15TH Multidimensional Chromatography Workshop

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Abstract book

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FG-1

ADVANTAGES AND LIMITATIONS OF GC×GC IN GOVERNMENT AND INDUSTRIAL LABORATORIES

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Abstract

Comprehensive gas chromatography (GC×GC) is a common technique used in government and industrial laboratories; however, it has struggled to gain widespread acceptance due to perceived complexity and a lack of standardized and validated methods. Furthermore, the technique is not directly comparable to historical data sets and previously used analytical techniques. Overcoming these challenges and limitations in non-academic laboratories is a critical aspect of research by experts and advanced GC×GC users. Advanced users must be vocal advocates, highlighting the advantages of GC×GC in cases where the additional separation data can be advantageous. By addressing the benefits and limitations of this technique, this discussion will aim to address how we may elevate GC×GC in industrial and government laboratories, including, but not limited to, the role of obtaining employment in these sectors, allowing for further integration into the GC×GC community.

FG-2

PRELIMINARY RESULTS IN THE DEVELOPMENT OF A SYSTEM PERFORMANCE STANDARD REFERENCE TEST MIXTURE FOR COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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Abstract

Comprehensive gas chromatography (GC×GC) is a common technique used in government and industrial laboratories; however, it has struggled to gain widespread acceptance due to perceived complexity and a lack of standardized and validated methods. Furthermore, the technique is not directly comparable to historical data sets and previously used analytical techniques. Overcoming these challenges and limitations in non-academic laboratories is a critical aspect of research by experts and advanced GC×GC users. Advanced users must be vocal advocates, highlighting the advantages of GC×GC in cases where the additional separation data can be advantageous. By addressing the benefits and limitations of this technique, this discussion will aim to address how we may elevate GC×GC in industrial and government laboratories, including, but not limited to, the role of obtaining employment in these sectors, allowing for further integration into the GC×GC community.

KL-1

FROM RESEARCH TO ROUTINE ANALYSIS -- THE ROLE OF GC×GC IN THE REGULATORY SPACE

Sarah Prebihalo

U.S. Food and Drug Administration, College Park, USA

Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) coupled with time-of-flight mass spectrometry (TOFMS) is a powerful analytical technique capable of providing valuable information about the chemical composition of complex samples. While GC×GC is an established method of analysis in academic and industrial laboratories, it has not yet been widely adopted in regulatory laboratories, in part due to the unique goals and challenges of regulatory science. Regulatory laboratories require robust, reliable, and validated methods which can perform rapid identification and/or quantification of target analytes. Frequently, these targeted methods are based on pre-existing knowledge of sample composition and provide a limited view of chemical profile. By utilizing GC×GC as an investigative tool, additional sample composition information may be achieved, potentially providing critical inferences, and informing on additional analytes of interest. In this presentation, we will discuss a recent study performed by the United States Food & Drug Administration, in which the chemical profiles of six hemp cultivars and fifty-four hemp-derived market samples (oils/tinctures) were investigated via GC×GC to complement chemical data obtained via targeted methods.

KL-2

TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY FOR SMALL MOLECULE PHARMACEUTICAL ANALYSIS – MORE KNOWLEDGE IN LESS TIME

Qinggang Wang, Yehia Baghdady, Ziqing Lin, Jonathan Shackman, Brian He, Yiyang Zhou, Catherine Miles, Lianjia Ma

Bristol Myers Squibb, New Brunswick, USA

Abstract

Pharmaceutical companies have been under consistent pressure to bring safe therapeutics to patients faster. In the meantime, the structural complexity of synthetic drug candidates has been increasing in the pharmaceutical development pipeline, from compounds with multiple chiral centers to peptides and oligonucleotides. Due to their larger molecular sizes and more complicated synthetic routes, these compounds usually consist of more diverse impurity profiles compared with those of traditional small molecules. Complete separation of all relevant peaks can be challenging in LC method development. This is especially true during early-stage process development, when the knowledge of process impurities is still limited. These challenges have prompted the evolution of innovative analytical techniques to facilitate knowledge generation in chemical process development, including using two-dimensional liquid chromatography (2DLC).

In the last few decades, application of 2DLC has grown rapidly in the pharmaceutical industry. Turnkey commercial instruments are now available from multiple vendors. Compared to conventional one-dimensional liquid chromatography, 2DLC can significantly improve separation power through unique selectivity pairings between the first and the second dimension separation. This presentation will give an overview of our efforts in exploring 2DLC for fast knowledge generation in chemical proceed development. The examples include peak purity verification by orthogonal RPLC-RPLC-MS, 2DLC quantitative impurity analysis, and quantitative enrichment of trace level impurities by trapping mode 2DLC. The results of these studies demonstrate that 2DLC is a powerful tool in understanding chemical processes, as well as ensuring analytical method quality for pharmaceutical development.

KL-3

ON-LINE MULTI-DIMENSIONAL LC/MS: THE NEXT-GENERATION TOOL FOR REAL-TIME MONITORING OF ANTIBODY QUALITY ATTRIBUTES IN BIOPHARMACEUTICAL PROCESSES

Thomas Bouvarel

Genentech, South San Francisco, USA

Abstract

Monitoring of PTMs mAbs is essential during their production in both upstream and downstream processes. However, characterization of PTMs using conventional peptide mapping procedure requires time-consuming and labor-intensive off-line sample preparation steps. This work describes for the first time, the implementation of a Protein-A affinity chromatography column as the first dimension (1D) in a multi-dimensional LC setup for the automated characterization of mAb variants from harvest cell culture fluid.

KL-4

FROM WILDFIRE ORIGINS TO COURTROOM VERDICTS: EXPLORING ARSON INVESTIGATIONS WITH MULTIDIMENSIONAL CHROMATOGRAPHY

Gwen O'Sullivan

Mount Royal University, Calgary, Canada

Abstract

The field of fire debris analysis is continually evolving to address challenges associated with identifying new types of ignitable liquids, complex matrices, and the presence of interferences, with more focus in the courtroom on the robustness and admissibility of generated evidence. The identification of ILR, accelerant type, and source in arsonous fires within a laboratory setting is crucial for legal proceedings and convictions. In this presentation, we will illuminate the current regulatory landscape governed by ASTM International standards, while outlining method development strategies to maximize the potential of GC×GC. This includes a focus on critical aspects such as column selection, modulator settings, and parameter optimization. Additionally, we will introduce a robust workflow for GC×GC analysis of ILRs, featuring retention times indices. Our exploration will extend to the potential of GC×GC analysis in detecting cross-contamination, involving a comprehensive investigation of the entire ILR volatility spectrum to fully characterize cross-contamination in a simulated scenario. Furthermore, we will assess packaging materials for their efficacy in sample preservation. The presentation will delve into the challenges associated with managing large and complex chemical data from this type of analysis, and we will introduce a novel chemometric workflow aimed at identifying relevant marker compounds.

