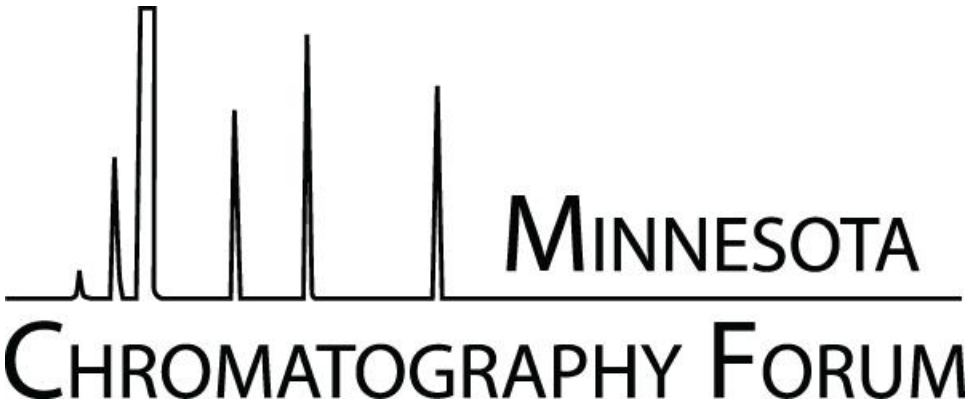


42nd Annual

MCF Spring Symposium

Heritage Center of Brooklyn Center

June 20-22, 2023

Table of Contents

Map of Heritage Center of Brooklyn Center

MCF SPRING SYMPOSIUM: June 20-22, 2023

Daily Program

Tuesday, June 20, 2023

7:30 AM	Registration & Check-In Breakfast Station & Beverages	Harvest Room (Door 4)
8:00 AM – 4:30 PM	Concurrent Short Courses " Basic Care, Maintenance, and Troubleshooting of Capillary GC Systems" " Applying Basic Chemistry to Improve Lab Results" " Ion Chromatography Fundamentals and Beyond"	Harvest Room
BREAKS:		
10:00 AM	Break (Snacks & Beverages)	Harvest Room
12:00 PM	Lunch	Garden City Ballroom
2:30 PM	Break (Snacks & Beverages)	Harvest Room

Wednesday, June 21, 2023

7:30 AM	Registration & Check-In Breakfast Station & Beverages	Harvest Room (Door 4)
8:00 AM – 12:00 PM	Concurrent Short Courses (Continued from Tuesday)	Harvest Room
10:00 AM	Break (Snacks & Beverages)	Harvest Room
12:00 PM	Lunch	Garden City Ballroom
12:00 PM – 6:00 PM	Vendor Exhibits Open	Carriage Hall
2:30 PM – 5:00 PM	Vendor Seminars	Harvest Room
3:30 PM – 6:00 PM	Reception (Hosted wine/beer, hors d'oeuvres)	Carriage Hall

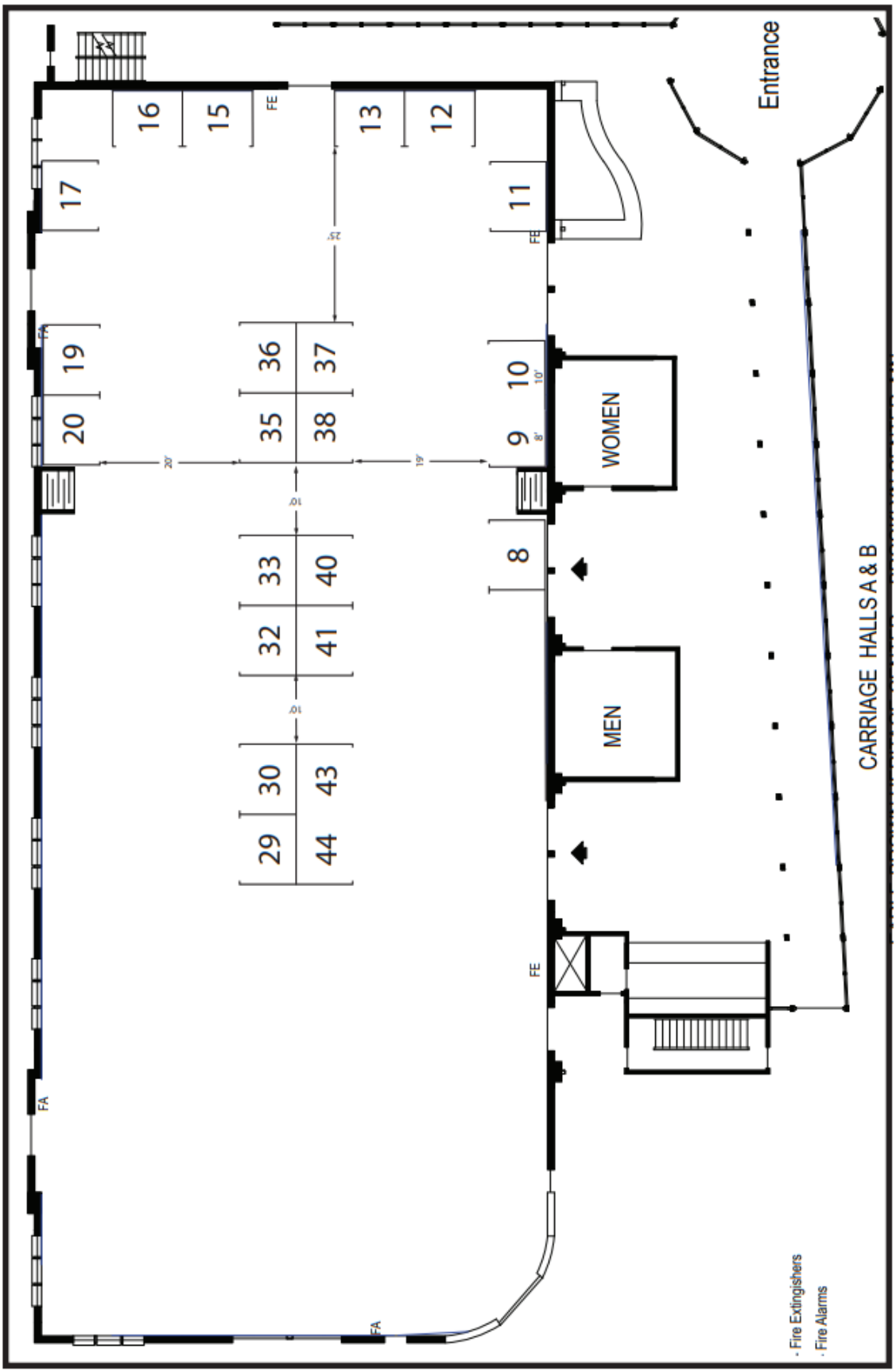
Please note: Registration is not required for the Vendor Exhibits, Vendor Seminars, and Reception on Wednesday.

