



Connections

In this month's installment, John Hinshaw reports about the 24th International Symposium on Capillary Chromatography and Electrophoresis held in May.

Gas Chromatography at the 24th International Symposium on Capillary Chromatography and Electrophoresis

The 24th International Symposium on Capillary Chromatography and Electrophoresis met in Las Vegas, Nevada, on 20–24 May 2001. This symposium was the latest in a series of symposia that has met in Europe, Japan, and the United States. Next year's silver jubilee meeting will be held 13–17 May in Riva del Garda, Italy.

Nearly 500 scientists, students, and commercial representatives from a diverse list of countries attended this year's meeting. The meeting format of selected oral presentations interspersed with a large number of posters closely followed that of previous capillary chromatography symposia in the United States. In all, more than 300 papers were presented. The symposium's sponsor held a reception one evening, but attendees otherwise were free to enjoy the many attractions of the gambling capital of the United States. I suspect, however, that gambling revenues were lower than expected due to the very high percentage of attendees with practical knowledge of probability and statistics.

The meeting began with the presentation of the Marcel J.E. Golay Award, sponsored by PerkinElmer Instruments (Shelton, Connecticut), to Fred E. Regnier (Purdue University, West Lafayette, Indiana) and Ben V. Burger (Laboratory for Ecological Chemistry, University of Stellenbosch, South Africa). Both recipients gave presentations that set the tone for the rest of the meeting. Regnier outlined the challenges of targeted proteomics for the study of disease markers by differential analysis of various proteins and protein fractions or digests associated with diseased and healthy organisms. Burger spoke about the potential of comprehensive two-dimensional gas chromatography (2-D GC or GC²) as applied to the

analysis of exocrine secretions of wild animals and the challenges posed by sample collection, separation, and characterization. These two themes — proteomics and comprehensive 2-D GC — comprised major portions of the liquid- and gas-phase separation presentations, respectively.

The meeting included 86 scheduled oral presentations in two parallel, four-day long sessions; 224 posters; and presentations from various manufacturers. It was impossible for one person to attend all the talks and look at all the poster presentations; therefore, this report contains a degree of selectivity that may not reflect the significance and relevance of all the presented papers. Instead, it mirrors my opinions of the presentations I attended and the posters I viewed. For space reasons, I have limited this report to presentations involving nonliquid mobile phases.

Multidimensional separations — specifically, comprehensive 2-D GC — played a major role at the symposium. Attendees and presenters also showed significant interest in micromachined devices for GC separations and in high-speed analysis. Other topics, as listed below, filled out the agenda.

Extraction and Sample Preparation

Solid-phase sorption sampling techniques continue to present a perceived potential for handling difficult sample matrices and for simplifying sample extractions that otherwise would require significant amounts of solvent or more complex devices such as automated headspace or thermal desorption samplers. Presenters and attendees also devoted a good deal of attention to devices specialized to meet the unique requirements of capillary chromatography, especially high-speed GC.

Carel Cramers (Eindhoven University of Technology, Eindhoven, The Netherlands) spoke about the relative merits of sorption-based sample preparation techniques using polydimethylsiloxane-packed beds or stir-bar sorption. These techniques produced higher sensitivities than open-tubular column trapping or solid-phase microextraction (SPME).

René J.J. Vreuls (Vrije University, Amsterdam, The Netherlands) presented data from miniaturized sample extraction techniques that permit at-line or on-line interfacing with capillary GC columns. The

supercritical fluid extraction and microwave-assisted extraction were suitable for the isolation of less-volatile polar components.

C.A. Lacerda (University of São Paulo, São Carlos, Brazil) presented a study of selectivity of SPME fibers coated with various polymethylcyanopropylsiloxanes and reported a significant degree of selectivity for fatty acid methyl esters that depended on the cyanopropyl content of the SPME fiber coating. Nobuo Ochiai (Yokogawa Analytical Systems Inc., Osaka, Japan) used stir-bar sorption followed by thermal-desorption GC-MS to analyze preservatives

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exact mechanisms of solid-phase extraction are not well-characterized, and Janusz Pawliszyn (University of Waterloo, Waterloo, Ontario, Canada) discussed a unified theory of extraction, based upon mathematical modeling of sorption and desorption processes. J. Roeraade (Royal Institute of Technology, Stockholm, Sweden) presented preliminary results for trace aqueous volatile polar analyte concentration on a lithium chloride-packed, programmed-temperature vaporizer in which he found high selectivity against nonpolar compounds and good linearity with injection volumes as large as 120 μ L. Several presentations dealt with the special sample preparation challenges associated with high-speed GC, as mentioned below.

