Meeting Review: Advances in GC IV

The Heath Business Park, Runcorn. Wednesday 30th October 2013

by Paul Ferguson, Vice-President, The Chromatographic Society

The fourth 'Advances in GC' meeting was held at The Heath Business Park on Wednesday 30th October. The meeting was organised by The Chromatographic Society and Royal Society of Chemistry North-West Division with over 120 delegates from a variety of fields in attendance. Additionally, around 35 vendors representing 17 companies (including the principal meeting sponsors Agilent and Thermo-Fisher Scientific) presented the latest from their product portfolios making for a vibrant and informative atmosphere. See Table 1 for a full list of vendors.

Alan Handley (LGC Ltd) opened the meeting and welcomed the audience. He also warmly thanked the vendors who provided financial sponsorship and support for the meeting allowing a number of bursaries to be provided for students undertaking their doctoral studies to attend. Alan then handed the meeting over to the co-organiser Dr Stewart Forbes (Shell and representing the RSC NW Region) who chaired the morning session.

The first presentation was provided by **Dan Carrier** of **Anatune** who presented *'Sample preparation solutions for Gas Chromatography'*. Dan gave an overview on a number of different sample preparation approaches and how they may be applied. The main areas he discussed were as follows:

Stir-bar sorbtive extraction (SBSE, also known as 'Twister' technology). This approach was developed by Professor Pat Sandra (University of Gent) in 2000. The 'Twisters' are essentially magnetic stirrer bars coated with a thin film of either polydimethyl siloxane (PDMS) or polyethylene glycol (PEG) which are inserted into a sample solution to absorb analytes. The PDMS coated twister has hydrophobic absorption properties similar to octanol and this can be used to determine potential analyte absorption and recovery via Log P (Log $K_{o/w}$) values. Anatune provide a 'Twister calculator' which based on analyte Log P or compound CAS number and the sample size will calculate as a percentage how much of the material will absorb onto different size 'Twisters'. The capacity of the 'Twister' bar is 63-126 µl (dependent on dimensions) which is far in excess of solid phase micro extraction (SPME) approaches which are have *ca.* 0.5 µl capacity.

Figure 1. Delegates and vendors discussing the latest GC technologies at the 'Advances in GC' meeting.

Twisters must be conditioned before use through thermal cycling above 200°C under nitrogen flow to remove any residual water. These bars are then placed in the test solution for two hours, removed and rinsed with water, dried and then analysed in a thermal desorption unit (TDU) at temperatures around 180°C (split/splitless injection for maximum sensitivity). Examples were demonstrated for determination of malodours in water and PAH's in water. A headspace twister was also discussed for the collection of chocolate aromas.

Dan also described the use of dynamic headspace (DHS) injection which is an instrumental option compatible with Anatune's multi-purpose sampler (MPS). The

Table 1. Vendor organisations in attendance at the 'Advances in GC IV' meeting (listed in alphabetical order).

Agilent *(Principal Sponsor)*
Anatune
Aquilant Scientific/PreSearch
BOC Speciality Gases
Crawford Scientific
Csols Ltd
Ellutia
Hichrom
Thames Restek
Thermo Fisher Scientific *(Principal Sponsor)*
Kinesis
Leco
LGC
Markes International
Perkin Elmer
Phenomenex
Sage Analytical & Prochrom
Sigma Aldrich

Figure 2. An Agilent GC 7890A GC and 7000 MS triple Quad with MPS 2 XL (Dual Head) CIS Multiflex Inlet used to determine environmental pollutants in water. Picture courtesy of Anatune Ltd.

system works by passing nitrogen gas into a sealed headspace vial forcing volatile materials onto a sorbent trap (typically Tenex). The trap is then transferred into the GC injector and desorbed using a temperature program. Compared to static headspace, this approach demonstrates much improved analyte transfer and therefore detection sensitivity. Extremely small liquid samples can be anlaysed by this approach. By using a large excess of the volatilising gas, trace levels of components can be dramatically concentrated and allows the analysis of volatile, non-volatile and hydrophilic analytes. An example was presented where Jagermeister components were sampled using SPME, SBSE static HS and DHS with DHS demonstrating the best results.