Registration is required to attend Thursday's sessions
(Continues on next page)

Thursday, June 22, 2023 (Registration Required)

8:00 AM	Registration Breakfast	Carriage Hall (Door 1) Garden City Ballroom
8:45 AM	Technical Program Introduction	Garden City Ballroom
9:00 AM	Keynote Address "Unleashing the Potential of GCxGC-TOFMS for Emerging Challenges in Complex Sample Analyses" by Dr. Rob Synovec, University of Washington	Garden City Ballroom
9:55 AM	Presentation of the Jubilee Medal of the Chromatography Society to Professor Jared Anderson Presented by Dr. Daniel Meston	Garden City Ballroom
10:00 AM	Morning Break; Exhibits Open	Carriage Hall
10:30 AM – 12:30 PM	Morning Sessions: LC Materials and Instrumentation Advances	 Captain's Room (Main Level) Tack A/B (Lower Level) See Page 10 for Full Program
12:30 PM – 2:00 PM	Exhibits Open	Carriage Hall
12:30 PM – 2:00 PM	Lunch	Garden City Ballroom
2:00 PM – 3:30 PM	Afternoon Sessions: GC Environmental Analysis	 Captain's Room (Main Level) Tack A/B (Lower Level) See Page 11 for Full Program
3:30 PM – 4:30 PM	Exhibits Open	Carriage Hall
4:00 PM – 4:30 PM	Student Research Award Presentation Door Prize Drawing MCF Board Elections	Carriage Hall

Exhibitor Booths and Exhibit Floorplan (June 21 & 22)



2023 Symposium Exhibitor Location & Contact Information

Vendors Alphabetically with Booth Number

Agilent Technologies	43, 44
Aminoacids.com	12
Bruker	11
BUCHI	17
Chrom Tech, Inc.	9, 10
Fisher Scientific	19
Gerstel	13
Matheson Gas	8
Metrohm	35
Oxygen Service Company	15
Pace Life Sciences	29
Peak Scientific	30
Quantum Analytics	38
Restek	41
Sciex	40
Shimadzu Scientific Instruments, Inc.	33
Thermo Fisher Scientific	20
Waters Corporation	36, 37

Vendors by Booth Number

Matheson Gas	8
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Peak Scientific	30
Shimadzu Scientific Instruments, Inc.	33
Metrohm	35
Waters Corporation	36, 37
Quantum Analytics	38
Sciex	40
Restek	41
Agilent Technologies	43, 44

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Technical Presentations – Thursday, June 22, 2023

8:45 **Introduction**
Garden City Ballroom

9:00 **Keynote Address: Dr. Rob Synovec**
Department of Chemistry, University of Washington
"Unleashing the Potential of GCxGC-TOFMS for Emerging Challenges in Complex Sample Analyses"

9:55 **Presentation of the Jubilee Medal of the Chromatography Society to Professor Jared Anderson**
Presented by Dr. Daniel Meston

10:00 **Morning Break –** Exhibits – Carriage Hall

Time	Captain's Room (Main Level)	Tack A/B (Lower Level)
	Liquid Chromatography	**Materials and Instrumentation Advances**
10:30	Applications of Targeted and Untargeted Metabolomics in Agronomic and Horticultural Sciences Katrina Freund Saxhaug	Advances in Ionic Liquid-Based Stationary Phases and Sorbent Materials for Chromatography and Sample Preparation Jared Anderson
11:00	Forensic Analysis of Benzodiazepines in Blowfly Larvae and Puparia Using reverse-phase HPLC/HR-TOF-MS: Method Development and Quantitation Zienab Rabiei	Modulating π-Complexation in Silver(I) Ion-Olefin Separations using Coordination Chemistry Nicholas Tryon Tasson
11:20	An Automated High Throughput Approach for Large Scale Retention Measurement in Liquid Chromatography Trevor Kempen	The Development of an Automated and Self-contained Instrument for Ice Concentration Linked with Extractive Stirrer Kyle Burch
11:40	Development of a High-Throughput Micro-Scale Solid-Phase Extraction Method for HPLC-MS Analysis of Pyridine Nucleotide Metabolism in Maize Seedlings Evan Larson	Green Sample Preparation: It's All Green Doug Raynie
12:00	Analysis of Selenate in Human Plasma using Ion Pair Reverse Phase Chromatography Usha Mishra	Renewable Small-Scale Synthesis of Ammonia and its Improved Separation with Reactive Absorption Chinomso Onuoha
12:20	Predicting Isocratic Retention Factors from Gradient Elution Conditions Using a Re-parameterized Neue-Kuss Model Kathryn Cash	Development of Monolithic Immobilized Enzymatic Reactors for Complex Proteome Profiling Daniel Meston

