Advances in Gas Chromatography

November 3rd, 2009, LGC Ltd Runcorn The Heath Business Park.

Alan Handley, Head of Pharmaceutical Services LGC Ltd

The Heath Business Park

On November 3rd 2009, The Chromatographic Society staged a one day joint scientific meeting with the RSC North West Region Analytical Division entitled "Advances in Gas Chromatography" .It was held at LGC Ltd "The Heath Business Park" Runcorn. This is one of the Chromatographic Society's series of biennial meetings.

Gas Chromatography (GC) is still the technique of choice for analysing both volatile and semi volatile compounds, and as we move to more complex and difficult matrices, much is now being asked of the technique in terms of separation and limits of detection.

The meeting set out to look at newer detection/separation solutions and profile case studies from the pharmaceutical, petrochemical, forensic and environmental areas.

In parallel to the full meeting program there was an instrument exhibition with representatives from all the major GC instrument and consumables suppliers.

The meeting was attended by some 130 delegates from both Industry and Academia and as with the 2007 meeting the event was a sell out with registration having to close some weeks before the event - highlighting the popularity and relevance of the technology to modern day analytical laboratories.

As an integral part of the symposium, 16 companies had tabletop displays of their latest product offerings with Agilent and Thermo providing the major sponsorship for the meeting and other companies such as Shimadzu, Thames Restek and Leco helping to sponsor speakers. The companies exhibiting included:

Agilent Technologies - www.agilent.co.uk

Anatune - www.anatune.co.uk

Crawford Scientific - www.crawfordscientific.com

ELGA - www.elgaprocesswater.co.uk

Genevac - www.genevac.org

Hichrom - www.hichrom.co.uk

ILM publications - www.ilmpublications.com

Leco UK - www.lecouk.com

Markes International - www.markes.com

Perkin Elmer - www.PerkinElmer.co.uk

Phenomenex - www.phenomenex.com

Prochrom - www.prochrom.co.uk

SGE - www.sge.com

Shimadzu - www.shimadzu.co.uk

Thermo Fisher Scientific - www.thermo.com

Thames Restek - www.thamesrestek.co.uk

Alan Handley the current president of The Chromatographic Society and President Elect of the RSC Analytical Division chaired the meeting and described the wide role and importance that GC technology plays in today's society and gave an overview of the themes covered by the meeting.

The first talk of the morning session was given by Ray Perkins of Anatune Ltd on "Dealing with Difficult Matrices- Active SPME with Large Volume Headspace"; he described the problems when conventional static headspace sampling is used for the analysis of volatile organic compounds in liquid and solids. The matrix only comes into contact with the walls of the sample vial and the portion of the sample transferred to the GC or GC-MS is in the vapour phase - whilst this makes the technique a very robust and trouble free analytical technique, there are significant limitations, such as the volume of headspace that can be injected and the size of samples that can be accommodated is sample vial .He spoke of a new technique, "Active SPME" which has been developed by Entech Instruments Inc. This enables the pre-concentration of gas phase samples, up to 1 litre in volume and the use of a large scale auto-sampler which allows for a wide variety of large and small volume sample containers to be used (up to 1 litre in capacity).This ability to work with large volumes of headspace lowers detection limits to the part per trillion level and makes it much easier to work with representative samples. In addition, headspace and other air samples may be captured in passivated canisters (or glass bottles) and analysed using the same hardware. For further information contact: Ray.Perkins@anatune.co.uk

Some of the issues of GC column technology were addressed by the next speaker Jaap De Zeeuw from Restek in the Netherlands. His talk concentrated on the analysis of gases and volatiles using a new range of bonded PLOT columns. PLOT columns are widely used in many applications. Their main advantages are there that they are highly selective and can be operated at much higher compared with liquid type stationary phases. However because the absorbent layer is built up from particles this can result in detector contamination from the particles and some cases non reproducible flow.

Ray Perkins showing the audience the new larger volume headspace jars.

The challenge has always been to stabilize the adsorption layer in PLOT columns, especially for porous polymers. Restek have successfully stabilized porous polymers, alumina and mol sieve adsorbents and deposited these layers in fused silica and MXT (metal) capillary columns. A new way to measure openness of PLOT columns was proposed, using a flow-restriction factor. Also a simple test procedure was developed

using the pressure pulses which are programmable with today's hardware. MXT as well as fused silica PLOT columns coated, showed excellent stability resulting with virtually no particle elution under challenging conditions. These porous polymers have high capacity for volatiles as well as improved inertness for eluting polar compounds like formaldehyde, methanol and water. These new columns can be made on 0.53-0.18mm capillary tubing showing the flexibility of the latest PLOT coating techniques.

For further information contact:
Jaap.deZeeuw@restek.com

A number of talks then followed by representatives from Industry .The first was by Tom Lynch from BP Ltd a past recipient of The Chromatographic Societies Jubilee Medal.

Tom's talk concentrated on micro fluidics; he explained that for many years researchers have been looking for the "Holy Grail" of complete resolution by GC of all components in complex mixtures. Such complex mixtures in the case of the petroleum industry could run into some thousands of components .This goal he said is starting to become more of a reality with the development and commercialisation of comprehensive two dimensional GC systems (GC x GC) .He stated that although this technology is now available it has yet to be fully embraced by Industry who require not only selectivity, but also sensitivity, speed of analysis and above all low cost solutions. These areas he said are now being addressed by microfluidics. He described Agilent's new generation of GC systems with their new two and three way flow micro capillary splitting systems. This had served to reinvent the "Deans" switching technologies which had been used extensively in the past for packed column and process GC, and provide much more flexibility and separation options than before.

