
14TH Multidimensional Chromatography Workshop

January 30 - February 1, 2023

Workshop Guidebook



Thank you to our sponsors for making this event possible. It is your generous support that enriches the conference program and allows us to operate the conference with free registration for all attendees.



Local information

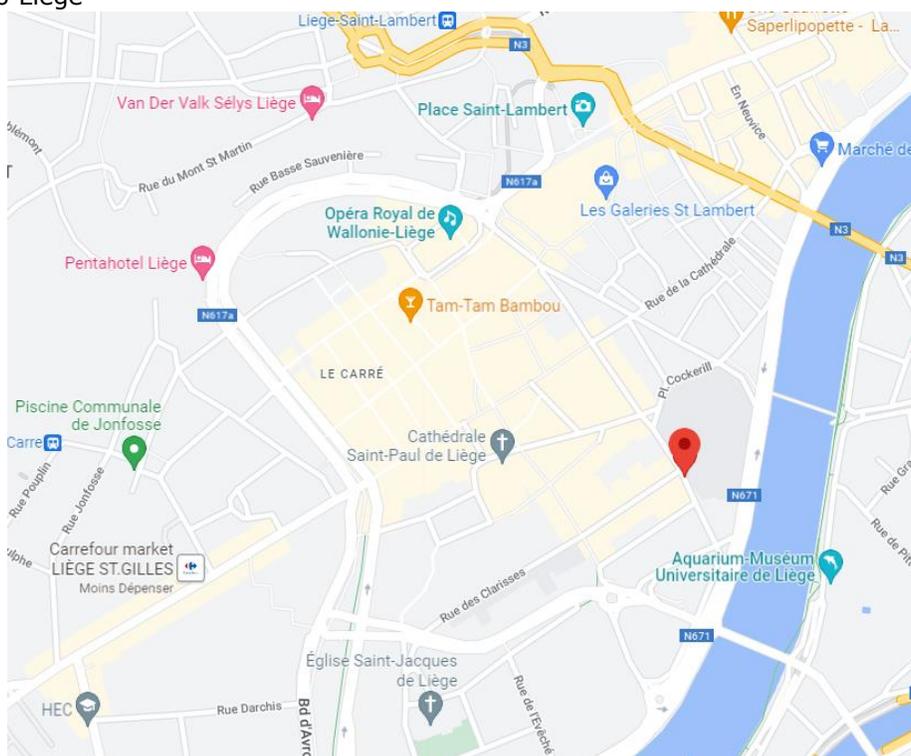
Venue (Red Pin)

Liège University
Place du 20 Aout 7
4000 Liège
Belgium

Main Room: Salle Academique

Cocktail

Aquarium-Muséum Universitaire de Liège
Quai Edouard Van Beneden 22
4020 Liège



Certificate

If you need an attendance or presentation certificate, please email us after the conference concludes at: obiachem@uliege.be

Full Program – MONDAY JANUARY 30, 2023

8:30 - 9:00 AM	Registration
9:00 - 9:30 AM	Opening Remarks
9:30 - 10:00 AM	KL01 Petr Vozka - Quantitative analysis of aliphatic olefins in fuels made from plastic waste by comprehensive two-dimensional gas chromatography
10:00 - 10:30 AM	KL02 Bob Pirok - Challenges to achieve unsupervised optimization of heart-cut and comprehensive two-dimensional liquid chromatography separations
<hr/>	
10:30 - 11:00 AM	Coffee Break
<hr/>	
11:00 - 11:20 AM	OL01 Marie Pardon - Systematic study of a selective comprehensive two-dimensional liquid chromatography interface with active solvent modulation to overcome the mobile phase incompatibility between HILIC and RPLC
11:20 - 11:40 AM	OL02 Ali Amini - Prototyping microfluidic devices for spatial multi-dimensional liquid chromatography by using Digital light processing 3D-printing
11:40 - 12:00 PM	OL03 Turaj Rahmani - Hyphenation of temperature-responsive chromatography and ultrafast chiral chromatography as a generic comprehensive two-dimensional method for the analysis of chiral pharmaceuticals
12:00 - 12:20 PM	OL04 Giorgia Purcaro - LC-GC×GC-TOF MS/FID: a powerful multidimensional technique for automated and reliable characterization of complex samples
<hr/>	
12:20 - 1:30 PM	Lunch sponsored by Agilent
<hr/>	
1:30 - 1:50 PM	OL05 Grant Ochoa - Developing advanced chemometric analysis methods for GC×GC-TOFMS to facilitate in-depth jet and rocket fuel characterization
1:50 - 2:10 PM	OL06 Laura McGregor - Comprehensive analysis of vehicle emissions using thermal desorption (TD) and GC×GC-TOF MS
2:10 - 2:30 PM	OL07 Eliane Lazzari - Qualitative screening of catalytic pyrolysis wood-oil by means of GC×GC-TOFMS and soft ionization
2:30 - 2:50 PM	OL08 Romaine Klein - Characterization of automobile material emissions by TD-GC×GC-TOFMS and correlation with odor hedonic perception in humans

2:50 - 3:50 PM	Coffee Break and Poster session
3:50 - 5:20 PM	Guided Discussion 1: Removing the barriers from adoption of comprehensive two-dimensional chromatography - Caitlin N. Cain, Timothy J. Trinklein, Sonia Schöneich, Grant S. Ochoa, Lina Mikaliunaite, and Soraya Chapel
6:30 PM	Conference cocktail (<i>Aquarium-Muséum Universitaire de Liège</i>)

Full Program – TUESDAY JANUARY 31, 2023

8:30 - 9:00 AM	Registration
9:00 - 9:15 AM	Opening Remarks
9:15 - 9:45 AM	KL03 Arnaud Delobel - 2D-LC/MS in a regulated biopharma environment: Challenges and applications
9:45 - 10:15 AM	KL04 Taylor Hayward - Assessment of fruit quality through volatile analysis using SPME and thermal desorption with GC×GC-TOFMS
10:15 - 10:35 AM	FL01 Christina Kelly - Simplifying method development for routine petroleum analysis using flow-modulated GC×GC-MS/FID FL02 Agathe Legendre - Renewable gases exploration by TD-GC×GC-TOFMS
10:35 - 11:05 AM	Coffee Break sponsored by JEOL
11:05 - 11:25 AM	OL09 Jan Leppert - Modular simulation of complex gas chromatographic systems
11:25 - 11:45 AM	OL10 Timothy Trinklein - Simulating GC×GC-TOFMS data with realistic run-to-run shifting to evaluate the robustness of chemometric software
11:45 - 12:05 PM	OL11 Daniel Geschwender - Automated alignment for quantitative pairwise differencing of two-dimensional chromatography data
12:05 - 12:25 PM	OL12 John Dane - A new generation high resolution MS for GC×GC analysis
12:25 - 1:30 PM	Lunch
1:30 - 1:50 PM	FL03 Caitlin Cain - Discovering compositional differences between aerospace fuels using comprehensive two-dimensional chromatography with time-of-flight mass spectrometry and chemometrics FL04 Nemanja Koljančić - Food metabolomics by GC×GC-TOF MS and tandem ionization: Understanding the impact of climate events on edible crops quality
1:50 - 2:10 PM	FL05 Elsa Boudard - Sampling body odor for healthcare monitoring: The need to control influential factors FL06 Kinjal Bhatt - Lipid profiling of boar tainted and untainted pig plasma using GC×GC-TOFMS

2:10 - 2:30 PM	<p>FL07 Lina Mikaliunaite - Computational method for untargeted determination of cycling yeast metabolites using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry</p> <p>FL08 Wan Sin Heng - Rapid detection of bacteria in food using static-headspace comprehensive two-dimensional gas chromatography (HS-GC×GC)</p>
2:30 - 2:50 PM	<p>FL09 Rushali Dargan - Using two-dimensional gas chromatography to understand decomposition odour in the Canadian environment</p> <p>FL10 Sonia Schöneich - Tile-based fisher ratio analysis of comprehensive three-dimensional gas chromatography with mass spectrometry detection data</p>
2:50 - 3:20 PM	Coffee Break sponsored by JEOL
3:20 - 4:50 PM	Guided Discussion 2: GC×GC, will it ever be in common use in the petroleum laboratories? - Lenny Kouwenhoven, Jop Bezuijen, Christina Kelly, and Jon Sims
5:00 PM	LECO Whiskey Tasting and Science Event

Full Program – WEDNESDAY FEBRUARY 1, 2023

8:30 - 9:00 AM	Registration
9:00 - 9:15 AM	Opening Remarks
9:15 - 9:35 AM	OL13 James Harynuk - Blueberries and wheat and beer, oh my! Adventures in the application of GC×GC to foodomics
9:35 - 9:55 AM	OL14 Tatiana Cucu - Lager beer flavour profiling by stir bar sorptive extraction, GC×GC separation and time-of-flight mass spectrometry
9:55 - 10:15 AM	OL15 Andrea Schincaglia - Chromatographic fingerprint of Pistacia vera fruits: an aromatic tour around the world
10:15 - 10:35 AM	FL11 Anika Lokker - Non-destructive identification of prehistoric adhesives by HS-GC×GC-TOFMS: Preliminary study FL12 Micaela Galletta - Untargeted characterization of the volatile fraction and targeted determination of chiral lactones in Marsala wines by means of flow-modulation headspace SPME-chiralGC×polarGC-ToFMS
10:35 - 11:05 AM	Coffee Break sponsored by Merck
11:05 - 11:25 AM	OL16 Mariosimone Zoccali - Determination of xenobiotics in food samples through reduced sample preparation coupled to cryogenic-modulation GC×GC combined with triple-quadrupole mass spectrometry
11:25 - 11:45 AM	OL17 Thomas Gröger - The use of comprehensive two-dimensional gas chromatography for pharmaceutical applications: Investigation of complex drugs
11:45 - 12:05 PM	OL18 Marco Beccaria - Two-dimensional gas chromatography-based techniques for lipidomics investigations
12:05 - 12:25 PM	OL19 Flavio A Franchina - Method development and optimization for monitoring probe exhaled breath metabolites using parallel MS-based analytical platforms
12:25 - 1:30 PM	Lunch
1:00 - 1:20 PM	OL20 Caroline Gauchotte-Lindsay - Novel pipeline for elucidation of high-level chemical mechanisms using non-targeted analysis by comprehensive two-dimensional gas chromatography coupled with mass spectrometry

1:20 - 1:40 PM	OL21 Steven Mascrez - Bursting the chromatographic fingerprint by combining vacuum-assisted headspace, multi-cumulative trapping SPME, and GC×GC
1:40 - 2:00 PM	OL22 Joe Binkley - Application of a unique dual detection GC×GC-TOFMS/FID setup for reliable qualitative and quantitative fragrance analysis
2:40 - 3:10 PM	OL23 Damien Eggermont - Exploring the cup of coffee using GC×GC-MS combined with multiple combination of headspace extractions
3:10 - 4:30 PM	<i>Closing and Awards</i>

POSTER LIST

- P01 Anika Lokker** Non-destructive identification of prehistoric adhesives by HS-GC×GC-TOFMS: Preliminary study
- P02 Grégory Bauwens** Validation of the LC-GC×GC-ToFMS/FID platform for mineral oil analysis through the comparison with the result of interlaboratory trials
- P03 Sheri Schmidt** Multiomics study of wheat volatiles
- P04 Lina Mikaliunaite** Development of a valve-based GC×GC-QMS instrument for highly volatile sample analysis
- P05 Laura McGregor** Comparing the aroma profiles of whisky by SPME-GC×GC-TOF MS
- P06 Hans-Gerd Janssen** Using only the second half of your GC×GC instrument: an easy way to fast GC
- P07 Allie Ferranti** Volatile profiling of bananas and banana pulp during ripening
- P08 Thibaut Dejong** Simultaneous multiple SPME fibers sampling to maximize the sample potential
- P09 Clémence Gély** Separation of cross-linked hyaluronic acid hydrogel digestates by LC×LC-MS
- P10 Dwight Stoll** Guiding the development of two-dimensional liquid chromatography separations using simulations and big(ger) data
- P11 Sebastiano Panto** Statistical differentiation of the Chinese liquor baijiu using SPME-GC×GC-TOFMS and Chromatof Tile software
- P12 Sebastiano Panto** Hydrogen carrier gas and comprehensive two-dimensional chromatography applied to the analysis of pesticides.
- P13 Daniela Peroni** Advancing MOSH/MOAH analysis towards speciation and contaminant identification
- P14 Ali Moussa** Modelling of analyte loss and dispersion generated by modulation loops used in multi-dimensional liquid chromatography
- P15 Niels Verhoesel** Evaluation of oxygenates in plastic pyrolysis oil by GC×GC-TOFMS
- P16 Eliise Tammekivi** Off-line LC×SFC-HRMS/MS method development for the non-target analysis of depolymerized lignin

- P17 Dawn Brown** Taste testing comparisons paired with volatile profile on cherries by TD-GC×GC-TOFMS
- P18 Genesis Barzallo** Quantitative analysis of alkenes in alternative fuels made from plastic waste conversion via comprehensive two-dimensional gas chromatography
- P19 Liesa Verscheure** Multidimensional LC-MS with multi-method option and parallel middle-up and bottom-up MS acquisition for the in-depth characterization of antibodies
- P20 Lukas Schwab** Adding discrimination dimensions with the application of selective ionization for two-dimensional comprehensive gas chromatography in the analysis of complex drugs
- P21 Sandra Piel** Benefits of higher mass resolution for the application of GC×GC-MS in drug research: application of a new generation of ultra-high resolution TOF-MS for identification of complex pharmaceuticals
- P22 Thibault Massenet** The beer's volatolome, a comparative study by comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry
- P23 Nemanja Koljančić** Food metabolomics by GC×GC-TOF MS and Tandem Ionization: understanding the impact of climate events on edible crops quality
- P24 Nathália Brilhante** Artificial intelligence smelling by GC×GC-MS/FID as a tool for food aroma blueprinting: the unique aroma of Brazilian olive oils
- P25 Simone Squara** Valorisation of premium Italian wines by volatile signature exploration with GC×GC-TOF MS and Computer Vision
- P26 Chiara Cordero** Computer vision enables effective detection of compositional differences in complex samples: validation of a workflow based on chromatographic fingerprinting and pattern recognition
- P27 Miloš Auersvald** Detailed insight into wheat/barley straw bio-oil composition using GC×GC-MS/FID/NCD/SCD

POSTER AWARDS



The American Chemical Society's Subdivision on Chromatography and Separations Chemistry (ACS SCSC) sponsors the Multidimensional GC Award and the Multidimensional LC Award at the 14th Multidimensional Chromatography Workshop. Each award holds a value of \$250 USD distributed directly by SCSC to the top posters in each category. Awards are distributed during the closing ceremony of the conference.

Sponsors

Features at a Glance

- Direct MS, LC/GC-MS and GCxGC-MS compatible
- Supports all major instruments and legacy data files
- Powerful chromatographic deconvolution
- Automated feature determination
- Targeted and non-targeted component analysis
- Statistical analysis and sample differentiation
- Visualization of complex data
- Intuitive workflow to reduce processing bottleneck
- Accurate mass compatible

ANALYZER PRO[®] XD

Simplifying your MS data processing workflow



AnalyzerPro XD is the modern and highly intuitive MS data processing software you have been waiting for. Designed to quickly and objectively process your data. From single sample processing to sample-to-sample comparison, AnalyzerPro XD is the perfect tool to accelerate your data mining workflow and achieve results you can be confident of.

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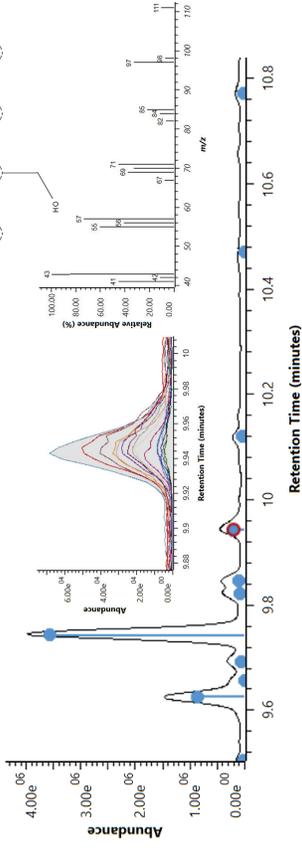


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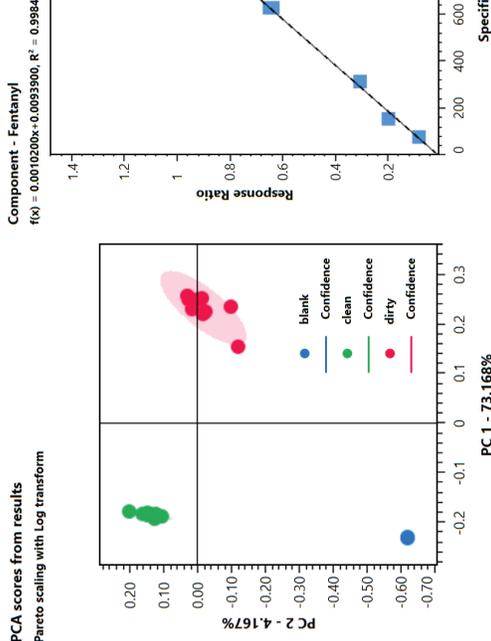


GC-MS / LC-MS



Statistical Analysis

PCA scores from results
Pareto scaling with Log transform



Direct-MS

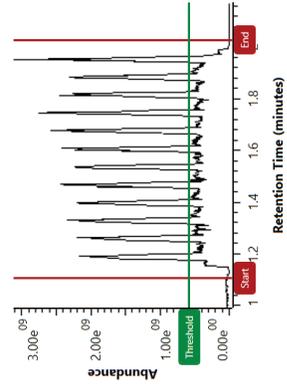
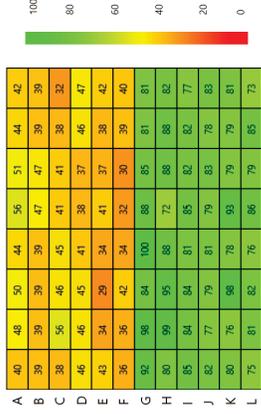
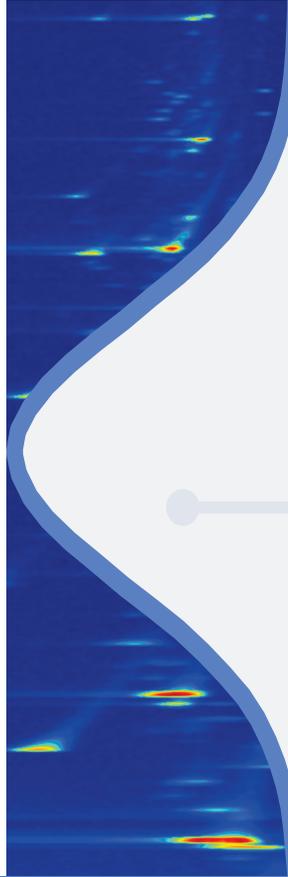


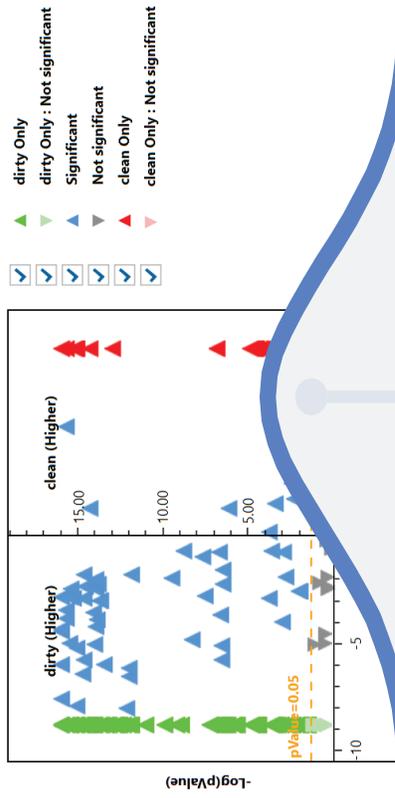
Plate Map Heat Plot
Target 151



GCxGC-MS / LCxLC-MS



Volcano Plot - clean / dirty



ANALYZER^{PRO} XD

One platform for all your MS Data Processing Requirements

JMS-T2000GC Specifications



1 Model

The JMS-T2000GC (AccuTOF GC-Alpha) is a gas chromatograph/high-resolution time-of-flight mass spectrometer designed for complex GC-MS chemical analysis.