Exhibit Hall Open 12:00-2:00 PM		
12:30	Lunch (12:30-2:00) – Garden City Ballroom	
	Gas Chromatography	**Environmental Analysis**
2:00	The HydroInert Source Improves GC/MS Analyses When Using H_2 as Carrier Gas Daron Decker	Utilizing Polymeric Ionic Liquid Sorbent Coatings in Thin Film Microextraction to Isolate Pesticides from Cannabinoids for Chromatographic Separations Victoria Zeger
2:30	Investigation of Wood Windows Aging Using Thermal Desorption-Pyrolysis Gas Chromatography-Mass Spectrometry Nafisa Bala	Precursor Ion Mass Spectrometry as a Selective Method of Detection for Target and Nontarget Pesticide Residues Aiden Berndt
2:50	Detection of Dicamba in the Gas Phase Using a Field Simulating Gas Chamber and GC-MS Taylor Johnson	A Comprehensive Workflow Approach for the Determination of PFAS in Wastewater Andy Johnson
3:10	A Comparative Study of Volatile Organic Compounds Liberated During 3D Printing Using Solid-Phase Microextraction and the Solid-Phase Microextraction Arrow Geometry Coupled to Gas Chromatography/Mass Spectrometry Bhawana Thapa	Investigating thermal destruction of per- and poly-fluoroalkyl substances (PFAS) by combining evolved gas analysis and thermal desorption – pyrolysis – gas chromatography and mass spectrometry Katerina Litvanova
3:30	Olefin Separation by Gas Chromatography using Polymer Electrolytes Incorporating Silver(I) and Copper(I) Ions Dongyun Ryoo	Sample Preparation Techniques for PFAS Analysis in Complex Environmental Matrices Daron Decker
3:50	End of Technical Program	
	Exhibit Hall Open Until 4:30 PM; Student Research Award Presentation & Door Prize Drawing at 4:00 PM	

Keynote

Unleashing the Potential of GC×GC–TOFMS for Emerging Challenges in Complex Sample Analyses: Application to Biomarker Discovery

Robert E. Synovec

University of Washington, Seattle, WA, USA

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. Compared to one-dimensional gas chromatography with mass spectrometry (GC-MS), GC×GC–TOFMS provides a 10-fold or more peak capacity than GC-MS, which translates into many more separated analyte peaks for a given sample to inform the analyst. To achieve this peak capacity advantage, complementary stationary phases need to be applied to "spread out the peaks." Finally, chemometric data analysis software tools can be applied to fully unleash the information initially trapped in the dense GC×GC–TOFMS data set. A wide variety of applications can be addressed with this experimental and software platform, dealing with metabolomics, food safety and quality, environmental studies, fuels, and so on. In this presentation biomarker discovery will be highlighted: (1) aroma profiling of clean coffee versus coffee impacted by the potato taste defect (PTD), (2) biomarker discovery of metabolites correlated to orthopedic knee-ligament injury, and (3) metabolome profiling of pacu fish farmed in Argentina. For these studies, the peak capacity advantage of GC×GC–TOFMS over GC-MS will be demonstrated. Also, recently introduced software to confidently discover, identify, and quantify meaningful biomarkers will be implemented.

LC-1

Applications of Targeted and Untargeted Metabolomics in Agronomic and Horticultural Sciences

Katrina Freund Saxhaug, Adrian Hegeman

University of Minnesota, St. Paul, USA

Abstract

Metabolites of agricultural and horticultural crops are tightly linked to crop phenotype through influences on inter-organismal interactions, characteristics of consumer preference like color, and response to biotic and abiotic environmental conditions. Metabolomics, a field of study focused on the measurement and analysis of all metabolites within a system, has increasingly been used to explore the chemical diversity of crops to develop improved varieties and agricultural products. At the Plant Metabolomics Facility of the University of Minnesota, we utilize metabolomics approaches to 1) explore biomarkers for specific genotypes and phenotypes, 2) assess the content and quality of plant materials, and 3) analyze the production of plant metabolites in response to environmental conditions. Targeted and untargeted HPLC-MS methods, in combination with observational studies and genomic analyses, have been used to examine differences between crop cultivars exhibiting resistance and susceptibility to insect pests, identify pigments in oats and cold-hardy grapes, and assess the influence of growing conditions on metabolite profiles. Plant samples were collected from field, greenhouse, and growth chamber experiments and extractions performed following standard procedures. Metabolomic profiles were obtained using ultra-performance liquid chromatography (Ultimate® 3000 HPLC) and electrospray ionization-hybrid quadrupole-orbitrap mass spectrometer (Thermo Fisher Scientific Q Exactive) with reverse phase columns. Data were processed with MZmine and analyzed using multivariate statistical methods in R, and feature identification was explored using MS/MS data and GNPS molecular networking. With several ongoing projects in crop and cultivar improvement, metabolomic analyses continue to be a valuable tool in the agricultural and horticultural sciences.