In the application area, Cláudia A. Zini (University of Waterloo) described results using SPME with polydimethylsiloxane, coupled with GC-ion-trap mass spectrometry (MS) to identify volatile organic compounds (VOCs) in eucalyptus leaves. Elena E. Stashenko (Industrial University of Santander, Bucaramanga, Colombia) presented data that compared different extraction methods for roasted coffee and found that dynamic headspace sampling (purge-and-trap) yielded the greatest number of compounds, solvent extraction-distillation also produced many compounds, SPME provided only the major components, and

in beverages. Pat Sandra (Ghent University, Ghent, Belgium) applied stir-bar sorption to the analysis of dicarboximide fungicides in wine.

Multidimensional Separations

Multidimensional GC has undergone a remarkable resurgence of interest during the past few years in the form of comprehensive two-dimensional GC. J.B. Phillips (1) pioneered comprehensive 2-D GC, and two recent reviews appear in the chromatographic literature (2,3). In comprehensive 2-D GC, partially separated solutes are repeatedly trapped as they are eluted from a first column and released into a second column that has a different selectivity. The timing of the trap-and-release cycles, the columns' temperatures, and the flow rates are adjusted so that adjacent solute fractions in the second column do not impinge on each other. By choosing a more-or-less conventional first column and a high-speed second column, the fractions from the first column can be trapped and released into the second column at relatively short intervals — on the order of the first-column peak width — of less than 1 s to more than 10 s. A series of chromatograms are produced at the second column exit, and they can be deconvoluted with the trap-and-release cycles to produce a composite 2-D gas chromatogram in which the retention

time of the first column is plotted on one axis and the retention time of the second column is plotted on the other axis. The signal intensity can be represented as a color spectrum, and sometimes the intensity is plotted in the z direction to produce a 3-D representation.

A 2-D GC chromatogram appears strongly reminiscent of a 2-D thin-layer chromatography (TLC) plate with colored spots distributed in the x and y directions, and indeed, a close relationship exists between the two techniques (4). Peak resolution increases as a product of the resolution on either of the two columns. Peaks separated on the first column maintain their separation as they pass into the second column, much as 2-D TLC spots retain their separation from migration with the first solvent as the second migration begins orthogonally to the first. In 2-D TLC, selectivity differences from the first to the second migration arise from using different solvents; in 2-D GC, the differences arise from using two stationary phases.

Comprehensive 2-D GC presents some instrumentation challenges because of the high speed of the chromatograms from the second column and the design and implementation of trapping or switching devices between the first and second columns. At this time, no major instrumentation company has embraced a complete instrument package for comprehensive 2-D GC. Trapping devices, however, are commercially available as GC accessories.

Symposium presentations about comprehensive 2-D GC encompassed theoretical, instrumental, and application topics. In a daylong session about this topic, Keith Bartle (University of Leeds, Leeds, United Kingdom) reported of his group's work with RMIT University in Melbourne, Australia, in applying comprehensive 2-D GC to the isolation and classification of more than 500 VOCs in urban air. He attributed increased sensitivity to narrower peak widths as well.

Jan Beens (Vrije University) showed a thermal modulator based upon dual liquid carbon dioxide cryotrap with no moving parts in the GC oven. John V. Seeley (Oakland University, Rochester, Michigan) presented a 2-D GC system that uses flow modulation to send solute fractions alternately into dual secondary columns. Philip J. Marriott (RMIT University) discussed his group's work with more novel applications of comprehensive 2-D GC, including the study of dynamic intramolecular interconversion of isomers as they pass through

a chromatographic system and the effects of nonlinear partition isotherms. He predicted that the future application of comprehensive 2-D GC to many routine samples will yield increased sensitivity and considerably more information than that previously available.

Robert E. Synovec (Center for Process Analytical Chemistry, University of Washington, Seattle, Washington) reported how he applied chemometric principles to the challenges presented by the high speed and complexity of comprehensive 2-D GC. A simulation of the generalized rank annihilation method applied to comprehensive 2-D GC demonstrated the method's potential for analyzing unresolved peaks in this type of system. Kevin L. Johnson (also from the Center for Process Analytical Chemistry) discussed independent temperature programming of both columns to optimize both separations and ran the second column chromatography at intervals of less than 1 s with data acquisition frequencies greater than 200 Hz. The group at Vrije University also presented results from comprehensive 2-D GC coupled with high-speed, time-of-flight (TOF) MS, which adds a fourth dimension — mass spectra — to the data.