O-1

APPLICATIONS OF MULTIDIMENSIONAL LIQUID CHROMATOGRAPHY IN MODERN DAY PHARMACEUTICALS

CJ Venkatramani

Genentech, South San Francisco, USA

Abstract

In the past several years many pharmaceutical companies have ventured into mixed modalities like peptides, oligonucleotides, cell therapy to address the growing needs of ageing population. This has created significant challenges and opportunities for the analytical chemists. Detailed characterization of new modalities mandates the use of multidimensional liquid chromatography as traditional techniques are inadequate.

Characterization of peptides involves the use of RPLC to assess chemical stability and SEC to assess physical stability. RPLC resolves sample components based on their hydrophobicity and SEC based on hydrodynamic volume. Ideally, RPLC purity should be lower than SEC as latter has limited resolving power, however, there are instances where its other way around as bigger multimers might not elute from RPLC column. This makes it difficult to assess the chemical purity. We have developed a selective comprehensive SEC-RPLC system where SEC resolves the peptides based on hydrodynamic volume and RPLC based on hydrophobicity. The product of primary and secondary column purity gives the overall purity.

On the other hand, highly polar oligonucleotides require ion-pair liquid chromatography to retain, resolve short-mers and long-mers from desired component, HILIC and IEC for additional characterization. Coupling RPLC with HILIC would be quite valuable, however, the mobile phase incompatibility makes it challenging. We have addressed the incompatibility is addressed using in-line mixing modulation, a simple, novel approach to address mobile phase incompatibility in liquid chromatography.

The presentation will cover achiral-chiral using RPLC-RPLC, RPLC-SFC, peptide purity using SEC-RPLC, oligo characterization using RPLC-HILIC, PEG characterization using HILIC-RPLC.

O-2

ESSENTIAL SEPARATIONS: ANALYSIS OF AROMA OILS BY ONE-DIMENSIONAL AND TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Robert Cody, Kirk Jensen, John Dane

JEOL USA, Inc., Peabody, MA, USA

Abstract

Five aroma oils were analyzed by both one-dimensional gas chromatography and comprehensive two-dimensional gas chromatography combined with mass spectrometry. Electron ionization and soft ionization data were collected for all samples.

Statistical analysis of fresh and 35-year-old peppermint oil samples was carried out for both the GC-MS and the GC×GC-MS data to identify differences in compositions. Conventional GC-MS with quadrupole and time-of-flight mass spectrometers using chromatographic deconvolution data analysis was generally effective in characterizing and identifying differences in the samples. Unsurprisingly, GC×GC-MS revealed components that would be difficult or impossible to separate by conventional one-dimensional gas chromatography. High-resolution accurate-mass data obtained for both electron ionization and soft ionization added confidence to the assignment of known components and aided in the identification of unknowns.

O-3

SAMPLING BODY ODOR FOR HEALTHCARE MONITORING: HOW TO AVOID THE PITFALLS OF INDIVIDUAL'S ODOR VARIATIONS AND CONTAMINATIONS BY THE SAMPLING ENVIRONMENT

Elsa Boudard[1,2], José Dugay[1], Isabelle Rivals[1], Nabil Moumane[2], Jérôme Vial[1], Didier Thiébaut[1]

[1]ESPCI, Paris, France. [2]Sense-Detect Health-Care, Aigremont, France

Abstract

The human body constantly emits numerous volatile organic compounds (VOCs): they constitute the body odor and are affected by various factors such as pathologies. Thus, body odor analysis can enable efficient, non-invasive and large-scale health monitoring. Dogs have a very acute sense of smell, and are therefore commonly used to perform olfactive detection (explosives, narcotics...). However, dogs are also likely to be disturbed by environmental conditions, so that it is necessary to confirm their detections through a more objective technique. So, sampling on a solid sorbent followed by thermodesorption into comprehensive two-dimensional chromatography coupled with time-of-flight mass spectrometry (TD-GC×GC/ToFMS) allows the needed high sensitivity and high resolution for the analysis of this complex matrix.

Study's initial step was the development of a user-friendly sampling system with materials having minimal VOCs emissions. These requirements are mandatory in order to obtain TD-GC×GC/ToFMS results suitable for chemometric treatment, and a reliable search of volatile biomarkers of the disease by comparing samples belonging to positive and negative groups. However, the use of Fisher tests or volcano plots is not enough in this case and, once a biomarker is highlighted, it is necessary to check whether it is specific of the disease or of the sampling process, including the sampling environment. Examples given in this lecture will use COVID-19 as model pathology. Another concern regarding the constancy of one person’s body odor over time will also be discussed. This gives a first overview of the temporal and spatial constancy of body odor.

O-4

A HOLISTIC VIEW OF RIVER WATER QUALITY USING PASSIVE SAMPLING AND GC×GC–TOF MS

Jonathan Grandy[1], Matthew Edwards[1], Laura McGregor[2], Steve Smith[3], Nick Bukowski[3]

[1]SepSolve Analytical, Waterloo, Canada. [2]SepSolve Analytical, PETERBOROUGH, United Kingdom. [3]SepSolve Analytical, Peterborough, United Kingdom

Abstract

Routine monitoring of water quality is now a requirement of environmental legislation, e.g. the EU's Water Framework Directive (WFD). The cause of a poor water quality status is often unknown and extensive investigative monitoring is needed to determine what chemical may be responsible.

To monitor all such analytes in a single run using one method demands high sensitivity across the entire sampling and analytical system. Sampling of water has historically been carried out using grab-samples, but passive samplers (e.g. silicone rubber, semi-permeable membrane devices (SPMD and LDPE) are now available that indirectly lower detection limits, by concentrating pollutants over time.

Here, silicone rubber samplers were deployed for several weeks in a UK river course, to sequester large volumes of water and provide a concentrated, representative extract for analysis. However, the sample complexity resulting from passive sampling calls for enhanced separation.

The combination of passive sampling and GC×GC–TOF MS allows for the detection and identification of a wide range of organic pollutants, including pesticides, pharmaceuticals, and emerging contaminants, at trace levels. This non-target approach provides a more comprehensive assessment of the chemical composition of river water and a better understanding of pollution sources and trends.

This abstract emphasizes the potential of passive sampling coupled with GC×GC–TOF MS as a powerful tool for environmental monitoring, offering a holistic view of river water quality.