LC-2

Forensic Analysis of Benzodiazepines in Blowfly Larvae and Puparia Using reverse-phase HPLC/HR-TOF-MS: Method Development and Quantitation

Zeinab Rabiei, Lavinia Iancu, Alena Kubatova

University of North Dakota, Grand Forks, USA

Abstract

Benzodiazepines are a class of psychoactive drugs commonly prescribed around the globe to treat symptoms associated with anxiety and sleep disorders. There is an increase in death report regarding their abuse. For example, heroin and cocaine abusers use them to boost their "high" or decrease the effects associated with narcotic withdrawal. In cases when human tissues are severely decomposed, or inadequate for sampling, necrophagous insect species could be used to investigate the presence of putative drugs by investigating their bioaccumulation in insect tissues. Blowflies (Diptera: Calliphoridae) are the primarily colonizers of human bodies, making them suitable candidates for entomotoxicology studies.

A sensitive and selective method for the simultaneous screening and quantitation of two benzodiazepine compounds (clonazepam and flunitrazepam) on the development cycle of Calliphora vicina Robineau-Desvoidy, 1830 (Diptera: Calliphoridae) using the reverse-phase HPLC/HR-TOF-MS (high pressure liquid chromatography with high resolution time of flight mass spectrometry) is developed. A homogenization with zirconia beads, followed by precipitation step with ice-cold acetonitrile was used for the isolation of benzodiazepines from the insect specimens. Consequently, homogenization step followed by precipitation process and analyzing with reverse-phase HPLC/HR-TOF-MS, yielded a 110±22 recovery percentage and limit of detection (LOD) was determined to be 175 ppb.

This technique is appropriate for accurately identifying analytes at their minimum reported dosage concentrations with the use of only 62.52 milligrams of insect tissue. The ultimate objective is to utilize this method for forensic investigations that deal with low levels of benzodiazepines.

LC-3

An Automated High Throughput Approach for Large Scale Retention Measurement in Liquid Chromatography

Trevor Kempen[1], Tina Dahlseid[1], Bob Pirok[2], Dwight Stoll[1]

[1]Gustavus Adolphus College, Saint Peter, USA. [2]University of Amsterdam, van 't Hoff Institute for Molecular Sciences, Amsterdam, Netherlands

Abstract

Many contemporary challenges in liquid chromatography - such as the need for "smarter" method development tools, and deeper understanding of chromatographic phenomena - could be addressed more efficiently and effectively with larger volumes of experimental retention data than we have been accustomed to historically. The paucity of publicly accessible, high-quality measurements has been due, at least in large part, to the high cost in time and resources associated with traditional retention measurement approaches. Recently we described an approach to improve the throughput of such measurements by using very short columns (typically 5 mm), while maintaining measurement accuracy. The automated high throughput approach processes chromatograms during acquisition and creates new methods with conditions that are designed for a specific compound/stationary phase system before appending them to a dynamic work list. In addition to describing the automated workflow, we will also discuss the characteristics of a dataset containing results for 35 different small molecules, nine different stationary phases, and several mobile phase compositions for each analyte/phase combination. A critically important observation from these analyses is that selectivity (defined here as retention of a given analyte relative to the retention of a reference compound: kx/kref) is a much more consistent measure of retention over time (months) compared to the retention factor alone. This approach will enable the compilation of large databases (>> 10,000 measurements) of retention values over long time periods (years), which can in turn be leveraged to address some of the most important contemporary challenges in liquid chromatography.

LC-4

Development of a High-Throughput Micro-Scale Solid-Phase Extraction Method for HPLC-MS Analysis of Pyridine Nucleotide Metabolism in Maize Seedlings

Evan Larson, Adrian Hegeman, Jerry Cohen

University of Minnesota, St. Paul, USA

Abstract

Pyridine nucleotides such as NAD+/NADH are central to cellular energy metabolism. Two pathways are used to metabolize pyridine nucleotides, while the active pathway depends on the organism. The consensus is that the tryptophan pathway is active in animals and fungi, while the aspartate pathway is active in plants. However, there is uncertainty in plants where certain genomic studies claim the presence of the tryptophan pathway in monocots, while other genomic studies disagree. Previously, there have been no metabolomics studies on the tryptophan pathway in plants.

The current work aims to develop a high-throughput HPLC-MS method to quantify six of the compounds in the tryptophan pathway to pyridine nucleotides to confirm the presence of this pathway using minimally sized plant samples to enable spatial-temporal studies. As a simple liquid extraction from plants is far too complex to analyze directly, a robust solid-phase extraction method was necessary to isolate the six compounds with varying chemical moieties. After a broad screen of resins and further method development, a micro-scale ion-exchange SPE method was developed to capture the range of compounds. The SAX resin is added to specially designed TopTip cartridges, similar to pipette tips, which are centrifuged to drive the liquid through the column. The small bed volume (25 µL) allows for a low plant material requirement (50–100 mg), while tips can be run in parallel for high-throughput analysis. Preliminary results from maize seedlings show the presence of all six compounds, which can be quantified using spiked isotopically labeled standards.

LC-5

Analysis of Selenate in Human Plasma using Ion Pair Reverse Phase Chromatography

Usha Mishra

University of Minnesota, Minneapolis, USA

Abstract

Selenium is an essential trace element required for cellular functions, therefore, deficiency in selenium may result in diseases. To prevent the selenium deficiency, the blood selenate level is frequently monitored. However, an ion chromatographic system is required for detection of selenate. Often most labs do not have ion chromatographic system available for selenate detection, Therefore, an ion pair RP-HPLC method is developed for detection of selenate in human plasma. The selenate is separated on a reverse phase C18 column using tetra butyl ammonium bisulfate as the ion pair reagent. It is detected using UV at wavelength of 205nm within five minutes, and a good linearity is achieved in the concentration range from 62µg/mL to 1000 µg/mL-1 (r2 >0.99 in human plasma.