In the application area, Glenn S. Frysinger (U.S. Coast Guard Academy, New London, Connecticut) presented comprehensive 2-D GC data about the detection of arson accelerants in fire debris. This technique greatly enhanced the ability to distinguish pyrolysis products from various accelerants and building materials. Peter Haglund (Umeå University, Umeå, Sweden), working with researchers from RMIT University, spoke about using comprehensive 2-D GC to analyze polychlorinated biphenyls (PCBs) with a liquid-crystalline stationary phase in one column and a 5% phenyl-methylsilphenylene phase in the other column. In its smectic state, the liquid-crystalline column separated groups of PCB congeners on the basis of shape, and the other column distinguished them on the basis of their volatility.

In a related talk, Hans-Gerd Janssen (Unilever Research, Vlaardingen, The Netherlands) addressed the application of comprehensive LC-GC to the characterization of triacylglycerides in fats and oils. He studied the feasibility of using off-line coupling from a silver-phase LC column, which separated a triacylglyceride mixture according to the number of double bonds, followed by GC separation based upon the carbon number or fatty-acid distribution of

the triacylglyceride. This information, presented as two-dimensional bubble plots similar to comprehensive 2-D GC plots, provides various characterizations of single or mixed fats and oils.

Supercritical Fluid Chromatography

Several papers about supercritical fluid chromatography (SFC) and related topics demonstrated the benefits of this somewhat neglected technique that uses carbon dioxide, often as a methanol mixture, as the mobile phase under GC pressures and temperatures. Steven H. Hoke II (Procter & Gamble Co., Mason, Ohio) showed greatly increased analysis speeds for pharmacokinetic separations with packed-column SFC using tandem MS (MS–MS). The increased analytical speed was a result of the decreased viscosity of a carbon dioxide–modified mobile phase and the correspondingly higher average flow velocity. Sandra discussed the hyphenation of packed-column SFC with MS–MS detection using silver coordination ion spray to overcome the spectral complexities and interpretation difficulties that analysts encounter with atmospheric-pressure chemical ionization and SFC.

J.C. Rodrigues and F.M. Lanças (University of São Paulo) presented preliminary results of transition-phase chromatography (also called *solvating GC*) in micropacked fused-silica GC columns in which the mobile phase undergoes a state transition from supercritical to subcritical along the pressure gradient through the column and as the column temperature changes during the run. This type of separation is related to unified chromatography, in which controlled mobile-phase transitions between liquid, supercritical, and gaseous states through dynamic temperature, pressure, and chemical composition changes give users access to GC, LC, and SFC separations on a single column, thereby greatly expanding the range of materials that a single system could separate successfully. The practical realization of this system is difficult for many reasons, and transition-phase chromatography possibly represents a more realistic approach.

Miniaturized Devices

Symposium attendees showed considerable interest in miniaturization and micro-sized devices for biochemical analysis. The μ TAS meetings — the next of which will be held 21–25 October 2001 in Monterey,

California — address miniaturization for chemical and biochemical analysis on a broad basis. Although the primary emphasis has been on microfluidics and liquid-phase separations in recent years, miniaturized devices continue to hold the interest of gas chromatographers. Portability, speed, and application to micro-sized samples are some of the perceived benefits. At the symposium, several GC presentations dealt with questions of miniaturization.

Glenn E. Spangler (Technispan LLC, Pikesville, Maryland) and Edward S. Kolesar (Texas Christian University, Ft. Worth, Texas) discussed the theory and fabrication of rectangular cross-section columns and showed some developments that could provide a better theoretical model for columns with height-to-width ratios less than 0.1. In a second presentation, they demonstrated fabrication and sealing by anodic bonding of silicon micromachined columns.

Richard Sacks (University of Michigan, Ann Arbor, Michigan) discussed the application of vacuum outlet operation and stopped-flow column switching for resolution enhancement in an autonomous gas chromatograph that would use micro-sized components and micromachined columns.

High-Speed Analysis

High-speed GC encompasses separations that proceed at significantly higher speeds or rates than conventional separations. The words *fast* and *high-speed* appear in many places, but they sometimes have vastly different meanings for GC separations. Not only do they signify peaks that are eluted more rapidly, they also imply considerations of the entire analysis process from sample preparation to report generation. As chromatographic analysis times become shorter, the sample preparation, sampling, and data-handling times become major contributors to the overall time for individual analyses from start to finish. In general, most chromatographers at this meeting who reported about high-speed GC were able to use commercially available instrumentation for their high-speed components. These devices are becoming more readily available; high-speed mass spectrometers, high-frequency data-acquisition devices, rapid column heating arrangements, fast operating cold traps, and injection systems all have become more common in the past few years. Five years ago, this situation was not the case, and gas chromatographers had to resort to special one-of-a-kind devices.