2 Description

The AccuTOF GC-Alpha is a 6th generation GC-HRMS system that provides state-of-the-art capabilities for the identification of compounds in highly complex mixtures. Our new hardware design offers 30,000 resolving power and 1 ppm accuracy for applications demanding high resolution, and 50 Hz spectrum acquisition rate for Fast GC and GCxGC experiments. Combination EI/FI/FD and/or EI/PI ion sources provide flexibility for sample ionization without breaking vacuum, and our specialized software msFineAnalysis can combine hard- and soft-ionization HRMS data to provide identification capabilities far beyond standard database searching.



3 Specifications

Mass Spectrometer

Resolving Power:	30,000 (FWHM)
Mass Accuracy:	1 ppm
Mass Range:	4 to 6,000 u
Acquisition Rate:	50 spectra/s maximum
Digitizer Speed:	4 GS/s maximum
IDL (EI):	18.7 fg (from 8 replicates of 100 fg OFN)
Ion Sources:	EI, PI, PCI/NCI, FI/FD
Combo Sources:	EI/PI & EI/FI/FD
Probes:	DIP, DEP, FD
Filament Current (EI):	0 to 600 μ A
Ionization Energy:	0 to 200 eV
IS Temp. Range:	300°C maximum
Accel. voltage:	9 kV
Analyzer:	Two-stage reflectron with grid
Detector:	Two-stage MCP
Evacuation:	260 L/s (N ₂) TMP × 2
Carrier Gases:	He, N ₂

Gas Chromatograph

Oven Temp.:	Room temp. +4 to 450 °C
Stability:	0.01 °C/1 °C ambient temp. change
Heating:	0 to 120 °C/min in 0.01 °C/min steps
Inlet Type:	Split/splitless, PTV/LVI, & COC
Inlet Press.:	0 to 680 kPa
Inlet Temp.:	400 °C maximum
GCxGC:	Available as add-on

Hardware Requirements

Dimensions:	143 (W) × 79 (D) × 248 (H) cm
Mass:	348 kg
Power (MS):	Single phase, 50/60 Hz, AC 190 to 210 V or 220 to 240 V, 20 A
Power (GC):	Single/split phase, 50/60 Hz, AC 220/230/240 V (Fast GC), 15 A
Room Temp.:	15 to 30 °C ± 3 °C
Humidity:	20 to 70% (no condensation)
Grounding:	Class D (100 Ω or less)
Power Supply:	Voltage Fluctuation ±10% or less

[Click Here for Product Webpage](#)

Contact us: ms@jeol.com

*Specifications subject to change without notice

Document date: 4/1/2021

GC Image

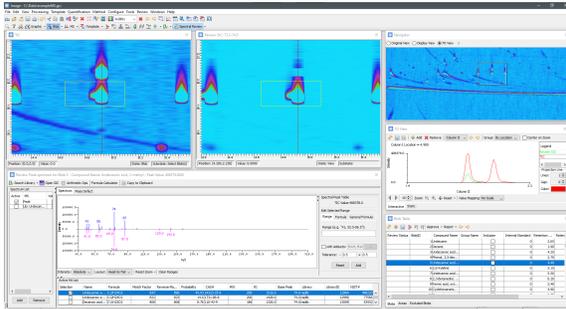
Software for Multidimensional Chromatography

GC Image, LLC; Lincoln, NE USA
www.gcimage.com | info@gcimage.com

Informatics for GCxGC and LCxLC

Unequaled data analysis toolkit for comprehensive two-dimensional chromatography.

GC Image® provides a software suite designed for customization to user-specific multidimensional chromatography (MDC) applications, with tools for data visualization, processing, analysis, multisample comparisons, and reporting.



Broad and Flexible Support for Data Inputs

Import your data from many chromatographic, mass spectral, and UV inputs, and standard data tables and formats.

Batch Processing with Command-Line Interface

Automate advanced processing for faster analyses across multiple samples and comparing chromatograms, peaks, and peak sets.

Multifaceted Visualization & Data Review

Inspect results quickly with a variety of interactive visualizations including 1D graphs, 2D plots, chromatographic images, 3D views, and tables.

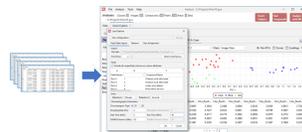
Advanced Peak Alignment, Identification & Analysis

Identify chromatographic patterns and spectral signatures with highly effective chemical identification, advanced peak alignment, and cross-sample analysis technologies.

MDC Investigator™ / Analysis

MDC Investigator™ provides an array of tools for an analyst performing multi-sample analyses including:

- Built-in calculations and plots of common statistics and trends for assisting multi-sample analysis.
- Interactive visualization for comparing pairwise differences among samples and sample classes.
- Multi-class analysis tools with principal component analysis (PCA), Fisher ratios, F-tests, and machine learning.
- Tools for detecting common and unique compounds across many samples based on statistical characteristics, and chromatographic and mass spectral information.

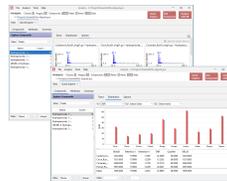


1D and 2D Peak Table Support

MDC Investigator performs multiple-sample analysis directly on peak tables acquired by both one-dimensional and two-dimensional chromatographic and spectrometric techniques (GC-MS, LC-MS, GCxGC, LCxLC, etc.). With the functionality enabled by Smart Feature Templates™ and alignment algorithms, MDC Investigator provides a high degree of selectivity and implicit cross-sample matching of peaks in peak tables.

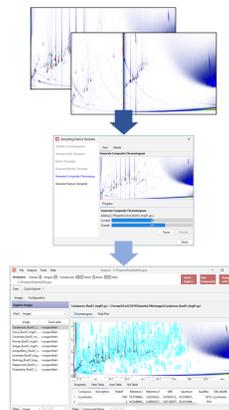
Data Visualization and Analytics

Visualizing your data is easy with MDC Investigator. The software includes a variety of customizable charts to highlight interesting trends, features, outliers, and class differences.



Alignment

MDC Investigator has the capabilities to perform peak alignment across multiple samples using automated template matching and transformation algorithms. The aggregated peak tables after alignment can be exported for further modeling and analysis.



Find Common and Unique Compounds

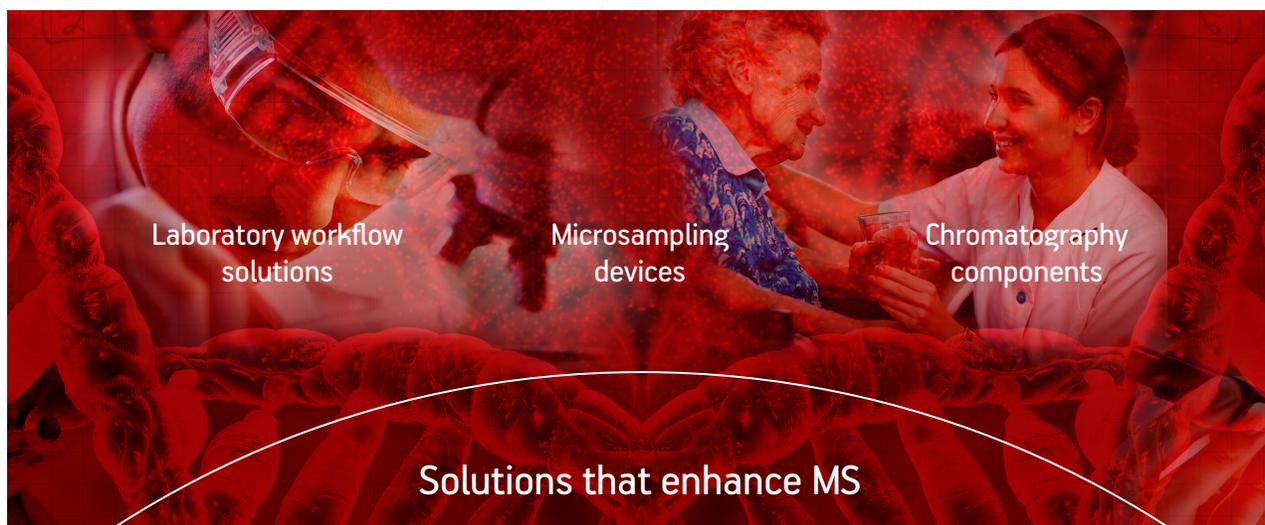
MDC Investigator's Find Compounds tool aids in the discovery of common and unique compounds using statistical characteristics, and chromatographic and mass spectral information. It also provides quick access to detailed compound information.



Machine Learning

Perform advanced classification and analysis using the Investigator ML™ machine learning tool. This tool performs supervised pattern recognition and classification using a variety of algorithms and supports visualization and reporting on the chromatograms, features, feature patterns, classification models, and classification results.



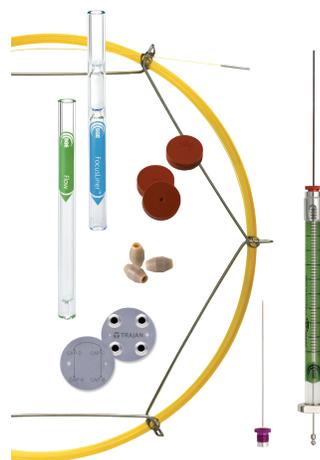


Chromatography components

The parts of a GC are intimately interconnected and quality is explicable only by reference to the whole system.

A properly maintained GCMS instrument should be capable of consistently achieving sub ng detection limits.

Using modern, high performance instrumentation, it is the user replaceable parts that represent the greatest barrier to maximum performance.

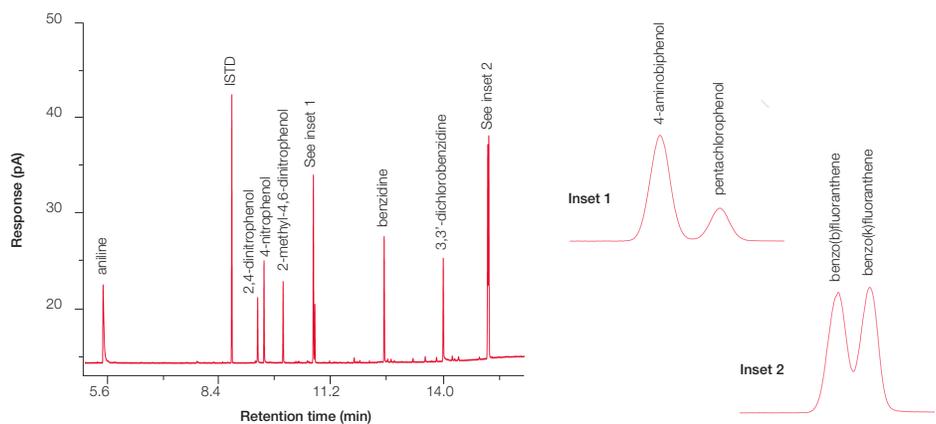


Holistic approach to GCMS sample flow path inertness

Trajan is supporting best practice chromatographic analysis by taking a holistic approach to inertness of the sample flow path to remove barriers to maximum performance.

We are supporting GC users to make informed choices around selection of user replaceable parts in the GC flow path.

Trajan SGE Inlet liners for 8270 semivolatiles analysis



Improving sensitivity

Trajan's CRS GC septa is founded on unique technologies that optimize the performance of the injection port. All CRS GC septa are made with a high grade silicone material to minimize needle coring.

CRS GC septa ensures:

- Very high temperatures of operation
- Exceedingly tight requirements for low emission of volatile and liquid components
- Resistance to sticking

crs GC septa



To maximize accuracy and precision, it is recommended that the minimum volume injected from a syringe is 20% of the total syringe capacity.

TIP

Minimizing sample loss



Choosing the right inlet liner and injection parameter can increase peak areas and improve detection limits by up to 300 % [Kende, A et al. Chromatographia, 2006; 63 (3/4): 181-7]

SGE Inlet liner for USEPA 8270

Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from many types of solid waste matrices, soils, air sampling media, and water samples.

Several compounds in Method 8270 are susceptible to excessive degradation in the GC flow path, becoming problematic to analyze if the inlet liner is not properly deactivated.

Trajan SGE Inlet liners for 8270 semivolatiles analysis are treated using a deactivation approach and have been extensively tested at 2 ng on column using a test mix containing the potentially problematic compounds:

- N-nitrosodimethylamine, aniline-2,
- 4-dinitrophenol, 4-nitrophenol, 2-methyl-4,
- 6-dinitrophenol, 4-aminobiphenol, pentachlorophenol, benzidine, benzo(b)fluoranthene, benzo(k)fluoranthene, and 3,3'-dichlorobezidine.



When changing your column, inlet liner or septum, lower the injector temperature to <math><100^{\circ}\text{C}</math> to prevent stripping the liner deactivation. This is especially important for the analysis of trace levels of active compounds.

TIP

Optimizing performance through GC column inertness



The GC column is at the heart of any separation.

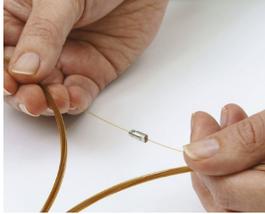
Proprietary deactivation approaches are used to make MS-grade inert GC columns and a wide range of stationary phases synthesized in-house for specialized applications.

Even if you are not using MS if you are performing trace analysis of active compounds, choose an MS-grade inert GC column eg. BP5MS-UI.

TIP

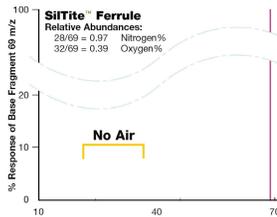
Solutions that enhance MS

Creating connections to improve analysis



The GC capillary column connector SilTite® μ -Union is specifically designed and precision engineered for use in capillary GC.

- Inert - Enabled by our expertise in surface chemistry, features chemically deactivated stainless steel ferrules alleviating active sites.
- Zero dead volume - Giving you optimized peak shapes.
- Robust - Stable for both extreme temperature and pressure cycling
- FingerTite technology - Ensures it's easy to install and leak free.
- SilTite ferrules - No more leaks and no need to re-tighten after installation.
- Only 9 mm in total length and a mass of <0.5 g - Low thermal mass.



MS trace using a SilTite ferrule after 5 temperature cycles. (Using a MS no leaks can be detected, even after 400 temperature cycles between 70°C and 400°C)

Always use SilTite® or Graphite/Vespel® ferrules when connecting a column to a GC/MS interface.

TIP

Removing barriers to maximum performance



Improve your GC connectivity with Trajan's stainless steel micro-fluidic platform SilFlow®.

SilFlow is an innovation in design and fabrication resulting in a highly efficient and reliable micro fluidic platform that improves GC connectivity to enable maximum chromatography performance.

Enabled by Trajan's expertise in surface chemistry, SilFlow features chemically deactivated stainless steel channels avoiding active sites experienced with conventional connections.



A well executed back-flush using a SilFlow® microchannel device can reduce analysis time while extending detector maintenance intervals by maximizing system cleanliness.

TIP

Trajan Scientific and Medical

Science that benefits people

Trajan is actively engaged in developing and delivering solutions that have a positive impact on human wellbeing. Our vision focuses on enriching personal health through scientific tools and solutions.

Environmental & Agricultural GC Column Selection Guide



Ensuring Optimal Method Performance

Because your application can have quite demanding requirements it is critical to choose a column that can provide the necessary resolution, inertness, and stability.

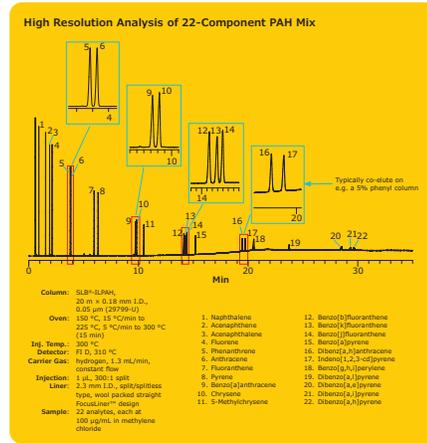
We have developed the most extensive line of special purpose columns designed for industry specific applications.

These columns are manufactured to deliver high resolution, great analyte response, low bleed, and long column life to achieve the analytical performance you require.

Let's find the right column for your process.

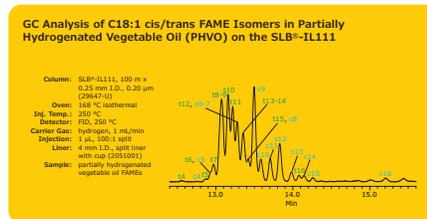
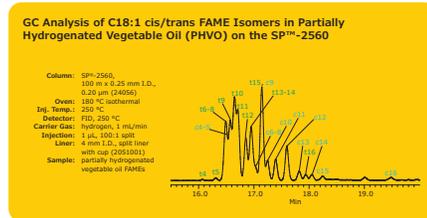
Environmental Industry

	SPB®-Octyl	SLB®-5ms*	Equity®-5*	SPB®-624*	VOCOL®*	Equity®-1701*	SPB®-608	Sup-Herb™	SPB®-35	SPB®-50	SPB®-225	SPB®-1000	SLB®-IL59	SLB®-IL60*	SLB®-IL82	SP®-2331*	SLB®-IL1111	Chiral	SLB®-ILPAH*	SLB®-PAHms*	
Volatiles by GC-MS																					
Volatiles by GC																					
Semivolatiles by GC-MS																					
Semivolatiles by GC**																					
Fuels (GRO, DRO, TPH)																					
Dioxins by GC-HRMS																					
PCBs by GC-HRMS																					
PBDEs by GC-MS																					
PAHs by GC or GC-MS																					
Oil Spill Dispersants																					
Odor Compounds (Geosmin, 2-MIB)																					

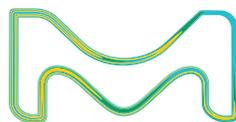


Agriculture Industry

	Equity®-1*	SLB®-5ms*	SAC™-5	Equity®-1701*	SPB®-608	SPB®-225	SPB®-PUFA	Nukol™	SPB®-1000	Omegawax®	SUPELCOWAX® 10*	SLB®-IL59	SLB®-ILPAH*	SLB®-PAHms*	SLB®-IL60*	SP®-2331*	SP®-2380	SP®-2560	SLB®-IL1111	Chiral	Watercol™ 1910*	
Edible Oils																						
Free Fatty Acids																						
FAMES by Boiling Point Elution																						
FAMES by Degree of Unsaturation																						
Omega 3 and Omega 6 FAMES																						
cis/trans FAME Isomers																						
Pesticides																						
Dioxins																						
Flavors and Fragrances, Aroma																						
Moisture Analysis																						
PAHs																						



* Indicated columns are available in Intuvo format
 ** Includes: organochlorine pesticides, PCBs as Arctics, herbicides, organophosphorus pesticides, nitroaromatics, phenols, phthalate esters, halobenzoic acids, disinfection by-products and solvents, and PAHs.



The life science business of Merck operates as MilliporeSigma in the U.S. and Canada.



PEGASUS[®] BT Series



LECO
EMPOWERING RESULTS

GC-TOFMS

Mass spectrometers are perhaps the greatest tool available for the analytical chemist. With the ability to ionize, sort, and measure complex chemical mixtures by their mass-to-charge ratio (m/z) with incredible sensitivity, it is no wonder that mass spectrometers are widely used across many industries.

With the ability to acquire the full mass range of your sample with exceptional spectral continuity and fast data acquisition rates, Time-of-Flight mass spectrometers (TOFMS) are ideal for discovering new compounds, quantifying targeted compounds in complex samples, and increasing throughput with fast chromatography. Non-targeted data mining is available with the results from TOFMS, while they also yield high quality library matches through mass spectral deconvolution and accurate quantitation using fast gas chromatography (GC). There is no compromise in data acquisition speed or sensitivity when collecting the full mass range, and it creates a historical catalog of information about a sample that can be referenced in the future if new questions arise. In addition, the spectral profile is always consistent across a peak, regardless of intensity, allowing ChromaTOF® software's industry leading deconvolution algorithms to perform optimally.