LC-6

Predicting Isocratic Retention Factors from Gradient Elution Conditions Using a Re-parameterized Neue Kuss Model

Kathryn Cash[1], Dwight Stoll[1], Sarah Rutan[2]

[1]Gustavus Adolphus College, St Peter, MN, USA. [2]Virginia Commonwealth University, Richmond, VA, USA

Abstract

The ability to predict isocratic retention factors from data acquired under gradient elution conditions may provide a more efficient path to establishment of retention databases compared to the use of isocratic conditions alone. Such databases can be used to develop retention models and support simulations of separations, however past work has shown that isocratic retention factors predicted in this way are different from experimentally determined retention factors. In this presentation we will describe the use of a re-parameterized Neue Kuss (NK) model, along with a Design of Experiments approach that aims to enable the accurate prediction of isocratic retention factors from experimental retention data acquired under gradient elution conditions. The results show that the fits of gradient data to the NK model yielded average (absolute value) prediction errors for model parameters in the range of 6 to 11%, however the errors in isocratic retention factors predicted using this approach were much better, with an average error of 1.59% provided that the prediction does not involve an extrapolation to mobile phase conditions not used in the gradient elution experiments used to build the model. This is an important result that has the potential to simplifying the acquisition of retention data for large database efforts.

Materials-1

Advances in Ionic Liquid-Based Stationary Phases and Sorbent Materials for Chromatography and Sample Preparation

Jared Anderson

Iowa State University, Ames, USA. Ames National Laboratory, Ames, USA

Abstract

Ionic liquids (ILs) can be designed to exhibit unique properties for their use in a number of applications in analytical and bioanalytical chemistry. This talk will focus on the design and synthesis of ILs, magnetic ionic liquids (MILs), and polymeric ionic liquids (PILs) as well as the use of these materials in a number of applications within multidimensional chromatography and sample preparation. A series of monocationic/dicationic ionic liquid-based and silver-containing stationary phases were evaluated as secondary columns in comprehensive two-dimensional gas chromatography (GC×GC) for the separation of aliphatic hydrocarbons from kerosene as well as the separation of olefins from paraffins. Finally, nucleic acids are biopolymers that constitute important diagnostic molecules for a broad range of applications from clinical testing to forensic analysis. A major challenge faced by DNA and RNA analysis techniques is the selective extraction of particular nucleic acid sequences using rapid and sensitive methodologies. It will be shown that ion-tagged oligonucleotides (ITOs) can be used in conjunction with MILs to efficiently capture DNA sequences from complex samples. The ITOs can be created through thio-lene “click” chemistry and the nature of the ion tag can influence the partitioning of the ITO to the hydrophobic MIL. This novel liquid-phase approach towards sequence-selective DNA capture provides superior extraction efficiencies to conventional magnetic bead technology as well as a platform for using external fields to manipulate the liquid droplets.

Materials-2

Modulating π-Complexation in Silver(I) Ion-Olefin Separations using Coordination Chemistry

Nicholas Tryon-Tasson[1,2], Philip Eor[1,2], Jared L. Anderson[1,2]

[1]Iowa State University, Ames, USA. [2]Ames National Laboratory, Ames, USA

Abstract

Argentation chromatography is a method in which silver(I) ions are added to a chromatographic stationary phase to exploit the highly selective, reversible nature of silver(I)-olefin complexation. In argentation-gas chromatography (Ag-GC), silver(I) ions are most commonly found uncoordinated, in the form of silver nitrate, dissolved in a supporting media for separations. Currently, very few commercial Ag-GC columns exist with little development since its origins. Ionic liquids (ILs) are an ideal supporting media for Ag-GC separations as they possess inherently good properties such as low vapor pressure and high thermal stability. Recently, silver(I) ion-containing ILs have been employed as Ag-GC stationary phases demonstrating great promise for olefin-paraffin separations. To date, very few studies have explored the coordination environment of silver(I) ion and the role that various ligands play in its interaction with olefins. In this presentation, coordinating ligands and their effect on silver(I)-olefin complexation within Ag-GC will be discussed. A variety of silver(I)-coordinated salts were synthesized, dissolved in an IL, and employed as GC stationary phases. The retention behavior of various probe analytes including alkenes, alkynes, dienes, esters, and aromatics were used to understand the role of coordination on p-complexation behavior. This presentation will provide insight into how silver(I)-olefin complexation can be adjusted by altering the coordination environment around silver(I) ion.

Materials-3

The Development of an Automated and Self-contained Instrument for Ice Concentration Linked with Extractive Stirrer

Kyle Burch, Brian Logue, Jay Shore

South Dakota State University, Brookings, USA

Abstract

Ice Concentration Linked with Extractive Stirrer (ICECLES) is a novel technique that combines both freeze concentration (FC) and stir bar sorptive extraction (SBSE) for extracting compounds from aqueous matrices at ultra-trace levels. Previous implementations of ICECLES utilized the combination of a chiller, jacketed beaker, and stir plate and limits the sample size to 10 mL or less, restricts control of parameters affecting ICECLES extraction efficiency, provides minimal ability to automate the process, and limits the number of samples which can be prepared simultaneously. A novel and self-contained ICECLES prototype was produced using electromagnetic stirring (EMS) of the SBSE stir bar, thermoelectric cooling (TEC), and computer control. The EMSTEC prototype allows for detailed temperature control, regulation of stir speed, larger sample sizes (up to 40 mL), and is fully automated. Direct comparison of the previous instrumentation and the EMSTEC for 5 mL and 10 mL samples produced nearly equivalent extraction efficiency while the EMSTEC provides the advantages of shorter sample preparation duration, better accuracy and precision, and automation with programmable runs for routine analysis of different volumes of solution.

