The Column
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Instrumental Innovations 2018

Selected highlights of innovative chromatography products

UBM

Cover Story

Features

Regulars

Instrumental Innovations 2018

Photo Credit: Ivnl/Shutterstock.com

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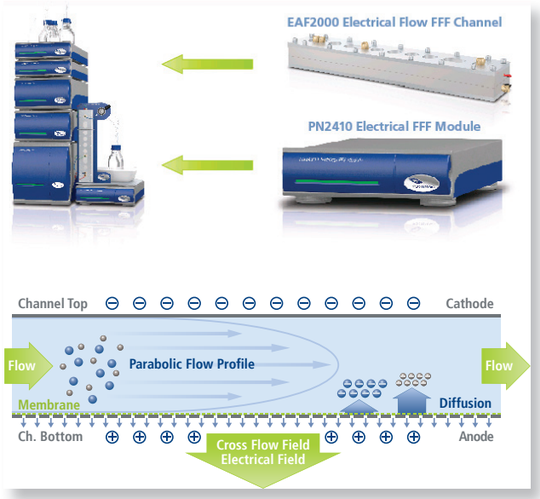
FFF Products

Electrical/Asymmetrical Flow Field-Flow Fractionation



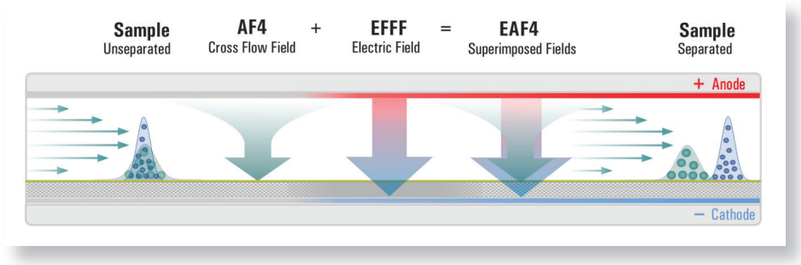
Traditional separation technologies for biopharmaceutical and nanoparticle applications provide particle size or molar mass distributions as the final result. However, it is clear that particle and molecular charge play a primary role in many applications such as protein aggregation, polymer flocculation, particle agglomeration, and in pharmaceutical formulations in general. The Postnova EAF2000 instrument using electrical asymmetrical flow field-flow fractionation (EAF4) technology allows the particle size or molar mass distributions to be further differentiated and transformed into charge distributions. This identifies charge heterogeneities present within the different size and molar mass fractions and will help to aid research or establish more efficient product development processes.

The instrument works by combining the principle of electrical and AF4 in one system. According to the company, this instrument is a key tool, particularly for protein research, because existing techniques for zeta-potential are limited by concentration and are simple batch techniques giving just an average value for all components in the solution. The EAF2000 can determine the zeta-potential of each individually separated component, such as protein monomer and dimer (or higher aggregates) or antibody monomer and fragments–aggregates.

www.postnova.com/overview_759.html

GC Products

Electrical/Asymmetric Flow Field-Flow Fractionation



Wyatt Technology's Eclipse asymmetric flow field-flow fractionation (AF4) system is a versatile tool for separating and characterizing particles in complex fluids ranging in size from 1–10,000 nm. The new Mobility module combines electrical and flow fields to produce bi-modal fractionation, EAF4. EAF4 serves three purposes:

- Improved AF4 performance when particles tend to stick to the membrane;
- Separation of similarly sized species with different electrical charges;
- Determination of complete distributions of size/zeta potential.

These new capabilities of the Eclipse Mobility enhance isolation and characterization of many types of macromolecules and sub-micrometer particles, such as gene vector VLPs and polymersomes, exosomes, lipoproteins, liposome-encapsulated drugs, inks, and magnetic nanoparticles. According to the company, the system is an especially powerful characterization tool when combined with Wyatt's online multi-angle light scattering (MALS) and dynamic light scattering (DLS) detectors as well as UV, fluorescence, or ICP-MS instruments.

www.wyatt.com/mobility

Dry Scroll Vacuum Pump

The IDP Dry Scroll vacuum pump for GC–MS removes the need for oil in analytical processes. Dry scroll pumps create a vacuum using a dual-scroll mechanism where one nested scroll orbits the other creating moving zones of captured gas. This design and assembly offer benefits such as low noise and vibration, simple and infrequent maintenance, and elimination of catastrophic failure modes.

Common complaints regarding vacuum pumps are problems associated with the oil itself: oil leaks, oil changes, and oil waste. A unique collaborative approach between MS and vacuum pump divisions was deployed to develop the technology and offer customers sustainable products that aim to reduce waste and system downtime, while helping to make the laboratory a better environment to work in. Working towards sustainability is an integral part of how Agilent conducts business and responds to the challenges of customers.

With the introduction of the 7010 GC/QQQ with the IDP10 dry pump option, Agilent has now completed its offer of oil-free GC–MS across 5977B GC/MSD, 7010 GC/QQQ, and 7200 GC/Q-TOF. Oil-free pumps are offered on new GC–MS systems and as upgrade kits to cover the installed base of Agilent GC–MS.

www.agilent.com/chem/ecobonus

Automated Multi-Mode VOC Sampling

April 2018 saw Markes International launch Centri, an automated multi-mode sampling and concentration system for GC–MS.

Centri combines market-leading robotics and analyte-trapping technologies to offer enhanced throughput and performance for VOC and SVOC sampling, using high-capacity sorptive extraction, headspace, SPME, and thermal desorption.

The company says that Centri is ideal for environmental, food, fragrance, forensic, and clinical laboratories who struggle with time-consuming manual sample preparation, and who want improved sensitivity for organic compounds in solids or liquids. The company adds that it is also valuable for streamlining workflows by performing several sampling techniques in a single automated sequence.

A key feature of Centri is the ability to automate high-capacity sorptive extraction from liquids and solids using Markes' HiSorb probes, which use a relatively large volume of PDMS sorbent on a metal probe to simultaneously offer high sensitivity and robustness. Centri can also automate headspace and SPME sampling (with optional trap-based focusing), as well as desorb industry-standard thermal desorption tubes in compliance with standard methods. Across all these modes, Centri is able to re-collect split flows onto clean sorbent-packed TD tubes, which allows valuable samples to be analyzed multiple times without having to repeat sample extraction.

chem.markes.com/SamplePrep

GC–MS/MS System

The Thermo Scientific TSQ 9000 triple quadrupole GC–MS/MS system is designed to provide exceptional productivity and sensitivity for any laboratory targeting the quantitation of trace compounds in complex sample matrices. According to the company, users can benefit from reduced cost for each sample in a routine analysis environment, without compromising analytical performance or uptime through selective reaction monitoring sensitivity.

The TSQ 9000 triple quadrupole GC–MS/MS system can be equipped with an advanced electron ionization source designed to provide ionization of target compounds with high sensitivity while also extending challenging detection limits. In addition, the patented Thermo Scientific NeverVent technology is available in the system's ExtractaBrite ion source configuration, which is engineered to enhance uptime by removing the need to vent the mass spectrometer during routine maintenance operations. For robust sample analysis and data management across multiple chromatography platforms, the Thermo Scientific Chromeleon XTR laboratory management software is also available and equipped to manage every aspect of sample analysis: from sample login to testing and final reporting. This enables adherence to internal standard operating procedures and regulatory compliance with a full audit trail.

www.thermofisher.com/unstoppableGCMS

GPC/SEC

Comprehensive 2D

Modern high performance polymers are often multicomponent systems, where the molar mass distribution is only one of several distributions present. Two-dimensional chromatography combining GPC–SEC and interaction polymer chromatography (IPC) is therefore an essential tool for in-depth polymer characterization.

Comprehensive 2D is simple and automation is feasible with the PSS 2D Analyzer, which is used by many chromatography experts around the world.

For novice users of IPC and two-dimensional chromatography, PSS has developed two new solutions that add multidimensional separation capabilities without the need to use this solution exclusively for 2D. In this way, significantly higher equipment utilization in the laboratory is achieved, while the tools for more modern and efficient separations are also directly at hand.

The PSS 2D Fractions Analyzer and the 2D Heart-Cutting Analyzer make the transition between one-dimensional and two-dimensional separations fast and straightforward without the need for extensive training in new skills. New valve solutions (manual or fully controlled by WinGPC UniChrom MCDS) suitable for all three systems allow operation without manually changing columns, capillaries, or tubing.

www.pss-polymer.com/products/lc-instruments-and-detectors/2dpolymeranalyzer/

Ion Chromatography

IC Suppressor

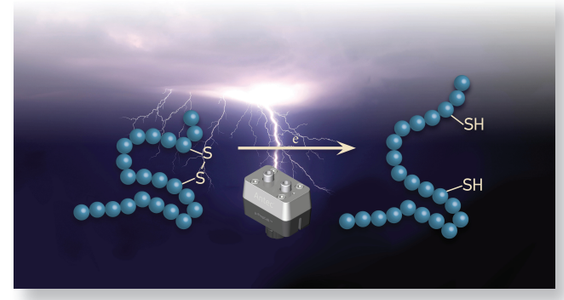
Diduco has brought membrane suppressors into a new era. The new Xenoic ASUREX-A200 automatic regenerator enables the Xenoic XAMS suppressor to handle everything from standard ion chromatography analysis using carbonate-based eluents, to hydroxide gradients, with one device. The ASUREX-A200 regenerator reportedly contributes to lower baseline drift and faster start-up, making the system attractive for many different routine analyses.

According to the company, the XAMS/ASUREX-A200 suppressor setup is capable of trace analysis of anions with detection limits in water from low ppb (µg/L). This satisfies established analysis methods for drinking water (US EPA 300.0 and 300.1), and in power plants (for example, boiler feedwater and steam condensate). It is also suitable for new assays of inorganic ions and organic acids in modernized pharmacopoeia methods and for impurity profiling in battery electrolytes, because hydroxide eluents up to more than 50 mM can be suppressed without a significant increase in noise and background conductivity. The suppressor is designed to operate with columns of several different brands and is suitable for flow rates from 0.5 to 2 mL/min, and can thus be implemented in numerous existing instruments regardless of manufacturer, according to the company.

www.diduco.com/asurex-a200

LC Products

Electrochemical Flow Cell



Fast, efficient online cleavage of disulfide bonds in proteins and peptides from biopharmaceuticals such as mAbs is now possible using a novel electrochemical flow cell for use with the Roxy EC System and developed by Antec Scientific.

The Antec Scientific µ-PrepCell-SS consists of a two-electrode configuration with a new counter electrode design for continuous operation for several days without contamination or loss of efficiency. Different electrode materials are available to widen the application scope of the µ-PrepCell-SS. The flow cell can be used in pre- and post-column HPLC configurations prior to MS detection and is suited for reduction of high disulfide-stabilized proteins. Online reduction occurs within several seconds as compared to conventional offline chemical methods, which can take hours or longer to achieve a similar result. A high-pressure version for HDX-MS and a low-dispersion variant to preserve chromatographic separation are also available. Overall much higher sequence coverage has been found in HDX-MS when compared to chemical reduction (TCEP, DTT) and new cysteine peptides could be identified in post-column settings.

www.AntecScientific.com

Miniature Detectors

Small and modular. Robust and intelligent. The new range of Runge Mikron detectors recently introduced by Biotech AB unites many attractive features in a tiny package, according to the company. Different modules can be combined to measure absorption, fluorescence, or conductivity in a variety of fluidic systems, including liquid chromatography.

Thanks to several available LED-based fixed-wavelength light sources with a lifetime of more than 5000 h, power consumption below 2.5 watts, and start-up within seconds, the Runge Mikron detectors are reportedly ideal for incorporation into portable field instruments and online monitoring devices. This also allows the detectors to be operated in refrigerated laboratory environments down to 4 °C (39 °F), without virtually any heat production. Flexibility in sampling frequencies, detector cell sizes, port connections, and choice of wetted materials make the Runge Mikron detectors suitable for many flow rate conditions and eluent compositions.

The Runge Mikron detectors are easy to connect as they communicate through, and draw power from, one single USB-C port, according to the company. Drivers are provided for several chromatography software packages, alternatively, an open protocol can be used for customized implementation. The detectors conform to international standards and are CE marked.

www.biotechfluidics.com/products/detectors/mikron

UHPLC HILIC Columns

Hilicon is a leading company in developing and manufacturing hydrophilic interaction liquid chromatography (HILIC) products for the separation of polar and hydrophilic compounds. It has recently launched two product lines of 1.8-µm UHPLC HILIC columns with two complementary surface chemistries, iHILIC-Fusion and iHILIC-Fusion(+). These columns are versatile for the analysis of polar compounds in "-omics" research, pharmaceutical discovery, food and beverage analysis, clinical diagnostics, and environmental studies.