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Pegasus BT

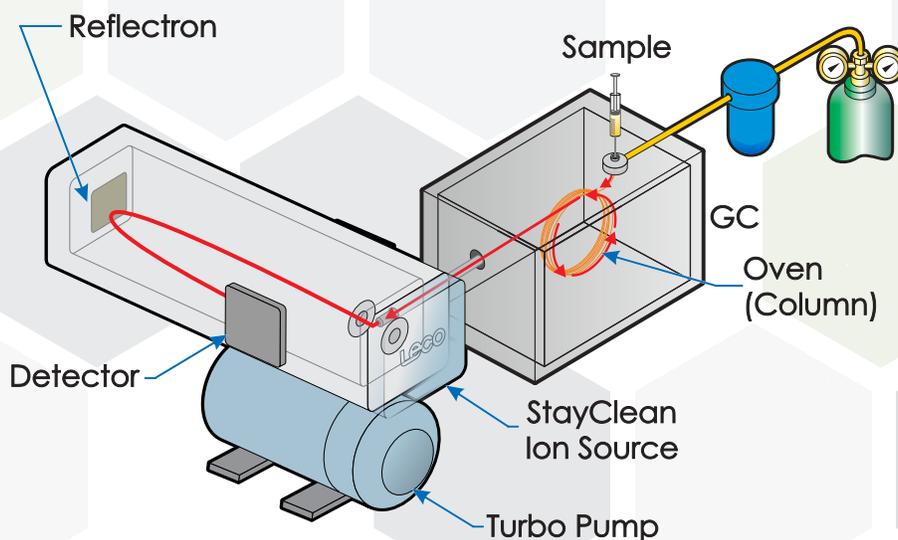
Today's laboratories are being asked to do more everyday—run more samples, acquire more data, process more chemical information, and achieve more results—all in less time, and for less money.

A smart investment for any laboratory looking to perform qualitative or quantitative analysis of targeted and non-targeted compounds, the Pegasus BT GC-TOFMS is the first benchtop GC time-of-flight mass spectrometer to develop higher sample throughput, better chemical information, and very low maintenance costs, resulting in improved overall productivity in your laboratory and results that are of the highest quality.

Advantages of the Pegasus BT

- Find and quantify an unlimited number of analytes, in every run, every time
- Market-leading deconvolution algorithms yield clean, high-quality mass spectra
- TOF eliminates spectral skewing associated with scanning mass analyzers
- Deconvolution ensures clean spectra are obtained from coeluting peaks and matrix interferences are drastically reduced, providing the most reliable chemical information for your samples
- Complete historical record of mass spectra for each sample for future data mining
- Lab tried and tested reliability and durability
- Low-maintenance StayClean[®] ion source virtually eliminates downtime with no need for cleaning even after dirty samples*
- Improved productivity is directly related to higher quality results, with higher sample throughput, better chemical information, and lower maintenance costs due to its reliability and minimal downtime

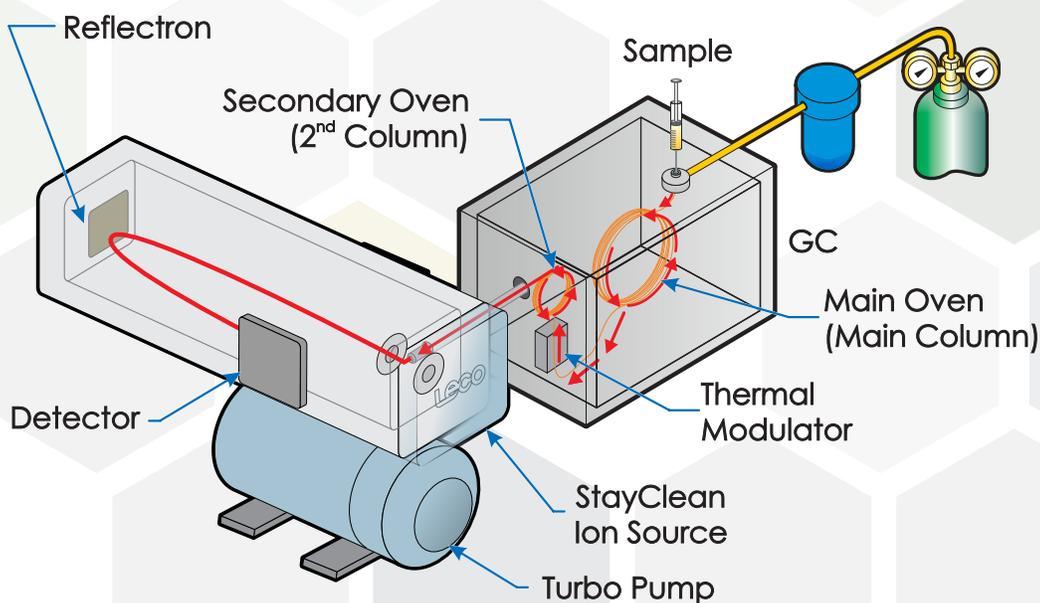
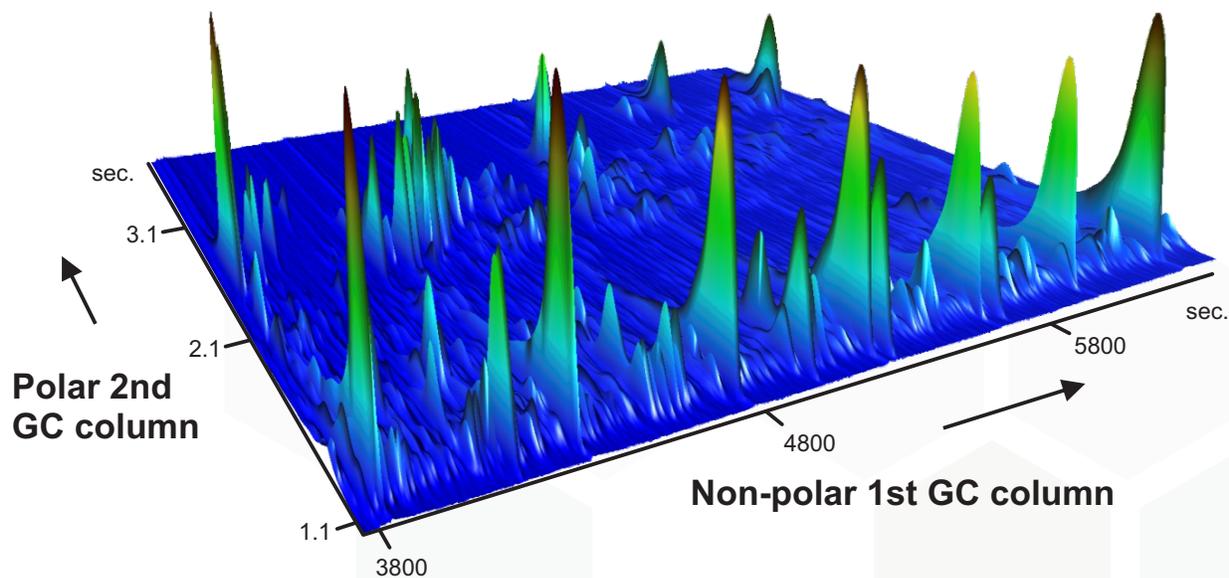
**After 3,000 sludge injections, all performance specifications were still achieved.*



GCxGC

Real-world samples are rarely clean, and heavy matrix interference is commonplace. A single injection might have thousands of different compounds. The more compounds in a sample, the higher the chance of coelution, and even LECO's proprietary deconvolution algorithms might not be enough. This is where a second dimension of chromatographic separation shows its strength.

Comprehensive two-dimensional gas chromatography (GCxGC) increases analyte detection and identification. On average, a thermally modulated GCxGC analysis has five times the sensitivity and offers three times the number of compounds identified compared to typical GC-MS runs. By running a sample through a second, orthogonal column phase, analytes can be easily separated from matrix interferences or other coeluting compounds. The increased chromatographic resolution allows better automatic library matches, leading to faster, more confident peak identification.



Pegasus BT 4D

Not all GCxGC systems are the same, and not all analyses have the same focus. LECO offers the Pegasus BT 4D with a variety of GCxGC modulators with various performance and operational focuses so you can choose the best setup for your laboratory's specific needs.



	QuadJet™ LN ₂	QuadJet™ CF	Flux™ DF
Modulator Type	Thermal	Thermal	Diverting Flow
Performance Attributes			
Sensitivity	Excellent	Excellent	Good
Chromatographic Resolution	Excellent	Excellent	Very Good
Quantitative	Excellent	Excellent	Very Good
Volatility Range	Very Good	Good	Excellent
Operation Attributes			
Robustness	Very Good	Very Good	Excellent
Consumables	\$\$\$	\$\$	\$
Instrument Cost	\$\$\$	\$\$\$	\$
Method Optimization	Excellent	Excellent	Very Good

Pegasus BT 4D Modulators

QuadJet LN₂ Thermal Modulator

Industry-leading sensitivity is made possible with cryogenic focusing at the modulator using liquid nitrogen cooled jets to sharpen the peaks prior to detection, increasing the S/N ratio and improving deconvolution. Analytes that are typically too low in concentration to detect are brought into sharp focus and clearly identifiable.

QuadJet CF Thermal Modulator

A lack of cryogenics means cost-per-analysis for the Consumable-Free QuadJet is lower than its Liquid Nitrogen counterpart, but it also means the QuadJet CF doesn't get as cold, leading to a small loss in performance for highly volatile compounds. Otherwise, the QuadJet CF is similar in design, performance, and initial cost to the QuadJet LN₂.



Flux Flow Modulator

The simplest of LECO's modulators, the Flux is a diverting-flow-based modulator for robust GCxGC analyses that do not need the full sensitivity of a thermal modulator. With no cryogenics required, consumable costs are low, and the integrated ChromaTOF brand software handles all of the timing and flow requirements so your lab can save time and boost efficiency with the introduction of comprehensive GCxGC.



Sample Introduction Tools

L-PAL3 Autosampler

LECO's L-PAL3 offers increased vial capacity, discrimination-free, ultrafast GC injections, an automatic tool exchange option to switch between injector types (liquid, headspace, or SPME), minimized carryover, and the sensing of vial bottoms to avoid mis-injections. All of these advantages come on a highly robust and integrated platform. The LECO L-PAL3 GC autosampler allows you to safely focus on characterizing your samples without experiencing downtime and uncertainty in your lab.

All L-PAL3 models are CTC-based robots that combine an autosampler and an injector that operates in three dimensions of space.



Standard Features

- 5-position solvent wash station
- Mounting kit for GC
- Tray holder with three trays (54 positions each, 162 samples total) for 2 mL vials
- Complete injection cycle times down to 100 milliseconds
- Bottom-sensing technology to sample even very small volumes

Models

	Liquid	Headspace	SPME	ATX	DRV
Liquid Syringe	Yes	Yes	Yes	Yes	Yes
Heated Headspace Tool	No	Yes	No	Yes	Optional
SPME Fibers tool	No	No	Yes	Yes	Optional
Tool Exchange	None	Manual	Manual	Automatic	Automatic
SPME Fiber conditioning station	No	No	Yes	Yes	Optional
Heated Agitator	No	Yes	Yes	Yes	Yes
Derivatization	Manual	Manual	Manual	Manual	Automatic
Additional tray holder with three trays (15 positions each, 45 samples total) for 10/20 mL vials	No	Yes	Yes	Yes	Yes
Additional Options Available	No	Yes	Yes	Yes	Yes

L-PAL3 Options

Dilutor

- Allows automated preparation of analytical standards
- Fast wash module
- Additional syringe sizes
- Vortex mixer

SPME Arrow

- Larger sorptive properties for immersion or headspace applications
- Various sizes and coating materials available

ITEX Dynamic Headspace

- Rapid and sensitive enrichment of volatile and semi-volatile compounds from solid, liquid, and gaseous samples
- A choice of different adsorbents for best sensitivities
- No sample loops, transfer lines, or valves; no contamination issues
- L-PAL3 Automatic Tool Exchange (ATX) enables head space, SPME, and ITEX-sampling within one sequence

Peltier

- Storage of up to 3 racks or plates under user-defined temperature conditions
- Temperature range between 4 °C and 40 °C
- Capacity:
 - Multi Titer Plates
 - VT54 (54 x 2 mL)
 - VT70 (70 x 1 mL)
 - VT15 (15 x 10/20 mL)
 - or combinations

Other Accessories

Thermal Desorption (TD)*

An automated Thermal Desorption (TD) unit made possible by combining an OPTIC-4 inlet, LINEX head for automatic transport and insertion of TD tubes, and cryotrap for collecting desorbed sample prior to analysis.

Pyrolyzer*

An automated TD and pyrolyzer made possible by combining an OPTIC-4 Pyro inlet (increases upper temp to 700 °C for pyrolysis), LINEX head for automatic transport and insertion of TD/pyrolysis tubes, and cryotrap for collecting desorbed or pyrolyzed samples prior to analysis.

Cryotrap*

The cryotrap can be used as a standalone device for effective cryofocusing of headspace or headspace SPME injections, as well as in conjunction with thermal desorption or pyrolysis accessories.

OPTIC-4*

A multi-mode inlet which can be used as a standalone inlet for hot, cold, large volume, and on-column injections, or as the base for automated TD (up to 600 °C), or liner exchange applications when coupled with a LINEX head which allows automated transport and insertion of inlet liners and TD tubes. A cryotrap is utilized for collecting thermally desorbed sample prior to releasing for analysis.

OPTIC-4 Pyro*

A multi-mode inlet which can be used as a standalone inlet for hot, cold, large volume, and on-column injections, or as the base for automated TD, pyrolysis (up to 700 °C), or liner exchange applications when coupled with a LINEX head which allows automated transport and insertion of inlet liners, TD/pyrolysis tubes. A cryotrap is utilized for collecting thermally desorbed or pyrolyzed sample prior to releasing for analysis.

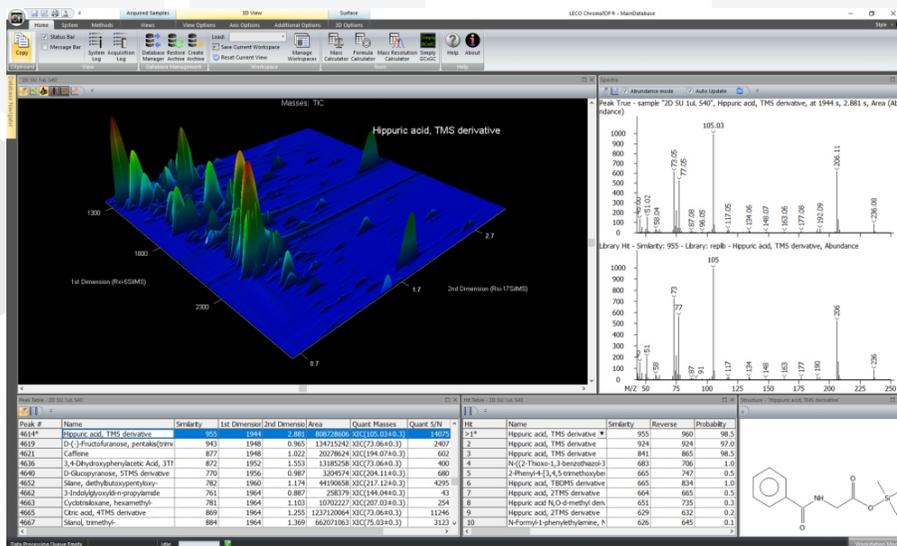
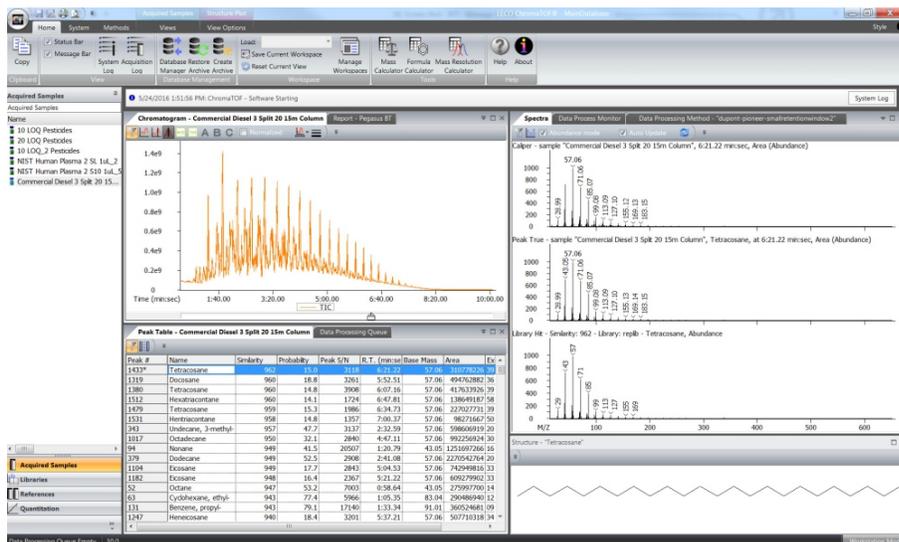
*GL Sciences

ChromaTOF Software

Developed exclusively by LECO, ChromaTOF is uniquely designed to meet the needs of today's laboratory professionals by processing and analyzing the large amounts of data that are acquired with our time-of-flight instruments. ChromaTOF offers seamless control of both the instrument and its accessories, as well as an intuitive interface with highly integrated data processing. ChromaTOF is the first mass spectrometry data system to fully accommodate multidimensional chromatographic data (GCxGC).

What Makes ChromaTOF Unique?

- Data processing is automatically saved within the file system—no extra steps are needed and you can always come back to where you left off
- File management system stores and manages meta data (AS, GC, MS, and Processing Methods) with each data file
- Industry-leading deconvolution algorithms yield clean, high-quality spectra with higher quality spectral hits for more reliable results and more confident reports
- Integrates with commercially available mass spectral data bases, i.e. NIST, Wiley, and also allows custom library creation
- Frequently updated for improved maintenance and additional feature development



Optional Software Tools

ChromaTOF|TILE

ChromaTOF Tile revolutionizes how GCxGC data is analyzed by comparing GCxGC data files quickly and easily. Statistically significant differences rise to the top so you can spend less time finding the differences between your data and more time finding out what they mean.

Designed for Sample Group Differentiation

ChromaTOF Tile finds differences between two or more classes of samples.



Biomarkers distinguishing healthy from not...



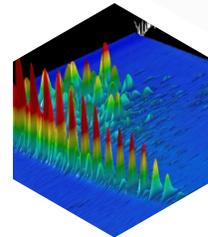
Off-odor detection in food samples that passed or failed quality control...



Water samples up- and down-stream from an outflow source...



Petroleum samples from various geographical origins...

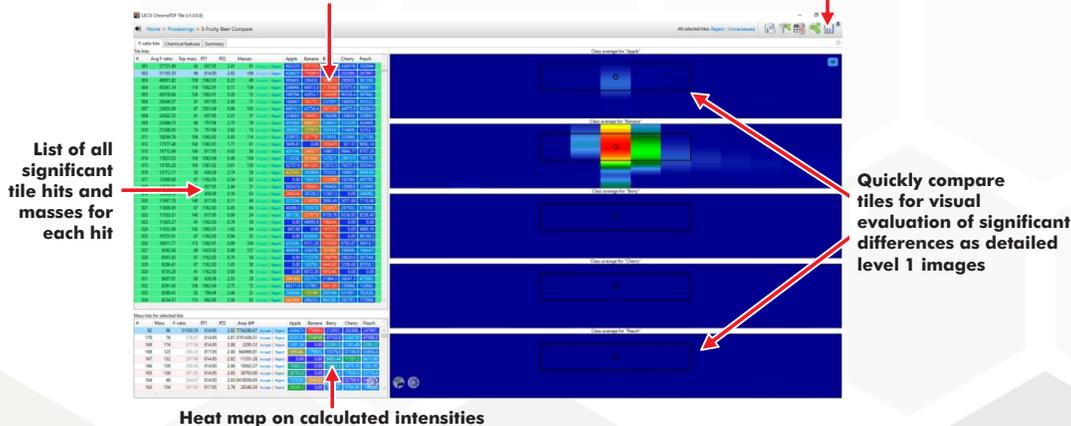


And anything else you can imagine

Fisher Ratio Hits Pane

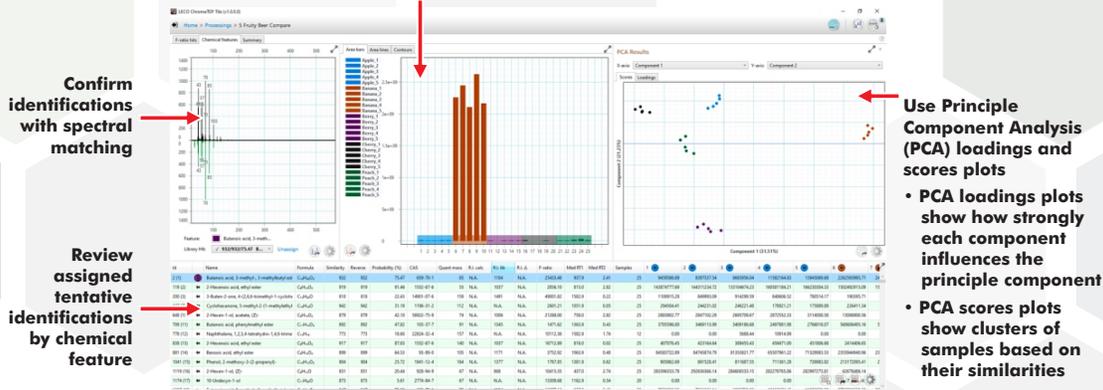
Immediate feedback on class distinctions

Automated curation of tiles to chemical features



Chemical Features Pane

View the trends across classes



Optional heatmap tables are incorporated throughout the interface to give instant feedback on relative intensities.