For example, Nicholas H. Snow and Panagiotis Tavlarakis (Seton Hall University, South Orange, New Jersey) applied temperature program ramps of 160 °C/min and higher to reduce the analysis time of pharmaceutical residual solvents from approximately 30 min to 1–3 min. They also presented the results of a systematic study of GC performed on short, resistively heated columns. Rick Parry (Leco Corp., St. Joseph, Michigan) examined environmental as well as agricultural sample extraction, rapid GC separation, TOF MS detection, and automated quantitative data-processing algorithms to reduce the total analysis time for these complex samples. Frank David (Research Institute for Chromatography, Kortrijk, Belgium) discussed sample preparation techniques such as static headspace, thermal desorption, and SPME and their miniaturization and compatibility with fast separation methods. Roman Szücs (Pfizer Global Research and Development, Sandwich, United Kingdom) applied static headspace sampling of residual pharmaceutical solvents to narrow, 150- μ m i.d. capillary columns and reduced chromatographic analysis times from 35 min to less than 7 min.

Jim Luong (Dow Chemical Canada, Ft. Saskatchewan, Alberta, Canada), in association with the Eindhoven University of Technology, reported that vacuum-outlet GC with a pulsed-discharge detector and an inlet restrictor (to keep the inlet system at greater than ambient pressure) produces analysis speeds approximately threefold faster than the times obtained with an atmospheric-pressure outlet. Luong attributed the faster times to an increase in the optimum average linear carrier-gas velocity under vacuum outlet conditions.

Andrew Tipler (PerkinElmer Instruments) presented a cold on-column injector with a split vent that enables column backflushing of unwanted high-boiling sample components or retention gap backflushing of volatile solvent, and thereby reduces the net analysis times. Bart Tienpont (Ghent University) reported about coupling pyrolysis sampling with fast capillary GC.

Columns

The development pace of GC columns has slowed in recent years. Several new column types have appeared, such as the sol-gel columns mentioned below, but columns

have undergone only incremental advances in deactivation, stationary-phase chemistry, and materials science for the most part. Abdul Malik (University of South Florida, Tampa, Florida) presented data from the coating, chemistry, and performance of hybrid sol-gel coatings and monolithic beds in capillary GC columns and showed unique GC selectivity for example test mixtures. Frank L. Dorman (Restek Corp., Bellefonte, Pennsylvania) discussed computer design of application-specific stationary phases with optimum resolution for targeted compounds.

Luong also showed separations on a bonded carbonaceous stationary phase of volatile hydrocarbons and chlorinated hydrocarbons in corrosive matrices. With Jaap de Zeeuw (Varian, Inc., Middelburg, The Netherlands), Luong reported about the successful analysis of polar compounds, including sulfurs, alcohols, glycols, chlorinated hydrocarbons, chlorinated phenols, and fluorinated hydrocarbons, on a capillary column designed primarily for highly polar volatile amines. De Zeeuw also reported about the use of porous-layer open tubular and bonded-phase columns

for the rapid analysis of sulfur odorant compounds in natural gas.

Angus Hibberd (SGE International Pty. Ltd., Ringwood, Victoria, Australia) presented results from columns that incorporated a polyethylene glycol stationary phase or a methylsilicone phase immobilized in a sol-gel matrix layer on the column inner surface. This arrangement distributes the stationary phase into a thinner film with a higher surface area than that of comparable thick-film columns with similar phase ratios. This process appears to result in a more stable, lower bleed column with no appreciable effect on column polarity or performance.

Conclusion

Considered a mature technique by many, GC continues to advance technologically and to play a very significant role in separation science. As evidenced by the GC-related posters and oral presentations at the 24th International Symposium on Capillary Chromatography and Electrophoresis, chromatographers are spending considerable time and effort investigating and characterizing diverse techniques and materials in the GC field. At the top of the list, fast

analysis and the concomitant extraction of as much information as possible from single or multidimensional chromatography seem to dominate those efforts. Miniaturization of GC components is driven by considerations of speed and portability. Solutions for problems that arise from complex sample matrices also are significant in the form of advances in extraction and sorption techniques, both general and analyte-specific variations. Chromatographers also continue to investigate alternatives to conventional chromatographic modes such as transition-phase chromatography. GC column technology keeps advancing toward better column performance as well as unique, compound-class-specific selectivities.

Symposia and conference series such as the International Symposium on Capillary Chromatography and Electrophoresis provide attendees with snapshots of technological advances in their respective fields. As a leading forum on capillary chromatography and certainly the premier forum for gas chromatography, this meeting continues to give chromatographers an occasion to share and discuss their developments with others in their profession. In

2003, the symposium is slated to return to the United States. Those who attend will have another opportunity to observe how much researchers and scientists have advanced the fields of chromatography.

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