The packed UHPLC iHILIC stationary phases are charge-modulated amide silica particles that are covalently bonded with various neutral, positively charged, and negatively charged hydrophilic functional groups, following the company's innovative and unique surface-bonding technologies. iHILIC-Fusion is neutral and slightly negatively charged at pH 2–8, while iHILIC-Fusion(+) is constantly slightly positively charged. According to the company, the columns provide customized and complementary selectivity, ultimate separation efficiency, and ultra-low column bleeding, and are particularly suitable for LC–MS-based applications. Furthermore, they also simplify method development and improve the productivity and data quality in chemical and biological analysis.

www.hilicon.com

Nitrogen Generator

In June 2018 Peak Scientific launched the latest evolution of its Genius Series of nitrogen generators, Genius XE. Designed specifically to provide on-demand gas for high performance analytical applications, such as triple-quadrupole LC–MS, Genius XE offers variable flow of analytical-grade nitrogen gas of up to 70 litres per minute, and at purities up to 99.5%.

Peak Scientific has positioned Genius XE as "the most advanced laboratory nitrogen generator on the market". According to the company, Genius XE combines everything proven successful in the Genius line (launched 2010) with new technologies and design principles, aimed at delivering greater performance and giving end-users in the laboratory more confidence and convenience.

The smaller and quieter range of generators (XE 35 and XE 70) now incorporate multi-stage purification including proprietary hydrocarbon removal technology, producing nitrogen at up to 99.5% purity, ECO mode (Electronic Compressor Optimization) for lower energy consumption and enhanced compressor performance, and PeakOS touchscreen system control, for ease of operation and fast service diagnostics.

Built upon decades of innovation in gas generation for the laboratory, Genius XE reportedly sets a new benchmark in performance and confidence. With increasingly sensitive applications and productivity demands, laboratories cannot afford to compromise on instrument gas.

www.peakscientific.com

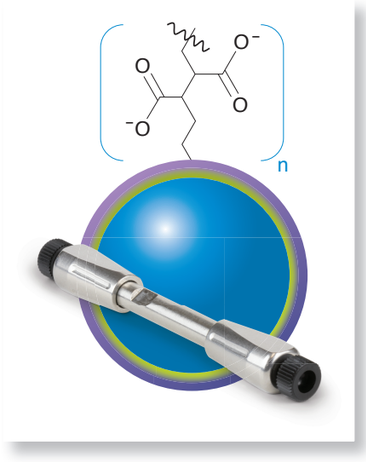
Triple Quadrupole LC–MS/MS

In November 2018, PerkinElmer launched the QSight 400 Series, the latest version of its QSight triple quadrupole liquid chromatography coupled with mass spectrometry (LC–MS/MS) instrument. The key feature of the QSight 400 is its superior sensitivity. With the ability to detect analytes present at parts per trillion concentrations, the QSight 400 is one of the most sensitive LC–MS/MS instruments on the market. This makes it ideal for any laboratory analyzing trace analytes such as allergens, residual pesticides, or environmental contaminants. For the industries where contaminant testing is common, innovative technology, that is capable of quantifying residual pesticides or mycotoxins at both current regulatory limits, and adapt to any updates, is needed. The improved sensitivity of the QSight 400 offers scientists a comfortable margin between quantitation limits and regulatory levels.

At the core of the QSight 400 Series are unique patented technologies: StayClean Source and Dual Source technologies. By reducing the amount of scheduled cleaning and maintenance, StayClean technology helps improve laboratory efficiency and instrument uptime by 15%. Dual Source technology offers two separate ion inlets, which can be set to electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) sources, enabling the detection of a wider list of contaminants. These two technologies, combined with exceptional sensitivity, make the QSight 400 Series a future-proof instrument for any food, cannabis and environmental testing laboratory.

www.perkinelmer.com/product/qsight-420-multi-opt-dual-source-system-bc003844

Protein Characterization



This year Phenomenex introduced bioZen, an LC column and sample preparation portfolio for the characterization of protein therapeutics, such as monoclonal antibodies, antibody–drug conjugates, and biosimilars. The bioZen product line includes three complementary particle technologies, eight stationary phases, a titanium bio-inert hardware, and a new HILIC SPE 96-well plate. The offering includes specific LC chemistries for the analysis of aggregates and total mAb, intact mass and fragments, peptide mapping, peptide quantitation, glycan mapping, and charge variants. As an added benefit, all bioZen UHPLC and HPLC media, particle sizes, and phases are available in Phenomenex's BioTi biocompatible titanium hardware, which minimizes secondary reactions, carryover, and other recovery issues to provide better overall reproducibility than stainless steel hardware, according to the company. It also minimizes the amount of time typically spent on column priming and does not interfere with protein or peptide integrity. The newest overall addition to this growing product line is the bioZen WCX, which improves protein and variant IEX recovery, selectivity, and reproducibility through a combined monodispersed nonporous polymer particle and tightly controlled carboxylate chain (1 million Da) stationary phase.

www.biozenbioseparations.com

SFC Columns

With over 50 years of experience in creating chromatography products, Regis is proud to now offer innovative achiral SFC columns. The Celeris family of achiral stationary phases has been specifically designed for SFC separations, delivering high capacity, broad selectivity, excellent peak shapes, and reproducible performance over long column lifetimes. According to the company, Celeris high performance phases provide rapid separation and recovery of purified components, enabling use of larger column sizes to reduce the number of purification cycles required to achieve purity of the batch.

Regis currently offers five phases for preparative- and process-scale SFC purifications. Celeris 2EP (2-ethyl pyridine) and 4EP (4-ethyl pyridine) media are designed to be highly reproducible based on tight product specifications and low metal content. Amino, PEI, and Arginine phases offer different selectivities than the ethyl pyridine phases while still offering the performance and savings associated with Celeris media. Columns are readily available in analytical to preparative sizes and in 5- and 10-µm media.

www.registech.com

Microflow Quantitation

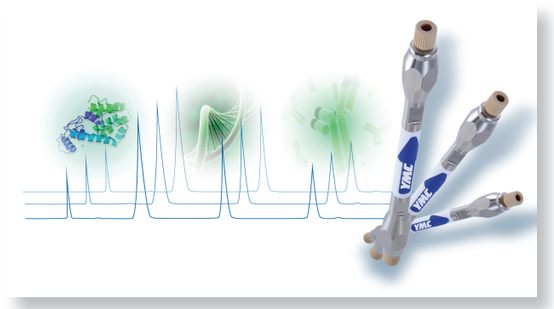
The Sciex OptiFlow Quant solution aids the biopharmaceutical community by providing high-sensitivity microflow quantitation for biomolecules. The system is comprised of the M5 Microflow LC with Phenomenex microflow columns and the new OptiFlow Turbo V Source paired with a 6500+ Triple Quad or QTRAP MS system for high quality quantitation data. This easy-to-implement setup provides a powerful tool for development of novel biotherapeutics.

Detection and quantification of biotherapeutics, such as peptides, ADCs, and mAbs, presents a challenge for drug developers in pharmaceutical companies and contract research organizations. For bioanalytical studies to support drug development, researchers require quantitation methods that are both sensitive and selective. The OptiFlow Quant solution offers researchers the robustness and usability of analytical flow systems, but with the powerful sensitivity of a microflow LC system. According to the company, usability stems from its innovative source with intelligent spray design, which requires no manual adjustments over a wide range of flow rates. This greatly increases the throughput of the system and eliminates problems associated with low-flow workflows, according to the company. The OptiFlow Quant solution also allows high flexibility and can be used with any microflow column and any column chemistry. The robustness and flexibility of this solution ensure it can be used for the novel biotherapeutics coming down drug discovery pipelines.

https://sciex.com/products/integrated-solutions/optiflow-quant-solution

Mass Spectrometry Products

Biochromatography Columns



With more than 10 years' experience in the production of BioLC solutions, YMC launched further products for the analysis of peptides, proteins, and (monoclonal) antibodies in 2018.

For reversed-phase separations, the YMC-Triart Bio C4 is a widepore phase for (U)HPLC. According to the company, this phase offers the perfect solution of outstanding selectivity for peptide and protein analyses as well as antibody separations with its 300 Å pore size. Method flexibility is enhanced by the high pH (pH 1–10) and temperature stability (up to 90 °C).

For selectivity for antibody analysis, the YMC-SEC MAB offers simultaneous analysis of the antibody together with its fragments and aggregates in just one run. According to the company, it is the ideal choice for users developing methods for QC for biologicals because of its outstanding reproducibility.

Effective separation of antibodies, antibody–drug conjugates (ADCs), and proteins is provided by the high-resolution of the hydrophobic interaction column BioPro HIC BF. The butyl-bonded polymer phase provides cost-efficient long-term stability and the excellent lot-to-lot reproducibility assures a consistent QC. The column reportedly improves analysis throughput with virtually no carryover effects.

www.ymc.de/biochromatography-columns.html

QTOF-MS

Shimadzu's LCMS-9030 is a research-grade quadrupole time-of-flight (QTOF) mass spectrometer designed to deliver high-resolution, accurate-mass detection with fast data acquisition rates, allowing scientists to identify and quantify more compounds with greater confidence. The system uses the same engineering DNA as Shimadzu's rugged, high performance triple quadrupole platform, and reportedly helps to transform high mass accuracy workflows, bringing together high sensitivity, high speed, and high-resolution detection.

Key technology drivers include bringing together core ion beam technologies developed for the triple quadrupole platform to deliver exceptional sensitivity, and unique approaches in TOF design to generate highly stable, high mass accuracy data. Shimadzu has introduced the UFaccumulation technologies in the LCMS-9030 as a unique approach to packaging high ion volume pulses into the TOF mass analyzer. Using very high voltage and a mechanically strong grating design, high ion volume pulses are delivered into a thermostatically stabilized TOF tube. According to the company, the result is exceptional sensitivity and stability at high scan rates, helping scientists to achieve better analyses and better science.

As with the triple quadrupole platform, the LCMS-9030 system can acquire MS and MS/MS data at high sampling rates, opening new possibilities for qualitative and quantitative challenges. Acquiring 100 scans per second in MS and MS/MS, the LCMS-9030 has game-changing capability in routine quantitation and identification of unknowns, according to the company.

www.shimadzu.eu

Sample Preparation Products

DART QDa System

The Waters DART QDa System with LiveID is a direct-from-sample analytical system that assesses the quality and authenticity of food samples. The system couples the Waters Acquity QDa Detector with the IonSense DART Ion Source for rapid fingerprinting of foods and food ingredients. The system allows laboratories to answer these questions, and more: Is the sample authentic? Has the composition of the sample changed? Is sample quality good or bad?

Direct analysis in real time (DART) is a direct and rapid analytical technique for use on various sample types requiring minimal sample preparation and no chromatographic separation. The source directs heated, ionized gas at the surface of the sample between the DART interface and the Waters QDa detector where the ionized molecules are detected. The LiveID software gives the analyst the ability to train and validate multivariate statistical models using the chemical profile obtained from the analysis. The LiveID models can be used to classify the identity of unknown samples generating results in near real time and a simple "yes/no" answer in seconds.

www.waters.com/dartqda

Extraction System

The EDGE combines dispersive solid-phase extraction and pressurized fluid extraction in a single automated system, reducing the bottleneck of sample preparation prior to LC or GC analysis. Unlike traditional techniques that require substantial amounts of solvent and operator intervention, the system can perform extractions of even complicated matrices in as little as 5 min (including cooling and washing steps) and will automatically process up to 12 samples for each run without operator intervention.

The system supports a wide variety of applications including pesticides in foods, total fat extraction, additives in plastics, and environmental extractions, such as EPA 3545A. Multiple different types of sorbets can be layered in the Q-Cup sample holder, combining the extraction and cleanup steps into a single step and reducing the amount of waste generated.

According to the company, the benefits include: automated sample handling (reducing operator intervention and error), rapid and complete extraction, simple operation, and applicability across a wide variety of samples.

www.cem.com/edge

Pyrolysis for HPLC

The Gerstel PyroVial enables pyrolysis procedures in a dedicated sample vial up to 800 °C. Volatile pyrolysis products can be sampled directly from the headspace for GC–MS determination. Less volatile pyrolysis products can be taken up in a suitable solvent for subsequent GC–MS or LC–MS determination—or for analysis using other techniques. The pyrolysis process is fully automated based on the Gerstel MultiPurpose Sampler (MPS). Placing the sample into the reaction chamber is simple and the PyroVial can be used as a micro-scale reaction chamber. The gas phase in the vial can be replaced by an inert gas or a reactant as needed. Food preparation processes, such as the Maillard reaction, can be simulated in small scale and the formed flavour compounds determined. Pyrolysis of polymers—such as those based on polar acrylic resins—can be followed by HPLC determination of the reaction products. The addition of reagents or catalysts before pyrolysis even enables the simulation of complex industrial processes.

www.gerstel.com

Software Products

Automated QuEChERS Method

LCTech has developed an automated, modified non-dispersive QuEChERS method that is dedicated not only to standard matrices, but also to difficult dried matrices such as tea or spices, or samples with high fat content, which have never been insertable in QuEChERS procedures before.

The clean-up step is transferred to automation using a non-dispersive procedure with specifically adapted columns. After the SPE step, the extract can be collected or directly injected into the LC–MS/MS system via the HPLC Direct-Injection module. According to the company, this results not only in clean samples but also in excellent results in one working step from raw extract to chromatogram. Process and run time of the LC–MS/MS system are overlapping sample to sample, therefore a perfect throughput is achieved.