Materials-4

Green Sample Preparation: It's All Green

Doug Raynie

South Dakota State University, Brookings, USA

Abstract

The aims of green chemistry, chemical analysis, and sample preparation are not contradictory. In fact, the new extraction techniques developed over the past generation, while created for their performance advantages, address green chemistry concerns of waste, solvent use, energy efficiency, and toxicology. We will look at an overview of new and emerging sample preparation technologies, their performance in various applications, and the resulting green benefits.

Materials-5

Renewable Small-Scale Synthesis of Ammonia and its Improved Separation with Reactive Absorption

Chinomso Onuoha, Alon McCormick, Paul Dauenhauer

Department of Chemical Engineering and Material Science, University of Minnesota, Minneapolis, USA

Abstract

Ammonia is a key component in fertilizer required for global food production as well as a variety of specialty chemicals including electrolytes for batteries, food additives, analytical reagents, and as a fuel for medium-to-long-term energy storage. The conventional method (Haber-Bosch) to produce ammonia is unsustainable considering its large energy utility and greenhouse gas emissions. The availability of renewable resources like wind energy coupled with its co-location in areas with high fertilizer demand, give rise to the possible synthesis of carbon-free ammonia at small scale close to the end user. There is a growing interest in this method of ammonia synthesis as excess renewable energy can be stored as ammonia and converted back into electricity or hydrogen fuel during periods of high-power demand. Through our pilot scale process, we have demonstrated that ammonia can be made using air, water, and wind energy but this product is however more expensive than one based on fossil-fuels. One way of reducing this cost is by replacing the traditional ammonia separation by condensation with reactive absorption using metal halides. Although this method of ammonia separation is more efficient, pure absorbent material is unstable and shows decreasing capacity with prolonged usage. Here, we discuss the role of absorber-effluent gas analysis in the development of better absorbents and optimum operating conditions for improved ammonia separation.

Materials-6

Development of Monolithic Immobilized Enzymatic Reactors for Complex Proteome Profiling

Daniel Meston

Gustavus Adolphus College, St Peter, USA

Abstract

Conventional comprehensive proteomics workflows suffer from significant variation in sample preparation. While a number of techniques have been developed to combat this problem, a major disadvantage of these protocols is the multiple handling steps necessary which ultimately impact sample recovery. Immobilized enzymatic reactors (IMERs) provide a facile methodology to address both the variation as well as the slow digestion times in global proteomics studies. IMER technology involves the covalent attachment of bioactive proteins to a framework which allows for ultrafast protein digestion (minute to second scale) by catalyzing the proteolysis of proteins. Monolithic frameworks represent a particularly apt format to produce IMERs due to the tunable porosity which can allow for optimal surface area to porosity ratios to efficiently immobilize bioactive enzymes, as well as low backpressure allowing faster flowrates and subsequent digestion speeds in comparison to packed particle columns. Herein, we present the development of novel on-line IMER LC-MS workflow optimized for minimal peptide carryover and digestion reproducibility. A tertiary monomeric polymer was produced in a single porogenic solvent to produce monoliths inside 100 µm I.D capillaries capable of being integrated into nanoLC-MS setups. We optimized the hydrophobicity to reduce non-specific hydrophobic interactions to decrease sample carryover as well as fine-tuned the maximal concentration immobilized trypsin enzyme. In this way it was possible to comprehensively characterize complex proteome samples in less than 1 hour with good repeatability. IMERs represent a suitable technology to be seamlessly integrated into current nanoLC-MS setups, removing the need for conventional sample preparation methods.

GC-1

The HydroInert Source Improves GC/MS Analyses When Using H_2 as Carrier Gas

Daron Decker

Agilent Technologies, Pearland, TX, USA

Abstract

Hydrogen has been used in gas chromatography (GC) for quite some despite some concerns with its explosive nature and reactive properties. With Helium increased prices and pressure on helium availability, hydrogen as carrier gas is getting even further examination. Hydrogen can be generated in the lab in a cost-effective manner and produces fast chromatography and high sample throughput. Most detectors have little issues with the introduction of hydrogen as carrier but the biggest exception is the mass spectrometer (MS) which has become a standard detector in most labs. Since hydrogen is a reactive gas, reactions can and do occur in the mass spectrometer electron ionization (EI) source. A newly designed extractor source for the Agilent 5977B Inert Plus GC/MSD and Agilent 7000D/E Inert Plus triple quadrupole GC/MS systems addresses these hydrogen-related issues and helps improve performance with hydrogen carrier gas in GC/MS and GC/MS/MS. The Agilent HydroInert source with H2 carrier gas retains mass spectral fidelity and can allow users to continue to use existing helium-based mass spectral libraries.