ID	Name	Formula	Similarity	Quant mass	Formula	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
2300 (26)	2-Buten-1-one, 1-(2,6-dimethyl-1-cyclohexylidene)	C ₁₄ H ₂₄ O	874	56	1318.93	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2403 (27)	Benzaldehyde	C ₇ H ₆ O	917	105	799.29	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2406 (28)	1-Heptanol	C ₇ H ₁₄ O	928	56	1324.10	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2675 (40)	2-Hepten-1-ol acetate, (E)	C ₉ H ₁₆ O ₂	901	77	774.36	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2710 (41)	6-Octen-1-ol, 1,7-dimethyl-, (E)	C ₁₀ H ₂₀ O	902	81	1194.15	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2771 (42)	Fatalkene	C ₁₀ H ₁₈	739	91	1549.20	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2888 (43)	3-Methyl-2-butene-1-ol acetate	C ₇ H ₁₂ O ₂	944	89	240.17	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2936 (44)	Butyl 2-methylbutanoate	C ₁₀ H ₂₀ O ₂	940	712	1034.00	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2907 (45)	2-Heptanol	C ₇ H ₁₄ O	915	87	707.76	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2917 (46)	Pentane, 2-cyclopropyl-	C ₈ H ₁₆	828	86	896.44	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
2952 (47)	Butyl 2-methylbutanoate	C ₁₀ H ₂₀ O ₂	944	57	100.87	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
3020 (48)	Butanoic acid, 2-methyl-, ethyl ester, (Z)	C ₈ H ₁₄ O ₂	706	87	1222.64	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
3021 (49)	2-Methylbutanoic acid, ethyl ester, (Z)	C ₈ H ₁₄ O ₂	706	87	1222.64	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07

21 CFR Part 11

ChromaTOF software is now fully compliant to the United States FDA Code of Federal Regulations Title 21 Part 11 and its European equivalent (Eudralex Chapter 4, Annex 11). These regulations document the requirements for ensuring the integrity of electronic records and electronic signatures for regulated environments.

A dedicated user login, electronic signature capabilities, and audit trail are core capabilities now implemented within the software to enhance ease-of-use when meeting federal regulations. All aspects of data are secured within the GC-MS data system. ChromaTOF manages the meta-data for users and ensures its security, eliminating the management of complex file structures within the data system. All data structures are under the secure umbrella of ChromaTOF with CFR enabled. Electronic signatures can be required for acquisition, all methods, data processing, and reporting. A new Network Administrator tool securely handles the setup and management of users and roles for easy integration into your laboratory's IT environment.

Incorporating these features into our powerful ChromaTOF ensures that submissions to the FDA or other regulatory bodies are properly validated, secure, and correct, simplifying what can often be a complex process.

Achieve Compliance at All Levels

- Instrument Users—Prove product quality and provide electronic signatures for changing methods, results, tuning, and more. Additional options include Audit Trail Viewer and Client Configuration.
- Lab Administrators and Managers— Monitor instrument usage and assign roles using the Administrator tool.
- Network Administrators—Get everyone up and running quickly with an easy-to-use, clearly defined set-up process.



LECO's Simply GCxGC online tool walks you through the steps of developing and optimizing a GCxGC method, whether you're creating a method from scratch or converting an existing GC method to GCxGC. Unnecessary testing is eliminated with this free tool from LECO.

The screenshot shows the LECO Simply GCxGC online tool interface. It is divided into several sections:

- Guide Me:** A vertical sidebar on the left with buttons for "Convert GC to GCxGC", "Stationary Phase Combinations", "Evaluate Sample Loading", "Determine Secondary Oven Offset", "Evaluate Stationary Phase", "Evaluate Peak Capacity", "Increase Peak Capacity", "Increase Secondary Column Peak Capacity", "Decrease Run Time", "Limits / Settings", "Inventory", and "Contact Us".
- Configuration:** The main area contains input fields for "Secondary Column ID (mm):" (0.25), "Secondary Column Phase thickness (µm):" (0.25), "Desired Flow (ml/min):" (1.4), and "Desired Oven Ramp Rate (°C/min):" (3.6). It also includes text indicating optimal flow rate (1.4 ml/min) and oven ramp rate (3.6 °C/min) for the current configuration.
- Buttons:** "Modify" and "Add" buttons are located below the configuration fields.
- History:** A table at the bottom left shows a list of previous runs with columns for "#", "Run Time", "PC 1", "PC 2", and "PC Not".
- Summary:** A detailed overview on the right side, including "Overview" (Peak Capacity Gain: 6.3, Run Time: 73 min, Acquisition Rate: 202 cps), "Columns" (Primary Column: PwL501 MD, Stationary Phase: 0.25 µm x 0.25 µm, Secondary Column: Stationary Phase: 0.25 µm x 0.25 µm), "Inlet" (Carrier Gas: Helium, Flow: 1.4 ml/min, Inlet Pressure at 300 °C: 40 psi, Primary Column Velocity: 23 cm/sec), "Temperature" (Oven Temperature Program: Initial Temperature 40 °C for 2.0 min, 3.6 °C/min to 300 °C, Secondary Oven Offset: 5 °C, Transfer Line Temperature: 340 °C), and "GCxGC" (Optimal Modulation Period: 2.3 sec, Method Modulation Period: 2.3 sec, Method Hot Pulse Time: 0.68 sec).

Service and Support

Instrument Training

At time of installation, your LECO Service and Installation Engineer will provide you with a basic overview of how to operate your instrument and get started. However, LECO knows that the key to success in the lab with any new instrument is understanding how it works for you. Our Separation Science instrument training classes will show you how to use your new instrument to its full potential. We now offer a variety of training options to meet your schedule and comfort level.



LECOlearn allows for 24/7 access to organized training videos for our QuadJet and Pegasus series instruments so you can learn on your time, at your own pace. Videos are presented in course format by topic and designed to walk you through the natural progression of a typical training class. Access and re-watch any video, or any part of the video, at any time when you need clarity or review on a topic.

Topics include:

- Databases and File Management
- Tuning and QC
- Methods and Acquisition
- Deconvolution and Quantitation
- Introduction to GCxGC
- Service Videos

Installation Qualification and Operational Qualification

Installation Qualification (IQ) and Operational Qualification (OQ) ensures your instrumentation and software are installed correctly as well as functions according to LECO's specifications. This procedure also confirms that all functionality operates as intended by LECO. The OQ service uses chemical standards supplied by LECO for system validation to ensure accuracy and precision of the installed system. The results of the IQ/OQ are fully documented.

IQ/OQ is performed on-site by a certified LECO service engineer, specially trained to validate LECO instrumentation. At the end of the IQ and OQ, documentation, including testing data, forms, and copies of the protocols used during the qualification procedures, are left at the customer site.

Annual OQs can be performed by a LECO service engineer.

LECO, Pegasus, ChromaTOF, StayClean, QuadJet, and Flux are trademarks of LECO Corporation.

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LECO Corporation



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INSTRUMENTATION – SOFTWARE – EXPERTISE

Enabling GC chemists to maximise every analysis



Sampling technologies



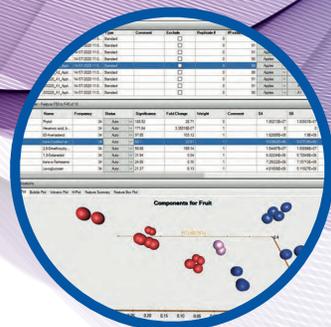
Thermal desorption



Sample extraction & enrichment

MARKES
international

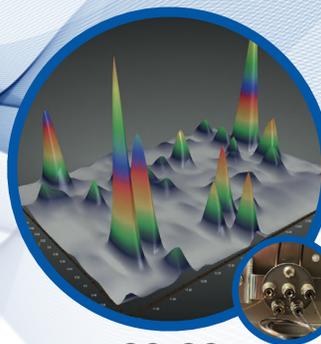
SepSolve
Analytical



Data mining & chemometrics



Time-of-flight mass spectrometry



GCxGC separation

Discover more – Deliver more

www.markes.com

www.sepsolve.com



LC | GC[®]

The logo consists of the letters 'LC' and 'GC' in a bold, black, sans-serif font. A red line, resembling a chromatogram peak, runs horizontally through the middle of the letters. The line starts at the bottom of the 'L', rises to a sharp peak between the 'C' and 'G', and then descends to the bottom of the 'C' before continuing horizontally to the right.

the
Analytical Scientist

Abstracts

KL01

QUANTITATIVE ANALYSIS OF ALIPHATIC OLEFINS IN FUELS MADE FROM PLASTIC WASTE BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

Petr Vozka

California State University, Los Angeles, Los Angeles, USA

Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) has become the state-of-the-art instrument for qualitative and quantitative analysis of volatile and semi-volatile complex mixtures and has emerged as a powerful separation tool for studying environmental samples, petroleum fractions, persistent organic pollutants, drugs, and many more. In the past 60 years, plastic waste has increased exponentially, while only 9% of plastic waste has been recycled and 12% incinerated. The remaining 79% (about 6 billion tons) of plastic waste has accumulated in landfills or oceans, where they slowly degrade and release microplastics and other toxic chemicals into the environment. To reduce the amount of plastic waste, conversion methods such as pyrolysis and hydrothermal processing are used to make oils, which can be further used to produce alternative fuels. These fuels have an alkene (olefin) content of up to 50 wt.%. Unfortunately, there are currently no methods for detailed quantitation of olefins in such concentrations. This talk aims to introduce a novel method applicable for the characterization and quantitation of aliphatic olefins in complex oils from plastic depolymerization, alternative, and petroleum-based fuels using GC×GC with a flame ionization detector. The talk also introduces teaching strategies for GC×GC technique inclusion to the laboratory portion of class syllabi.

KL02

CHALLENGES TO ACHIEVE UNSUPERVISED OPTIMIZATION OF HEART-CUT AND COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY SEPARATIONS

Tijmen Bos¹, Jim Boelrijk², Stef Molenaar², Dwight Stoll³, Bob Pirok^{2,3}

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Abstract

One and two-dimensional liquid chromatography (LC) technology is making remarkable advancements, however the number of potential users remains lagging behind for 2D separations. A prime obstacle for large-scale usage is the considerable investment needed for method development and data processing. Automation in any step of the method development reduces the required investment.

Recently a comprehensive, modular, closed-loop and interpretive algorithm for automated LC method development for complex samples of unknown composition was developed. The idea of these computer platforms is that they can directly and iteratively program the LC with new method parameters obtained from previous raw experimental data until convergence of a specified objective function was reached. Using peak tracking, multi-start regression, retention modelling and Bayesian optimization, such algorithms are capable to automate the selection of several method parameters.

This presentation will discuss the current challenges to scale this automated method development technology to heart-cut and comprehensive 2D-LC separations.

KL04

ASSESSMENT OF FRUIT QUALITY THROUGH VOLATILE ANALYSIS USING SPME AND THERMAL DESORPTION WITH GC×GC-TOFMS

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Apeel, Santa Barbara, USA

Abstract

Apeel uses plant derived materials that exist in nature to create a protective barrier that seals moisture in and keeps oxygen out. This allows our produce to last twice as long, leading to less waste throughout the supply chain.

Fruit quality can vary throughout growing seasons because of a multitude of factors such as climate, region of growth, soil and other environmental conditions. Determining incoming fruit quality can help impact the reliability of Apeel products. In nature, animals have been able to do this through characteristics such as enhanced vision and senses of smell. Volatile compounds play an important role in fruit physiology and metabolism and understanding their role can enable us to determine the quality of produce.

To measure these volatiles, we utilize sample enrichment and collection techniques such as SPME and thermal desorption, separation by GC×GC, and detection with mass spectrometry (TOFMS). Volatile collection through thermal desorption tubes on whole fruit allows for a non-destructive measurement, and the ability to study the fruit throughout its lifetime. This, paired with destructive measurements using SPME furthers our efforts to gain a fundamental understanding of the relationship between volatiles and quality.

Here, we demonstrate the application of these techniques to understand how volatile production of mangos relates to quality under anaerobic conditions. These conditions are a leading cause of off-flavors in these fruits. Further, the use of this comprehensive technique allows for modeling this process and identifying compounds of interest related to the onset of off-flavors.

Oral - OL01

SYSTEMATIC STUDY OF A SELECTIVE COMPREHENSIVE TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY INTERFACE WITH ACTIVE SOLVENT MODULATION TO OVERCOME THE MOBILE PHASE INCOMPATIBILITY BETWEEN HILIC AND RPLC

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Abstract

Two-dimensional liquid chromatography (2D-LC) is becoming increasingly popular for the analysis of complex samples, which is partly due to the recent introduction of commercial 2D-LC systems. One of these systems employs active solvent modulation (ASM) to deal with the mobile phase incompatibility between highly orthogonal retention mechanisms, such as hydrophilic interaction liquid chromatography (HILIC) and reversed-phase LC (RPLC). However, clear recommendations or guidelines regarding the optimal use of ASM are not available. Therefore, this study investigates possible configurations for the modulation of HILIC and RPLC using ASM in a selective comprehensive 2D-LC set-up (sHILIC x RPLC) to suggest guidelines for future users. Using a representative sample, the filling percentage of the sample loops and their loading/unloading configuration, the duration of the ASM phase and the dilution factor (DF) are investigated and optimized. It is observed that maintaining the sample loop filling at maximum 25%, unloading it in backflush mode, and using a DF of 10 with the shortest possible ASM phase results in the best peak shapes, intensities and recoveries for early eluting peaks, while keeping the analysis time minimal. Based on these results, some general recommendations are made: reduce the sample loop filling, the DF, and the duration of the ASM phase as much as possible, and operate in BF mode, in order to improve peak shapes and save analysis time. These recommendations could also be applied to other 2D-LC modes, such as LC x LC and LC – LC, and other chromatographic combinations with mobile phase incompatibility issues.

Oral - OL02

PROTOTYPING MICROFLUIDIC DEVICES FOR SPATIAL MULTI-DIMENSIONAL LIQUID CHROMATOGRAPHY BY USING DIGITAL LIGHT PROCESSING 3D-PRINTING

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Abstract

Spatial multi-dimensional liquid chromatography (MD-LC) is an emerging separation technology that potentially offers unprecedented resolving power. The maximum peak capacity that can be generated corresponds to the product of the multi peak capacities of the individual development stages, provided that orthogonal retention mechanisms are applied. Furthermore, analysis time is very short compared to conventional 2D-LC or 3D-LC systems, since all fractions in the second and third dimensions are analyzed in parallel. This novel separation concept requires the construction of a device in which analytes are separated by their position in a three-dimensional separation space. Digital light processing (DLP) 3D printing is one of the best suited techniques for the fabrication of complex microfluidic devices with many interconnected microchannels, as encountered in spatial MD-LC.

DLP 3D printing fabrication parameters were examined and optimized targeting the fabrication a spatial 2D-LC chip containing an interconnected microchannel structure allowing to perform isoelectric focusing followed by size-exclusion chromatography (IEF x SEC). of intact proteins. The effects of exposure time and layer thickness on printing resolution, microchannel geometry, and surface roughness were investigated. A novel methodology for localized synthesizing UV-photoinitiated polymer monolithic frits in-situ in microdevices created from a UV absorber 3D-printing resin was developed. Additionally, the parallel microchannels were packed with 5 μm SEC particles and employed for the separation of intact proteins. In the presence of organic solvents, the pressure resistance of the 3D-printed chips was found to be approximately 230 bar.

Oral - OL03

HYPHENATION OF TEMPERATURE-RESPONSIVE CHROMATOGRAPHY AND ULTRAFAST CHIRAL CHROMATOGRAPHY AS A GENERIC COMPREHENSIVE TWO-DIMENSIONAL METHOD FOR THE ANALYSIS OF CHIRAL PHARMACEUTICALS

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Abstract

Chirality is a prevalent property found in nature, caused by the presence of a (carbon) chiral center in a molecule. Many molecules with different chirality greatly vary in their chemical properties, therefore the ability for separation and detection of these molecules is of utmost importance in the biomedical and pharmaceutical industries.

However, obtaining effective separation of chiral analytes in complex (biological or synthetic) samples requires high resolving power. Which can be theoretically achieved by Comprehensive two-dimensional liquid chromatography (LC x LC), as this technique would allow for a large increase in peak capacity per unit of time. However finding appropriate solvents for the second dimension might be difficult. The slow speed of chiral separations, on the other hand, has hampered the use of chiral stationary phases as the second dimension in 2D-LC.

In this study, the enantioselective separation of a wide range of medicinal substances (log p: 0.9-4.1) is evaluated using a combination of temperature-responsive and reversed-phase chiral liquid chromatography. Temperature-responsive liquid chromatography (TRLC) in the first dimension enables analysis in purely aqueous conditions, allowing for complete (and more general) focusing of organic solutes prior to second-dimension separation. By combining this with small particle (sub-2 micron) based chiral stationary phases as the second dimension in TRLCxChiral-RPLC, a chiral screening platform may be built, which in principle has a lot of potential for tackling chiral screening challenges

Oral - OL04

LC-GC×GC-TOF MS/FID: A POWERFUL MULTIDIMENSIONAL TECHNIQUE FOR AUTOMATED AND RELIABLE CHARACTERIZATION OF COMPLEX SAMPLES

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Abstract

The introduction of multidimensional and comprehensive techniques has revealed that complex samples can be hidden behind apparent simple ones. This understanding has pushed many scientists to study possible approaches for further boosting separation power, mainly by adding extra dimensions. This presentation will focus on the potentialities of a fully integrated and validated LC-GC×GC platform coupled with a parallel dual detection, i.e., ToFMS and FID. The coupling of an LC system with a GC one was first published by Majors in 1980 and the first automated commercial instrument (Dualchrom 3000) was introduced in 1989 by Carlo Erba (Italy). The LC-GC systems were intensively studied in the 1980s and 1990s by Grob and his group, but the system was almost abandoned later. In 1991 Phillips introduced the comprehensive two-dimensional technique (GC×GC), a powerful technique that gained immediate attention and is still growing exponentially. The integration of the two two-dimensional techniques provides exponential benefits with an easy, robust and validated setup. The LC-GC×GC platform can provide an enhanced characterization of complex samples reaching efficient sample clean-up and/or a group-type separation of the analytes in the LC dimension and enhanced separation in the GC×GC dimension. It has been proved very useful to improve not only the full characterization of complex samples but also to simplify sample pre-treatment and provide more robust and validated routine analysis, particularly in the challenging topic of mineral oil analysis in food.