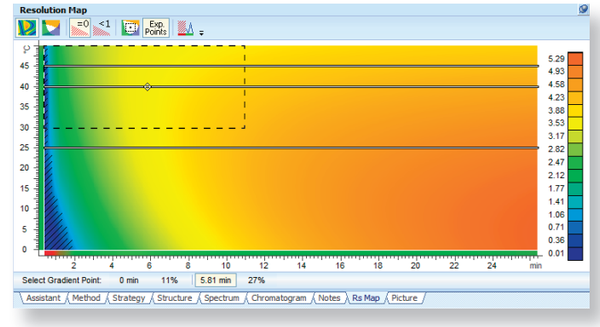
The non-dispersive property of the miniaturized ready-to-use SPE columns reduces ion suppression and results in high recoveries and high reproducibility.

The approved Freestyle system, on which the QuEChERS method is automated, offers easy operation, low maintenance, low purchase, and operating costs as well as processing 24/7—even during weekends.

Less manual work in combination with high clean-up efficiency makes the new QuEChERS method even more straightforward than the conventional method.

www.LCTech-online.com

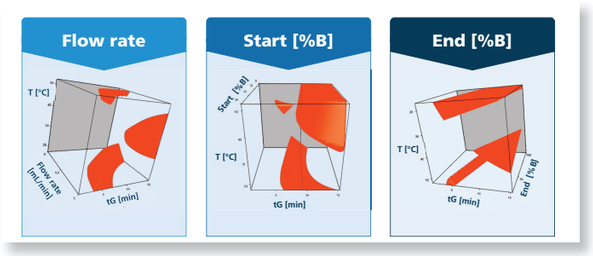
Method Development Software



ACD/Labs continues to innovate via the company's principal method development software solution: AutoChrom. The v2018.1 release of ACD/AutoChrom represents its most fully featured package to date, with significant workflow upgrades to further support quality by design (QbD) method development strategies, including systematic coverage of the design of experiment (DoE) space, multivariate optimization, and robustness modelling. According to the company, the experiment planning interface has been improved to promote greater ease-of-use, so that all relevant method development steps are presented both intelligently and sequentially. The user can search reference method databases, select key method conditions (column, pH, solvents, buffers), design and execute screening and optimization experiments, identify optimal method conditions, and perform robustness tests. Plus, AutoChrom includes direct operation of Agilent ChemStation (Open Lab ChemStation Edition) and Waters Empower instruments, streamlining execution of the selected method strategy. Other improvements include enhanced visualization of the method operable design region (MODR), including the means to identify which critical quality attributes (CQAs) determine method unsuitability in non-optimal DoE space. Additionally, the QbD reporting framework can add contextual notes to every major step in method selection and optimization, justifying each decision to simplify regulatory submission.

www.acdlabs.com/autochrom

Method Modelling Software



Molnár-Institute's DryLab software has a 35-year history in scientific method modelling. Using an accomplished DoE of twelve input runs, the software integrates the theory of solvophobic interactions and linear solvent strength (LSS) to reliably predict the movements of peaks, selectivity changes, and retention times of any multidimensional design space.

The software's automation module creates method sets in the most economic and ecologic order, executes runs, and acquires results from the CDS. Mass and other integrated data are retrieved and ambiguity in peak tracking is reduced to a minimum. An automated zoom algorithm presents chromatograms in the most clear-cut way, the align-peaks-option adds another helpful tool to identify peak movements across varied method conditions.

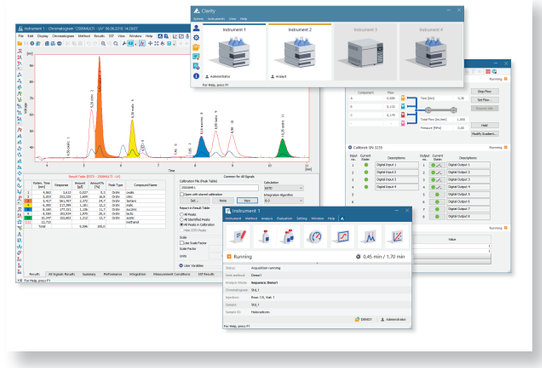
Recent advances in the modelling engine now allows for systematic designs with extra calculable parameters such as flow rate, gradient start-, and gradient end-%B, resulting in an extra dimension in critical resolution maps (CRMs). The software's visual method modelling provides insight and scientific understanding into the chromatography behind the method.

DryLab's Robustness module has been added to further instrument parameters, allowing for an assessment of a method's pitfalls in routine use. Understanding these at the earliest stage not only provides for the most substantial risk management, but allows for the redemption of less-than-optimal methods at later stages in the analytical lifecycle.

The software's reporting tool, its "Knowledge Management Documentation" (KMD), features a new set of project information windows allowing the operator to define and lay down statements as templates with regard to all areas of Analytical Quality by Design (AQbD) and the derived workflow.

www.molnar-institute.com

Chromatography Software



Clarity Chromatography Software is a general purpose chromatography software capable of controlling 700+ different instruments, including Agilent, Hitachi, Shimadzu, and many more, from one environment. It is a solution for not only the latest instrumentation, but also legacy instruments that can be connected via A/D converters.

The software is modular, and users can expand the software via optional SW extensions that support a variety of applications such as:

- PDA (Photo Diode Array) data processing
- MS (Mass Spectra) data processing
- GPC (Gel Permeation Chromatography) data processing
- NGA (Natural Gas Analysis) calculations
- DHA (Detailed Hydrocarbon Analysis) calculation
- SST (System Suitability Test)

Clarity can be deployed in laboratories from small to large and includes tools for regulated environments that can be interfaced to LIMS. The software accomdates six different languages—English, Chinese, Russian, Spanish, French, and German. Clarity offers easy to use operations, unmatched free user support, including free SW updates, and competitive pricing. Clarity OEM versions are available and a free demo version is accessible from DataApex's webpage.

www.dataapex.com

News

Crawford Scientific Acquires Anatune Ltd

Crawford Scientific has announced the acquisition of Anatune Ltd. Anatune Ltd will continue to operate as a separate legal and commercial entity while allowing Crawford Scientific customers access to Anatunes expertise in automation and trace analytical measurement.

"Over the many years we have known Ray Perkins and his team at Anatune, we have been impressed by their expertise in applications development for the most challenging analytical separations and their ability to automate these solutions," said Tony Taylor, Group Technical Director, Crawford Scientific Holdings Ltd. "We welcome Ray and his team to the Crawford Scientific family and look forward to many successful collaborations with our clients."

"Anatune becoming part of the Crawford Scientific Group means we can match the growing demand for automated sample preparation solutions. Both organizations are oriented around first-class technical support and have similar cultures and missions. We are excited by the new opportunities before us," said Ray Perkins, CEO of Anatune.

The acquisition of Anatune Ltd follows Crawford Scientific's acquisition of VR Analytical earlier in the year. Based out of Oregon, USA, VR Analytical partnered with Hall Analytical Laboratories in Manchester, UK, as part of the deal and offered clients extractables and leachables analysis, as well as, electronic nicotine delivery systems (ENDS).

"We are delighted to be joined by Ray Colton and his excellent team at VR Analytical, which presents exciting opportunities for our customers in this rapidly expanding and technologically challenging testing market," commented Sam Crawford, Managing Director of Crawford Scientific Holdings Ltd.

For more information, please visit: **www.crawfordscientific.com**, **www.anatune.com**, or **www.vranalytical.com**

Nanomechanical Resonators Expand the Reach of MS

A team of French researchers have demonstrated a new mass spectrometry technology based on nanomechanical resonators that is capable of measuring the mass of particles mega- to giga-dalton range.

Current technologies for mass measurement can weigh several tons down to a hydrogen atom mass, roughly one atomic mass unit, or dalton (Da). However, a gap exists in-between these extremes in which existing commercial technology were incapable of measuring accurately. The megadalton (MDa) to gigadalton (GDa) range, or nanoscale range, contains many scientifically interesting entities including most viruses, a diverse range of disease biomarkers, as well as synthetic nanoparticles for nanomedicine.

"In the mass range we are targeting, particles weigh the equivalent of 1 million to 1 billion hydrogen atoms. It is an intriguing range where some particles, just like objects of everyday life, are constituted of an unspecific number of atoms, while others are known to contain specific numbers of atoms of defined masses: like small molecules, they have a defined molecular mass," said Sebastien Hentz, Director of Research at CEA-Leti. "This is the case, for example, of the bacteriophage T5 virus capsid we have analyzed. To our knowledge, this is the highest molecular mass ever determined by mass spectrometry."

Conventional mass spectrometers have contributed to countless studies and brought forth new knowledge at an amazing pace and scale. Nonetheless, they struggle to analyze species above the MDa range, because they require ionization to manipulate particles, and this becomes particularly difficult for "heavy" particles (1). This new system instead relies on nanomechanical resonators that use a specific tone or frequency to measure the change in frequency which occurs when a particle lands on the surface of the resonator. The mass of the landed particle can then be inferred from this frequency change.

This is not the first time nanomechanical mass spectrometers have been attempted, however, previous iterations mimicked conventional system and used electromagnetic processes to transport ionized analytes to the resonator. The result was sample loss and incredibly long analysis times with a single analysis possibly taking weeks. To circumvent this the team based out of Grenoble, France, used a surface acoustic wave device to nebulize nanoparticles in solution into a mist of small droplets which are then aspirated into a vacuum system. The particles are then transported towards the nanomechanical detector using a flow of carrier gas to focus this down into a narrow beam. As the beam is still quite large an array of nanomechanical resonators are used to detect the mass of as many incoming particles as possible.

The new technology has been dubbed "neutral mass spectrometry" and could offer researchers around the world a new tool in their chosen pursuits.

Reference

1. S. Dominguez-Medina *et al.*, *Science* **362**(6417), 918–922 (2018).

Photo Credit: nobeastsofierce / stock.adobe.com

Peak Packaging On Point

Peak Scientific and Macfarlane Packaging have been awarded the "Supply Chain Solution of the Year Award" at the 2018 UK Packaging Awards.

The companies collaborated on "Project McLaren" to create protective and sustainable packaging for transporting the Peak's laboratory gas generation products to global exhibitions. The project takes its name from Peak's Exhibition Manager of 20 years, Ann McLaren.

The new compact exhibition packaging solutions is reusable, replacing the single use wooden crates previously used to transport its gas generators to exhibitions.

''I am delighted that Project McLaren has won Supply Chain Solution of the Year at this years' UK Packaging Awards. This award recognizes the collaborative and innovative work of both MacFarlane Packaging and Peak Scientific," said David Williamson, Global Supply Chain and Logistics Manager at Peak Scientific.

"This new packaging solution meets our exhibition packaging needs perfectly, transporting product more cost effectively and safely through the supply chain, while promoting brand awareness."

For more information please visit: **www.peakscientific.com**

Investigating Gaul Head Embalming Using GC–MS

The analysis of skeletal remains using gas chromatography–mass spectrometry (GC–MS) from Gaul settlement excavations in Southern France has confirmed the ritualistic practice of head embalming in ancient Gaul culture (1).

The practice of ritualistic head display is well documented within Celtic Gaul culture with classical textual sources documenting that decapitated enemy heads were hung around their horses' neck to be transported back to settlements to be displayed. The textual evidence is further supported by sculpting iconography recovered from the time (2) and the remains of human skulls with iron nails inside them — remnants of the mounting process. Pillars and lintels with cavities of the approximate dimensions and shape of a human skull have also being found.

Despite the practice being well-documented, the details surrounding the head preservation process have been lost to time. The only reference to the process is in Greek literature which asserts that the Celts embalmed decapitated heads with 'cedar oil'. However, historians have noted that this cedar oil may be the local Pinacea oil that the Greek authors misidentified because the two oils have a similar aroma. The discovery of severed heads in an excavation site in Le Cailar, France, offered an opportunity to perform analyses and verify the presence of possible embalming remnants on the cranial remains.

Using GC–MS researchers analyzed a large variety of skull fragments found at the site and compared them to animal bones recovered at the same site. The animal bones acted as blanks to compare against the results of the skull fragment analysis.

The analysis revealed the presence of saturated and unsaturated fatty acids, monoacylglycerols, sterols, alkanes, alkanols, and biomarkers of conifer resins (1). The presence of retene and the high amount of fatty acids in the samples was attributed to the process of resins beings heated and mixed with plant oils, which was a common practice in many ancient cultures. These mixtures were known for their anti-bacterial, anti-oxidative, and aromatic properties. The odour reduction and anti-bacterial properties of this mixture would have made it ideal for severed head preservation. None of the animal samples tested contained the conifer resin biomarkers.

Despite this new evidence confirming the embalming process, the precise method still remains unclear. The heads may have been dipped in the oil or covered with the pinacea mixture using a tool. The persistence of the embalming material in the samples could be attributed to large quantities of the preserving material being used during the first preservation process or evidence that multiple treatments were applied during the lifetime of the heads display in order to continue preservation. This would fit the Gauls' legendary attachment to their grizzly trophies as noted by ancient Greek historians Strabo and Diodorus of Sicily, who wrote: "They never gave back the head belonging to the most famous and brave person, even for an equal weight of gold" (2).