Next the ATEX (automated tube exchange) sample preparation system was discussed. This is an approach for analysing large volume dirty samples and is particularly appealing because the matrix is not transferred into the system. This works by injecting into a TDU (rather than directly into the inlet) which then focuses the analytes onto the column. The MPS can automatically replace the TDU liner as required meaning a 'fresh' system can be provided for each injection.

Next was the ITSP which is a small scale SPE cartridge (containing 15-35 mg of sorbent) which can be automated in conjunction with the dual-arm 'multiflex' MPS. Using this system all preconditioning and extraction steps may be performed before final reconstitution into the appropriate solvent diluents prior to analysis. An environmental example was discussed for the determination of trace levels of NDMA and metaldehyde in water samples. Using this approach, NDMA and metaldehyde could be determined down to 1 ng/l and 2ng/l respectively. The instrumentation used to perform this testing is shown in *Figure 2*.

The final approach discussed was the use of single drop micro-extraction (SDME) which again may be fully automated using the MPS. A type 2 injection needle is inserted into a heated headspace vial containing the analyte solution and a small drop of an appropriate solvent is moved onto the tip of the needle. The longer the drop is held in the vial the greater the uptake of analyte. This droplet is then directly injected into the GC and ppb detection limits are easily determined using this approach.

The next presentation was provided by **Dr Jaap de Zeeuw** of **Restek Corporation, The Netherlands** who discussed *'Column selection – there is more to life than a boiling point column'*. Jaap stated that around 70% of all GC work is undertaken on 'boiling-point columns' where retention is proportional to analyte boiling point, or more accurately solubility in the stationary phase. He demonstrated that for a series of alkane, ethers and alcohols analysed on an RTX-1 (100% PDMS) columns that within a homologous series, boiling point was indeed a good predictor of retention, but this was not the case when all analyte classes were considered together. PEG (polar) bonded phases also operate as boiling point columns but are more retentive for polar analytes.

PDMS bonded phases are extensively used in the petrochemical industry. However, for higher alkanes (>C_{100}), temperatures of up to 400°C are required (Choose a stationary phase that 'looks like' the components you want to separate" e.g. for hydrocarbon analysis use a 100% PDMS phase, for aromatic compounds use a 5% phenyl phase etc). However, at this temperature, standard columns can phase-bleed and become fragile leading to breakage. One solution is to use high temperature polyimides which may be used up to temperatures up to 380°C, but even these columns eventually pyrolyse and become brittle. An alternative approach is to use metal columns which are thermally stable up to temperatures of 450°C (see *Figure 3*). Historically, these columns were extremely active leading to poor chromatography, but later generations of these column types include an elemental layer of silicon coated onto the surface of the

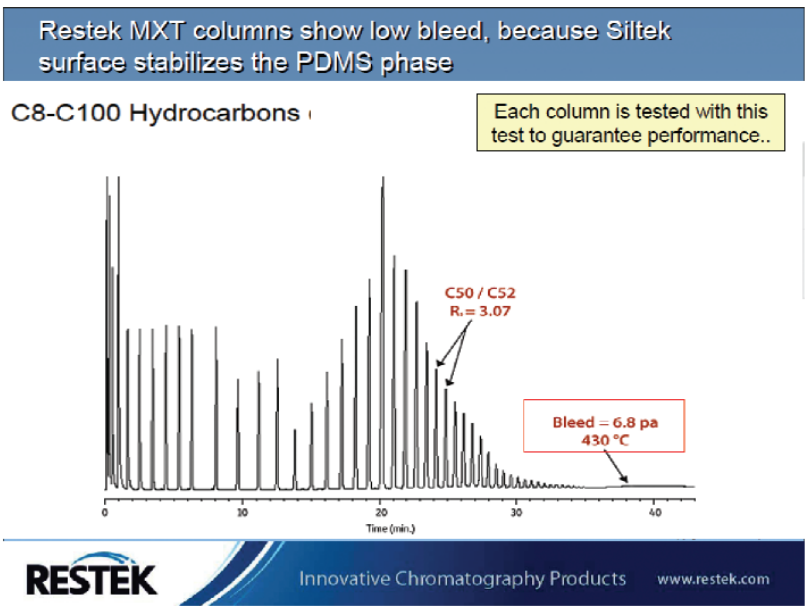

Figure 3. Slide taken from Jaap de Zeeuw's presentation illustrating the low-bleed characteristics of the Restek MXT (metal) column for hydrocarbon (oil) analysis.