Oral - OL05

DEVELOPING ADVANCED CHEMOMETRIC ANALYSIS METHODS FOR GC×GC-TOFMS TO FACILITATE IN-DEPTH JET AND ROCKET FUEL CHARACTERIZATION

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Abstract

Kerosene-based jet and rocket fuels are critical to the success of the aerospace propulsion industry. There is an ongoing need to assess fuel composition more fully for the purpose of improving quantitative connections between fuel composition, properties, and system performance. Addressing this challenge benefits from implementation of two-dimensional (2D) gas chromatography with time-of-flight mass spectrometry detection (GC×GC-TOFMS) coupled with robust chemometric data analysis tools. Working in the framework of implementing tile-based Fisher ratio (F-ratio) analysis, which discovers differences between sample classes, we have developed methodology to determine pure mass channels for discovered analytes for rapid and accurate quantification, which can be leveraged to facilitate class comparison-enabled mass spectrum purification (CCE-MSP) to obtain the pure mass spectrum for confident identification of discovered features. Since polar compounds play an important role in thermal performance, developing tools for determining the polar content is paramount. To this end, we have implemented solid phase extraction (SPE) with GC×GC-TOFMS and tile-based F-ratio analysis, and more recently 1v1 analysis, which requires only one chromatogram per class to discover class distinguishing compounds, to comprehensively categorize the fuel components due to bulk hydrocarbons and/or to minor polar compounds. Lastly, these approaches are integrated to gain an in-depth understanding of the SPE sampling for these fuels. By analyzing sequential fractions of fuel passed through a SPE cartridge we discover, identify, and quantify analytes affected by SPE using either silica or alumina phases. Ultimately, this research leads to improved SPE sampling of targeted polar compounds.

Oral - OL06

COMPREHENSIVE ANALYSIS OF VEHICLE EMISSIONS USING THERMAL DESORPTION (TD) AND GC×GC–TOF MS

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Abstract

With the increased uptake of hybrid and electric vehicles, the impact of non-exhaust emissions is of growing concern for human health and the environment. It is now important to obtain a comprehensive view of all possible sources of volatile organic chemicals (VOCs) from vehicles, including emissions from materials, such as foam, carpeting and trimmings, as well as those generated through tyre wear.

The recent global push towards a circular economy has also meant that automotive manufacturers are being urged to improve the sustainability of their operations by increasing the use of recycled or renewable materials, such as innovative plant-derived plastics. Robust quality control is therefore essential to ensure these novel products will not produce volatile emissions that could be considered harmful or malodorous.

However, the sample and matrix complexity, as well as an ever-expanding list of compounds of concern makes it challenging for those responsible for performing sampling and analysis. This has led to a need for innovative new methods to be created for complete emissions characterisation.

Here, we will demonstrate the use of thermal desorption (TD) for versatile sampling of emissions from exhausts, vehicle interiors and tyres. When coupled with GC×GC–TOF MS and novel chemometric analysis, this provides improved chemical fingerprinting of emissions to enhance our understanding of how vehicles may impact the environment and human health.

We will show how this future-proof system can go beyond current regulations to help accelerate research and development and guide the automotive industry towards better strategies to limit environmental impact.

Oral - OL07

QUALITATIVE SCREENING OF CATALYTIC PYROLYSIS WOOD-OIL BY MEANS OF GC×GC-TOFMS AND SOFT IONIZATION

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Abstract

The use of lignocellulosic biomass to produce chemicals and fuels through pyrolysis has gained increased attention in the last decades due to its abundance, renewable nature, and composition. 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, bidimensional gas chromatography (GC×GC) coupled to time-of-flight mass spectrometry (TOFMS) and supported by soft ionization has been exploited for the characterization of volatile and semi-volatile compounds in catalytic pyrolysis wood oil. The conventional, nonpolar at 1D and a polar at 2D, column set even promoted a structure-ordered chromatogram, especially in terms of naphthenes and aromatics, the reverse-phase combination allowed to better solve oxygenated compounds, which were previously gathered eluted with neighboring aromatics peaks. By understanding the soft ionization spectra insights into the structure of phenol monomers were achieved and a group-type analysis was obtained thanks to the detection of the molecular ion by photoionization (PI). A range of aromatics (mono; di; tri) and naphthenes have been identified in wood-derived oil and the presence of phenols was readily different in bio-oils derived from catalytic pyrolysis processes. This approach allowed explaining the bio-oil composition and checking the efficiency of catalytic pyrolysis that has been applied to reducing the concentration of the oxygenated compound and obtaining a biofuel that could be used as an alternative to fossil-based fuels.

Oral - OL08

CHARACTERIZATION OF AUTOMOBILE MATERIAL EMISSIONS BY TD-GC×GC-TOFMS AND CORRELATION WITH ODOR HEDONIC PERCEPTION IN HUMANS

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Abstract

The study of pollutants and odorous molecules is of growing interest to automotive manufacturers within the frame of Vehicle Interior Air Quality (VIAQ) programs. The most common method to analyse material emissions is to heat them, collect their emissions on sorbent tubes, which are later thermally desorbed and analysed by gas chromatography coupled with mass spectrometry. This method is suitable for the target analysis of the dozen most intense molecules, but fails to uncover the true molecular complexity of the samples.

In the present work, we used a new instrumental configuration combining thermal desorption (TD), comprehensive bidimensional gas chromatography (GC×GC) and Time of Flight Mass Spectrometry (TOFMS) to elucidate the detailed composition of vehicle material emissions. This implied the testing of several column sets, including normal and reverse polarity configuration, and several second column dimensions, while managing constraints due to the TD coupling.

Over a hundred of potentially odorous polar compounds were observed for each sample, which would not have been possible on monodimensional GC due to low intensities and coelutions with apolar compounds present in large amount.

The material samples were also presented to an untrained panel of human noses while collecting their hedonic perception and semantic descriptions, in the aim of establishing links between the material emissions and perception. According to their subjective hedonistic rating, materials were classified into two groups, and this classification was compared to objective olfactomotor data.

Oral - OL09

MODULAR SIMULATION OF COMPLEX GAS CHROMATOGRAPHIC SYSTEMS

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Abstract

A modular simulation for complex gas chromatographic systems is presented. It is based on the one-dimensional simulation of GC (GasChromatographySimulator.jl, [1]), which also allows for the simulation of gradients of the temperature along the column, gradients of the column diameter and gradients of the film thickness.

With the combination of different modules, like `GC Column`, `Transfer Line`, `Thermal Modulator`, `Flow Modulator` and `Pressure Regulators`, complex GC systems can be constructed. Also, multidimensional systems, like GCxGC and GCxGCxGC, even with multiple detectors are possible to set up. The migration and separation of the solutes through the different modules are simulated using the GasChromatographySimulator.jl. The results, retention time and peak width, at the end of one module are used as starting conditions for the next module.

To simulate such a system, it is necessary to know the flow throughout the system over the whole time of the program. Tools of graph theory are used to set up the equations to calculate the pressures of the mobile phase at the connections of the modules. With the knowledge of these pressures the flows through each module can be calculated. Therefore, the presented software is also a flow calculator for any GC system consisting of the used modules.

The simulation and the flow calculator will be presented on several examples of multidimensional GC systems to demonstrate its flexible usage.

[1] Leppert, Jan (2022): GasChromatographySimulator.jl. In: JOSS 7 (76), S. 4565. DOI: 10.21105/joss.04565.

Oral - OL10

SIMULATING GC×GC-TOFMS DATA WITH REALISTIC RUN-TO-RUN SHIFTING TO EVALUATE THE ROBUSTNESS OF CHEMOMETRIC SOFTWARE

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Abstract

We report a workflow to simulate GC×GC-TOFMS datasets with realistic run-to-run retention time shifting which are used to evaluate the robustness of chemometric software to shifting. By using simulated data, chromatographic modeling variables such as the amount of shifting, crowdedness (i.e., saturation), and peak area RSD% could be systematically varied. Data were shifted between runs by using low frequency "shift functions", which were compared to the shifting observed in a yeast metabolomic study to ensure the results were generalizable to real data. We focused on the evaluation of tile-based *F*-ratio analysis (FRA), a supervised, non-targeted analysis tool which segments chromatograms into "tiles" and uses the ANOVA *F*-ratio to identify regions containing class-distinguishing analytes, output into a table (i.e., "hit list"). A broad range of simulation parameters were tested to thoroughly evaluate the robustness of tile-based FRA to run-to-run shifting. For each set of simulation conditions, a broad range of tile sizes (a user-selected software input) were tested. The simulated datasets were then submitted to FRA. Since each hit in the FRA hit list was known a priori as either a true or false positive from the simulation, receiver operating characteristic (ROC) curves could be made and used to quantify the discovery "success" for all combinations of the modeling variables. Using these results, recommendations for tile size selection and experimental design are provided, and further supported by comparison to the results to previous applications. Finally, extensions of the simulation method to evaluate the robustness of other chemometric methods are investigated.

Oral - OL11

AUTOMATED ALIGNMENT FOR QUANTITATIVE PAIRWISE DIFFERENCING OF TWO-DIMENSIONAL CHROMATOGRAPHY DATA

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Abstract

Identifying chemical differences among samples is useful for process monitoring, sample classification or identification, correlative determinations, and other important tasks. Multi-dimensional chromatography (including GCxGC and LCxLC) is a powerful technique for highly effective chemical separations of complex mixtures, but it also produces highly complex data that require both interactive and automated comparative analysis methods.

One common case is to compare two types of samples to determine similarities and differences. Our existing side-by-side interactive differencing tool provides both comparative visualization of chromatograms and comprehensive characterization of sample differences down to individual peaks. It allows comparing chemical differences between two samples qualitatively and quantitatively. However, it requires that the analyst specify an initial peak correspondence in order to compute a transform from one retention time space to the other.

We propose a new automated matching algorithm that combines computer vision image registration techniques with the peak matching algorithm utilized in our Investigator framework. Computer vision-based registration provides an intuitive and unsupervised way to identify and match patterns across entire raw chromatograms. This registration computes an initial transform to seed our peak matching algorithm. The peak matching algorithm identifies and matches reliable peaks based on several criteria including retention time distance and spectral match scores. This matching is used to compute a refined transform that is then provided to the side-by-side interactive differencing tool in order to compare the chromatograms. We demonstrate the technique to compare across different samples as well as across different detectors using the same sample.

Oral - OL12

A NEW GENERATION HIGH RESOLUTION MS FOR GCxGC ANALYSIS

John Dane, Robert Cody

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Abstract

In this presentation, we will discuss a newly redesigned high-resolution time-of-flight mass spectrometer for GCxGC-HRMS analysis. This new HRMS features increased resolving power ($R > 30,000$) and high mass accuracy (< 1 ppm) while also offering a variety of ionization techniques that include electron ionization (EI) as standard with the system as well as three optional soft Ionization methods -- chemical ionization (CI), photoionization (PI), and field ionization (FI). Additionally, there are 2 combination ion sources (EI/FI/FD and EI/PI) that allow for switching between hard and soft ionization without breaking vacuum. Several applications will be presented to highlight the capabilities of this new-high performance HRMS when combined with GCxGC.

Oral - OL13

BLUEBERRIES AND WHEAT AND BEER, OH MY! ADVENTURES IN THE APPLICATION OF GC×GC TO FOODOMICS*

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Abstract

Due to GC×GC's unique capabilities for delivering separations of complex mixtures of small, organic molecules, it is no surprise that it is a key technology for the agri-food industry. After all, much of the sensory experience related to the food we love to eat is dependent upon its aroma, which is a direct result of mixtures of small, organic molecules. Whether for our gastronomic pleasure (blueberries), or to protect a plant from insect predation (wheat), GC×GC can provide insight into plant metabolism, aiding breeders looking to develop improved lines of crops, be it for flavour or yields. The need for GC×GC in foodomics continues beyond the fields, as exemplified by its use profiling the aromas of spontaneously fermented beers, supporting a multi-omics study of yeasts with the goal of developing new, interesting genetics for the brewing industry.

Scientific advancements in these areas made possible by GC×GC will be highlighted, along with some of the challenges being faced (and solutions being developed) as GC×GC takes a leading role in large omics studies with samples numbering in the thousands.

*This presentation may contain traces of coffee and/or other food/agricultural products beyond those listed in the title.

Oral - OL14

LAGER BEER FLAVOUR PROFILING BY STIR BAR SORPTIVE EXTRACTION, GC×GC SEPARATION AND TIME-OF-FLIGHT MASS SPECTROMETRY

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RIC, Kortrijk, Belgium

Abstract

Beer is one of the most popular beverages in the world. Its specific flavour is the result of the interaction of compounds from hops, grain and yeast during the brewing process. Identification of these compounds and determination of their influence on the overall quality of the beer is highly challenging due to the very high number of organic compounds present. Moreover, some compounds with low odour threshold values and high sensory impact are difficult to identify due to co-elution with major odour-inactive compounds. Accurate beer flavour profiling is important for brewers to optimize beer production and to guarantee odour quality and taste stability of the final products. This is especially the case for pale lager beers that represent the beer type with the largest worldwide production volume and consumption.

Efficient extraction is mandatory in flavour analysis of beer. In a previous study we have shown that stir bar sorptive extraction (SBSE), a solvent-free extraction method, is highly efficient for beer flavour profiling [1]. Combined with conventional (1D) GC separation and TOFMS detection it was possible to identify already over 400 flavour relevant compounds. In the current study, combination of SBSE extraction with a multidimensional separation, namely GC×GC, was used in trying to further increase the knowledge on the flavour profile of different brands of Belgian lager beer. The performances of GC-TOFMS and GC×GC-TOFMS are compared for in-depth flavour profiling and differentiation of lager beers.

Oral - OL15

CHROMATOGRAPHIC FINGERPRINT OF *PISTACIA VERA* FRUITS: AN AROMATIC TOUR AROUND THE WORLD

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Abstract

Aroma is a key organoleptic characteristic of pistachio that determines its quality and consumer acceptance. As for natural products, the aroma is highly dependent on many variables such as the cultivar, geographical origins, harvesting conditions and storage. Most of the pistachio production comes from countries with a warm, arid climate, indeed, the world's leading producers of pistachio are Iran, the United States (USA), Italy, Greece, Tunisia, Turkey, Syria, and Spain. Determining their characteristic aroma fingerprints is essential not only from a consumer acceptance viewpoint but also for standardizing pistachio-based product production in industries. In the present study, the volatile organic compounds (VOCs) of pistachio from different geographic origins, were evaluated. To perform this evaluation, a high-capacity concentration (HCC) tool, named HiSorb™, was used. HiSorb™ bridges the gap between solid phase micro-extraction (SPME) and stir bar sorptive extraction (SBSE); increasing sensitivity and repeatability, thanks to an automated and easy handling interface. Different HiSorb™ probes were evaluated to obtain the best results, as well as temperature and time of extraction. VOCs extracted with HiSorb™ were successively analyzed with two-dimensional comprehensive gas chromatography-mass spectrometry (GC×GC-MS), equipped with a reversed fill/flush flow modulator. The use of multidimensional gas chromatography allows an enhancement of separation power and maximises the level of information extracted, obtaining in this way a chromatographic fingerprint of pistachio's VOCs.

Oral - OL16

DETERMINATION OF XENOBIOTICS IN FOOD SAMPLES THROUGH REDUCED SAMPLE PREPARATION COUPLED TO CRYOGENIC-MODULATION GC×GC COMBINED WITH TRIPLE-QUADRUPOLE MASS SPECTROMETRY

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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 oils by using cryogenic-modulation comprehensive two-dimensional gas chromatography (CM GC × GC) combined with triple quadrupole mass spectrometry (QqQMS). The higher sensitivity of CM GC × GC, compared to one-dimensional GC, and the enhanced specificity of QqQMS, allowed the determination of xenobiotics in a simple manner in vegetable oil samples, with no need for analyte pre-concentration. Analyte introduction onto the first dimension column was performed through a programmed-temperature vaporizer. The exploitation of cryogenic modulation and QqQMS (in the multiple-reaction-monitoring mode) eliminated the need for a target-analyte concentration step. Furthermore, the use of two analytical columns with 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 sample contaminants, in relation to maximum residue limits set by the European Union.

Oral - OL17

THE USE OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY FOR PHARMACEUTICAL APPLICATIONS: INVESTIGATION OF COMPLEX DRUGS.

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Abstract

GC×GC has been used for more and more applications since its introduction in the 1980s. While it has become routine in areas such as fossil fuels and environmental studies, and is at least an integral part of research in other areas, its use in other areas is virtually undocumented. One of these areas is the analysis of pharmaceuticals. Not only is there still no harmonized method based on GC×GC used in the pharmaceutical industry, but also just very isolated proof-of-concept studies that can be found in the scientific literature.

In the first part of the presentation, we will briefly summarize the studies published so far and discuss possible reasons why GC×GC has not yet become established in the pharmaceutical field. In the second part, we will present a recent study in which GC×GC-high-resolution mass spectrometry was used to investigate the active pharmaceutical ingredient (API) sodium bituminosulfonate (SBS). The pharmaceuticals with the API SBS can tentatively be counted among the class of non-biological complex drugs (NBCD). Therefore, by definition, SBS cannot be comprehensively investigated by a single or -combined physiochemical method so far.

The results of our study show the advantages of the application of GC×GC but also its complexity. Special attention is given to the use of GC×GC for non-targeted analysis and the demands this implies in terms of method validation when the method is to be applied in the pharmaceutical field.

Oral - OL18

TWO-DIMENSIONAL GAS CHROMATOGRAPHY-BASED TECHNIQUES FOR LIPIDOMICS INVESTIGATIONS

Marco Beccaria

DOCPAS, University of Ferrara, Ferrara, Italy

Abstract

Lipids, organic compounds containing hydrocarbon chains, are molecules essential for the structure and function of living cells. They comprise a wide range of structures, characterized by predominantly non-polar and hydrophobic molecular skeletons. However, some exhibit a slight polar or hydrophilic character, giving them amphiphilic properties. Lipids can provide useful information in different fields of chemistry such as the origin of and overall quality of a food product (food chemistry), the physiological state of an individual (clinical chemistry), and the quality of biodiesel (petrol chemistry).

Two-dimensional gas chromatography (GC×GC) methodology, combined with dedicated sample preparation techniques, has been applied to investigate different lipid fractions, namely total fatty acid profile and minor lipid components.

Total fatty acid methyl esters (FAMES) were prepared using a single-step microwave-assisted extraction and derivatization coupled to a flow modulation GC×GC- flame ionization detector. The entire procedure was evaluated according to the PrepAGREE metric for greenness and comparable with reference methods.

Minor lipid components, which represent between 1-5% of total lipid components, have been fractionated and focalized from the lipid matrix by preparative liquid chromatography before GC×GC-high resolution mass spectrometry investigation, leading to the identification of different chemical classes (e.g., intact fatty acids, fatty alcohol, sterols) that together can be considered as the fingerprint of a lipid sample.

Finally, an explorative study on the advantages of using GC×GC for characterizing intact lipid samples (acylglycerols) from different origins has been carried out proving fascinating potential.

Oral - OL19

METHOD DEVELOPMENT AND OPTIMIZATION FOR MONITORING PROBE EXHALED BREATH METABOLITES USING PARALLEL MS-BASED ANALYTICAL PLATFORMS

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Abstract

The high potential of exhaled breath for disease diagnosis has been highlighted in numerous studies. However, exhaled breath analysis is suffering from a lack of standardized sampling and analysis procedures, impacting the robustness of inter-laboratory results, and thus hampering proper external validation. The aim of this work was to verify compliance and validate the performance of two different comprehensive two-dimensional gas chromatography coupled to mass spectrometry platforms in different laboratories by monitoring probe metabolites in exhaled breath following the Peppermint Initiative guidelines. An initial assessment of the exhaled breath sampling conditions was performed, selecting the most suitable sampling bag material and volume. Then, a single sampling was performed using Tedlar bags, followed by the trapping of the volatile organic compounds into thermal desorption tubes for the subsequent analysis using two different analytical platforms. The thermal desorption tubes were first analyzed by a (cryogenically modulated) comprehensive two-dimensional gas chromatography system coupled to high-resolution time-of-flight mass spectrometry. The desorption was performed in split mode and the split part was recollected in the same tube and further analyzed by a different (flow modulated) comprehensive two-dimensional gas chromatography system with a parallel detection, specifically using a quadrupole mass spectrometer and a vacuum ultraviolet detector.

Oral - OL20

NOVEL PIPELINE FOR ELUCIDATION OF HIGH-LEVEL CHEMICAL MECHANISMS USING NON-TARGETED ANALYSIS BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY

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Abstract

We aim to simplify complex data to elucidate high-level mechanisms of engineering processes using non-targeted (NT) analysis by two-dimensional gas chromatography coupled with mass spectrometry (GCxGC-MS). We present here sample and data pipelines to describe chemical transformations of by-products during the underground gasification of coal. By using NT analysis, chemical signatures and chemical markers of the reactions can be identified and related to the reaction conditions and parameters.