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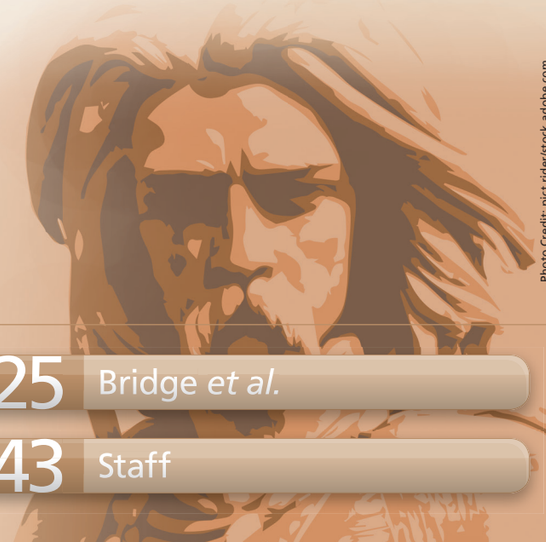

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Peaks of the Month

- **The *LCGC* Blog: Best Practice in HPLC Eluent Design**—I think it's fair to say that there has been a paradigm change in the way we approach mobile-phase design for HPLC in recent years. **Read Here>>**

- **Analyzing Phosphorylated N-Glycans with Full Recovery on Bio-Inert LC Systems and PEEK-Lined HILIC Columns**—Glycosylation is a critical quality attribute (CQA) that can impact on product safety and efficacy of protein biopharmaceuticals. Characterization of N-glycans is therefore of paramount importance for the pharmaceutical industry. This article demonstrates the analysis of phosphorylated glycans with full recovery on a bio-inert LC system and PEEK-lined HILIC column. **Read Here>>**

- **Mixing and Mixers in Liquid Chromatography—Why, When, and How Much? Part 2, Injections**—Is a mixer needed between the injector and column in high performance liquid chromatography (HPLC)? **Read Here>>**

Photo Credit: SkyeBergStudios, adobe.com

- **Tips & Tricks GPC/ SEC: What Are the Differences Between GPC, SEC, and GFC, and How Do You Get Started with the Technique?**—Molar mass distributions, molar mass averages, and polydispersity can be determined by gel permeation chromatography (GPC), size-exclusion chromatography (SEC), and gel filtration chromatography (GFC). This makes this technique indispensable for all scientists in quality control (QC) and R&D who have to work with large molecules. However, the technical terms used can be quite confusing for beginners. This instalment of Tips & Tricks explains more. **Read Here>>**

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- **Investigating Whale Shark Feeding Habits Using GC–FID**—Researchers from the Centro de Investigación y Estudios Avanzados de IPN, in Mérida, Mexico, have investigated the feeding habits of the whale shark (Rhincodon typus) in the Mexican Caribbean using gas chromatography–flame ionization detection (GC–FID). **Read Here>>**

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News In Brief

Restek has launched new pesticide residue standards to meet the cannabis analysis needs of Oregon and states with similar pesticide residue regulations/programmes. Restek's Oregon pesticide standards are certified reference materials (CRM) manufactured and QC-tested in ISO-accredited laboratories.For more information, please visit
www.restek.com

Agilent Technologies has announced the opening of a new extension to its Little Island facility in Cork, Ireland. The campus will focus of developing advanced technologies for the analysis of live-cells in real time. "Technological progression allowing researchers to examine cell health and function kinetically, and in real-time, are driving global demand for complete cell analysis solutions," said Todd Christian, general manager, Agilent Cell Analysis Division. For more information, please visit
www.agilent.com

Tosoh Bioscience has announced it has completed an equity investment in Semba Biosciences with the intention of acquiring full ownership. The two companies have been collaborating on various downstream biomanufacturing projects since 2007. "We are extremely pleased to team up with Tosoh Bioscience," said Robert Mierendorf, President of Semba Biosciences. "We are excited to work with Semba Biosciences' experts to extend the boundaries of downstream purification," added Ali Soleymannezhad, Director of Sales and Marketing at Tosoh Bioscience.
For more information, please visit
www.tosohbioscience.com

Talking About Your **Generation**

Incognito scrutinizes the behaviour of baby boomers and Generation X, Y, and Z in the laboratory. What do they want from the workplace?

In the last Incognito instalment (1), I discussed the issue of job satisfaction for analytical chemistry laboratory workers and the factors that contribute to how happy we are with our scientific lot.

In researching and writing the article, I became aware of some clearly defined differences in laboratory culture and practice, which seem to very closely correspond to the generational classifications of the past 60 years or so. It also struck me that this period of time matches the rise and development of instrumental chromatographic analysis. I therefore thought it would be fun to draw some comparisons between the evolution of analytical equipment and the evolution of those who are using the equipment—baby boomers, Gen X and Y, and now Gen Z—to draw some conclusions on what history might advise us we can do better in our current and future practices within the laboratory.

Baby Boomers (born 1945–1960, approximately 29% of US workforce in 2017 [2], although I suspect not many are working in the laboratory these days!): They are motivated by job security and are "organizational"; their career paths are largely dictated by their employers. They are the generation of the swinging sixties, the Apollo moon landings, youth culture, and the post-war boom. They saw the birth and rise of television and see the telephone as a useful means of communication. The prefer face-to-face communication, with telephone and e-mail second and third, respectively. Their decision-making is most strongly influenced by face-to-face interactions, but they are increasingly reverting to online sources for "backup" information.

These are the pioneers of chromatography, leading the way as both the science and instrumentation were in their infancy. They are in touch with the theory of separation science because they needed to design and adapt equipment to keep pace with evolving theories, communicated to them using a nascent academic literature and increasingly through the huge numbers of conferences and discussions groups—all required to keep pace and maintain order as new

technology, methods, and modes were born. Equipment was "modular", often with a different manufacturer for each part of the system (pump, detector), and "autosamplers" had not yet been invented.

As new manufacturers emerged, they needed to figure out novel ways of connecting equipment (hydraulically and electronically) and measuring output, predominantly via calibrated chart paper (of a known and reproducible weight) from which the "peaks" were cut out and weighed for quantitative analysis. They used 25-cm long high performance liquid chromatography (HPLC) columns packed with 10- or 40-µm irregular silica particles and glass gas chromatography (GC) columns (4 mm inner diameter [i.d.]) hand packed with a variety of media, from sieve-sized brick dust to small fossilized diatoms (diatomaceous earth). There were very few "coated" stationary phases for HPLC, and those which did exist were made mostly using GC support materials (GC was by far the dominant chromatographic technique in those early days) coated with a variety of not very stationary, stationary phase liquids (that is, they didn't stay coated onto the support materials for very long at all). Both HPLC and GC columns were frequently packed in-house. Preparing equipment for analysis might have taken multiple days, analyses may have been an hour or longer, and method development time was measured in weeks or months. Troubleshooting or technical support was provided by academicians or the few instrument or column companies that existed.

Generation X (born 1961–1980, approximately 34% of US workforce in 2017 [2]): They are much more interested in a work–life balance and were the pioneers of portfolio careers, loyal to a profession but not necessarily an employer. The early lives of the "latch-key kids" were influenced by the end of the Cold War, Regan and Gorbachev, Live Aid, and the fall of the Berlin Wall. They are the generation of the personal computer, e-mail, and text messaging, colloquially known as *digital immigrants*, many of whom started their career just as typewriters were rapidly being replaced with rudimentary computers for writing laboratory reports. They have a preference for e-mail rather than face-to-face communications, and whilst their decision-making is often underpinned by on-line information, their secret preference is still for face-to-face knowledge gathering.

In the laboratory, Gen X had a mixture of modular systems and fully integrated

systems (a single system from a single manufacturer), which were beginning to make an appearance. This is the generation of the computing integrator, an instrument that produced chromatograms on chart paper rolls with peak area measurements—a great leap forwards for quantitative analysis. During their working lifetime, Gen X workers have seen mass spectrometric (MS) detection techniques in GC become fully established and the meteoric rise in the development of LC–MS. Bonded phases for HPLC—C18 in the vast majority of cases—were commercialized, with 10- or 5-µm particles now becoming the norm. Whilst the majority of GC columns were still packed particles in glass columns, the revolution of the wall-coated open tubular (WCOT) silica capillary megabore (0.53 mm i.d.) had begun the inexorable march towards capillary column domination. There was a proliferation of academic literature, and whilst the number of conferences had consolidated, their attendance had not, and meetings, such as Pittcon, boomed in terms of both the scientific programme and vendor exposition. There were now more well-established instrument companies producing more reliable equipment, and even independent column manufacturers were becoming mainstream, all providing solid and fairly readily available technical support. Whilst columns were still packed or prepared in-house, purchasing columns from vendors had become commercially favourable. Instrument preparation was in the order of a day or less and chromatographic run times of 30 min or so had become established.

Generation Y (Millennials) (born 1981–1996, approximately 34% of US workforce in 2017 [2]): This is the generation of the 9/11 terrorist attacks, PlayStation, social media, and reality TV. The "digital native" generation are more interested in freedom and flexibility and work "with" employers not for them. Their main communication tools are smartphones and tablets and they communicate via Instagram, Snapchat, and occasionally the ageing medium of text message. They are the generation who, for the first time, communicate on-line rather than by telephone or face-to-face, preferring the speed and brevity of written communication as well as the ability to have multiple streams of communication in play simultaneously. They trust on-line information, sometimes to their detriment!

In the laboratory, equipment is now fully modular and the industrialization of equipment into black box format is well underway. The equipment is much more reliable, and it is the era of operators rather than experts in the technology. Separation science is now much better understood by organizations and the service has become an information or data provider rather than an expert provision whose experts are required to interpret the wider context of the data within the business. The age of the computing data system is fully upon us with automated quantitative and qualitative results reporting. A proliferation of HPLC-bonded phases is available and the quality of HPLC packing materials has improved significantly; some might say there is too much stationary phase choice. This is the era of the rise of hydrophilic interaction liquid chromatography (HILIC) separations, of UHPLC, sub-2-µm, and core–shell particles. HPLC technology might be said to be fully mature.

High efficiency GC capillary columns are fully established with standardized ranges of phases producing plate counts that could only have been dreamed of by the early pioneers. There are fewer scientific meetings with less novel scientific programmes and we see the rise (and some might say the beginning of the decline) of the SuperExpo as the behemoth instrument companies vie for the spend of the multinational corporations. On-

line support and instrument telemetry are now well established, but as competition increases, instrument companies often see training and support as an added cost of business and begin to rationalize these services and optimize profit margins, justified by the quality and reliability of instrumentation. Applications laboratories concentrate on the niche and emerging opportunities in what is now a rapidly maturing market. This is the age of the sub-5-min HPLC analysis, whilst GC analyses are in the 10–30 min range, and instruments, when well maintained, can last months between services with analytical preparation times of under 1 h.

Generation Z (born after 1995, approximately 3% of US workforce in 2017 [2]): This is the generation of the economic downturn, global warming, cloud computing, and wikileaks. Given the economic instability of their early years, they will for the first time since the baby boomers seek security and stability in employment, however they remain career multitaskers, moving seamlessly between employers, always confident that their 21st century education and technology skills will make them employable. They will be the generation of Google Glass, nanocomputing, 3D printing, and driverless cars. They are technoholics and know little else of alternative effective means of communication, effortlessly using cloud and on-line methodologies for information exchange, including FaceTime and Instagram. Their devices are handheld or integrated into clothing or wearable devices. They will have no problem making decisions based on crowd-sourced opinions or real-time polling.

So, what of the future for Gen Z in the laboratory?

Instruments will continue to become increasingly "inaccessible", and without good training on operating principles, use and preventative maintenance may truly be black box, with expertise falling upon the instrument vendor or the multi-vendor service organization. Chip-based separations will become the norm, with fully integrated chromatography systems being miniaturized onto chip size devices with no connective tubing. Perhaps this generation will see the first disposable chromatographic system—one chip "system" simply being replaced for another. MS detectors will continue their dominant position, perhaps with every chromatographic system having an MS detector as standard. Certainly, the science behind this fully industrialized discipline will become less well understood with automatically developed, generic methods taking the place of individually crafted separations.

Data will be fully automatically generated using advanced data systems, alongside all of the quality and statistical data required for a completed report. The days of the "load autosampler, select method, automatically report data to the cloud" paradigm will be upon us and sample preparation will also become increasingly automated, with perhaps only a rudimentary sample weighing being necessary. Perhaps this generation will see the first 1 million plate columns in regular use and I predict that the number of stationary phases will begin to decline in line with the increase in generic methods—efficiency taking the place of selectivity. Major vendors will have their own expos and scientific conferences will be confined to specific application areas as end users vie for advances in small margins rather than major breakthroughs. Support will be virtual, perhaps with parts and consumables being sent as digitally encrypted plans for a new instrument part or indeed a chip-based column printed on the laboratory 3D printer.