GC-2

Investigation of Wood Windows Aging Using Thermal Desorption-Pyrolysis Gas Chromatography-Mass Spectrometry

Nafisa Bala[1], Alena Kubátová[2], Kozliak Evguenii[2]

[1]University of North Dakota, Grand Fork, USA. [2]University of North Dakota, Grand Forks, USA

Abstract

Understanding wood window aging and resistance to weathering is essential for both manufacturers and users. Thermal desorption-pyrolysis gas chromatography-mass spectrometry (TD-Py-GC-MS) technique allows for the analysis of wood preservatives and studying the aging of wood-based materials without extensive sample preparation. This study introduces a new fast and effective TD-Py-GC-MS method for the quantitative determination of fungicides along with wood constituents. Various TD-Py temperatures and times were tested to quantitatively determine concentrations of various fungicides. The analytes' responses at different TD temperatures were compared and a temperature of 275°C for 20 seconds was determined as the optimum. The pyrolysis from 275°C with ballistic heating to 500 °C & 20 s hold showed the effective determination of characteristic wood constituents. The combination of optimal TD and Pyr steps in TD-Py-GC-MS in both scan and selected ion monitoring MS acquisition methods were employed in the characterization of aging in window-treated corner sections.

GC-3

Detection of Dicamba in the Gas Phase Using a Field Simulating Gas Chamber and GC-MS

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Abstract

Dicamba is a chlorinated herbicide commonly used on corn, genetically modified soybeans, and other commercial crops. These genetically modified soybeans are resistant to dicamba and allow the use of this herbicide for weed control, however dicamba is severely volatile and can easily drift into nearby non-resistant crops and vegetation, causing irreversible damage. Because of this, it's important to study the volatility of dicamba in the gas phase to further understand how it behaves after it's applied to crops. This study used SPME fiber technologies derivatized with BSTFA, a derivatization agent commonly used to limit steric hindrance of molecules while binding to sorption materials. This sorption material was used to absorb gas phase dicamba from a tabletop field-simulating gas chamber and analyzed using an Agilent GC-MS (gas chromatograph-mass spectrometer). We then used this method to examine the photochemical degradation of dicamba in the gas-phase. The ultimate goal in this project is to use the method development and optimization of SPME fibers, the GC-MS, and gas chamber to address the research question: "Are photodegradation and/or reaction with gas-phase oxidants changing dicamba on timescales relevant to vapor drift and volatilization?"

GC-4

A Comparative Study of Volatile Organic Compounds Liberated During 3D Printing Using Solid-Phase Microextraction and the Solid-Phase Microextraction Arrow Geometry Coupled to Gas Chromatography/Mass Spectrometry

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Abstract

Three-dimensional (3D) printing is an approach used to create 3D objects and is increasingly popular today owing to its ease of use, versatility, and low cost. One of the most commonly employed 3D printing methods is fused deposition modeling (FDM), where thermoplastic materials like polylactic acid, acrylonitrile butadiene styrene, and co-polyester+ are dispensed through a heated nozzle and deposited on a moving bed. During printing, the molten filament is heated and extruded resulting in the release of volatile organic compounds (VOCs). Concerns regarding potential health risks from released VOCs during 3D printing have risen with the growing indoor use of FDM printers. In a previous study using solid-phase microextraction (SPME) combined with gas chromatography/mass spectrometry (GC/MS), it was found that commercially available SPME fibers were capable of extracting VOCs, and the type of VOCs extracted was largely due to the chemistry of the sorbent coatings. In this work, the extraction performance of commercial SPME fibers is compared with SPME Arrow, a novel SPME geometry, based on the detected VOCs upon analysis by GC/MS. The phase area and volume of SPME Arrow can provide higher sensitivity for trace-level detection. Three commercial SPME coatings, namely, PA, PDMS and DVB/C-WR/PDMS in both geometries were used, resulting in a detection of total of 43 and 30 VOCs with SPME Arrows and fibers respectively. This presentation will discuss results obtained using commercial SPME fibers, and Arrow devices, particularly as it relates to identifying trace compounds liberated during 3D printing.

GC-5

Olefin Separation by Gas Chromatography using Polymer Electrolytes Incorporating Silver(I) and Copper(I) Ions

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Abstract

Silver(I) ion, which is commonly used for olefin separation due to its strong olefin complexation abilities, is susceptible to reduction to metallic silver when exposed to certain conditions. Copper(I) ion is a viable alternative to silver(I) due to its lower cost, but its use for olefin separation is limited by the instability of Cu(I) ion in the presence of oxidants. Ionic liquids (IL) and polymeric ILs (PIL) have been employed as stabilizers for metal ions to ensure high separation efficiency by preventing their degradation. Ionenes, a type of polyelectrolyte with charged moieties within polymer backbone, are also investigated as potential stabilizers. However, little is understood regarding structural features of PILs and ionenes and how they influence olefin separations when incorporating metal ions. This study employs gas chromatography (GC) to investigate retention of olefins on stationary phases composed of ionenes and PILs with various types of Ag(I) and Cu(I) ions. Inverse GC is utilized to evaluate characteristics of the Ag(I) or Cu(I)-containing polyelectrolytes that facilitate their complexation with olefins. The utilization of multi-dimensional GC resulted in enhanced retention of alkenes and alkynes. The composition of stationary phase, including silver salt anion, IL (and PIL) anion, and length of alkyl substituent of IL (and PIL) influenced Ag(I)-olefin interactions and thermal stability of Ag(I) ion. This work aims to elucidate the role of structural differences within polymer backbone in enhancing stability of Ag(I) and Cu(I) ions for olefin separations.