We focus here on the formation of semi-volatile organic compounds (SVOCs) during underground coal gasification (UCG) from two different experimental set-ups. Coal tar samples were collected from a shallow in situ UCG experiment and processed (or waste) waters from two ex situ experiments. The sample workflows include, for each type of sample, novel ultra-sound assisted exhaustive extraction and an adapted GCxGC chromatographic method. The data pipeline comprises tile-based alignment, Fisher ratio selection of features, sample normalisation and clustering of compounds rather than samples using affinity propagation. Affinity propagation is a clustering algorithm based on "message passing" between data points. The clusters grouped together compounds that have the same reaction kinetics patterns. It enabled us to better describe the coal gasification processes compared to the quantitative analysis of targeted compounds and to identify markers or exemplars of the reactions that could be used in future experiments to monitor progress and yield.

Oral - OL21

BURSTING THE CHROMATOGRAPHIC FINGERPRINT BY COMBINING VACUUM-ASSISTED HEADSPACE, MULTI-CUMULATIVE TRAPPING SPME, AND GC×GC

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Abstract

HS-SPME is an easy, solvent-free and selective technique for the analysis of semi- and volatile compounds. For the latter, long equilibration times are needed, which are typically shortened for routine applications. Therefore, a compromise between sensitivity and extraction time is necessary.

Two approaches have been recently proposed to improve extraction kinetics and thus the overall extraction yield: vacuum-assisted HS-SPME (Vac-SPME) and multi-cumulative trapping SPME (MC-SPME). Vac-HS-SPME showed a similar or an increment of extraction yield using a shorter time and milder temperature compared to conventional HS-SPME conditions [1]. Also MC-SPME has the potential to improve the overall sensitivity by using a cumulative shorter extraction time compared to a single long one [2]. In both cases, the extraction of semi-volatile has been significantly improved compared to the traditional approach allowing for a more comprehensive definition of the aroma profile.

In this work, we present the bursting combination of the two approaches, namely Vac-SPME and MC-SPME into Vac-MC-SPME, along with the enhanced separation capability provided by multidimensional comprehensive gas chromatography (GC×GC) and an advanced tile-based data handling. The synergic effect was shown by comparing the results with each of the two sampling techniques separately using targeted key compounds for the olive oil aroma definition. Moreover, the entire chromatographic fingerprint obtained in GC×GC was used to discriminate the different olive oil quality, comparing the performance of the three approaches, namely Vac-SPME, MC-SPME, and Vac-MC-SPME.

Oral - OL22

APPLICATION OF A UNIQUE DUAL DETECTION GC×GC-TOFMS/FID SETUP FOR RELIABLE QUALITATIVE AND QUANTITATIVE FRAGRANCE ANALYSIS

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Abstract

Fragrances are composed of tens or hundreds of ingredients, selected from a palate of thousands. The identification and quantification of individual species in a fragrance is challenging, and using numerous standards is not practically efficient. Therefore, a dual workflow is commonly employed using MS for identification and FID, with effective carbon number correction factors applied, for quantification. Additionally, due to the complexity of these samples, two analyses are often required to isolate the individual compounds; one using polar and another using a non-polar GC separation.

Here, we demonstrate a possible improvement to this workflow, using a prototype GC×GC-TOFMS/FID instrument. GC×GC provides enhanced chromatographic separation of individual analytes, removing the requirement for two separate 1D assays. Applying dual detection, using MS and FID, enables both identification from MS data and quantification via the FID. Quantification accuracy can be affected with many fixed or EPC splitters due to variation of the split ratio across the analytical run. The prototype instrument used in this study, uses a reverse fill flush modulator, allowing total transfer of the primary effluent to the secondary column, and a controlled splitter that maintains a consistent split ratio between the MS and FID. These characteristics help to ensure that biases are not introduced from changing split ratios over the course of the chromatographic separation, which could skew quantification results. Novel algorithms that align the MS and FID peaks facilitated data interpretation. Various fragrances were analyzed, with reliable analyte identifications and quantifications demonstrated from single injections.

Oral - OL23

EXPLORING THE CUP OF COFFEE USING GC×GC-MS COMBINED WITH MULTIPLE COMBINATION OF HEADSPACE EXTRACTIONS

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Abstract

The coupling of high-concentration capacity headspace extraction (HCC-HS) with gas chromatography (GC) and in particular with comprehensive multidimensional GC (GC×GC), has played a fundamental role to enhance significantly the level of information that can be extrapolated from a chromatographic fingerprint.

The aim of this presentation is to elucidate the potentiality of such a coupling and its further development to answer food-related questions. In this respect different approaches have been investigated, starting from different tools, namely SPME and HiSorb (higher sorbent volume), different coatings of extraction (liquid or porous sorbent or a combination of them), as well as the recently presented multi-cumulative trapping approach combined for both tools (i.e., SPME and HiSorb). The information obtained were elaborated separately, as well in different combination to evaluate comprehensively the aroma profile of an espresso coffee, in particular in relation with the different capsule materials used.

Flash - FL01

SIMPLIFYING METHOD DEVELOPMENT FOR ROUTINE PETROLEUM ANALYSIS USING FLOW-MODULATED GCxGC-MS/FID

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Abstract

Published in 2022, the flow-modulated GCxGC-FID ASTM Standard Test Method D8396 for Group-Type Quantitation of Hydrocarbons in Hydrocarbon Liquids demonstrates that GCxGC is gaining acceptance as a routine technique in the petroleum industry. With this acceptance comes the expectation for easy-to-understand, user-friendly interfaces and robust hardware that reliably provides full transfer of analytes throughout the separation space for accurate quantitation of chemical species that correlate to bulk physical properties of petroleum products. Preliminary results from testing both gravimetric standards and a variety of reference aviation and diesel fuels evaluate a variety of method parameters crucial to providing proper transfer of analytes from the primary to secondary column when using flow modulation. Clear workflows that simplify GCxGC method development for reverse fill-flush flow modulation are optimized for easier adoption in routine laboratories. Additional support in characterization of samples is provided using a prototype GCxGC-TOFMS/FID instrument which is equipped with a novel splitter design that ensures a consistent split ratio between the MS and FID detectors to avoid erroneous area percent determinations as well as a novel peak alignment algorithm that simplifies identification of FID peaks using corresponding MS spectra to assist in drawing regions for more accurate group-type quantitation of chemical classes.

Flash - FL02

RENEWABLE GASES EXPLORATION BY TD-GC×GC-TOFMS

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Abstract

In the context of the energy transition, the French gas network is diversifying to include renewable gases from innovative processes such as pyrogasification implemented at the moment in R&D pilots. Pyrogasification consists in heating solids such as biomass or Solid Recovered Fuel at high temperatures from 600 to 900°C. Yet, the detailed composition of the produced gas is far from being well known because focus is generally put on the analysis of major components. A better knowledge in the detailed composition of the produced gas is mandatory to adapt the purification steps. The aim of the present study was to characterize trace organic compounds, including alkanes, aromatics, oxygen-organic compounds, halogenorganic compounds and sulfur-organic compounds, at different steps of the process, by thermal desorption GC×GC-TOFMS.

First, a sampling system was investigated to ensure the representativity of the collected sample. Then, the TD-GC×GC-ToFMS method was developed to take into account the presence of a high content of light alkanes (C2 – C14) in the samples. To do this, the cryogenic modulation system has been optimized concerning the duration of cold and hot jets. A compound family approach, based on the use of one reference compound by chemical family, was proposed to perform a quantification by equivalent on real samples and map volatile organic impurities in biosourced gases. Finally, this method allowed the comparison of the composition of several real renewable gases from different inputs. The highlighting of specific differences in their composition was performed using a tile-based Fisher Ratio analysis.

Flash - FL03

DISCOVERING COMPOSITIONAL DIFFERENCES BETWEEN AEROSPACE FUELS USING COMPREHENSIVE TWO-DIMENSIONAL CHROMATOGRAPHY WITH TIME-OF-FLIGHT MASS SPECTROMETRY AND CHEMOMETRICS

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Abstract

The chemical composition of aerospace fuels directly impacts system performance, reliability, and operability. Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) has become a vital platform for characterizing the composition of these fuels to ensure regulatory compliance. However, the use of GC×GC-TOFMS to characterize these aerospace fuels can create a large amount of data for an analyst to manually interpret. Therefore, chemometric workflows are necessary to quickly reveal significant chemical information regarding the composition of these fuels. Herein, we demonstrate the use of an unsupervised feature selection algorithm to find analytes that correlate to the performance of aviation turbine fuels and kerosene-based rocket propellants. In contrast to supervised methods, which use class labels to discover analytes related to those differences, unsupervised approaches can uncover various chemical relationships hidden in the data. Visual interpretation and additional chemometric models will provide further insight into the relationship between the physical properties of the fuels and the differences discovered in their chemical composition. Ultimately, the presented workflow will aid in the continued effort to improve data analysis methods for discovery-based experimentation.

Flash - FL04

FOOD METABOLOMICS BY GC×GC-TOF MS AND TANDEM IONIZATION: UNDERSTANDING THE IMPACT OF CLIMATE EVENTS ON EDIBLE CROPS QUALITY

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Abstract

A better and comprehensive understanding of the relationship between climate conditions and nutrition is necessary to provide the human population with safe and secure access to food. The goal of the current study is to understand the effects of climate change on the detectable metabolome of hazelnuts regarding alternative post-harvest practices, as well as defects indirectly caused by global warming such as insect migrations that affect the quality of both peanuts and soy crops. The analytical strategy, aligned to food-metabolomics principles, exploits the information potential of multi-dimensional analysis that combine physicochemical discrimination/separation of analytes with spectrometric detection, such as comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS) operating in Tandem Ionisation™. The process known as untargeted and targeted (UT) fingerprinting is used in combination with chemometric algorithms to highlight metabolomic variations between composite-class images generated by re-alignment and fusion of raw data collected from samples belonging to distinct classes, thus highlighting metabolites pattern differences. Data fusion, obtained by merging hard and soft ionization data streams, is capable to increase the information potential by exploiting both the standard MS fragmentation and higher overall sensitivity of the hard ionization and the wider dynamic range of response with an increased signal-to-noise ratio typical of the soft ionization. Moreover, aroma precursors involved in the Maillard reaction such as amino acids (i.e., threonine, valine, and tryptophan) and reducing sugars (i.e., glucose, fructose, saccharose) of both peanuts and hazelnuts were investigated to understand the quality discrepancy in the roasted products.

Flash - FL05

SAMPLING BODY ODOR FOR HEALTHCARE MONITORING: THE NEED TO CONTROL INFLUENTIAL FACTORS

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Abstract

The human body constantly emits a lot of volatile organic compounds (VOCs) which are affected by numerous factors such as pathologies. This is why odor analysis can be a smart, non-invasive, and large-scaled way to perform health monitoring. Dogs have a very acute sense of smell, and are thus commonly used to perform olfactive detections. But since dogs are also likely to be disturbed by environmental conditions, it is important to confirm their detections through a more objective technic. Thermodesorption followed by comprehensive two-dimensional chromatography coupled with time-of-flight mass spectrometry (TD-GCxGC/ToFMS), with its high sensitivity and resolution, is indeed a good candidate for the analysis of a complex matrix such as body odor.

The first challenge lies in body odor sampling: the optimization of a sampling system, including an adsorbent, a holder and a fastening system, was required and had to consider the specific, unwanted emissions of these components. The type of sampling, through passive contact or without any contact with the skin, had also to be taken into account. Though most of the optimization was done on the armpits, we also cared to study body odor homogeneity by sampling other locations such as the inguinal area. As this type of sampling requires rigor, the impacts of other parameters such as hairiness have also been studied in order to optimize the whole process.

Flash - FL06

LIPID PROFILING OF BOAR TAINTED AND UNTAINTED PIG SERUM USING GC×GC-TOFMS

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Abstract

Boar taint is a strong, unpleasant smell or taste found in the meat of some uncastrated male pigs. The surgical castration of male piglets is a traditional practice to prevent boar taint meat worldwide. Furthermore, it is performed without anesthesia or analgesia, causing pain to the piglets. European pork production stakeholders agreed to prohibit surgical castration of piglets due to increased animal welfare concerns by 2018. These objectives are yet to be achieved successfully.

The aim of work was to understand the difference between boar-tainted (BT) pigs and untainted (UT) pigs based on the fatty acid profiling of pig serum using two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS).

In GC, conversion into a more volatile and stable component is essential to analyze saturated and unsaturated fatty acids. To improve measurement efficiency and obtain chromatographic separation of the lipids, a two-step sample extraction and derivatization (base-catalyzed transesterification and acid-catalyzed esterification) approach was optimized using DoE. The optimized condition has a composite desirability of 0.9159. A total of 40 pig serum samples were analyzed. The chemometric tests, unsupervised screening (PCA, HCA), univariate analysis (Volcano plot), and multivariate supervised analysis (PLS-DA) were performed.

The results suggested that the concentration of PUFA ω -6 and cholesterol derivatives were significantly increased in BT pigs, whereas SFA and PUFA ω -3 were increased in UT pigs. These differences in the lipid composition are opening new investigation routes to better understand boar taint deviation.

Flash - FL07

COMPUTATIONAL METHOD FOR UNTARGETED DETERMINATION OF CYCLING YEAST METABOLITES USING COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY TIME-OF-FLIGHT MASS SPECTROMETRY

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Abstract

A computational method for the untargeted determination of cycling yeast metabolites using a comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) dataset was developed. The yeast metabolomic cycle for the diploid yeast strain CEN.PK with a 5 hr cycle period relative to the O₂ concentration level is comprehensively examined to determine the metabolites that exhibit cycling. Samples were collected over only two cycles (10 hr with a total of 24 time-point sampling intervals at 25 min each) as an experimental constraint. Due to the limited number of cycles expressed in the dataset, a computational method was devised to determine with statistical significance whether or not a given metabolite exhibited a temporal signal pattern that constituted cycling in the context of the 5 hr cycle period. The computational method we report compares the experimentally obtained 24 time-point metabolite signal sequences to randomly generated signal sequences coupled with statistically based confidence level LOF metrics to determine whether or not a given metabolite expresses cycling, and if so, what is the phase of the cycling. Initially the GC×GC-TOFMS dataset was analyzed using tile-based Fisher ratio (F-ratio) analysis. Since there were 24 time-point intervals, this constituted 24 sample classes in the F-ratio calculation which produced 672 metabolite hits. Next, application of the computational method determined that there were 210 of the 672 metabolites exhibiting cycling: 55 identified metabolites and 155 unknown metabolites. Furthermore, the 210 cycling metabolites were categorized into four groups, and where applicable, a phase was determined.

Flash - FL08

RAPID DETECTION OF BACTERIA IN FOOD USING STATIC-HEADSPACE COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY (HS-GC×GC)

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Abstract

Microbial contamination of food is a serious threat to public health and a major hindrance to safe food production. Timely detection of pathogenic microbes is crucial for a secure food supply. Early detection of pathogenic microbes can minimise the spread of contaminated food, but current reliance on conventional culture-based methods is time-consuming and laborious. We postulated that detection of volatile organic compounds emanating from food samples (dairy milk) spiked with *Escherichia coli* (*E. coli*) might serve as putative markers to indicate *E. coli* presence. Our workflow employed quasi-stop-flow modulation headspace GC×GC to measure volatile organic compounds emanating from enriched milk samples spiked with *E. coli* and our investigation suggests that ethanol, 1-propanol, and acetaldehyde may be used as such markers.

Different incubation times (5, 10, 15, and 20 h) were investigated to determine the minimum enrichment time required to detect *E. coli*. Fifteen hours incubation proved adequate, with clear differentiation possible between spiked and control test solutions. Sample throughput was maximised by incorporating a back flushing step. Backflushing is readily achieved using the quasi-stop-flow column ensemble by reducing the GC inlet pressure to a value less than the second dimension (mid-point) pressure.

By using HS-GC×GC, the time-to-response can reduce by more than one-full day compared to the current conventional approaches at pre-enriched single-cell bacteria level. The developed method shows great promise to be utilised for rapid screening of microbial food contamination. Further work must investigate marker compounds for a range of bacteria in milk and other food matrices.

Flash - FL09

USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY TO UNDERSTAND DECOMPOSITION ODOUR IN THE CANADIAN ENVIRONMENT

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Abstract

Human decomposition odour is comprised of volatile organic compounds (VOCs) released during the process of decomposition. Decomposition is inherently governed by the environment in which it occurs thus, results from one environment type cannot be extrapolated to another. This study was the first human decomposition study to be conducted in the humid continental climate of Québec, Canada. VOCs were collected from the headspace of eight cadavers decomposing in an outdoor scenario at Canada's first human taphonomic research facility. Air samples were collected on sorbent tubes and analysed with comprehensive two-dimensional gas chromatography—time-of-flight mass spectrometry (GC×GC-TOFMS). The results indicated that compounds belonging to previously reported chemical classes such as acids, alcohols, aldehydes, aromatics, cyclic aliphatics, esters and analogues, ethers, halogen-containing, ketones, linear aliphatics, nitrogen-containing, and sulphur-containing VOCs were identified. This study presents a list of prominent (recurring) VOCs that are evolved during human decomposition. Identifying these VOCs is significant because, during their searches for human remains, cadaver detecting dogs (CDDs) might be potentially associating these with their target odour. A knowledge of which VOCs are decomposition-related is a crucial first step to improving their training and hence the outcome of CDD searches. Additionally, this study also found differences in VOC profile owing to variation in average ambient temperature resulting from the rapid progression of decomposition during warmer ambient temperatures. The VOC profile during the active and bloat stage was found to be the most variable compared to the fresh and late decomposition stages.

Flash - FL10

TILE-BASED FISHER RATIO ANALYSIS OF COMPREHENSIVE THREE-DIMENSIONAL GAS CHROMATOGRAPHY WITH MASS SPECTROMETRY DETECTION DATA

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Abstract

Comprehensive two-dimensional (2D) gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) is an excellent tool for the analysis of complex samples. However, many analytes remain poorly analyzed with GC×GC-TOFMS, so improvements in instrumentation and data analysis methods are warranted. To address this challenge, comprehensive three-dimensional (3D) gas chromatography with TOFMS detection (GC3-TOFMS) has been developed. Specifically, development of total transfer GC3 (100% duty cycle) boasts improvements in both selectivity and sensitivity relative to GC×GC. However, the 4D data obtained with GC3-TOFMS requires data analysis approaches that efficiently mine the data, especially when comparing numerous chromatograms, such as with Fisher ratio (F-ratio) analysis for the discovery of analytes that significantly differ in concentration between classes. Herein, we report expansion of tile-based F-ratio analysis originally developed for GC×GC-TOFMS data, now for GC3-TOFMS data, whereby both involve tiling and automated redundant hit removal. While tile-based F-ratio analysis of GC×GC-TOFMS data requires 4 grids in a 2D tiling format, F-ratio analysis for GC3-TOFMS data requires eight grids in a 3D "cube" tiling format to capture the analyte signal plus any retention shifting. Implementation is demonstrated on six replicates of a jet fuel spiked with a mixture of compounds at 400 ppm and six neat fuel replicates. F-ratio analysis of the GC3-TOFMS data discovered nearly all spiked analytes leveraging the selectivity of the third dimension. F-ratio analysis of the GC3-TOFMS data improved discoverability of the spiked analytes relative to the F-ratio analysis of the same data in a GC×GC-TOFMS format.

Flash - FL11

NON-DESTRUCTIVE IDENTIFICATION OF PREHISTORIC ADHESIVES BY HS-GC×GC-TOFMS: PRELIMINARY STUDY

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Abstract

Identification of prehistoric adhesives on stone tools is valuable as it might reveal something about tool use and human behaviour. Currently, prehistoric glues are chemically analysed by gas chromatography coupled to mass spectrometer (GC-MS) which requires extraction and derivatization of the residues¹. This is a major drawback as it is destructive for the glue and often, the required amount is not present. Moreover, the adhesives cover a wide range of materials (e.g., resin, animal glue, gum). Therefore, sensitive, universal, and non-destructive identification methods are needed. Headspace solid phase micro-extraction (HS-SPME) in combination with GC-MS and with comprehensive GC-time-of-flight mass spectrometer (HS-SPME-GC×GC-TOFMS) has been proposed^{2,3}. HS-SPME requires no extraction and derivatization, it is therefore a good opportunity for the chemical identification of prehistoric glues. Moreover, GC×GC-TOFMS has more peak capacity and is more sensitive than GC-MS³. But sensitivity remains a problem, therefore we investigated a different headspace method; dynamic headspace (DHS) coupled to GC×GC-TOFMS.