What can we learn from these reflections? There are three (and soon to be four) generations coexisting in the laboratory, all with very different

life and workplace philosophies, and we need to recognize this in the way laboratory work is organized, executed, and managed. Theory and knowledge should be passed from the few remaining baby boomers down through Gen X and Y, always bearing in mind that these generations may be more favourably placed to learn digitally. Develop more apps and mobile device software and play to the generational strengths; Gen Y and Z certainly won't want to be tied to a computer next to an instrument for example.

We need to recognize that we are in the age of the chromatography operator and exploit the digital and IT skills of Gen Y and Z to ensure that throughput is optimized, always recognizing that we need to guard against the production of data for data's sake, rather than valid information useful for the wider business. Younger generations, and especially Gen Z, need to be aware of the science and engineering that underpins separation science, otherwise they will not be able to differentiate good information from bad and certainly won't be emotionally engaged with the profession. They need to be aware of the data "in context" and taught how their information is used to inform business and scientific decisions. They need "stretch" and we need to develop new ways to challenge them to collect, organize, and present information, as well as encouraging them to investigate new technologies and implement them in the laboratory.

In a wider context, Gen Y and Z will value experiences more highly than possessions and therefore will place increasing emphasis on the quality of the workplace, additional benefits, and the work–life balance, rather than salary alone. These are the days of the "total compensation package".

In these recovering economic times, we need to realize that younger people have a choice of career and employer. Without challenge, a deep understanding of the science, and the ability to adopt new digital ways of working and communicating, we can be sure that they will revert to type and seek to work with (not for) an employer who is better able to understand their needs and allow them to become more emotionally attached to separation science.

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GC×GC–MS for Forensic Analysis

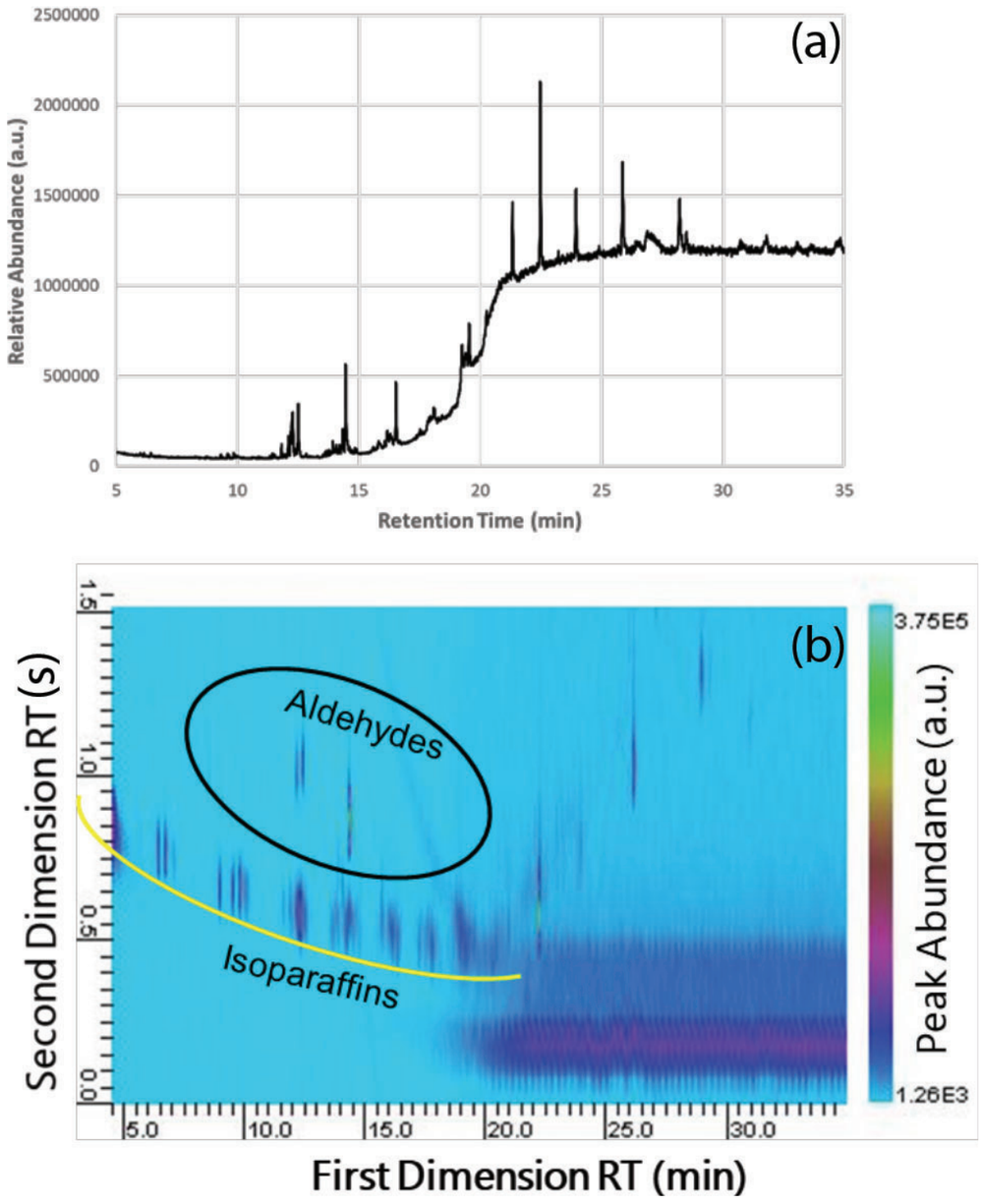
Candice Bridge[1,2], Mark Maric[1], and Kaitlin Jones[2], [1]National Center for Forensic Science, University of Central Florida, Orlando, Florida, USA, [2]Department of Chemistry, University of Central Florida, Orlando, Florida, USA

Gas chromatography–mass spectrometry (GC–MS) is considered the gold standard in forensic trace evidence analysis because of its ability to chromatographically separate and analyze components in mixtures. Although two-dimensional GC–MS (GC×GC–MS) has been used extensively in the oil and petroleum and flavour and fragrance industries, it has not been fully explored in the forensic sector. However, forensic scientists often encounter highly complex samples that would benefit from the capabilities of GC×GC–MS, such as, sexual lubricants, automobile paints, and tyres. GC×GC–MS analysis can allow for the deconvolution of coeluted components while providing increased sensitivity of minor components to help benefit any forensic laboratory.

Gas chromatography–mass spectrometry (GC–MS) is a "go-to" analytical technique primarily because of its versatility for isolating and analyzing different components in unknown mixtures without requiring substantial method development for each new sample. This is the primary reason why GC–MS is the gold standard in the forensic analysis of trace evidence, such as ignitable liquids, drugs. However, there are limitations in using GC–MS for all unknown mixtures because of the complexity of some of these mixtures. The primary limitation is coelution of the compounds in a mixture. This is where multidimensional gas chromatography (MDGC) can increase component separation with the potential to increase the sensitivity of compounds that may not meet the limit of detection in GC–MS.

There are a few types of multidimensional gas chromatography configurations, all of which can be coupled to a mass spectrometer: comprehensive (GC×GC–MS) or heart-cut (GC–GC–MS). There are three

Figure 1: (a) GC–MS and (b) GC×GC–MS of an oil-based lubricant.



types of commercially available MDGC–MS configurations: thermal modulation (TM), Deans switch (DS), and differential flow modulation (DFM). Discussions of TM and DS can be found in the literature (1,2). This article will discuss the use of the latter modulator for forensic trace evidence analysis to rapidly differentiate complex mixtures by observing the unique chromatographic "fingerprint" (3). These "fingerprints" are similar to a topography chart, which shows the trends of compounds that are chemically related, that is, normal alkanes, isoparaffins. As a result of increased sensitivity, this "fingerprint" shows both major components as well as those minor components that may have been hidden as a result of coelution.

GC×GC–MS systems have been used in the edible oil industry to investigate minor compounds (3,5) as well as the petroleum and biodiesel industries for rapid determination of the chemical formulation (6). However, the technique has yet to be evaluated for complex forensic evidence. This article discusses the use of GC×GC–MS for several forensic samples.

Experimental

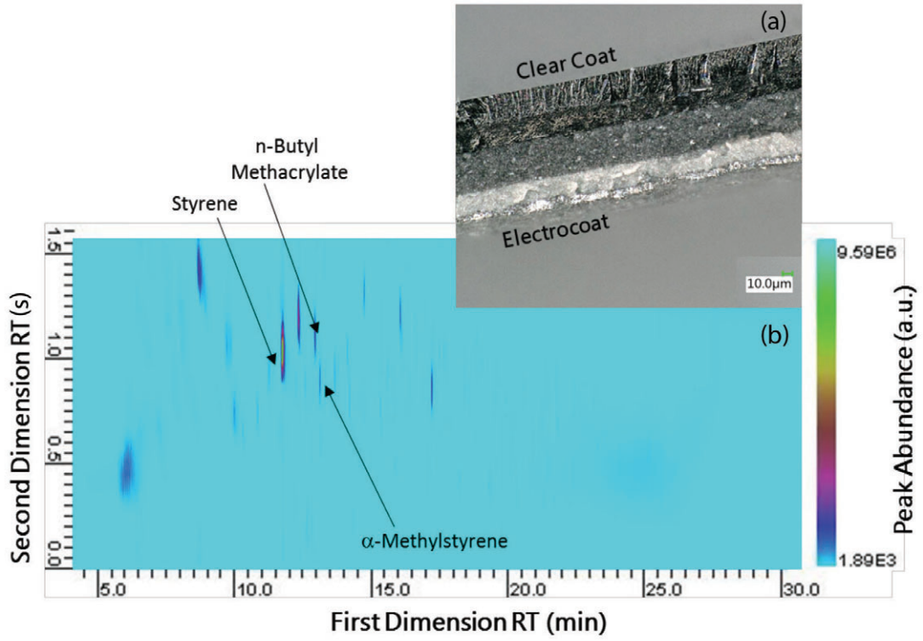
Both GC–MS and GC×GC–MS analysis of the trace evidence samples was performed on the same GC–MS system using the same column configuration. The GC system was a 7890B gas chromatograph equipped with a split–splitless injector coupled to a 5977 quadrupole mass spectrometer (Agilent) (7).

The pyrolysis analysis of automobile paint and tyres used the same GC×GC–MS method from the lubricant analysis. However, to conduct pyrolysis of the sample a Pryoprobe 4000 (CDS Analytical LLC) was used. The flash pyroprobe profile was started at 50 °C for 2 s and then was ramped to 750 °C at 50 °C/s and held for 2 s. All samples were analyzed in their natural, unmodified state.

Forensic Lubricant Analysis

A recent survey conducted by the National Center for Injury Prevention and Control revealed that approximately 1 in 5 women and 1 in 71 men will be sexually assaulted in their lifetime (8). Despite this staggering statistic, most criminal investigators primarily rely on DNA evidence to solve these crimes—from semen, skin cells underneath fingernails, or any other biological evidence. However, the use of condoms by sexual perpetrators has increased primarily because they think that it will mitigate the deposition of semen at the crime scene or on the victim, thus preventing their identification based on DNA. A study by Nancy Ritter demonstrated that approximately 30% of sexual assault kits do not contain any probative DNA profiles for the perpetrator (9).

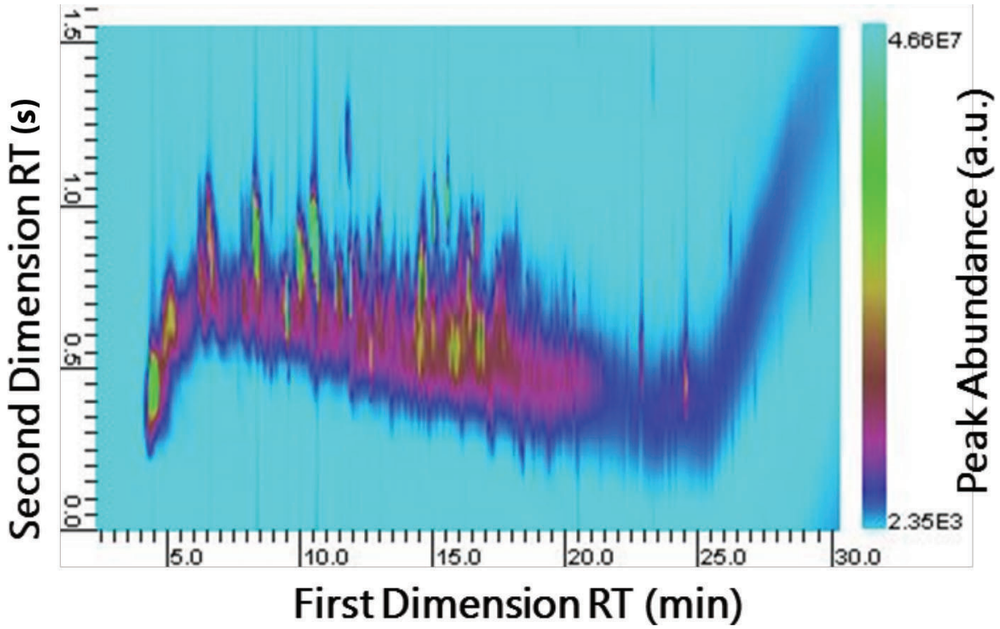
Figure 2: (a) Cross-section of automotive paint system, (b) Py-GC×GC-MS profile of the clear coat.