O-5

NON-TARGET SCREENING AND CONTAMINANT PROFILING OF HOUSE DUST COLLECTED ACROSS EUROPE BY COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY - MASS SPECTROMETRY AND MULTI-VARIATE STATISTICAL EVALUATION

Peter Haglund

Umeå University, Umeå, Sweden

Abstract

Seventy-five house dust samples were collected from 14 countries, spread across Europe, through a collective effort within the Norman research network. The dust was sieved and extracted with acetone:hexane (1:3) and acetone. The extracts were pooled and analysis by comprehensive two-dimensional gas chromatography - electron ionization - mass spectrometry (GC×GC-EI-MS). Data evaluation was performed using multi-variate statistical analysis by unsupervised as well as supervised principal component analysis (PCA). Unsupervised PCA was conducted using aligned peak table data (matrix of samples vs. dust contaminant peak volumes), whilst supervised PCA was performed on the raw data utilized Fisher Ratios of chromatographic regions (‘tiles’) to compare contaminant abundances between groups of samples, in this case samples from North-Europe, Mid-Europe, and South-Europe. The unsupervised PCA revealed that there are large variations in dust contaminant levels between countries, but also between dust samples originating from the same country. In fact, the within country variability was often as great or even greater than the between country variability. A 3D-score plot of the three first principal components is shown in the graph below. Country codes are used to indicate origin. The tile-based data evaluation and supervised PCA revealed a number of compounds that significantly differed between North, Middle and South Europe, including nicotine, fragrances, phthalates, pesticides, and personal care product ingredients.

O-6

CHEMICAL CHARACTERIZATION OF THE AIRCRAFT CABIN ENVIRONMENT UTILIZING GC×GC-TOFMS AND HARD AND SOFT IONIZATION.

Kevin Hayes[1,2], Gwen O'Sullivan[2], Scott Campbell[3], John Moncur[3], David Megson[1]

[1]Manchester Metropolitan University, Manchester, United Kingdom. [2]Mount Royal University, Calgary, Canada. [3]SpectralWorks Limited, Cheshire, United Kingdom

Abstract

Contamination of the aircraft cabin environment has been associated with an increased occupational risk and incidences of chemical injury in pilots and flight attendants. The aircraft environment is chemically complex with multiple potential contaminant sources: Interior furnishings are impregnated with halogenated and organophosphate flame retardants, pesticides and herbicides are regularity employed to prevent unwanted transmission or transport of pests, and air is bled from the engines to pressurize most commercial aircraft cabins. This air can contain chemicals originating from engine and hydraulic oil, their respective additives, and pyrolyzed products that may be generated in the high heat and pressure environment. When attempting to describe the occupational risk of the cabin environment it is essential to properly understand the importance and contributions of each potential pollution source.

To assess the aircraft cabin environment, wipe sampling was conducted on sixty-seven flights of varying duration and aircraft type. The samples and trip blanks were extracted and run with minimal cleanup, in triplicate, on a flow modulated GC×GC-ToFMS in tandem ionization mode (SepSolv BenchTOF). Suspect screening, followed by a pseudo non-targeted analysis was completed; hard and soft ionization coupled with the separatory power of multidimensional chromatography is used in this instance in the place of high-resolution mass spectrometry for compound identification. Data was analyzed using AnalyzerPro XD, and with the technical assistance of SpectralWorks LTD, greater than thirty categories of sample were examined using a variety of multivariate and summary statistical tools.

O-7

DON'T LET THE REALITY OF GC×GC-MS DATA BURST YOUR BUBBLE! OR HOW THE &@$#%^& AM I SUPPOSED TO MANAGE ALL THESE BITS AND BYTES?!?*

James Harynuk, Broderick Wood

University of Alberta, Edmonton, Canada

Abstract

Getting funding for a new GC×GC-MS system or two is super exciting! However, finding the funds and picking out the right chromatography hardware option for your needs is where your expertise as a chromatographer and scientist likely ends. You get computers to run the instruments and collect data provided by the vendor. Then the onslaught of data bursts your bubble as the reality of a busy GC×GC-MS lab sinks in.

Maybe the computer collecting the data from the instrument cannot handle the onslaught. Maybe your students are losing or misplacing portable drives or wiping data they thought they'd backed up. Maybe the computer you bought to process the data can process a couple of files but then things get super bogged down and slow, maybe it cannot even open the files, or maybe it can process and align the files, but the processing is too slow or impossible at the scale that you need. You have met the "minimum requirements" from the vendors, so what's wrong? Where should you spend money to boost performance to an acceptable level?

In this presentation, we dive into the nitty gritty of networking, storage, computer specs, processing performance, and attempt to answer the main question: how and where do I spend my money to get a solution that makes it easy to manage and protect my data, and where should I spend money when investing in new computers for crunching data?

*may also apply to LC×LC-MS etc too.

O-8

STREAMLINING GROUP TYPE ANALYSIS WITH STANDARD GC×GC TEMPLATES THROUGH COMPUTER VISION-ASSISTED ALIGNMENT

Daniel Geschwender, Qingping Tao, Chase Heble

GC Image, LINCOLN, USA

Abstract

Comprehensive two-dimensional gas chromatography (GC×GC) is a powerful technique for the group type analysis of complex sample mixtures. Standard methods using GC×GC-FID such as UOP 990 and ASTM D8396 have been established. However, these methods require careful alignment between the chromatograms and standard templates for accurate quantification.

To address this challenge, we have developed various models and interpolation methods for correcting retention time shifts in whole chromatograms. These models enable software to adapt the template to individual samples automatically. In addition, we are exploring several computer vision approaches for both automated peak matching and as a quality control measure of the alignment of individual groups. These approaches utilize a computer vision model that captures the location and distribution of reference peaks to assess the alignment of individual groups and ensure the reliability of the group type quantification results.

Together, these approaches provide a foundation to develop a workflow that streamlines the transfer of standard templates across GC×GC chromatograms, improve the accuracy and efficiency of group type quantification, and facilitate the adoption of standard methods for routine analysis.

O-9

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

Eliise Tammekivi[1], Magali Batteau[1], Dorothée Laurenti[2], Karine Faure[1]

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Abstract

Lignin is an abundant natural polymer that is by far the largest natural resource for aromatic compounds. Nevertheless, approx. only 2% of it is commercialised while the rest is mainly burned to power the paper industry, from which lignin is obtained by fractionating cellulose from lignocellulosic biomass. However, it has the potential to be valorised more by isolating valuable aromatic compounds, incorporating into materials (e.g., coatings, resins, thermoplastics), or used as biofuel. For making these valorisation processes efficient, thorough structural characterisation via a powerful chromatographic technique can be highly beneficial as the complex composition of lignin depends on the botanical origin, isolation, and depolymerisation processes.

Therefore, an off-line comprehensive two-dimensional (2D) chromatography method combining liquid chromatography, supercritical fluid chromatography, and high-resolution mass spectrometry with fragmentation (LC×SFC-HRMS/MS) was developed. The implementation of a 1-aminoanthracene column in the second dimension enabled a good class separation of lignin monomers, dimers, trimers, and tetramers with additional separation based on the number of hydroxyl groups and steric effects. The pentafluorophenyl column in the first dimension additionally improved the separation based on hydrophobicity, thus the first 2D-LC plot demonstrating classification of lignin compounds was obtained. The comparison of the technique to 1D-SFC showed that the 2D-LC method is also superior for separating isomers, which is especially beneficial for lignin as 77% of the detected compounds had at least one isomer. Advanced data analysis methods (MS-DIAL, SIRIUS, and FBMN) were integrated into the non-target workflow to rapidly visualise and study the detected compounds.