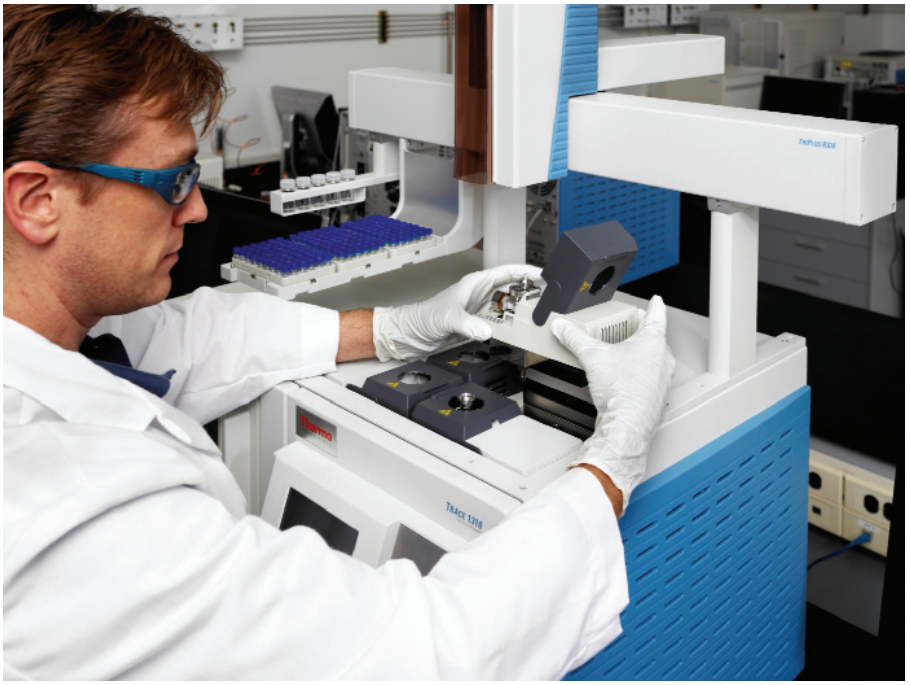

Figure 4. The Thermo Trace 1300 GC system showing the modular detector system. Picture courtesy of Thermo-Fisher Scientific.

capillary leading to up five-times less bleed than a deactivated phase ('Siltek' deactivation'). These types of columns can be used successfully for the analysis of higher alkanes and even oil-spill 'tar-balls' as seen in the Gulf of Mexico oil-spillage in 2010.

Jaap went on to state that selective detection provided by MS means that many analysts choose a boiling point column as selectivity generated by a column is not as important. He noted that there are times when column selectivity is still required however e.g. when a column exhibits low efficiency (especially with packed columns, but not common with the latest generation of capillary columns), when selective detection is unavailable, or when isobaric impurities are present. Restek provide a GC Chromatogram Modeler and a method translator software under their 'EZ-GC' services (EZ-GC is currently an on-line program available at www.restek.com/chromatogram/ezgc/). This program simulates separations using database information and provides GC conditions and column selection for analysis within *ca.* 5-10 minutes. The method translator will become public soon on line and also as a 'windows' program at a later date).

The last area touched upon was the use of multidimensional GC to increase peak capacity or selectivity. 2D column combinations include PDMS-WAX, 17 Sil-MS (polar)-5 Sil-MS (non-polar) and PDMS-cyclodextrin (structural isomer resolution) column combinations. Typical systems can easily generate peak capacities of 30000 which would require a 10 km long column in a single dimension. At this point Jaap showed a picture of the longest fused silica GC column ever produced (1300 m x 0.32 micron film thickness PDMS) for which he won a Guinness book of records award. This column produced excellent resolution of a petroleum sample, but took 3 hours to elute methane and 3 days to elute the last peak.

Professor Jean-Francois Focant from the **University of Liege, Belgium** gave an excellent presentation on '*Demystifying comprehensive GC*'. He started the presentation by outlining the issues with single dimension GC including limited peak capacity, the general elution problem (high temperature separation eluting polar molecules too rapidly while low temperature separations eluting high-boilers too late with poor peak shape) and dynamic range issues.