This is where the forensic analysis of sexual lubricants can support the current analysis of sexual assaults. In the absence of DNA, lubricant analysis can provide another link between the perpetrator and the victim or crime scene. However, many lubricants are made from natural oils, which are comprised of many compounds that may be difficult to differentiate using traditional GC–MS.

An example of a typical oil-based organic personal lubricant is one comprised of several organic butters (cocoa and shea) as well as vitamin E oil, bees wax, sweet almond oil, and even sunflower oil. Each of these oils and butters are comprised of many different oils and components themselves. Lubricant samples were prepared by hexane solvent extraction. Despite the fact that the oil-based lubricant only has six labelled ingredients, GC–MS analysis shows that there were more than the six labelled components, but there was a substantial amount of coelution between retention times (RTs) of 7 and 20 min (Figure 1[a]). However, using

Figure 3: Py-GC×GC–MS profile of a tyre sample.



GC×GC–MS analysis, more than 25 different components were readily observed. Between the 10- and 15-min first dimension retention times (FDRTs), several components were separated in the second dimension that were coeluted during GC–MS analysis (Figure 1[a]).

When compared to other natural oil-based or plant-based lubricants, the overall chromatographic profile is similar, but the differences are readily observed between the FDRTs of 7 min and 17 min. Isoparaffinic compounds make up the lower arc of the early GC×GC profile (underlined in yellow) and the aldehydes are above (circled in black). Many of the heavier oils elute later on the first-dimension column, such as vitamin E oil. This oil is not readily observed in this sample primarily because of the low concentration in the sample. Based on the analysis of other natural lubricants and lotions, vitamin E (also known as a-tocopherol) elutes off the second column adjacent to the column bleed located at the lower right-hand corner of the chromatographic plane. What is also immediately noticeable is the increased intensity.

It was not immediately clear why there was a background shadow observed between first dimension retention times 20 to 35 min (lower right hand of Figure 1[b]). It is possible that this "shadow" was a result of either a column bleed from the first-dimension column or the second-dimension column, considering the elevated oven temperatures at the end of the chromatograph run (280 °C).

Automotive Paint Analysis

Automotive paint is a type of forensic evidence collected at car accidents, hit-and-runs, and any other crime involving a vehicle. This type of evidence is encountered frequently, and thus it is critical to improve current analytical techniques as well as evaluate new options that could provide more information than current techniques can provide.

Automotive paint is chemically complex because it is multilayer system and different components are present in each layer. The four main components that make up automotive paint are pigments, additives, binders, and solvent. When automotive paint coatings are applied by the original equipment manufacturer (OEM), they are added in the following order: electrocoat, primer surfacer, basecoat, and clear coat. Each of the coatings have a different purpose with regards to the car's appearance. The electrocoat is used to

prevent corrosion and the primer surfacer provides the car with a smooth surface. The basecoat determines the colour of the vehicle, and the glossy finish is provided by the clear coat, which contains hindered amine light stabilizers and UV absorbers to protect the underlying paint layers from weathering and environmental effects (10).

Currently, there are three techniques used to analyze automotive paint: microscopy, infrared (IR) spectroscopy, and pyrolysis (py)-GC–MS. Py-GC–MS has the most discriminating power among these three techniques and can differentiate between samples with similar binders and pigments, not typically achievable with IR spectroscopy (11). The ability of py-GC–MS to discriminate between similar samples is significant, yet there is still room for improvement. Pyrograms of automotive clear coat samples analyzed using py-GC–MS have indicated that coelution occurs with certain compounds of interest, that is, toluene and 1,2-propandial, which can limit the ability to differentiate clear coats (11).

To overcome the obstacle of coelution, py-GC×GC–MS was used to analyze automotive clear coats. To our knowledge, there is no literature published on the analysis of paints using py-GC×GC–MS. Increased separation of paint components is demonstrated using py-GC×GC–MS, especially for peaks that typically coelute in GC–MS. The two peaks around FDRT 11.6 min (Figure 2[b]) illustrate the improved separation that is achieved in py-GC×GC–MS. α-methylstyrene (11.776 min FDRT) and n-butyl methacrylate (11.600 min FDRT) would normally coelute in the first column, however, the second column allows the two peaks to be distinguished from one another. With additional method development, we aim to increase the separation of clear coat peaks.

Tyre Analysis

Much like automotive paint, traces of tyre rubber are often encountered on road surfaces or on the victim of automotive-related incidents like hit-and-run accidents. The forensic analysis of tyre evidence is useful to investigators, specifically when attempting to reconstruct vehicle trajectories, velocities, and dynamics in incidents (12). Tyre impressions from a crime scene are routinely compared to the tread pattern of tyres from the suspect vehicle, however, in many instances the impression may be of poor quality, which is when the chemical analysis of the rubber traces may help to provide investigative leads. The physiochemical complexity of trace tyre particulates makes the characterization of this evidence challenging and time-consuming. Py-GC–MS is the technique primarily used by forensic scientists for the chemical analysis of tyre evidence (13,14). The pyrograms from rubber traces obtained from the tyre impressions can then be compared to the tyre from a suspect vehicle. Tyres are extremely chemically complex, often containing over 200 components, including natural and synthetic rubber, oils, plasticizers, antioxidants, antiozonants, accelerators, vulcanizing agents, accelerators, and curing systems (15). This chemical complexity can result in coelution of components, which may prevent a correct match and lead to significant errors.

A flash pyrolysis method was used to pyrolyze a small portion (~50 µg) of the main tread of a Firestone Destination LE tyre. Multidimensional separation of the pyrolysates was performed and the resultant GC×GC plot is presented in Figure 3. The complexity of tyre samples makes identification of the individual components difficult using one-dimensional py-GC–MS. py-GC×GC–MS was able to differentiate many components in the second dimension, which is beneficial to eliminate the ambiguity in making comparisons, and improves match determinations and reduces errors, which is imperative in forensic investigations.

Conclusions

With complex mixtures commonly encountered in forensic trace analysis, it is necessary to start evaluating techniques other than GC–MS. The use of GC×GC–MS or py-GC×GC–MS provide the forensic community with a new methodology that can achieve such separation. This could be the next frontier for increasing the actionable intelligence that forensic laboratories provide the criminal investigation system.

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Tips & Tricks GPC/SEC: What You Need to Know to Allow for Efficient GPC/SEC Troubleshooting

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Although modern gel permeation chromatography/size-exclusion chromatography (GPC/SEC) instruments are generally very reliable, scientists sometimes encounter problems. This instalment of GPC/SEC Tips & Tricks offers advice on how to efficiently identify the root cause of problems, such as dealing with a too high pressure, loss of resolution, or drifting baselines.

Liquid chromatography (LC) instruments are multicomponent systems comprising of at least one pump, an injector (automated or manual), one or more separation columns, and one or more detection system. To obtain reliable and accurate results, all components within such a system are required to work properly (1).

Scientists who work with gel permeation chromatography/size-exclusion chromatography (GPC/SEC) have to deal with (nasty) solvents. Very often mobile phase additives or modifiers, such as salts, are required to suppress undesired interactions or sample aggregation (2). In addition, sample preparation for macromolecular samples can be very demanding. Dissolution may take a long time and insoluble parts (for example, microgels) or contaminants can be present (3).

The most common problems that occur with GPC/SEC systems are therefore pressure increase, loss of column resolution, and drifting baselines, specifically when using refractive index (RI) detection.

If a problem occurs an efficient strategy can help to reduce the instrument downtime. This requires scientists to be familiar with their setup. Knowing a few important parameters can help to identify the root cause of a problem.

Pressure Issues

An (isocratic) pump is used to pump the LC mobile phase through the autosampler, the GPC/SEC columns, and the detectors. The inner diameter (i.d.) of the tubing used to connect the components and also within the components needs to be adapted to the system requirements. Narrow bore (0.17 mm [i.d.] and less) are typical for semi-micro and analytical setups to avoid band broadening. High viscous solvents or preparative setups sometimes require tubing with a larger inner diameter (0.25 mm or 0.5 mm).

Columns and tubing both generate pressure. This pressure value mainly depends on the viscosity of the mobile phase, the flow rate set at the pump, the number and type of columns, and the inner diameter and length of all tubing (in and outside of detectors). Each setup has its unique pressure value that should vary only slightly over time. A pressure change can be an indicator of a problem.

It is therefore recommended to monitor the pressure during analysis. In addition users should know the typical pressure value for their setup, applying their conditions (solvent, flow rate, temperature) with and without columns installed.

When installing new columns (4), a user should first document the pressure value for the pump, autosampler, and tubing to the precolumn. For this, set the desired flow rate at the pump, collect the waste at the tubing end, and write down the system pressure. Then install the precolumn according to the user documentation, set again the desired flow rate, and write down the value for the system with the precolumn. Install then the (first) analytical column and write down the pressure value; continue with this until all columns are in place. If the column manufacturer provides a pressure value on the column certificates this can be compared with your own values keeping in mind that different flow rates, different solvents, and different temperatures (as they influence the solvent viscosity) will generate different pressures. So deviations of these values are to be expected.

Figure 1: Results for plate count, asymmetry, resolution, baseline drift, baseline wander, and *S/N* determined with one injection. These parameters should be known for each setup. If results are out of spec, columns need to be tested individually.

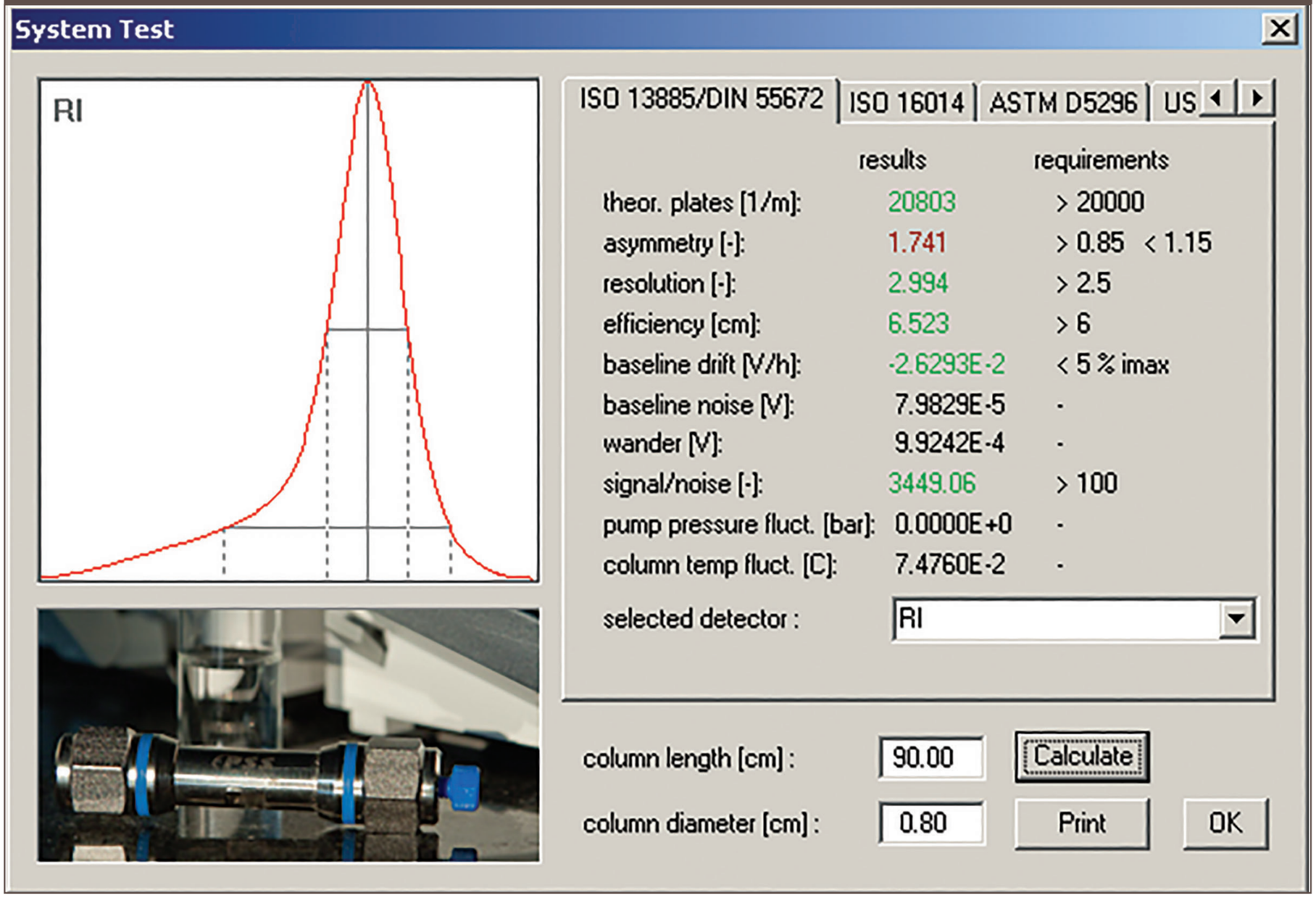

Table 1 shows an example of a well-documented setup.