O-10

USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY FOR DETERMINING BIOGENIC COMPONENTS IN RENEWABLE TRANSPORTATION FUEL BLENDS

Rafal Gieleciak, Anton Alvarez-Majmutov, Jinwen Chen

Natural Resources Canada, Devon, Canada

Abstract

The global effort to use more renewable resources in transport fuels aims to reduce greenhouse gas emissions. Two overarching strategies are employed to attain this objective: one entails straightforward blending of biofuels with traditional fuels, whereas the other centers on the co-processing of biocrudes with petroleum streams within existing refineries. The latter option presents a potentially cost-effective method for reducing the carbon footprint of transportation fuels. Accurate assessment of the renewable carbon content of refinery products is important in the context of domestic and international emission standards, as well as for regulatory credits and incentives. To effectively achieve these aspirations, it is crucial to monitor and quantify renewable constituents after blending or throughout the co-processing value chain. Furthermore, a nuanced understanding of the compositional changes during co-processing plays a pivotal role in foreseeing and mitigating potential disruptions to refinery operations. In current studies, including this one, the utilization of two-dimensional gas chromatography (GC×GC) technique has been proven to be excellent for resolving, identifying, and quantifying individual components in biocrudes and their fuel products. In this presentation, special attention will be given to determining oxygenates in the diesel and naphtha fractions. We will illustrate how GC×GC can be used to track renewable components during co-processing. Although this analytical technique may not completely address the complexity of biogenic carbon determination, it will significantly improve the understanding of the fate of renewable components in co-processed fuel streams.

O-11

ALKENE QUANTIFICATION IN PLASTIC WASTE-DERIVED ALTERNATIVE FUELS USING GC×GC-FID

Genesis Barzallo, Hung Gieng, Petr Vozka

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Abstract

In recent decades, the global accumulation of plastic waste has exceeded 10 billion tons, posing a significant environmental challenge. Conventional disposal methods like incineration and mechanical recycling have proven insufficient in addressing this crisis. However, through conversion techniques such as hydrothermal processing and pyrolysis, it is possible to transform plastic waste into alternative fuels containing varying olefin concentrations (up to 50 wt.%). Currently, no methods exist for quantifying olefin content at such high concentrations. In this study, we have developed a novel approach to characterize and quantify aliphatic olefins in plastic waste-derived fuels using comprehensive two-dimensional gas chromatography with a flame ionization detector (GC×GC-FID), a derivatization process involving dimethyl disulfide, and olefin standards from C_5 to C_{25}. Results obtained from GC×GC-FID closely align with established ASTM-approved methods, including D1159 (Bromine number), D5554 (Iodine value), and D1319 (FIA method). This study presents a robust and dependable technique for accurately quantifying olefins in fuels derived from plastic waste conversion.

O-12

CHARACTERIZATION AND QUANTITATIVE HYDROCARBON GROUP-TYPE ANALYSIS OF PLASTIC-DERIVED PYROLYSIS OILS BY GC×GC-TOFMS/FID

Christina Kelly, Joseph Binkley, John Hayes

LECO Corporation, Saint Joseph, USA

Abstract

An increase in the desire for waste plastics converted to pyrolysis oils to be used as fuel has led to the development of processes that create new potential feedstocks which, even with similar physical characteristics to traditional geochemical sources, carry higher risks of poisoning catalysts or otherwise reducing efficiency due to very different chemical characteristics. This presentation focuses on characterization of plastic-derived pyrolysis oils and the comparison of polar-nonpolar and nonpolar-polar column sets that target increased chromatographic resolution in different regions of the structured chromatograms, revealing clusters of compound classes not typically seen in traditional petroleum fuels, such as multi-branched paraffins and specific heteroatom-containing species of interest. The data provided by the LECO Paradigm Shift highlights the flexibility of this flow-modulator-and-splitter system for comprehensive two-dimensional chromatography (GC×GC) method optimization while utilizing the combined power of time-of-flight mass spectrometry (TOFMS) and simultaneous flame ionization detection (FID). With a splitter design ensuring that a constant ratio of analytes is sent to each detector throughout the GC temperature program to maintain uniform area % quantitation from the FID, the Paradigm Shift system preserves the integrity of the GC×GC separation of plastic-derived pyrolysis oils for analytical methods that concurrently provide rich qualitative and accurate quantitative information.

O-13

EXPANDING THE SCOPE OF TILE-BASED GC×GC–TOFMS DATA ANALYSIS

Robert Synovec, Caitlin Cain, Lina Mikaliunaite

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Abstract

Comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOFMS) is a powerful instrumental platform for the analysis of complex samples. Chemometric data analysis approaches play a pivotal role in the analytical workflow, translating the raw data into useful chemical information. We are developing and applying advanced approaches for the analysis of GC×GC–TOFMS data. Previously, we established tile-based Fisher-ratio (F-ratio) analysis, a statistically based data mining method to discover analytes that distinguish sample classes based upon a supervised experimental design. More recently, we have expanded the scope of using the same tile-based software platform for other purposes, such as the simple comparison of two chromatogram (1v1 analysis) and unsupervised feature selection using relative variance ranking, which can be used for principal components analysis (PCA) and partial least squares (PLS). For all of these chemometric approaches the same tile-based approach is used, but with different quantitative metrics for "hitlist" generation, enabling the rapid and high-quality extraction of the most useful analyte information. Recent advances are aimed at improving the overall hitlist ranking capability of the software, coupled with implementing in various chemometric methods. Applications dealing with metabolomics, fuel, food quality and safety, and environmental studies will be presented.

O-14

WORKFLOW DEMOCRATIZATION OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY – HIGH-RESOLUTION TIME-OF-FLIGHT MASS SPECTROMETRY DATA

Michael Sorochan Armstrong[1,2], Court Sandau[2,3]

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Abstract

Engineering advances for the application of multidimensional chromatographic data have enabled its use in a wide variety of settings where users demand high specificity and sensitivity in their chemical analyses. But from raw instrument signal to the final summary of chemical information as a "peak table", much of how the data is handled remains hidden within a black box. No single solution has been proven to overcome all known challenges associated with the analysis of hyphenated multidimensional chromatographic data. This is due to issues associated with an exhaustive comparison due to the diversity of data formats, unknown algorithmic steps, and practical issues with sharing the raw data from different studies using conventional repositories. The most persistent issue is that the comparison of unknowns within proprietary software platforms discourages attempts at a meaningful and actionable interpretation of the relative benefits and drawbacks of the different software offerings [1].