He discussed the system he has developed based on a design by Liu and Phillips (J. Chromatogr. Sci. (1991) **26** 227). The system is designed with a modulator ('slicing machine') so that only one detector is required on the system. For a system to be comprehensive (a) all parts of the sample must be subject to two independent retention mechanisms (orthogonality rule) and (b) the first dimensional separation must be maintained in the second dimension (conservation rule).

The modulator is key to comprehensive GC. There are three different types (i) valve, (ii) sweeper and (iii) cryogenic. The first two involve moving parts and are unreliable, whereas the latter uses jet modulation to trap and release peaks in a 4 second timescale. As only one detector is used for both dimensions, the data generated requires electronic deconvolution and is usually displayed as a 2D contour plot.

This approached was demonstrated for the analysis of 209 PCBs using the cryogenic modulator (which sits inside its own oven in the main GC oven). Using a DB-1/HT-8 combination or a HT-8/BPX column combination, trends where groups with increasing numbers of chlorine atoms were identified. He also discussed the potential for this technique to detect lung cancer through breath analysis using principal component analysis (PCA) for differentiation. Finally he briefly discussed how the time of death of a cadaver can be determined from the composition of around 600 volatile organic compounds (VOCs) produced during the decay process and analysed by comprehensive GCxGC-Tof MS.

Following lunch and the extensive vendor exhibition, the first presentation in the afternoon session (chaired by Karen Rome of AstraZeneca) was given by **Dr Greg Johnson** of **Thermo Fisher Scientific** – *'A fresh approach to managing GC in your laboratory'*. Greg discussed the new Thermo Trace 1300 GC which provides a high degree of flexibility using modular detection systems (see *Figure 4*). Whereas many labs have numerous GC's with fixed specific configurations, this instrument can switch detectors (2) in and out in under a minute. The detectors available as modules include FID, TCD, ECD, NPD, FPD, DID and MS.

The traditional split-splitless inlet system has been redeveloped to include a 'cool head' where the septum is kept well below the inlet temperature (e.g. septum is below 150°C even when inlet is set at 400°C) which gives less septum bleed and less sticking. The inlet design means it is very easy to change the liner and o-rings. The system also includes an activated charcoal filter on the carrier gas inlet and another on the split purge line to remove noxious compounds from the exhaust. The two inlets may also be removed and sonnicated to remove contamination.

The instrument also includes other novel features including an instant connect gas sampling valve (GSV) for gas analysis. Additionally, an auxiliary oven can be attached which provides extra valves, 8 independently heated transfer lines and 2 additional detector ports which allows the likes of GCxGC. Another new approach designed into the system is a helium saver system which is important given the ever

decreasing amount of helium on the planet. While other options for reducing He gas usage were noted e.g. use of hydrogen, backflushing and gas-saver mode all of these have limitations e.g. when hydrogen is used in place of helium, sensitivity is generally lower. During injection, only 0.1 ml/min helium is used and during analysis 4 ml/min, the rest of the flow being made-up form nitrogen. Nitrogen is prevented from entering the column by an anti-diffusion device. This is supplemented by higher nitrogen gas flows but dramatically decreases helium usage compared to other current systems.

The next presentation was given by **Dr Ken Brady** of **Agilent** on *'Exploring the extra dimension – Getting more out of your GC analysis'*. He discussed at length three key areas where Agilent feel they are market leaders – these being retention time locking (RTL), capillary flow technology (CFT) and low thermal mass (LTM).

RTL offers the ability to transfer methods between Agilent GC systems with identical chromatography irrespective of column length (e.g. after constant column trimming). This system works by varying the make-up flow pressure to maintain analyte retention time. Agilent offer RTL databases and guaranteed method kits for specific applications using this technology.

CFT was discussed next. Traditional switching valves have high dead volumes and are prone to mechanical wear and contamination. Agilent CFT valves are made from inert Ultimetal alloy which significantly decreases contamination and carryover. These valves also have a back-flushing capability which can be used to divert high boiling compounds back to waste which can be used to reduce column and detector contamination. In the examples discussed using back-flushing, improved RSDs for retention times and peak areas were observed. The back-flushing can be initiated as soon as the last peak of interest has eluted and does not significantly extend the analysis time of the method. Indeed, the total analysis time can occasionally be shortened if the back-flushing time is shorter than a temperature hold that may be required at the end of the method to elute all compounds.