As a too high pressure can damage the column packing and thus destroy the column entirely, it is good practice to set an upper pressure limit for the setup. If the limit is exceeded, this setting will cause a pump stop. Typically, the normal total pressure plus 20–30 bar is used as an upper limit.

Table 1 will now help to find the root cause in case of a pressure increase. Open the tubing at the entry port of the precolumn and check if the system pressure is too high. If this is the case, the pump, the autosampler, or the tubing is causing the problem. If this is not the case, most probably the columns are responsible.

Please note that the detector and tubing placed after the column may also cause the pressure increase. This could be double-checked by re-connecting the columns and by opening the connection at the exit of the last column. If the pressure reflects the value for the last analytical column installed, the detectors or the tubing after the columns is causing the issue.

After identifying the block of components that is causing the problem (pump/autosampler, columns, or, less common,

Table 1: Example of a well-documented GPC/SEC setup after column installation, all pressure values in bar

System	Conditions	System Pressure (No Detectors)	Precolumn Installed	Analytical Column 1 Installed	Analytical Column 2 Installed	Total Pressure
GPC 1	THF, 1 mL/min, 35 °C	5	11	31	53	57

detectors), each component in this block needs to be checked separately. For this remove piece by piece, starting from the end. Just loosen each subsequent connection while the flow rate is set as usual and check if an unusual high pressure drop occurs. It is good practice to replace any filters while the instrument is down.

In the case of a blocked tubing or needle, replace this part and immediately throw the blocked one away. If the precolumn is the root cause of the problem, it has done its job and should be replaced. In the case of an analytical column, applying a cleaning procedure or a replacement of the column frits can be an option. For this please refer to the column user documentation. If a detector is the cause of the problem, refer to the manual to see if and how you can clean the cell.

Column Performance

The columns in the setup are required to separate the molecules by size. A properly working GPC/SEC column has a high resolution power and generates narrow, symmetric peaks for monodisperse samples. If the resolution decreases, each of the columns in a set, even the precolumn, can be the single source of this behaviour. So in case of distorted chromatograms (broad peaks, double peaks, peaks with tailing or fronting) there is a realistic chance that only one of the columns in a set is malfunctioning.

Good measures to describe the column performance are the plate count, the asymmetry, and the specific resolution (5). These parameters should be determined for the complete column set immediately after installation. National and international standards provide acceptance limits for columns, often specifically for the mobile phase used. It is good practice to write down the parameters after installation and to compare these values with the data given on the column certificate. As the plate count depends on various parameters it is individual for each setup. If available, document the values of each column installed.

The plate count test should be repeated regularly, but at the very least when a problem is suspected. If the column set does not pass the acceptance limits any more, or if the deviations to previous measurements are too high, each column needs to be tested individually. Figure 1 shows an example where the asymmetry of a column set is out of spec as a result of peak fronting. The next step is to repeat the same test for each of the three columns individually to verify if only one column needs to be replaced or if the complete set is damaged. After identifying the faulty column it is good practice to review the samples previously analyzed to verify if one of them is causing the issue.

Please note that the behaviour shown in the example can sometimes be attributed to a wrong tubing connection. Each time new columns are installed (especially when the supplier has changed) the fittings and ferrules should be replaced to ensure low dead-volume connections with the matching stop depth.

Detector Performance

The detector is used to detect if sample fractions elute from the column. If pure effluent is passing the detector cell a baseline is obtained. The quality of detector signals is generally described by reviewing baseline drift and wander and the signal-to-noise ratio (S/N). National and international standards provide acceptance limits for drift and S/N. The influence of these values on GPC/SEC results has been investigated intensively (6).

To identify if a problem is related to chromatographic issues or detection issues it is best to measure uncritical samples. Plate count test substances can be used to determine the parameters for concentration detectors, such as RI, ultraviolet/diode array detection (UV/DAD), or evaporative light scattering detection (ELSD). If S/N, drift, and wander for this injection is documented after system installation troubleshooting will be easier.

Figure 1 also shows the results for drift, wander, and for S/N determined using the injection of the plate count test substance for a refractive index detector. All requirements by ISO13885 are met. In case of out-of-spec results, a baseline drift can often be assigned to temperature fluctuations. Here the conditions in the laboratory need to be reviewed (influence of draught of air conditioning, column compartment). A low S/N for concentration detectors is often an indicator of a dirty

flow cell. Refer to the user documentation for cleaning procedures.

Summary

- Knowing the pressure of the system with and without the separation columns installed helps to quickly identify if the columns or the instrument is responsible for a pressure increase.
- Single column testing helps to identify a blocked (too high pressure) or malfunctioning column (low plate count, asymmetry, resolution).
- The sample used for plate count determination can also be used to verify detector performance (drift, S/N).

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Solid-Phase Microextraction Liners for Headspace Volatile Organic Compounds

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Appropriate gas chromatography (GC) inlet liner selection often appears to be a challenge for end users. The recent release of new traditional solid phase microextraction (SPME) fibers and SPME Arrow has resulted in numerous questions surrounding SPME and liner selection. In an attempt to answer one of the more common questions, the following article provides data for the impact of straight wall liner dimensions on analytical response when using SPME for headspace (HS) volatile organic compounds (VOCs) in water.

In 1990, Janusz Pawliszyn (University of Waterloo) developed solid-phase microextraction (SPME) and published the first article on the technology (1). Nearly 30 years later, traditional SPME and SPME Arrow are reaching an entirely new set of end users, who did not previously use SPME. These new end users have a plethora of questions because it relates to SPME. More specifically, some end users are coming forward with the following liner questions:

- Must I have a 0.75-mm liner for my traditional SPME?"
- "Can I run a 1.1-mm SPME Arrow in a 1.8 -mm liner?"
- Will I lose a lot of sensitivity with a straight walled 2.0-mm liner?"

It appears that a lot of end users have strong preconceived notions on what liner is best for SPME, while a large portion have no idea what is best for their specific SPME application.

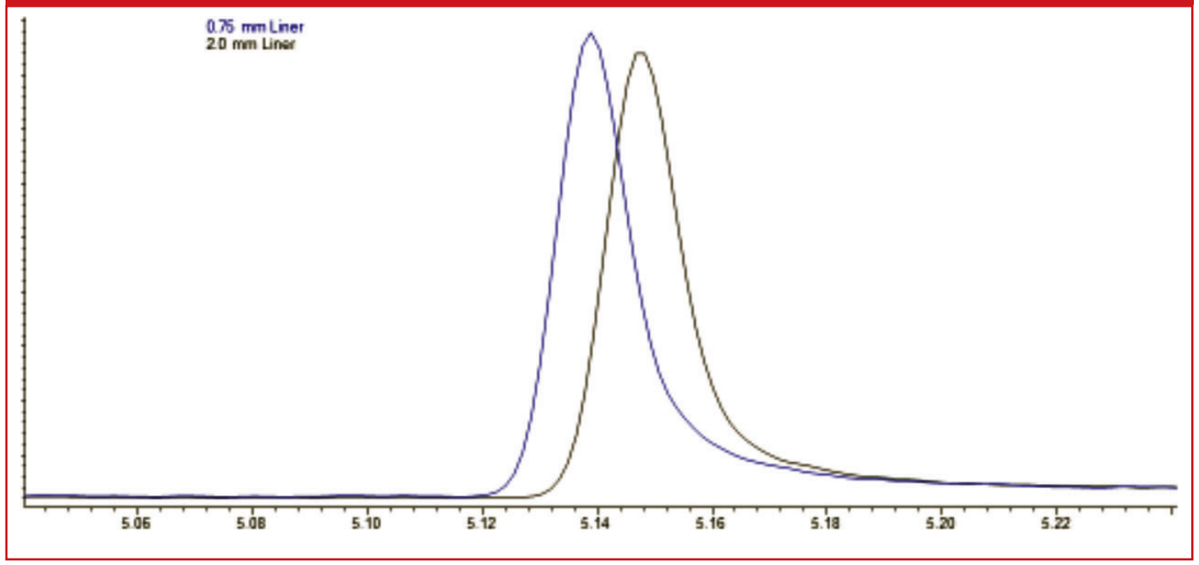
Table 1: ISO 17943 VOCs in DI water HS with 0.75 mm and 2.0 mm liners

Compound	0.75 mm			2.0 mm			Abs. % Diff.	P-Value
	Average	St dev.	% RSD	Average	Stdev.	% RSD		
Pentafluorobenzene	537734	44638	8.30	512355	20890	4.08	5.0	0.213
Diethyl ether	18686	2322	12.4	14848	1925	13.0	26	0.008
1,1-Dichloroethene	36437	2481	6.81	31990	2213	6.92	14	0.006
Carbon disulfide	156154	11971	7.67	132929	3208	2.41	17	0.002
Iodomethane	14143	1084	7.67	12641	333	2.64	12	0.010
Allyl chloride	30958	2889	9.33	24381	1330	5.45	27	0.000
Methylene chloride	239086	42619	17.8	186514	42623	22.9	28	0.049
Acetone	35075	8429	24.0	34917	2082	5.96	0.5	0.963
trans-1,2-Dichloroethene	114347	9725	8.51	97551	2953	3.03	17	0.003
Methyl tert-butyl ether (MTBE)	44022	4007	9.10	41165	6875	16.7	6.9	0.397
tert-Butanol (TBA)	8747	3157	36.1	8664	2108	24.3	1.0	0.956
Diisopropyl ether (DIPE)	120685	11152	9.24	101452	6889	6.79	19	0.003
Acetonitrile	21042	3399	16.2	18908	3342	17.7	11	0.279
Chloroprene (2-chloro-1,3-Butadiene)	87669	5637	6.43	74433	2707	3.64	18	0.000
1,1-Dichloroethane	61206	5062	8.27	49172	3366	6.85	24	0.000
Acrylonitrile	87167	5294	6.07	75368	5437	7.21	16	0.002
Ethyl-tert-butyl ether (ETBE)	95104	10613	11.2	80731	4853	6.01	18	0.011
cis-1,2-Dichloroethane	63258	4874	7.71	53603	2330	4.35	18	0.001
Bromochloromethane	16844	1337	7.94	14115	805	5.70	19	0.001
Chloroform	269267	110344	41.0	242763	72505	29.9	11	0.615
Methyl acrylate	34832	5138	14.8	31013	2696	8.69	12	0.120
Carbon tetrachloride	46207	14623	31.6	54093	3727	6.89	15	0.212
Dibromofluoromethane	40016	3165	7.91	35715	2448	6.85	12	0.019
Tetrahydrofuran	624755	351729	56.3	376440	202098	53.7	66	0.144
1,1,1-Trichloroethane	59309	5070	8.55	50195	3269	6.51	18	0.003
2-Butanone (MEK)	141203	74759	52.9	88172	44322	50.3	60	0.145
1,1-Dichloropropene	45150	4027	8.92	38586	1076	2.79	17	0.004
Benzene	476410	37530	7.88	429683	5839	1.36	11	0.016
tert-Amyl methyl ether (TAME)	30913	3995	12.9	29363	4763	16.2	5.3	0.543