To address many of these issues, we outline a paradigm shift from semi-supervised workflows within proprietary desktop environments. The workflow embraces the suite of open-source tools available to handle similar challenges in the context of big data analytics. This suite of community-driven tools within the Python ecosystem are used to shed some light on the black box and move chromatographic data pre-processing towards wider scrutiny and actionable improvements.

[1] Weggler, Benedikt A., et al. "A unique data analysis framework and open-source benchmark data set for the analysis of comprehensive two-dimensional gas chromatography software." Journal of Chromatography A 1635 (2021): 461721.

O-15

INVESTIGATING SENSORY-CLASSIFIED ROASTED ARABICA COFFEE WITH GC×GC-TOFMS AND CHEMOMETRICS TO UNDERSTAND POTATO TASTE DEFECT

Caitlin Cain[1], Meriem Gaida[2], Pierre-Hugues Stefanuto[2], Jean-François Focant[2], Robert Synovec[1], Susan Jackels[3], Kristen Skogerboe[3]

[1]University of Washington, Seattle, USA. [2]University of Liège, Liège, Belgium. [3]Seattle University, Seattle, USA

Abstract

As coffee consumption increases globally, demands for specialty and/or high-quality coffee beans are primarily driven by consumer preferences toward the taste and aroma of the final brew. However, the presence of chemical defects can negatively impact the sensory properties of coffee. Potato taste defect (PTD), unique to East African coffee, is characterized by a distinct musty, vegetable, raw potato aroma due to the presence of 2-isopropyl-3-methoxypyrazine (IPMP). This work develops a volatile fingerprint of PTD in roasted arabica coffee using headspace-solid-phase microextraction-comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (HS-SPME-GC×GC-TOFMS) and chemometrics. Tile-based Fisher ratio (F-ratio) analysis discovered over 300 volatiles that discriminated clean (i.e., no off-odor) coffee samples from those identified as having a strong PTD odor (p-value < 0.01). Analytes associated with unpleasant sensory descriptions were positively correlated with the odor of PTD, while analytes associated with desirable aromas were found to be negatively correlated with odor severity. Principal components analysis (PCA) highlighted that the coffee samples clustered based on the presence of PTD. Furthermore, use of the class-distinguishing analytes discovered by F-ratio analysis for partial least squares (PLS) regression produced accurate models of IPMP concentration with low prediction errors (~ 10 % error). Investigation of the PCA and PLS loadings revealed the volatile compounds which are most important to predicting PTD in roasted coffee. Ultimately, these results reveal the complex volatile signature of PTD in East African coffee beans, demonstrating that the defect has outcomes that extend well beyond the concentration of IPMP.

O-16

LONGITUDINAL CHANGES VALIDATE BREATH SIGNATURES OF ACUTE RESPIRATORY EXACERBATIONS

Michael Wilde[1], Rebecca Cordell[2], Matthew Richardson[2], Wadah Ibrahim[2], Paul Monks[2], Chris Brightling[2], Erol Gaillard[2], Neil Greening[2], Salman Siddiqui[3], on behalf of the EMBER consortium[2]

[1]University of Plymouth, Plymouth, United Kingdom. [2]University of Leicester, Leicester, United Kingdom. [3]Imperial College, London, United Kingdom

Abstract

The measurement of exhaled, low-molecular weight metabolites in breath offers new opportunities for the discovery of non-invasive diagnostic and prognostic biomarkers of acute cardiorespiratory disease. Analysis by multidimensional gas chromatography-mass spectrometry (GC×GC-MS), coupled with rigorous clinical phenotyping, revealed signatures of exhaled volatile organic compounds (VOCs) with high diagnostic accuracy (79% sensitivity, 85% specificity). The increased confidence in chemical assignment of VOCs afforded by GC×GC-MS resulted in the discovery of breath metabolite networks associated with clinical subtypes of cardiorespiratory exacerbation. Breath samples were then collected from the same cohort of patients 6 months post recovery to evaluate longitudinal changes in the exhaled chemical signatures. The temporal trends of significantly enriched metabolite sets with high chemical similarity were consistent exhaled VOCs being associated with acute exacerbation.

O-17

MULTI-OMICS WORKFLOW FOR BLOOD SERUM SCREENING USING GC×GC-TOFMS

Pierre-Hugues Stefanuto

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Abstract

According to the world health organization (WHO), colorectal cancer (CRC) ranks as the third most frequently diagnosed cancer and the second leading cause of cancer-related deaths. The current endoscopic-based or stool-based diagnostic techniques are either highly invasive or lack sufficient sensitivity. Thus, there is a need for better screening approaches.

The rapid advancement of high throughput "omics" approaches, such as meta-genomics, transcriptomics, proteomics, metabolomics, lipidomics, microbiomics, and volatolomics, offer a potentially less invasive alternative than available techniques to develop novel biomarkers for colorectal cancer screening that could contribute to its clinical management.

For small molecules "omics" screening, gas chromatography coupled to mass spectrometry (GC-MS) represents a method of choice to screen biofluid samples. However, GC-MS is mostly used for targeted analysis due to the high complexity of the matrices. To tackle this limitation, comprehensive two-dimensional gas chromatography coupled to mass spectrometry provided increased separation capabilities, making it a method of choice for untargeted small molecule metabolomics.

In this study, we analyzed 64 human serum samples representing three different groups of colorectal cancer using cutting edge GC×GC–LR/HR-TOFMS techniques. We analyzed samples with two different specifically tailored sample preparation approaches for lipidomics (fatty acids) (25 µL serum) and metabolomics (50 µL serum). In-depth chemometric screening with supervised and unsupervised approaches and metabolic pathway analysis were applied on both datasets. To ensure the high quality of the data produced, we have established a strict QAQC protocol including pooled sampled, serum SRM, and standard mixtures injections.

O-18

DIRECT FLOW MODULATION METHOD FOR COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY

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Abstract

The flow modulation method is a simple and low-cost modulation method for comprehensive two-dimensional gas chromatography. According to the flow path construction, it can be classified as either direct flow modulation or flow switch (or indirect) modulation. Comparing with the flow switch modulation method, the direct flow modulation method can provide longer secondary separation time (a 120 s secondary time has been achieved), higher compression ratio to enhance the peak height, and simpler construction (less connectors). The downside is that the modulation gas has more influence on the primary column flow, therefore, it needs more time to set up an experiment. In this presentation we will discuss the structure, operation conditions, and performance of the direct modulation method. We will also demonstrate the applications of this method on gasoline and reference gas oil standard.

O-19

LC×SFC VALVE TECHNOLOGIES: GUIDELINES TOWARDS A SUCCESSFUL ONLINE MODULATION

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Abstract

In recent years, on-line two-dimensional liquid chromatography has been significantly developed in many fields of application. Various separation modes are possible but are sometimes limited in terms of orthogonality. The use of SFC in the second dimension offers a wide choice of mobile and stationary phases, suggesting retention properties orthogonal to those of the first dimension. Initial works on LC×SFC on-line coupling published in the literature highlighted the first difficulties of solvent compatibility [1] or potential problems of bubbles created by CO_2 in partial loop filling mode [2].