The DHS method is optimized and validated via design of experiment on pine resin and hide glue. Subsequently, the method is tested on several different adhesives and compared to SPME-GC×GC-TOFMS.

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Flash - FL12

UNTARGETED CHARACTERIZATION OF THE VOLATILE FRACTION AND TARGETED DETERMINATION OF CHIRAL LACTONES IN MARSALA WINES BY MEANS OF FLOW-MODULATION HEADSPACE SPME-CHIRALGC×POLARGC-TOFMS

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Abstract

The present research is focused on the untargeted characterization of the volatile fraction of Marsala wines (a dessert wine), along with the targeted determination of chiral lactones, by using flow-modulation headspace SPME-chiralGC×polarGC-ToFMS. Chiral lactones are, in general, considered as markers of alcoholic beverage aging in wood barrels. In such a respect, and considering important aspects related to food authenticity, their determination can provide information on such aging processes. Furthermore, the untargeted characterization of the volatile fraction of alcoholic beverages can be exploited for the differentiation of products of the same type, but produced under different conditions, among others. Such analytical objectives were herein achieved by using: a triple-phase SPME fiber, an enantioselective column in the first dimension and a polyethylene glycol one in the second, low duty-cycle flow modulation and low-resolution ToFMS. Several types of Marsala wines were subjected to analysis, showing in many cases, highly complex chromatogram profiles. Finally, attention was devoted to a total of 15 chiral lactones, entirely-resolved through chiralGC×polarGC, many of which were identified and quantified in the samples subjected to investigation.

Poster - P01

NON-DESTRUCTIVE IDENTIFICATION OF PREHISTORIC ADHESIVES BY HS-GC×GC-TOFMS: PRELIMINARY STUDY

Anika Lokker¹, Pierre-Hugues Stefanuto², Ronè Oberholtzer², Dries Cnuts², Veerle Rots², Jean-François Focant²

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Abstract

Identification of prehistoric adhesives on stone tools is valuable as it might reveal something about tool use and human behaviour. Currently, prehistoric glues are chemically analysed by gas chromatography coupled to mass spectrometer (GC-MS) which requires extraction and derivatization of the residues¹. This is a major drawback as it is destructive for the glue and often, the required amount is not present. Moreover, the adhesives cover a wide range of materials (e.g., resin, animal glue, gum). Therefore, sensitive, universal, and non-destructive identification methods are needed. Headspace solid phase micro-extraction (HS-SPME) in combination with GC-MS and with comprehensive GC-time-of-flight mass spectrometer (HS-SPME-GC×GC-TOFMS) has been proposed^{2,3}. HS-SPME requires no extraction and derivatization, it is therefore a good opportunity for the chemical identification of prehistoric glues. Moreover, GC×GC-TOFMS has more peak capacity and is more sensitive than GC-MS³. But sensitivity remains a problem, therefore we investigated a different headspace method; dynamic headspace (DHS) coupled to GC×GC-TOFMS.

The DHS method is optimized and validated via design of experiment on pine resin and hide glue. Subsequently, the method is tested on several different adhesives and compared to SPME-GC×GC-TOFMS.

1. D. Cnuts, K. A. Perrault, P. H. Stefanuto, L. M. Dubois, J. F. Focant, and V. Rots, *Archaeometry*, 2018, 60, 1361.
2. M. Regert, V. Alexandre, N. Thomas, and A. Lattuati-Derieux, *J. Chromatogr. A*, 2006, 1101, 245.
3. K. A. Perrault, P. H. Stefanuto, L. Dubois, D. Cnuts, V. Rots, and J. F. Focant, *Separations*, 2016, 3, 8.

Poster - P02

VALIDATION OF THE LC-GC×GC–ToFMS/FID PLATFORM FOR MINERAL OIL ANALYSIS THROUGH THE COMPARISON WITH THE RESULT OF INTERLABORATORY TRIALS

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Abstract

The determination of mineral oil, a potentially toxic food contaminant, represents a real challenge from an analytical viewpoint. In fact, its quantification is characterized by a significant variability, caused for up to 20% by chromatogram interpretation and integration, beside the additional variability due to the sample preparation methods. Recently the Joint Research Center (JRC) organized a ring test to validate a standard operating procedure (SOP) for mineral oil analysis in infant formula. At the same time, DGF (German society for fat science) and ITERG (French Technical Institute for the Study and Research of Fats) organized another ring test to update the official EN 16995:2017 method with the aim of lowering the limit of quantification from 10 mg/kg to 1mg/kg. We took advantage of these two ring test to validate the novel fully integrated LC-GC×GC–ToFMS/FID platform that we have recently presented [1, 2]. The goal was to validate the entire system along with the novel software recently developed to quantify in 2D mineral oil contamination. The 2D data collected were compared with the results in 1D with the same platform and the entire results were put in perspective of the outcome of the ring tests.

Beyond the more detailed information provided by the 2D chromatogram, the benefit of using the integrated platform has been clearly demonstrated, providing mainly less space for interpretation of the chromatograms thanks to a superior separation of interferences and separation from the bleeding.

[1] Bauwens et al., 2021

[2] Bauwens et al., 2022

Poster - P03

MULTIOMICS STUDY OF WHEAT VOLATILES

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Abstract

Volatile organic compounds (VOCs) are one of the most important groups of metabolites produced by plants; these molecules play an important role in relationships between plants and insects. For example, some VOCs will attract pollinators, while other VOCs can provide protection against pests. Orange Blossom Wheat Midge (*Sitodiplosis mosellana*; WM) is globally one of the most devastating insect pests impacting wheat production. Average losses in Canada are ~\$60M per year, but can be as high as \$300M in bad years. There is one gene, *Sm1*, which confers some protection against WM, but there is concern that this will be overcome by WM mutation. It has been observed that some lines of wheat are not susceptible to WM damage and that they are also capable of protecting other plants nearby. It is hypothesized that this is due to differences in the VOC profiles of these lines of wheat. Wheat volatiles from a variety of different lines of wheat with known genetics were cultivated, and sampled by active sampling onto thermal desorption tubes, which were subsequently analyzed by TD-GC×GC-TOFMS. Data were mined to identify differences in VOC profiles that are correlated with WM deterrence. Ultimately, we will identify specific genes in wheat responsible for the biosynthesis of VOCs that deter WM, and provide breeders with specific genetic traits to breed into new lines of wheat with stacked VOC and *Sm1* protection from WM.

Poster - P04

DEVELOPMENT OF A VALVE-BASED GC×GC-QMS INSTRUMENT FOR HIGHLY VOLATILE SAMPLE ANALYSIS

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Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) with quadrupole mass spectrometry (qMS) detection employing valve-based modulation is developed. The qMS provides a low cost mass spectrometer option, however due to being a scanning mass spectrometer, it can produce non-integer scan rates, which make it challenging to be used with a GC×GC set-up, due to reshaped data appearing as if it has wraparound. Due to flow rate limitations while using qMS detector, valve-based modulator was used, which provides less expensive cryogen free flow modulation, with uncoupled flow rates between first and second dimension columns. We explore the use of this affordable valve-based GC×GC-qMS instrument for the separations of highly volatile samples, by employing porous layer open tubular (PLOT) column on the first dimension (¹D) and a wall coated open tubular (WCOT) column on ²D. We also present a computational way to deal with the wraparound effect caused by using a quadrupole mass spectrometer detector with comprehensive two-dimensional gas chromatography.

Poster - P05

COMPARING THE AROMA PROFILES OF WHISKY BY SPME–GC×GC–TOF MS

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Abstract

Over 1000 compounds from a wide range of chemical classes are known to contribute to the aroma of whisky, including alcohols, phenolics and esters. It is important to be able to confidently identify these volatiles, for quality control and authentication purposes, as well as for engineering new aromas.

Solid-phase micro-extraction (SPME) coupled with GC–MS is commonly used for such aroma profiling studies, but it typically results in complex chromatograms with multiple co-elutions, meaning that important trace compounds may be masked by higher-loading constituents.

Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOF MS) is an ideal alternative, as the enhanced separation capacity allows the entire composition to be screened in a single analysis, with confident identification of compounds that would ordinarily co-elute.

However, this increased separation capacity results in data-rich chromatograms which must then be distilled into meaningful conclusions. Here, we apply automated untargeted comparisons using a novel tile-based approach. Firstly, chromatographic alignment accounts for any retention time drift over the course of the study. The software then splits the raw chromatograms into small tiles and sums the signal for each m/z channel in each tile. This information is collated and compared for every sample, allowing the significant differences to be highlighted.

In this study, we perform headspace sampling of multiple brands of whisky using solid phase microextraction (SPME) followed by flow-modulated GC×GC–TOF MS, with tile-based chemometrics for fast and simple identification of chemical markers of quality.

Poster - P06

USING ONLY THE SECOND HALF OF YOUR GC×GC INSTRUMENT: AN EASY WAY TO FAST GC

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Abstract

The second dimension of a comprehensive GC×GC set-up is a very fast GC separation. For analytical applications that are not too complex, sometimes the separation afforded by the second dimension suffices. In such cases by-passing the first dimension is an easy route to flexible use of your comprehensive GC×GC instrument. The injector is used to evaporate the sample and the first-dimension column is replaced by a transfer line.

An additional application that could benefit from this is the analysis of rapidly changing gas-streams. Here the gas-stream is fed to the modulator and narrow time slices are injected into the second dimension. An application we studied using this approach is the release of food flavours from an ice cream melting in an artificial mouth. This process takes 20 to 30 seconds. With the fast second dimension of the GC×GC set-up we could collect up to 10 time slices and reproduce the flavour release profile very accurately.

Poster - P07

VOLATILE PROFILING OF BANANAS AND BANANA PULP DURING RIPENING

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Abstract

The aroma of bananas is an important indicator of the fruit's flavor and can be an important characteristic of overall quality. Various factors such as storage and transport conditions, ripening protocols, and other conditions within the supply chain can have an effect on the overall volatile profiles, which have been studied using solid phase microextraction and gas chromatography with mass spectrometry (SPME-GC-MS) on the pulp. These studies have shown to observe over 250 compounds including esters, alcohols, acids, aldehydes, ketones, and terpenes.

With such a complex mixture, the use of comprehensive two dimensional gas chromatography (GCxGC) can lead to improved separation and group classification to enable a better understanding of the produce physiology in these supply chain conditions. Additionally, these studies usually involve the destruction of the banana to analyze the pulp.

Here we are employing the non-destructive sampling of bananas, along with pulp analysis using thermal desorption and SPME sampling to monitor the ripening process of bananas. The green and yellow stages of bananas will be demonstrated. The use of GCxGC-MS shows >300 identifiable compounds and with chemometric processing, important volatiles in the ripening process can be determined within these stages.

Poster - P08

SIMULTANEOUS MULTIPLE SPME FIBERS SAMPLING TO MAXIMIZE THE SAMPLE POTENTIAL

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Abstract

In omics research setting, access to sample is usually a key factor of the experimental design. Here, we evaluate simultaneous multiple SPME fibers sampling. Using three fibers simultaneously, we generated three technical replicates from one biological sample. Each fiber was then analyzed by GC×GC-TOFMS in separated runs. The robustness of the procedure was tested on a 24-standards mixture, human whole stool matrix, and human whole stool samples from the National Institute of Standards and Technology (NIST). In addition, we studied three fiber storage conditions: storage at room temperature and at -20°C in Headspace (HS) vials, and storage in specially designed glass storage vials at -20°C. For the storage condition, the RSD mean value based on the area of 18 of the 24 standards is 38.4 % for the storage of fibers at room temperature and 19.8 % for the storage at -20°C, both in HS vials. The best RSD value is 10.0 % and it was obtain using the designed glass vials at -20°C. The cold temperature storage and the decrease of the vial volume allow decreasing the RSD mean value by a factor of two. The mean area values for two targeted fecal biomarkers on the PegasusTM BT 4D are 100 times higher than the PegasusTM 4D HRT. The former detects more than 11 times more compounds than the later. However, the high resolution of the PegasusTM 4D HRT system offers stronger mass accuracy and enable a more robust compound identification.

Poster - P09

SEPARATION OF CROSS-LINKED HYALURONIC ACID HYDROGEL DIGESTATES BY LC×LC – MS

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Abstract

Hyaluronic acid is a glycosaminoglycan formed by a repetition of disaccharide units composed of a glucuronic acid and a N-acetyl-glucosamine. This naturally occurring polysaccharide in the body is widely used in some medical and aesthetic applications. The body fastly metabolizes hyaluronic acid. For this reason, it is necessary to cross-link it to improve the resistance to degradation and the mechanical properties of the resulting hydrogel.

To better understand the interconnections of the polysaccharide chains with the crosslinker in the hydrogel, methods to characterize their structure are needed.

For this purpose, a method of two-dimensional liquid chromatography coupled with mass spectrometry (LC×LC-MS) was developed. During hydrogel depolymerization, a complex mixture of highly polar and chemically related compounds is formed, including anionic derivatives of hyaluronic acid and zwitterionic fragments. The HILIC mode was chosen in order to separate compounds resulting from enzymatic digestion according to the polysaccharide chain length. The RP and cation exchange mixed mode were selected to separate the compounds according to the number of cross-linker molecules linked to the polysaccharide. Due to their high polarity, digested products are poorly soluble in acetonitrile, making it difficult to inject the sample directly into HILIC. In addition, the use of HILIC just prior to the detection improves the mass detection. Accordingly, the RP mode was used as the first dimension and the HILIC mode as the second dimension. After optimization of the different two-dimensional parameters, the method was applied for the comparison of hydrogels presenting different degrees of cross-linking.

Poster - P10

GUIDING THE DEVELOPMENT OF TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY SEPARATIONS USING SIMULATIONS AND BIG(GER) DATA

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Abstract

Two-dimensional liquid chromatography (2D-LC) is increasingly being adopted to resolve a variety of challenging separation problems, ranging from high-throughput determination of therapeutic antibody titer and purity to high-resolution identification of complex surfactant mixtures. However, method development for 2D-LC separations is still driven more by user experience than well-established protocols and tools. Developing conditions for the second dimension is both challenging (e.g., short times, small columns), and rich with performance potential, since the performance of each second dimension (²D) separation amplifies whatever separation is gained by the first dimension (¹D). This poster will highlight recent efforts to fill these gaps in fundamental understanding through the development of an online, web-based, 2D-LC simulator built on real data from experimental measurements. The simulator is available, free of charge, for use in academic research and education. Strategies used to streamline the measurement, processing, and publication pipeline for the massive amount of data needed to power the 2D-LC simulator will also be shown.

Poster - P11

STATISTICAL DIFFERENTIATION OF THE CHINESE LIQUOR BAIJIU USING SPME-GC×GC-TOFMS AND CHROMATOF TILE SOFTWARE

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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 classical one-dimensional GC. In this study, we evaluate the use of comprehensive two-dimensional GC×GC-TOFMS to significantly improve separation, detection, and thus identification of species in Baijiu to provide significantly higher quality and more informative characterization ability.

The optimized analytical parameters allowed for a comprehensive characterization of the individual Baijiu samples, but beyond that, a non-targeted differentiative analysis to determine trends and patterns among the different Baijiu types was realized. 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.

Poster - P12

HYDROGEN CARRIER GAS AND COMPREHENSIVE TWO-DIMENSIONAL CHROMATOGRAPHY APPLIED TO THE ANALYSIS OF PESTICIDES.

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LECO, Berlin, Germany

Abstract

Analysis of pesticides in foodstuffs is a routine, yet often complex analytical requirement, particularly in food materials containing significant levels of interfering matrix materials, which can adversely affect the identification and quantification of numerous pesticides with satisfactory confidence.

One approach, using comprehensive two-dimensional gas chromatography (GCxGC) coupled to Time-of-Flight mass spectrometry (TOF-MS), allows the impact of interferences from complex food matrices to be better resolved, by a combination of significantly enhanced separation capacity together with fast acquisition, unskewed, full mass range data collection. This results in far superior chromatographic resolution of pesticides and allows effective use of mass spectral deconvolution, therefore improving the detection and quantification confidence.

Currently, due to significant issues with helium supplies, both in terms of availability and increasing costs, much attention is focused on the use of hydrogen, as an alternative carrier gas, due to the ease of using generators to source it abundantly and at high purity.

In this study, we performed a proof-of-concept evaluation of the analysis of various pesticide chemistries with hydrogen carrier gas, using GCxGC and a unique TOFMS technology design. Comparisons of mass spectral fragmentation, dynamic range, sensitivity, robustness, chromatographic resolution, and run times, obtained with both helium and hydrogen, were performed.

The results demonstrated both carrier gases gave very similar mass spectral fragmentation and similarity for NIST MS library matching, similar sensitivity, and dynamic range, and also the possibility to reduce analysis time using hydrogen.

Poster - P13

ADVANCING MOSH/MOAH ANALYSIS TOWARDS SPECIATION AND CONTAMINANT IDENTIFICATION

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Abstract

Contamination of food products attributed to mineral oil (MO), consisting of saturated (MOSH) and aromatic (MOAH) hydrocarbons, has been for years at the center of attention for its potential impact on consumers' health. The presence of aromatic compounds raises concern for increased risks due to their known toxicity and suspect carcinogenicity and genotoxicity, especially for species with 3 or more aromatic rings and low alkylation degree.

Current reference methodologies, based on the LC-GC-FID hyphenation, allow separate quantification of the aliphatic and aromatic fractions. Nevertheless, the task is challenging due to matrix variety and complexity as well as for the presence of interferences. Furthermore, FID detection does not permit to obtain qualitative information about the type of MOSH or MOAH present, to distinguish between MOSH and hydrocarbons of synthetic origin, and to confirm or not the occurrence of synthetic hydrocarbons such as polyolefin oligomers (POH) or endogenous hydrocarbons (terpenes, olefins residues, etc.).

As a consequence, laboratories tasked with MOSH/MOAH analysis would benefit from advanced analytical tools capable of in-depth characterization for samples found positive to contamination.

This contribution presents a two-dimensional platform for MOSH/MOAH analysis based on a preliminary HPLC separation followed by comprehensive gas chromatography (GC×GC) with parallel FID detection and high-resolution mass spectrometry. This solution can increase characterization capability and deliver a more insightful classification of the hydrocarbon profiles and act as confirmatory tool to classify contamination. A real-life case study highlights the value added for a identification of contamination origin in extra-virgin olive oil.

Poster - P14

MODELLING OF ANALYTE LOSS AND DISPERSION GENERATED BY MODULATION LOOPS USED IN MULTI- DIMENSIONAL LIQUID CHROMATOGRAPHY

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Abstract

With the increased interest in multi-dimensional LC separations in recent years, several sophisticated commercial 2D-LC systems have been introduced to the market. However, there is still a lack of a complete theoretical foundation upon which sound developments can be made. Two parameters that are not fully understood are the amount of sample loss from the loop tip during the filling of the loop by the first dimension effluent, and the variance of the analyte band entering the second dimension column when emptied from the loop. In this poster we will show both numerical simulation methods and experimental measurements that are used to understand and quantify the analyte loss and the emptying profiles variances.

To predict the amount of sample loss during filling a model was developed to estimate the fraction of the loop that can be filled before analyte loss occurs, as a function of loop geometry, flow rate and sample properties. When emptying the sample in the first-in-last-out (FILO) modulation mode, a model depending only on a single dimensionless parameter and the ratio of the filling and emptying flow rates $F_{\text{empty}}/F_{\text{fill}}$ was developed to predict a profile variance (as measured at the loop outlet). In the first-in-first-out (FIFO) modulation mode a model with the same function was also developed however in this case the filling fraction of the loop (f) needed to be included.

Poster - P15

EVALUATION OF OXYGENATES IN PLASTIC PYROLYSIS OIL BY GCxGC TOF MS

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Abstract

Issues around plastic waste have gained global attention. To resolve this, Value Chain Partners are working towards a plastic circular economy. In this context, Dow has evaluated multiple pyrolysis oil samples produced from plastic waste as a potential circular feedstock. Before considering Plastic Pyrolysis Oils (PPOs) as a circular feedstock (replacing fossil-based naphtha), a detailed compositional analysis is required. PPOs have an intricate composition; next to a broad and complex hydrocarbon composition (PIONA), hetero-atoms, such as Cl, O and/or N, are also present. Therefore, advanced analytical techniques are required to understand PPOs' detailed composition.