He also discussed how these valves can be split accurately to multiple detectors with accurate splitting and flow to each channel. It was interesting to learn that when splitting is used, a decrease in MS sensitivity is not always observed. While the analyte zone is split (and therefore the absolute analyte quantity is split), the reduced flow into the MS instrument is optimal and results in more efficient analyte ionisation.

Due to time constraints, LTM was briefly discussed. This technology uses resistively heated columns to generate extremely rapid heating and cooling for very fast separations. Some applications were demonstrated and also how these columns could be used in GCxGC.

After a coffee break, **Neil Owens** of **Givaudan UK Ltd** delivered a presentation on *'What has deconvolution ever done for us?'*. Givaudan are a fragrance company that synthesise scents for many applications such as perfumes and toiletries. He discussed how scents are classified into families such as 'Floral', 'Citrus', 'Woody' or 'Green' and the raw materials that contribute to these families can range from simple (of synthetic origin) to complex (naturally occurring such as Vetiver which is a complex oil containing ~100 components). It was noted that the human nose can 'selectively detect' different analytes which are structurally very similar. He outlined an example where the addition of a methyl group to a cyclic pentanone improved the noses' limit of detection down to 4 pg from 100 ng.

GC and GC/MS is used to understand olfactory response and the active ingredients contributing to this effect. A range of scenarios were shown covering increasing complexity of the raw materials used, and how the similarity of these to one another and the matrix they are found in can cause significant interference during analysis. The methods (two) employed are relatively old (old column technology and long analysis times) by contemporary standards but are well calibrated through retention indexes allowing excellent peak identification when coupled with FID and MS detection. It was noted that for these long runs RTL is not possible (mid points calibrate well, but early and late eluting peak retentions can vary).

These methods feed into 'AMDIS' – Automated MS Deconvolution ID System which can extract spectra and identify if the components are targets or not for a desired scent. This approach was shown to have improved the effectiveness of the analysis significantly, but also provided other benefits including systematic naming conventions for reports; single point MS library management and calibrated, aligned methodologies. This system is used globally and updated by multiple users given a comprehensive database for the identification of components from new sources or competitor fragrances.

The last presentation of the day was given by **Lewis Jones** of **Mars Waltham** (the largest part of the Mars group) titled *'Are GC techniques comparable to the human nose?'*. Lewis started the presentation by discussing the capabilities of the human nose has which around 400 olfactory receptors which are able to identify ~4000 individual aromatic compounds down to *nano*gram levels or below. Odours can be identified via *ortho* delivery (via the front of the nose) or **retro** via the mouth.

Instrumentation is required to identify the chemical components of a foodstuff which lead to particular odours. His group achieve this using GCxGC/MS with an odour port (ODP) which allows human assessment of odours as they elute from the column alongside GC preparative capability for trapping these compounds. A pulsed flow photometric detector (PFPD) is often used as this type of detector is sensitive to sulphur which is often a major constituent in odours. The instrument is located in its own lab to ensure that the human assessor is not distracted by any interfering smells in the atmosphere.

Sample preparation is performed using a sorbent trap (Tenex) which was found to not be the cleanest absorbent, but traps analytes of wide polarity range. The instrumentation uses a LTM column in the first dimension leading into a Deans switch. The Deans switch splits to a splitter plate in one direction (which in turn splits to the ODP and MS detector), and can be split again if required to include FID detection too. The other line from the Deans switch connects to a SIMS cryotrap collector which can cool to -20°C without need of liquid coolant. Detection sensitivity for a specific analyte can be increased by pooling fractions and injecting these onto the second LTM dimension which in turn is connected to the splitter plate and the detectors.

Lewis concluded his presentation with examples of where this system has been applied within his organisation and their plans for further additions to enhance the system...finances permitting!

Alan Handley brought the meeting to a close and highlighted future Chromatographic Society and RSC meetings running through to 2015 (see the meetings list in Chromatography Today for further details). The meeting was again a great success and left the delegates looking forward to Advances in GC V in 2015.