This present work highlights the impact of the interface between the LC and SFC dimensions on the performances of the 2D separation. Four different configurations have been evaluated, along with make-up flows. Their performances with empty loops eliminated the need of complex trapping columns, whatever the LC mobile phase. Injection in partial fill mode was possible without any problems of CO_2 bubbles, solvent miscibility, pressure, or modulation repeatability in each of the studied configurations. Selected configurations even allowed the use of a mobile phase split upstream of the valve. Guidelines present the best interface depending on chromatographic conditions.

For the very first time, the online LC×SFC instrumentation is optimized and can be used as easily as LC×LC instrumentation.

[1] M. Sun et al. / J. Chromatogr. A 1541 (2018) 21–30
[2] M. Sarrut et al. / J. Chromatogr. A 1402 (2015) 124–133

O-20

EXTENDING ANALYTE BOILING POINT RANGE USING THINNER FILM POROUS LAYER OPEN TUBULAR COLUMNS PAIRED WITH GC×GC-MS

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Abstract

We explore the extension of the boiling point range of samples for GC×GC-qMS with valve-based modulation using thin film porous layer open tubular (PLOT) column on the first dimension (^{1}D) and a wall coated open tubular (WCOT) column on the second dimension (^{2}D). PLOT columns are traditionally made with relatively thick stationary phase films, as they are typically used to separate permanent gases and extremely volatile compounds. We have previously investigated the benefits of using PLOT columns for separating volatile compounds by valve-based GC×GC-qMS, especially when many isomeric compounds are present in the mix, but herein we focus on expanding the scope of PLOT column use for GC×GC-qMS even further by using thinner film PLOT columns on ^{1}D. A commercially available 8 µm film PLOT column is compared to 4 µm and 2 µm prototype film columns. We demonstrate the added benefit of these thinner film PLOT columns, as they still provide adequate separation of permanent gases, but concurrent with the separation of analytes with a wider boiling point range.

O-21

INTRODUCING AUTOMATED ONLINE MULTICOLUMN TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY SCREENING AS A RAPID AND EFFICIENT TOOL FOR METHOD DEVELOPMENT OF MULTIPLE PIPELINE MODALITIES

Heather Wang, Zach Dunn, Andrew Singh, Rodell Barrientos, Imad Haidar, Erik Regalado

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Abstract

Two-dimensional liquid chromatography (2D-LC) has become a valuable tool for improving peak capacity and selectivity. Though powerful, standard 2D-LC instrumentation and software can often lead to tedious method development that is poorly suited for a fast-paced industrial environment. In this regard, the introduction of an automated online 2D-LC setup that could screen multiple columns in both dimensions without manual intervention will undeniably serve to streamline column/mobile phase selection and secure the viability of 2D-LC as a mainstay instrument for industrial applications. Herein, we introduce and investigate a multicolumn online 2D-LC approach that simplifies column screening and method development dramatically enabling us to combine multiple columns in both dimensions. This strategy in conjunction with diode array detection (DAD) in both dimensions and mass spectrometry (MS) acquisition in the second dimension serves to explore different columns and mobile phases as a framework for screening targeted compounds in multicomponent mixtures without having to perform chromatographic purification. Multiple achiral – achiral and achiral – chiral online 2D-LC-DAD-ESI-MS methods combining several stationary phase selectivity in an automated fashion are successfully applied to the separation and analysis of (bio)pharmaceuticals, where in many instances, traditional 1D-UHPLC fails or delivers sub-optimal results.

P-1

DEVELOPMENT OF A FISHER RATIO CONTRAST METRIC FOR SIMULTANEOUS DISCOVERY OF COMPOUNDS INDICATING EITHER MOLDING KINETICS OR BEAN GEOGRAPHICAL REGION IN MOISTURE DAMAGED COCOA BEANS

Lina Mikaliunaite, Owen Lee, Robert Synovec

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Abstract

Herein the development of a Fisher ratio contrast metric for chemometric analysis of simultaneous processes in comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC×GC-TOFMS) datasets is presented. The metric was developed to analyze the dataset of moisture damaged cocoa beans where molding of six different bean types was monitored over seven days. This presented an opportunity to investigate two processes that were present inherently in the dataset at once: molding kinetics and bean type based on geographical location. Usually, this study would require the initial generation of two separate hitlists using F-ratio to find a separate list of compounds of molding and bean type. However, generation and subsequent analysis of two separate hitlists would be extremely time-consuming, it would be hard to match analyte peaks across the two hitlists, and most importantly it would not show how much a compound is contributing to molding over bean time and vice versa. To address this challenge, an F-ratio contrast metric was developed to provide a method to analyze both processes simultaneously, resulting in one hitlist of compounds. The F-ratio contrast metric takes the ratio of the F-ratio using the molding time points as classes versus the F-ratio using bean geographical location type as the other set of classes, where for a given analyte hit, the larger of the two F-ratios is always used in the numerator. Using the F-ratio contrast metric, we evaluated a moisture damaged cocoa beans dataset and found ~200 compounds that contribute to either process.

P-2

ADVANCING FINGERPRINT DEPOSITION MODELING THROUGH THE INTEGRATION OF COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND TIME-OF-FLIGHT MASS SPECTROMETRY FOR AGE ESTIMATION

Elena Mosham, Rayana Ramirez, Katherine Roberts, Petr Vozka

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Abstract

Fingerprints are widely used for personal identification in forensic casework due to their individualizing characteristics. However, more information can be obtained beyond the external features of a fingerprint. We propose developing a time frame model of the chemical degradation process based on the compounds extracted from fingerprints to estimate how long a fingerprint has been deposited on a surface. This project aims to use comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry (GC×GC-TOF/MS) to develop a method for estimating the time since deposition. This will provide more definitive circumstantial evidence of an individual's presence at a crime scene. Preliminary research is being conducted using LECO's Pegasus BT 4D GC×GC TOF/MS. Eccrine and sebaceous fingerprints are collected on microscope glass slides and analyzed at varying times post-collection, ranging from immediately to four months. Preliminary results indicate the presence of squalene and cholesterol in fingerprints. Continuous research is being conducted to determine how aging fingerprints affect the concentration ratio of squalene and cholesterol.

P-3

FROM DATA TO DECISIONS: USING NOVEL SOFTWARE TOOLS FOR AUTOMATED PAIRWISE COMPARISON OF GC×GC DATA

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Abstract

Comprehensive two-dimensional gas chromatography (or GC×GC) is now used regularly to improve the separation of complex mixtures of volatile and semi-volatile organic compounds – in fields as diverse as metabolomics, environmental forensics and food authenticity. By coupling GC×GC with time-of-flight mass spectrometry (TOF MS), there is the added benefit of data-rich chromatograms containing detailed mass spectral information – making it ideal for non-target screening applications.