This study focused on the (heavy) oxygenates in the PPO. A measurement for C1-C5 oxygenates is a standard request within the petrochemical industry (ASTM D7754). However, it has been observed that a significant amount of C5+ oxygenates are also present. Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GCxGC TOF MS) was able to provide a better insight in the full carbon range and types of oxygenates present in the PPOs.

Poster - P16

OFF-LINE LC×SFC-HRMS/MS METHOD DEVELOPMENT FOR THE NON-TARGET ANALYSIS OF DEPOLYMERIZED LIGNIN

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Abstract

Lignin is an abundant renewable resource that is mainly obtained as a by-product of the wood industry. Most isolated lignin is considered a waste, and only 2% is commercialized. However, because of the phenolic structure, it has high potential to be used more as a natural resource for various compounds. The BIOPOLIOL (Bio-based Polymers from Lignin Oligomers) project aims to valorize lignin to manufacture polyhydroxyurethanes (PHU) that could replace polyurethane (synthesis requires toxic isocyanates) foams applied in construction. In this joint project, lignin is depolymerized using soft catalysis into monomers and oligomers, which are demethylated to increase the number of hydroxyl groups beneficial to the PHU synthesis. The complex mixture has to be analyzed to monitor and improve the valorization of the processed lignin via a powerful chromatographic and mass-spectrometric technique.

For that aim, an off-line comprehensive two-dimensional reversed-phase liquid chromatography combined with supercritical fluid chromatography (RPLC×SFC) was developed and applied for the non-targeted analysis of a depolymerized lignin sample. A set of 33 lignin monomer standards was used to demonstrate the higher orthogonality of the RPLC×SFC setup compared to RPLC×RPLC. The chromatographic dimensions were fully optimized, including injection conditions, make-up additive, and ESI(-) parameters. The overall peak capacity and ability to distinguish compounds with the same m/z ratio was compared with optimized 1D-LC.

A valuable advantage of using the technique in the off-line mode is the possibility to perform high-resolution MS/MS, which gives information about the compound's fragments in addition to the exact mass, formula, and DBE.

Poster - P17

TASTE TESTING COMPARISONS PAIRED WITH VOLATILE PROFILE ON CHERRIES BY TD-GC×GC-TOFMS

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Abstract

Volatile compounds can play an important role in the flavor profile of cherries. Primary volatile compounds that are attributed to cherries include compounds such as benzaldehyde, linalool, and hexanal to name a few. While many factors can influence the taste of cherries, the storage conditions within a supply chain may potentially lead to off-flavors.

Working with a trained taste testing panel, we have performed a volatile profile of cherries using thermal desorption with comprehensive two dimensional gas chromatography and mass spectrometry to compare the taste descriptors with the compounds identified. Additionally, we have profiled cherries throughout a cold storage supply chain to determine the influence on the cherry volatile profile.

From the taste testing panel, specific compounds were identified and targeted for the analysis. GC×GC enabled separation of compounds for improved quantification and showed a direct correlation with the taste testing panel.

Poster - P18

QUANTITATIVE ANALYSIS OF ALKENES IN ALTERNATIVE FUELS MADE FROM PLASTIC WASTE CONVERSION VIA COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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Abstract

Over the previous several decades, there has been a substantial buildup of plastic waste in landfills and the environment, amounting to over 10 billion tons. Conventional methods including incineration and mechanical recycling are ineffective in reducing plastic waste. Alternative fuels made from plastic waste can be produced using conversion techniques like hydrothermal processing and pyrolysis. The alkene (olefin) content in these fuels may vary from a few ppm to tenths of a wt. %. However, at these high concentrations, there are currently no methods for the detailed quantitation of olefins. In this work, we developed a novel method applicable for the characterization and quantitation of aliphatic olefins in fuels (gasoline, kerosine, diesel) made from plastic waste pyrolysis. Comprehensive two-dimensional gas chromatography with flame ionization detector (GC×GC-FID) and the derivatization method utilizing DMDS was used for this analysis and was tested with olefin standards ranging from C₅ to C₂₅. Results were compared to those obtained via ASTM D1159 (Bromine Number), ASTM D5554 (Iodine value), and ASTM D1319 (FIA method).

Poster - P19

MULTIDIMENSIONAL LC-MS WITH MULTI-METHOD OPTION AND PARALLEL MIDDLE-UP AND BOTTOM-UP MS ACQUISITION FOR THE IN-DEPTH CHARACTERIZATION OF ANTIBODIES

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Abstract

Monoclonal antibodies (mAbs) have become the fastest growing class of therapeutics in the pharmaceutical industry. These biotechnology-derived products are large and highly heterogenous resulting in hundreds of possible variants that differ in post-translational modifications (PTMs), amino acid sequence, higher order structure, etc. Inherent to this, many challenges are encountered in analytics to secure the quality, efficacy, and safety of the product.

To unravel the structural complexity of mAbs, several complementary analytical tools and methodologies are applied with chromatography and mass spectrometry (MS) at the forefront. In recent years, multi-attribute analysis has become a hot topic in the biopharmaceutical analysis domain where the number of characterization assays is reduced by using, for example, multidimensional liquid chromatography (mD-LC) with optionally, chemical, electrochemical or enzymatic reactors incorporated.

In this project, a next-generation protein analyzer is presented allowing sequential assessment of size, charge, and hydrophobic variants combined with parallel middle-up and bottom-up MS analysis for the determination of molecular weight, amino acid sequence and PTMs. The set-up consists of a first dimension multi-method option (choice between SEC/CEX/HIC) where the peaks of interest are collected and transferred to a second dimension RPLC column for desalting and reduction prior to middle-up MS analysis. Simultaneously, the reduced protein is subjected to on-column trypsin digestion in a third dimension and bottom-up MS-based peptide mapping in the fourth dimension. The applicability of this versatile mD-LC-MS protein analyzer was demonstrated for the full characterization of a therapeutic antibody fragment.

Poster - P20

ADDING DISCRIMINATION DIMENSIONS WITH THE APPLICATION OF SELECTIVE IONIZATION FOR TWO-DIMENSIONAL COMPREHENSIVE GAS CHROMATOGRAPHY IN THE ANALYSIS OF COMPLEX DRUGS

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Abstract

Further development, understanding of the pharmaceutical mechanisms and authorization for alternative uses of a pharmaceutical demand an in-depth characterization of the active pharmaceutical ingredients (API). The combination of comprehensive gas chromatography and high-resolution mass spectrometry with standard electron ionization (GC×GC-EI-HRMS) allows a comprehensive characterization of very complex APIs for the first time. We used this method to describe sodium bituminosulfonate (SBS), a sulfur-rich API known for centuries for treating various skin disorders and promising antimicrobial effects for further application. We extracted the API from the aqueous matrix and methylated the sulfonates with trimethylsilyl diazomethane. However, the thermal instability of the non-derivatized sulfonic acids poses a high hurdle for data interpretation. The number of heteroatoms and the variety of substance classes with overlapping elution profiles complicates the identification. We will demonstrate that applying an alternative ionization method like negative chemical ionization (NCI) offers a higher selectivity for target compounds and adds an extra dimension to the analysis. Although NCI is a soft ionization technique, it provides characteristic fragments for the functional group of the sulfonates. In combination with the core-structural information of the EI, this approach allowed for the successful detection and identification of aromatic sulfonates without the interference of artifacts.

Poster - P21

BENEFITS OF HIGHER MASS RESOLUTION FOR THE APPLICATION OF GC×GC-MS IN DRUG RESEARCH: APPLICATION OF A NEW GENERATION OF ULTRA-HIGH RESOLUTION TOF-MS FOR IDENTIFICATION OF COMPLEX PHARMACEUTICALS

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Abstract

Characterizing active pharmaceutical ingredients (APIs) is challenging, in particular if they are complex mixtures. This is especially true for non-biological complex drugs (NBCDs), many of which have been in use for centuries although lacking understanding of their exact composition. To identify chemical components of a NBCD such as sodium bituminosulfonate (SBS), a treatment for skin disorders with a promising antimicrobial effect, two-dimensional gas chromatography (GC×GC) offers unmatched chromatographical separation power. Major components of SBS are sulfonated arenes with a high number of heteroatoms. The subsequent identification of the separated compounds is intrinsically linked to the method of detection. A powerful method is high resolution mass spectrometry (HR-MS) where a frequently encountered problem is the "sulfur split" which refers to the distinction of ³²S₄ and ¹²C₃, a mass difference of only 3.4 mDa. Most commercial systems do not have sufficient mass resolution and therefore depend on high chromatographic resolution to resolve intermolecular mass splits. Increasing mass resolution enables the identification of intramolecular mass splits and the possibility of direct inlet probing (DIP), thereby omitting upstream chromatography. We present a comparison of multiple GC×GC/DIP-HR-MS measurements with rising generation of devices and increasing mass resolution to investigate SBS samples. The upcoming GC×GC-HR-MS device offers most information in this pilot study and shows great potential for future applications not limited to complex pharmaceuticals. This highlights the importance of continuous improvement in mass resolution to a point where GC×GC is still valuable for exploratory studies but no longer needed for monitoring.

Poster - P22

THE BEER'S VOLATOLOME, A COMPARATIVE STUDY BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY TIME-OF-FLIGHT MASS SPECTROMETRY

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Abstract

Fermented beverages, such as beer, are considered as complex mixtures by flavor and food chemists. The beer volatolome contains hundreds of compounds, which affect the taste and the mouthfeel. In this highly competitive market, it is crucial for brewers to master each step of the process to understand and control the taste and to guarantee aroma quality and stability. Aroma compounds are essentially derived from the raw ingredients and the conditions used to produce beers. This study aims to determine the impact of the yeast used for bottle fermentation on beer's volatolome.

We brewed 5 different beers with the same feedstock. During the bottling, we used 5 distinct yeasts generally used by brewers. After an aging period of 8 weeks, all samples were analyzed using solid-phase microextraction couple with comprehensive two-dimensional gas chromatography coupled to mass spectrometry (SPME-GC×GC-TOFMS). A dedicated data processing workflow was then optimized. Principal component analysis (PCA) was used to visualize the clustering between samples.

After data curation, peaks area of VOCs founds in each beer were used to carry out unsupervised statistical analyses. Three distinct groups were observed on PCA; two beers are considered very different regarding the VOCs while the remaining three constitute another cluster. Based on these results, the aroma profile of the different beers could be dressed. While the two first beers were dominated by specific ethyl esters giving fruity aromas, less associated fruity fragrance esters were expressed in the other group.

Poster - P23

FOOD METABOLOMICS BY GC×GC-TOF MS AND TANDEM IONIZATION: UNDERSTANDING THE IMPACT OF CLIMATE EVENTS ON EDIBLE CROPS QUALITY

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Abstract

A better and comprehensive understanding of the relationship between climate conditions and nutrition is necessary to provide the human population with safe and secure access to food. The goal of the current study is to understand the effects of climate change on the detectable metabolome of hazelnuts regarding alternative post-harvest practices, as well as defects indirectly caused by global warming such as insect migrations that affect the quality of both peanuts and soy crops. The analytical strategy, aligned to food-metabolomics principles, exploits the information potential of multi-dimensional analysis that combine physicochemical discrimination/separation of analytes with spectrometric detection, such as comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS) operating in Tandem Ionisation™. The process known as untargeted and targeted (UT) fingerprinting is used in combination with chemometric algorithms to highlight metabolomic variations between composite-class images generated by re-alignment and fusion of raw data collected from samples belonging to distinct classes, thus highlighting metabolites pattern differences. Data fusion, obtained by merging hard and soft ionization data streams, is capable to increase the information potential by exploiting both the standard MS fragmentation and higher overall sensitivity of the hard ionization and the wider dynamic range of response with an increased signal-to-noise ratio typical of the soft ionization. Moreover, aroma precursors involved in the Maillard reaction such as amino acids (i.e., threonine, valine, and tryptophan) and reducing sugars (i.e., glucose, fructose, saccharose) of both peanuts and hazelnuts were investigated to understand the quality discrepancy in the roasted products.

Poster - P24

ARTIFICIAL INTELLIGENCE SMELLING BY GC×GC-MS/FID AS A TOOL FOR FOOD AROMA BLUEPRINTING: THE UNIQUE AROMA OF BRAZILIAN OLIVE OILS

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Abstract

Extra virgin olive oil (EVOO) has a complex aroma, which is related to the *cultivar*, the pedoclimatic conditions where trees are grown, olives maturation stage, and extraction process applied. Brazil is the second largest importer of olive oil in the world, but, despite the high consumption, the growing of olives in the country and, therefore, the extraction of oil, are quite recent and small in relation to the size of its domestic market.

This work aimed to explore the Brazilian EVOO *volatilome* by GC×GC-MS/FID and evaluate the effectiveness of chromatographic blueprinting to recognize characteristic patterns of odorants for different cultivars (*Arbequina* and *Koroneiki*) and production regions (Rio Grande do Sul and Serra da Mantiqueira).

Samples from *Arbequina* and *Koroneiki* cultivars from the two main production regions in Brazil in 2021 and 2022 harvest were analyzed. GC×GC was performed with a polar × semi-polar column combination followed by qMS/FID parallel detection. Untargeted/targeted fingerprinting workflow was carried out combining template matching strategies on the 2D-patterns of volatiles. Quantification of target volatiles (n=42) was achieved via Multiple Headspace SPME, external standard calibration and FID predicted relative response factors (RRF).

HS-SPME combined to GC×GC-MS/FID and accurate quantification by predicted RRF resulted to be a great tool in the quality assessment of EVOO samples. By the effective exploration of the information encrypted in EVOOs *volatilome* and the accurate quantification of key-odorants an Artificial Intelligence smelling machine is realized with peculiar comparative possibilities for EVOOs aroma qualities.

Poster - P25

VALORISATION OF PREMIUM ITALIAN WINES BY VOLATILE SIGNATURE EXPLORATION WITH GC×GC-TOF MS AND COMPUTER VISION

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Abstract

Computer vision is a branch of artificial intelligence (AI) that allows systems to extract useful information from digital files to execute actions or make predictions based on that information. Computer vision was applied in the data processing of 54 samples obtained by microvinification of Corvina and Corvinone grape cultivars harvested in five different vineyards, all located in the Veneto region, Italy. Wines' headspace was sampled with an SPME device after the addition of sodium chloride to enhance the repartition equilibrium at the condensed/gas interface, and further analysed through comprehensive two-dimensional gas chromatography coupled with Time-of-Flight mass spectrometry (GC×GC-ToF MS). The AI approach entails creating a cumulative class-image from the combination of chromatographic data from various samples. It is a data-fusion technique in which the pixels (spectral events) from many 2D images are realigned, registered, and arithmetically summed to create a cumulative pattern that resembles the compositional complexity of all samples within a given group. Composite images were then pairwise-compared to extract crucial biological information from samples, such as cultivar and geographical location of the vineyards. Despite the location of the vineyard not showing meaningful impact on the wine volatilome with unsupervised approaches, the grape cultivar achieves up to 90% correctness in classification accuracy with supervised chemometrics algorithms. Alcohols such as 2-hexen-1-ol, penten-3-ol, and 3-hexen-1-ol were the primarily discriminating analytes (eight) mainly prevalent in Corvina cultivar, followed by esters (seven) and terpenes (five), the last two showing a higher relative distribution in the Corvinone one.

Poster - P26

COMPUTER VISION ENABLES EFFECTIVE DETECTION OF COMPOSITIONAL DIFFERENCES IN COMPLEX SAMPLES: VALIDATION OF A WORKFLOW BASED ON CHROMATOGRAPHIC FINGERPRINTING AND PATTERN RECOGNITION

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Abstract

Within Artificial Intelligence (AI) approaches Computer Vision conceptually allows "computers and systems to derive useful information from digital images" giving access to higher-level information and "take actions or make recommendations based on that information" [1]. By comprehensive two-dimensional chromatography, we have access to highly detailed, accurate yet unstructured information on the sample's chemical composition, the possibility to exploit the AI concepts at the data processing level (e.g., by Computer Vision) for rationalizing raw data explorations could quickly drive toward the understanding of the biological phenomena interrelated to a specific/diagnostic chemical signature.

The novel workflow for Computer Vision based on pattern recognition algorithms (i.e., UT fingerprinting) includes:

- 1) Generation of composite class images for representative samples' classes;
 - 2) Generation of a feature template with reliable peaks and peak-regions by processing composite class images from Step 1;
 - 3) Feature template pruning/editing to include targeted components, and eliminate bleeding peaks and artifacts;
 - 4) Application of the feature template from Step 3 to all samples' images and composite class images from Step 1;
 - 5) Pair-wise comparisons to highlight quantitative pattern differences -> link to the chemistry (targeted compounds) and tracked features (untargeted compounds).
- As an explanatory application, a sample set originated from a Research Project on artisanal butter (from raw milk to ripened butter) is explored, capturing the evolution of volatile components patterns along the production chain.

[1] <https://www.ibm.com/topics/computer-vision>

Poster - P27

DETAILED INSIGHT INTO WHEAT/BARLEY STRAW BIO-OIL COMPOSITION USING GC×GC-MS/FID/NCD/SCD

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Abstract

Wheat and barley straw is a promising feedstock that can be utilized for conversion to advanced biofuels using fast pyrolysis followed by hydrotreatment. Compared to woody bio-oils, bio-oil made from straw is characterized by an increased sulfur content (ca 650 wppm) and a much higher nitrogen content (0.7 wt%). Only little is known about the speciation of these heteroatoms in bio-oils. An excellent resolution of GC×GC allowed us to reveal the composition of the GC-detectable fraction of straw bio-oil at the highest possible level of detail.

The second dimension of GC × GC helped us in the identification of more than 60 different hydrocarbons in crude straw bio-oil. The presence of aliphatic hydrocarbons is typical for catalytic bio-oils, but it is quite rare for thermal bio-oils. Long-chain aliphatic alcohols, ketones and acids were determined in the sample at high concentrations. Most of these compounds, including also highly abundant 14,16-hentriacontanedione, have been identified in lipid extract from unprocessed wheat straw.

Using the SCD detector, we determined that hydrogen sulfide, methanethiol, dimethyl disulfide, and several thiophenes were the most abundant sulfur-containing compounds. Using the NCD detector, we revealed that nitrogen was present in wide spectra of functional groups covering e.g., amines, nitriles, pyridines, quinolines, amides and pyrrolidones. Using sulfur and nitrogen selective detectors, we determined that around 60% of sulfur and 18% of nitrogen were present in the GC-detectable fraction of the studied bio-oil. The information obtained in this study is useful for further development in straw bio-oil upgrading to advanced biofuels.

Guided Discussion 1

REMOVING THE BARRIERS FROM ADOPTION OF COMPREHENSIVE TWO-DIMENSIONAL CHROMATOGRAPHY

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Description

Comprehensive two-dimensional gas (GC×GC) and liquid (LC×LC) chromatography are well-established separation techniques that exhibit enhanced resolving power over their one-dimensional counterparts. With improvements in commercial instrumentation and data analysis platforms, performing a GC×GC or LC×LC separation and analyzing its output are easier now than ever before. However, despite these developments, the broader analytical community often perceives comprehensive two-dimensional chromatography as complex, difficult, and intimidating. How do we address this stereotype and make these separation techniques approachable to the broader community? Following each step in the established analytical workflow, this discussion group will identify common misconceptions about instrumentation, method development/optimization, and data analysis. By addressing these concerns, this discussion will aim to instill confidence in analysts and provide them tools for applying these separation methods to various application areas.

Guided Discussion 2

GCxGC, will it ever be in common use in the petroleum laboratories?

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Description

Legislation, commercial contracts or process control require standardized methods or procedures to ensure product results from all parties involved can be compared to meet contract requirements and resolve disputes.

Standardized method development and adoption is a collaborative process which requires buy-in from many competing interests before new methods are accepted. Innovative or unfamiliar technologies need to overcome market resistance to change, bureaucratic inertia within standardization committees, and the tendency of legacy market suppliers to protect their economic interest. All of these pre-existing stakeholders need to be brought into agreement to allow the new technology into the market space. With these difficulties as background, Lenny Kouwenhoven will talk about her real world experience in bringing the first GCxGC test method for the petroleum market through the ASTM method development process. In addition, the first preliminary ILS data for the GCxGC method will be presented and discussed. The path forward for European and Asian adoption will be overviewed and contrasted with ASTM procedures.