Table 1: ISO 17943 VOCs in DI water HS with 0.75 mm and 2.0 mm liners

Compound	0.75 mm			2.0 mm			Abs. % Diff.	P-Value
	Average	St dev.	% RSD	Average	Stdev.	% RSD		
Trichloroethene	295076	44494	15.1	285983	10900	3.81	3.2	0.618
Difluorobenzene	2695265	206935	7.68	2478537	102137	4.12	8.7	0.037
Dibromomethane	29351	2300	7.84	25501	1220	4.78	15	0.004
1,2-Dichloropropane	90089	9585	10.6	76503	6524	8.53	18	0.012
Bromodichloromethane	123703	17309	14.0	110395	7945	7.20	12	0.103
Methyl methacrylate	82025	10171	12.4	70339	3212	4.57	17	0.023
1,4-Dioxane	25088	5467	21.8	15957	3990	25.0	57	0.005
2-Chlorethyl vinyl ether	43713	4474	10.2	36829	2363	6.42	19	0.006
cis-1,3-Dichloropropene	116333	9218	7.92	104824	3370	3.22	11	0.016
Toluene-d8	927844	101263	10.9	839070	30900	3.68	11	0.062
Toluene	1227942	112607	9.17	1101668	42114	3.82	11	0.025
2-Nitropropane	78496	8165	10.4	70317	4504	6.40	12	0.047
2-Hexanone	77450	8679	11.2	70129	4457	6.35	10	0.082
trans-1,3-Dichloropropene	120541	9118	7.56	115235	4606	4.00	4.6	0.209
Tetrachloroethene	282000	20302	7.20	255948	8353	3.26	10	0.014
Ethyl methacrylate	135802	17992	13.2	125051	10514	8.41	8.6	0.211
1,1,2-Trichloroethane	82373	10351	12.6	81422	7055	8.66	1.2	0.849
Dibromochloromethane	86607	8322	9.61	79353	3028	3.82	9.1	0.065
1,3-Dichloropropane	134375	12686	9.44	122762	10493	8.55	9.5	0.098
1,2-Dibromoethane	82358	7085	8.60	77112	3911	5.07	6.8	0.125
4-Methyl-2-pentanone (MIBK)	172335	73913	42.9	143650	15019	10.5	20	0.351
Ethylbenzene	1539755	115327	7.49	1475360	39908	2.71	4.4	0.206
Chlorobenzene-d5	5593929	404374	7.23	5505346	205212	3.73	1.6	0.623
Chlorobenzene	803100	61745	7.69	759384	25019	3.29	5.8	0.124
1,1,1,2-Tetrachloroethane	136975	12555	9.17	124006	4392	3.54	10	0.035
m-Xylene	2983994	242401	8.12	2852997	82214	2.88	4.6	0.218
p-Xylene	2983994	242401	8.12	2852997	82214	2.88	4.6	0.218
o-Xylene	2984768	239725	8.03	2599512	585069	22.5	15	0.179
Styrene	993524	77479	7.80	986956	36640	3.71	0.7	0.846
Bromoform	68136	5125	7.52	61692	3492	5.66	10	0.022
Isopropylbenzene	1592008	119035	7.48	1516677	56865	3.75	5.0	0.171
1-Bromo-4-fluoro-benzene (BFB)	521390	38310	7.35	523098	22073	4.22	0.3	0.922
cis-1,4-Dichloro-2-butene	276680	19852	7.18	274596	10593	3.86	0.8	0.815
n-Propylbenzene	2112486	148826	7.05	2119247	70922	3.35	0.3	0.917
1,1,2,2-Tetrachloroethane	150198	14797	9.85	141351	8247	5.83	6.3	0.206
Bromobenzene	877219	68882	7.85	868984	32910	3.79	0.9	0.785
1,3,5-Trimethylbenzene	1724075	125952	7.31	1706122	63220	3.71	1.1	0.748
2-Chlorotoluene	1347214	90113	6.69	1380635	59951	4.34	2.4	0.443
trans-1,4-Dichloro-2-butene	276712	19841	7.17	274619	10654	3.88	0.8	0.814
1,2,3-Trichloropropane	197688	18210	9.21	187022	8910	4.76	5.7	0.204
4-Chlorotoluene	1347214	90113	6.69	1380635	59951	4.34	2.4	0.443
tert-Butylbenzene	1515301	133925	8.84	1465810	109225	7.45	3.4	0.479
1,2,4-Trimethylbenzene	1730054	122319	7.07	1779107	73886	4.15	2.8	0.395
Pentachloroethane	110696	9905	8.95	108799	3796	3.49	1.7	0.652
sec-Sutylbenzene (1-methylpropyl)	1755439	122135	6.96	1775593	55318	3.12	1.1	0.704
p-Isopropyltoluene	1600699	88654	5.54	1661484	60648	3.65	3.7	0.174
1,3-Dichlorobenzene	749597	53134	7.09	788119	39840	5.06	4.9	0.165
1,4-Dichlorobenzene-d4	4239692	230274	5.43	4692347	224598	4.79	9.6	0.004
1,4-Dichlorobenzene	735644	42801	5.82	791454	43795	5.53	7.1	0.042
n-Butylbenzene	1397476	68690	4.92	1549372	77500	5.00	9.8	0.004
1,2-Dichlorobenzene	675574	46132	6.83	699870	36364	5.20	3.5	0.312
1,2-Dibromo-3-chloropropane	41824	4692	11.2	40877	2295	5.61	2.3	0.648
Hexachlorobutadiene	263029	14506	5.51	276044	15568	5.64	4.7	0.151
Nitrobenzene	28753	3396	11.8	21564	2109	9.78	33	0.001
1,2,4-Trichlorobenzene	381384	20857	5.47	458375	39215	8.56	17	0.003
Naphthalene	901831	81778	9.07	982766	70703	7.19	8.2	0.082
1,2,3-Trichlorobenzene	376527	22819	6.06	431547	35441	8.21	13	0.011
Average			11.8			5.41	11.6	

Figure 1: Benzene (ion 78) overlay for 0.75 mm and 2.0 mm liners.



Intuition states that a 23-gauge traditional SPME fibre is going to more effectively desorb in a 0.75-mm liner than in a 0.8-, 1.0- , 1.8- , or 2.0-mm liner. This statement applies for the same flow rate, split rate, desorption time, and temperature. However, a rather extensive literature search only produces a few studies discussing SPME liner dimensions. Ouyang et al. have demonstrated that a 1.0-mm Drilled Uniliner has higher SPME sample transfer efficiencies than a 0.8-mm SPME liner; and also concluded that the cross-sectional area between the GC column inserted into the liner and the inside of the liner is the most important factor in sample transfer for both liquid and SPME injections (2). It is important to note that the aforementioned observation is in contradiction to intuition and not supported by any significance tests. Despite an apparent lack of data and contradicting data, there are some claims that narrow-bore liners are more efficient for SPME; however, again the data to support this statement appears to be absent. Therefore, the following short study was undertaken. The goal of the current study was to evaluate the significance of liner selection when using traditional SPME fibers for headspace (HS) volatile organic compounds (VOCs) in water. The null hypothesis was that the liner has no significant impact.

Method

Experiment details were as follows. ISO 17943 VOCs were evaluated in the HS of 10 mL of deionized (DI) water spiked at 125 ng/L (ppt). A 23-gauge traditional SPME fiber with 95 µm of carbon (Restek cat.# 27479.1) was used. The only variable that changed during the study was the use of a 0.75-mm liner (Restek cat.# 23434) versus a 2.0-mm liner (Restek cat.# 23313). Both were straight walled. The two extreme ends of the SPME liner spectrum were chosen, so as to elicit the largest change in response. Seven unique samples were run in each liner (14 in total).

HS VOCs were sampled with the following conditions.

HS-SPME Parameters: Tool: SPME and SPME; agitator speed: 250 rpm; agitator temperature: 30 °C; incubation time: 120 s; heatex stirrer (CTC Analytics) speed: 1000 rpm; heatex stirrer (CTC Analytics) temperature: 30 °C; extraction time: 120 s; vial penetration depth: 35 mm; injector penetration depth: 50 mm; desorption time: 10 s; preconditioning: true; postconditioning: false; conditioning time: 60 s; conditioning temperature: 250 °C

GC–MS Parameters: Instrument: Agilent 7890B/5977A; inlet: 280 °C, split 5:1; column: 40 m × 0.18-mm, 1-µm Rtx-VMS (Restek); oven: 40 °C (hold 3 min) to 240 °C at 60 °C/min (hold 1.65 min), GC Accelerator Oven Insert Kit; carrier: type: helium, mode: constant flow; flow: 1.44 mL/min; detector: type: single quadrupole MS, mode: scan, transfer: 250 °C, source: 230 °C, quad: 150 °C, electron: 70 eV, tune: BFB, ionization: EI.

Results

Table 1 shows the results for 88 VOCs (including four internal standards [ISTDs], one surrogate standard [SS], and the tuning standard 1-Bromo-4-fluorobenzene [BFB]). Without going into the details on a compound-by-compound basis, the following trends can be observed within the data:

1. The average absolute percentage difference was 11.6% between the two liners. This was in favour of the 0.75-mm liner.
2. Twenty-two of the 88 VOCs (1/4) showed a statistically significantly ($p < 0.01$) different response between the 0.75 mm and 2.0-mm liners.
3. Not all of the statistically significant differences favoured the 0.75-mm liner (for example, 1,4-dichlorobenzene-d4, n-butylbenzene, and 1,2,4-trichlorobenzene).

Figure 1 gives a brief insight into the chromatography between the two liner choices. Aside from a slight retention time shift, the difference in liner diameter had little impact on the chromatography. For example, the peak width at half-height of benzene was 0.016 min and 0.017 min for the 0.75 mm and 2.0-mm liners, respectively.

For the current experimental scenario (that is, HS VOCs from water), most (75%) of the time the SPME liner diameter had no statistically significantly impact on analytical response. The significant results did favour the 0.75-mm liner over the 2.0-mm liner, which is consistent with intuition. However, it is important to note that the largest statistically significant result was only a 57% difference (1,4-dioxane) and the average was 11.8%. Therefore, unless the SPME end user is really pressed to increase sensitivity (that is, they are near a detection limit) perhaps other variables should be given their attention, as it is clear from the current study that liner dimensions do not affect analytical response by orders of magnitude. It is also important to note that these differences were obtained by picking the two most extreme ends of the SPME liner spectrum (that is, 0.75 mm versus 2.0 mm). Although the results are not present in the current study, the current results combined with intuition would suggest that the difference between a 0.75 mm and a 1.0-mm liner would be almost non-existent. Again, all of this may only be true for HS VOCs. The liner dimensions may have a more significant influence for direct immersion (DI) or semi-volatile organic compounds (SVOCs) with SPME.

The take-away message from the current study is that a SPME end user may confidently grab any straight-wall liner and have the assurance that for volatiles with HS-SPME, they are not sacrificing orders of magnitude in analytical response. If the SPME end user is interested in significantly increasing analytical response, there are more important details surrounding SPME extraction and desorption that deserve their time and consideration. The SPME end user has over a dozen extraction and desorption conditions (for example, extraction temperature, desorption duration) they may manipulate, and some of these parameters have a more significant impact on analytical response and method run times.

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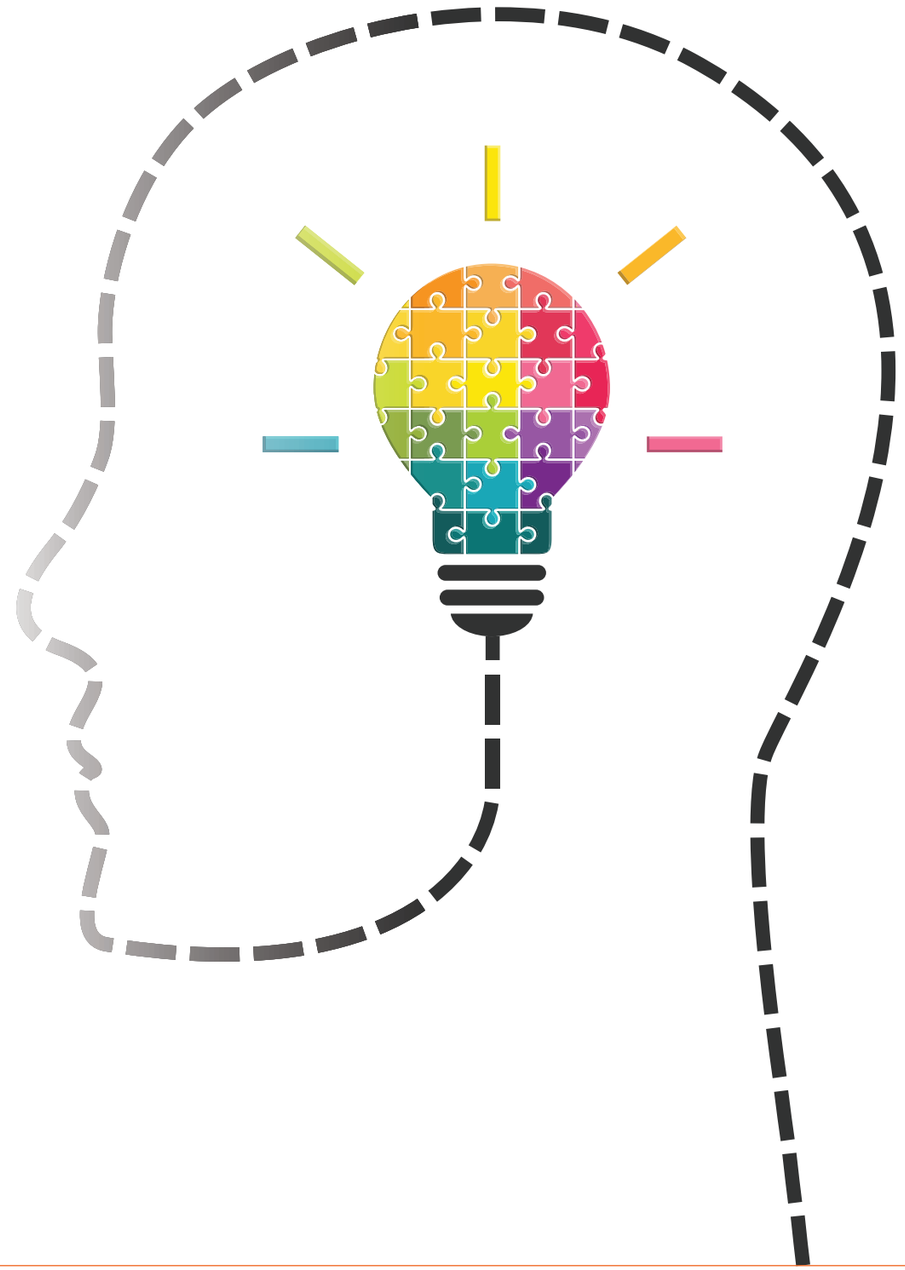

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