Environmental-1

Utilizing Polymeric Ionic Liquid Sorbent Coatings in Thin Film Microextraction to Isolate Pesticides from Cannabinoids for Chromatographic Separations

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Abstract

Analysis of pesticides in cannabis plant material is challenging due to the complexity of the matrix. Since commonly regulated pesticides are found in low abundance (ppb levels) and span a wide range of polarities, extraction methods tend to be non-selective for these analytes. During chromatographic analysis, cannabinoids present within samples may co-elute with low-polarity pesticides. Thus, current analysis methods rely heavily on the sensitivity and selectivity of expensive mass spectrometers to differentiate co-eluting analytes. However, microextraction sample preparation methods can be used in conjunction with chromatographic methods to better isolate analytes of interest. These methods can also preconcentrate analytes in low abundance allowing for detection with less sensitive detectors. In this work, we developed an analyte-selective extraction methodology for pesticides using robust polymeric ionic liquid (PIL) sorbent coatings in direct-immersion thin film microextraction (DI-TFME). PIL sorbent coatings, consisting of polymerizable IL monomers and crosslinkers, can be designed to interact preferentially with analytes of interest by incorporating different functional groups into their chemical structures. For this study, modifications including aromatic moieties and polar substituents, specifically hydroxyl and/or sulfonate groups, were integrated into the PIL chemical structure in an effort to enhance pesticide-cannabinoid selectivity. Pesticides and cannabinoids were extracted in parallel and monitored using high-performance liquid chromatography with ultraviolet detection. Conditions including salt content, percentage of organic solvent, extraction temperature, extraction time, desorption solvent, desorption volume, and desorption time were all optimized. Partition coefficients and selectivity factors were analyzed to identify sorbent functional groups influencing the separation under optimized conditions.

Environmental-2

Precursor Ion Mass Spectrometry as a Selective Method of Detection for Target and Nontarget Pesticide Residues.

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Abstract

Neonicotinoids are the most widely used insecticide in the world. This has led to the contamination of ecosystems everywhere. These pesticides are not inert in the environment; previous studies have shown their degradation via photolysis. However, many of the residues and degradation pathways of neonicotinoids are not currently well understood. We employ liquid chromatography precursor ion mass spectrometry methods to analyze surface waters for both known and previously unidentified neonicotinoid residues. Precursor ion mass spectrometry works by capitalizing on the structural similarities between the residues and the parent insecticide. Due to these structural similarities, these analytes frequently fragment to the same common fragment ions via collision induced dissociation. These common fragment ions allow us to separate analytes based on their fragmentation and only detect ions that fragment to the correct common fragment ion. Using this separation technique, we can selectively detect a plethora of insecticide residues while still filtering out the other contaminants in a complex sample. Our precursor ion mass spectrometry method has led to the detection of many novel residues of both imidacloprid and clothianidin (common neonicotinoids). This study shows how precursor ion scanning methods have the potential to help track a multitude of environmental contaminants and their residues in complex samples.

Environmental-3

A Comprehensive Workflow Approach for the Determination of PFAS in Wastewater

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Abstract

Per- and polyfluoroalkyl substances (PFAS) pose an increasing threat to the environment, animals, and human beings due to extreme chemical stability and bioaccumulation potential. Their detection at the trace level is often interfered with by the environmental matrices and background contaminants. A comprehensive workflow was developed for the PFAS analysis in wastewater, based on the existing EPA draft Method 1633 with additional PFAS of varying size and functional group. This workflow contains off-line solid phase extraction (SPE), clean-up step, followed by LC-MS/MS analysis, and automatic reporting. The workflow demonstrates a reliable solution for the targeted analysis of PFAS in complex matrices with high robustness.

Environmental-4

Investigating thermal destruction of per- and poly-fluoroalkyl substances (PFAS) by combining evolved gas analysis and thermal desorption – pyrolysis – gas chromatography and mass spectrometry

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Abstract

Pyrolysis is the thermochemical breakdown of compounds in an inert environment. This method has the potential to remediate group of prevalent pollutants, poly- and perfluoralkyl substances (PFAS), commonly referred to as "forever chemicals". PFAS are man-made compounds with a variety of uses in cookware, food packaging, fabrics, etc. Because of their widespread use and in addition to their chemical resistance to environmental degradation, PFAS are prevalent in the environment primarily in soils and water. As a result, most people have been exposed to PFAS leading to possible health issues, and therefore, new approaches to remediate and destroy PFAS from the environment are being researched. One of the possible remediation and destruction methods combines evolved gas analysis – mass spectrometry (EGA-MS) with Thermal desorption – Pyrolysis – GC-MS (TD-Py-GC-MS) within one instrument. This method can be used for compound volatilization, breakdown and subsequent identification. EGA, as a screening method, provides information about volatilization and breakdown conditions, TD-Py-GC-MS can be used to focus on those conditions allowing compound separation and identification. The method was tested on perfluorooctanoic acid (PFOA) and helped identify the breakdown temperature in a range of 200-300 °C and the main product of this breakdown was identified as perfluorohept-1-ene. The translatability and applicability of the method was further validated on other common PFAS of different structures and functional groups, such as perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), 1H,1H,2H,2H-perfluoro-1-decanol (8:2 FTOH) and hexafluoropropylene oxide-dimer acid (HFPO-DA), also providing information on behavior of each compound, breakdown conditions and preliminary information for breakdown product identification.

Environmental-5

Sample Preparation Techniques for PFAS Analysis in Complex Environmental Matrices

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Abstract

There is an increasing demand for PFAS analysis of complex matrices - biomass, wastewater, fish and other aquatic fauna are just a few examples. These sample types are presenting a very different challenge from the established drinking water methods which mainly focus on analyte enrichment by Solid Phase Extraction. Various matrix removal techniques (QuEChERS, Lipid Removal, Carbon clean up) will be discussed and data from fish and milk samples will be presented.