We know we can gain greater insight into sample composition with GC×GC–TOF MS, but the challenge then becomes "what am I going to do with all of this data?". Unfortunately, this has led to GC×GC developing a reputation as being difficult and time-consuming, often making it less attractive for GC–MS users who could truly benefit from the extra separation capacity.

In this poster, we demonstrate a workflow that solves this challenge, with automated alignment and comparison of the raw data, as well as fast reporting of the key differences. This automated approach allows complex GC×GC datafiles to be compared in minutes, instead of days (or even weeks).

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P-4

ASSESSMENT OF EXHALED BREATH VOC STABILITY ON TENAX® GR THERMAL DESORPTION TUBES

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Abstract

The analysis of exhaled breath volatile organic compounds (VOCs) is increasingly being leveraged to study human health and disease including respiratory infections, asthma, and metabolic disorders. Sampling of breath VOCs typically involves exhaling into collection bags and pumping the breath over sorbent-packed thermal desorption tubes (TDTs). Due to constraints such as time and instrument capacity, however, samples cannot always be analyzed same-day and must be stored for a future date. This brings forth questions regarding the most appropriate storage method, specifically with regards to storage length, as sample integrity must be maintained. Studies aimed at robustly evaluating the stability of exhaled breath VOCs are limited. In light of this, we conducted a stability study to examine the effects of (1) storage at 4 °C, (2) overnight air shipping, and (3) standard ground shipping on exhaled breath VOCs up to 32 days. For each of the three experiments, breath was collected from four subjects and split onto duplicate Tenax® GR TDTs. TDTs were stored at 4 °C and analyzed using TD–GC×GC–TOFMS after 0.5, 1, 2, 4, 8, 16, and 32 days; air- and ground-shipped samples were analyzed after 8, 16, and 32 days. We found no significant effect of storage after 32 days nor from air or ground shipping on the relative abundance and the numbers of detected VOCs. These results show that exhaled breath VOCs collected under these conditions can reasonably be stored for upwards of a month without jeopardizing sample integrity.

P-5

CHARACTERIZATION AND COMPARISON OF FRESH AND DRIED HERBS WITH GC, GC×GC, AND TOFMS

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Abstract

Gas Chromatography (GC) and mass spectrometry (MS) are well-established techniques for the characterization of a wide range of food, beverage, and flavor samples. The chemical components with important aroma contributions tend to be volatile and semi-volatile, thus amenable to GC analysis. Extending the analytical separation to two dimensions, with comprehensive two-dimensional gas chromatography (GC×GC), enhances the peak capacity and can allow for exploring more complex samples and determining more individual analytes within complex samples. Coupling GC (or GC×GC) to TOFMS leads to identification information for these isolated analytes and supports non-target analyses where analytes of interest and importance can be determined through data evaluation. Software tools that compare sets of GC×GC samples facilitate these analyses and can effectively reveal useful information from this rich data. In this work, we evaluate the aroma characteristics for herb samples, with a particular focus on differences between fresh and dried versions of the herbs. This type of characterization provides a better understanding of these types of products and ingredients, and can be useful for quality control, product development, and batch comparisons. Here, we show the characterization and comparison of herbs and the analytical benefits of these approaches.

P-6

COMPARISON OF NEW AND USED VACUUM PUMP OIL USING TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND HIGH-RESOLUTION TIME-OF-FLIGHT MASS SPECTROMETRY

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Abstract

New and used vacuum pump oil were measured using two-dimensional gas chromatography coupled with high-resolution time-of-flight mass spectrometry. Standard electron ionization was used to collect library-searchable mass spectra, and field desorption was used to observe the molecular weight distribution of both samples. One-dimensional GC profiles for both samples showed a broad, unresolved "hump." Two-dimensional GC revealed that the base oil components are represented in an unresolved complex mixture (UCM); however, it was possible to identify differences attributed to additives by GC×GC-TOFMS. Antioxidant class compounds were observed in the new pump oil, while oxidized additives were detected in the used pump oil. Because of the complex nature of the samples, it would not have been possible to identify the additives and their oxidation products by conventional GC-MS.

P-7

IDENTIFYING PUTATIVE VOLATILE BIOMARKERS FOR *S. AUREUS* METHICILLIN-RESISTANT AND SMALL-COLONY VARIANT SUBTYPES

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Abstract

Seventy percent of persons with cystic fibrosis (pwCF) in the US are respiratory culture positive for *Staphylococcus aureus*, and this rate is climbing (1). With increasing *S. aureus* infections, the detection of clinically-relevant subtypes, such as methicillin-resistant *S. aureus* (MRSA) and small-colony variants (SCVs), is also increasing. Both subtypes, but especially thymidine-dependent SCVs, have been associated with worse patient outcomes (2, 3). Due to the high rates and co-occurrence of SCVs and MRSA (2), detecting and tracking the emergence of each of these *S. aureus* subtypes in CF lung infections is important for understanding the progression of CF lung disease and for formulating effective treatment options. We are working to develop breath tests for detecting *S. aureus* MRSA and SCV lung infection subtypes in situ. As a first step in this process, we have characterized the *in vitro* volatile organic compounds (VOCs) produced by 110 *S. aureus* isolates from CF lung infections, representing four classes: methicillin-sensitive *S. aureus* normal colony variants (MSSA-NCVs), MSSA-SCVs, MRSA-NCVs and MRSA-SCVs. We expect to identify distinct volatile biomarkers for discriminating MRSA vs MSSA and SCV vs NCV isolates, in vitro, with an accuracy of >80% for each classification.

References

1. Cystic Fibrosis Foundation. Patient Registry Annual Data Report. Cystic Fibrosis Foundation; 2021.

2. Wolter DJ et al. The Lancet Respiratory medicine. 2019;7(12):1027-38.

3. Dasenbrook EC et al. JAMA. 2010;303(23):2386-92.

P-8

AUTOMATED QC POOLING BY THERMAL DESORPTION TUBE RECOLLECTION OF GASEOUS MIXTURES FOR METABOLOMIC STUDIES

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Abstract

Quality control (QC) samples in metabolomic studies are used to assess the analytical variance of the data. These samples should ideally be a qualitative and quantitative representation of the entire collection of samples in the study, which are typically made by combining a small aliquot of each sample as a pooled QC sample. This pooled sample represents both the sample matrix and composition of analytes and is analyzed intermittently to monitor method variance as well as determine high- and low-quality data in the processing of the results.

Combining gaseous mixtures can prove challenging to make QC pool samples and typically surrogates are used, which may not include all compounds of interest. The recollection feature on commercial thermal desorption units can be a means to collect and pool gaseous mixtures for metabolomic studies, such as in breath analysis. Here, we apply this feature to a small sample set to demonstrate viability in larger studies.

P-9

IDENTIFYING THE PRIMARY SOURCES OF VARIANCE IN A BREATH BIOMARKER EXPERIMENT

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Abstract

Exhaled breath is rich in volatile organic compounds (VOCs) and serves as a valuable source of novel biomarkers for a diverse range of diagnostics and monitoring applications. As part of a team of investigators, we are conducting experiments to identify breath biomarkers of fatigue by collecting and analyzing breath samples from 60 subjects as they undergo five different experimental protocols. The subjects are grouped into small cohorts (6 to 10 subjects) who undergo the five experimental protocols over the same five-to-six-week period. In total we aim to collect >2800 breath samples over the span of 18 months. This creates a prime opportunity to study the multiple sources of variance that may confound the downstream analyses to identify breath biomarkers. Thus, we performed an interim analysis of the breath VOCs data using the first 19 subjects and 668 breath samples, representing two experimental cohorts, to identify the primary sources of variance in the data. Breath VOCs were analyzed using comprehensive two-dimensional gas chromatography- time-of-flight mass spectrometry (GC´GC-TOFMS). After data processing and alignment, the samples were visualized using principal component analysis (PCA) and t-distributed stochastic neighbor embedding (t-SNE), labelling the observations by experimental protocol, subject, cohort, and analytical batch. We observed that samples from the two cohorts clustered separately, and in cohort 0 we observed further clustering by experimental/analytical batch. These results indicate that batch correction may be required to harmonize the cohort data prior to machine learning to identify fatigue biomarkers.

P-10

A FEASIBILITY STUDY OF SAMPLE RECOLLECTION IN THE ANALYSIS OF SELECTED VOLATILE ORGANIC COMPOUNDS IN BREATH SAMPLES USING GC×GC-TOFMS

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Abstract

Exhaled breath is a non-invasive window into our health. The breath sample contains volatile compounds that can act as a unique chemical signature for lung diagnostic purposes [e.g., 1, 2] Thermal desorption (TD) is a well-established as a method to selectively concentrate VOCs from breath samples. However, generally, only one breath sample at one time point can be collected that is used up during chemical analysis. Sample re-collection can create a technical replicate to address this issue by directing the split flow onto one or more than one TDT enabling additional analyses as well as banking for future analyses [3].

In this study, we assessed the feasibility of re-collecting breath samples using the Centri® (Markes International, Bridgend, UK) instrument followed by GC×GC-ToFMS analysis. In Phase 1, we evaluated the accuracy and precision of five recollection steps by spiking Grob mix onto TDTs. Intra-day and inter-day accuracy was in the range of 80.5%-97.4% and 78%-92.5% respectively. Intra-day and inter-day precision was in the range of 00.7%-14.4% and 3.2%-11.1% respectively. We also prepared a standard mix of 20 "breath-related VOCs" that covered different chemical classes found in breath. Intra-day and inter-day accuracy was in the range of 67%-127% and 73%-129%, respectively. For most compounds, the intra-day precision for recollection using same TDT and different TDTs is less than 20% and 25% respectively. In Phase 2, we evaluated recollection accuracy and precision in breath analysis. In total, we performed 70 breath recollection tests and obtained on average 500 features per sample.

P-11

DEVELOPMENT AND APPLICATION OF A WEB-BASED SIMULATOR FOR TWO-DIMENSIONAL LIQUID CHROMATOGRAPHY SEPARATIONS

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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 (^{2}D) separation amplifies whatever separation is gained by the first dimension (^{1}D). 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.

P-12

FLOW MODULATED GC×GC IN COMBINATION WITH ATMOSPHERIC PRESSURE MASS SPECTROSCOPY USING THE SICRIT IONIZATION SOURCE

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Abstract

A new ambient ionization source, SICRIT, has been developed that utilizes a plasma-based core to provide a dielectric barrier discharge ionization to gaseous analytes. The SICRIT ionization source directly attaches to the inlet of any atmospheric pressure MS, utilizing the vacuum of the instrument to constantly pull in volatiles for direct analysis. As these volatiles are drawn into the source, they are softly ionized by the dielectric barrier discharge ionization, providing parent ions for a wide range of analyte polarities. Additionally, chromatographic techniques such as gas chromatography can be coupled to an atmospheric pressure MS with the SICRIT source. These mass spectrometers have more powerful vacuum systems that can therefore handle higher flow rates than a typical GC-MS, making it a perfect fit for flow modulated GC×GC. Further, hydrogen can be used as a carrier gas without a loss in sensitivity.

Here, a flow modulated GC×GC was coupled to both an LC-QTOF and triple quadrupole via the SICRIT ionization source for volatile analysis. Hydrogen is used as a carrier gas, with second dimension flow rates greater than 20 mL/min. The entire effluent is directed to the mass spectrometer for sensitive detection and identification of analytes.

P-13

COMPARISON OF DIESEL SAMPLES MEASURED BY USING GC×GC-HRTOFMS

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Abstract

Petroleum samples are complex materials that can be difficult to analyze by traditional methods like gas chromatograph-mass spectrometry (GC-MS) that use only electron ionization (EI). Furthermore, given the complexity of this material, it can be difficult to determine differences between samples when measured.

In this work, a high-resolution time-of-flight mass spectrometer (HRTOFMS) equipped with a thermal modulator GC×GC system was used to analyze diesel samples form different vendors by using an electron ionization/field ionization/field desorption (EI/FI/FD) combination ion source. The FI data was used to characterize analyte families using Type Analysis strategies involving KMD analysis. Additionally, new software capabilities were used to identify unique compounds in each sample. The results for this work will be presented.

P-14

OPTIMIZATION OF HEADSPACE SOLID-PHASE MICROEXTRACTION OF BRONCHOALVEOLAR LAVAGE SAMPLES FROM PEOPLE WITH CYSTIC FIBROSIS AND METHOD EVALUATION

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Abstract

Headspace solid phase micro-extraction (HS-SPME) is a prevalent technique in metabolomics and volatolomics research. However, the performance of HS-SPME can vary considerably depending on the sample matrix. As a result, fine-tuning of parameters for each specific sample matrix is crucial to maximize extraction efficacy.

In this context, we conducted a comprehensive HS-SPME optimization for bronchoalveolar lavage fluid (BALF) samples using two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-ToFMS). Our exploration spanned several HS-SPME parameters, including vial size, dilution factor, extraction time, extraction temperature, and ionic strength. The 10 mL vial size, no sample dilution, extraction time of 50 minutes, extraction temperature of 45 °C, and 40% salt were identified as the optimized parameters. The optimized method was then evaluated by a pair-wise comparison of ten sets of samples. The results revealed that the optimized method yielded an increase of 340% in total peak area and an increase of 80% in total peak number. Moreover, enhancements were observed across nine major chemical classes in both peak area and number. Notably, the optimized method also doubled the number of volatile compounds consistently detected across BALF samples from 52 to 108.