A number of case studies were described highlighting the easy of method development using this microfluidic technology for the analysis such complex samples as engine oils ,Biodiesel and lubricants.

He then went on to describe the linking of microfluidic systems to GC x GC for the comparison and characterisation of complex Biodiesel samples.

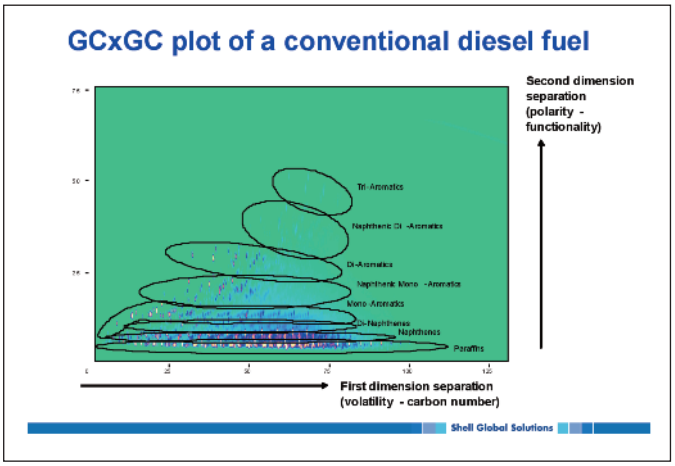
He concluded that the new commercially systems now offer great potential and flexibility for both problem solving and routine methodology and are a readily affordable "upgrade option" to exploring GC x GC applicability for your operations.

The talks moved into the area of detection options with Martin Sims from AstraZeneca speaking on "A New Hyphenation GC-APCI-TOF".

Accurate mass measurement (to produce elemental formulae) is an essential tool for impurity identification, therefore, the provision of robust technology to provide accurate mass GC-MS for this type of activity is essential. The speaker presented the findings from accurate mass GC-TOF-MS analysis of a series AstraZeneca compounds used in the development of new drug molecules. This data was produced using an APCI source to couple a GC to a Bruker Daltonics micrOTOF mass spectrometer. The APCI source is an accessory that can be coupled to all Bruker TOF and QTOF instruments, in exactly the same manner as LC-MS sources. The instrument does not require major modification and therefore can provide accurate mass GC-MS in a robust fashion. This approach allows both accurate mass LC-MS and GC-MS to be carried out on a single mass spectrometer. To fully test the potential of the new interface, a large number of compounds used in synthesis at AstraZeneca were analysed by GC-TOF-MS. He described the study which was carried out to evaluate the range of compounds that are amenable to technique. The sample set was also analysed by GC-EI/CI-MS to understand the capability of GC-APCI-MS relative to these established techniques. An evaluation of optimum instrumental parameters was also reported."

The afternoon session started with a talk from Stuart Forbes from Shell Ltd who talked specifically on the experiences of GCxGC in a talk titled "Comprehensive Two-Dimensional Gas Chromatography in the Petroleum Industry"

As with the talk previously given by Tom Lynch, he said the ability to resolve thousands of components present in complex analytes is clearly the main strength of GCxGC. Whereas gasoline, which contains ~200 components, can be fully characterised using one-dimensional capillary GC, the middle distillate fuels (kerosene, diesel) contain many thousands of individual components and GCxGC has enabled us to provide a far more detailed characterisation of these products than previously possible. Moreover, the two dimensional chromatographic representation of these materials, in which the first dimension corresponds to increasing molecular weight and the second dimension to increasing polarity, provides a comprehensive chemical description of the substance which is not possible by examining a series of peaks on a conventional chromatogram.



He stated that this is particularly well illustrated when one compares the GCxGC trace obtained from conventional diesel fuel (i.e. manufactured from crude oil) with that obtained from a gas-to-liquid (GTL) diesel fuel (i.e. manufactured from natural gas); the low concentration of naphthenics and absence of aromatics in the GTL fuel compared with conventional diesel can be clearly seen from the respective GCxGC plots. In addition to providing information on how the different chemical functionalities present influence the performance characteristics of these products, GCxGC has proved invaluable in providing detailed compositional information to support the registration of petroleum products under the new REACH legislation.

The ability to resolve traces of impurities present in complex sample matrices by GCxGC was illustrated in their examinations of jet fuel contaminated with Biodiesel.

He concluded that although the majority of the GCxGC work had been carried out using non-selective detection (i.e. flame ionisation), they have achieved ever greater analytical selectivity by combining the high resolving power of GCxGC with selective detection such as mass spectrometry or chemiluminescence.

This was followed by a presentation from Sam.Whitmarsh of AstraZeneca on the work they have been doing to look at "Reducing Costs in Pharmaceutical GC Analysis"

He said that R&D organisations within the pharmaceutical industry are having to become increasingly lean. In addition, the demand from larger early project portfolios and regulatory submission (QBD) grows, requiring a proportional increase in sample capacity. This 'do more with less' business model represents a significant challenge to the scientific community. Recent advances in multi-column Low Thermal Mass (LTM) GC technologies presented an interesting opportunity to develop more flexible instrument portfolios which address these problems.

Work carried out on an Agilent 7890 equipped with a four column LTM system was presented assessing the impact this technology could make to productivity and capability. The system was shown to be robust and highly flexible whilst providing a high degree of control over chromatographic parameters through the use of fast heating and cooling, hydrogen carrier gas and the range of column phases and dimensions available on the single instrument. It was capable of functioning in three different modes: High throughput (multiple users with predefined methods); Fast method development (column scouting, fast method optimisation) and enhanced functionality (increased sensitivity, single injections split onto multiple columns). This flexibility has the potential to reduce instrumentation and down time, in turn reducing capital and maintenance costs all whilst increasing capacity and technical capability. Disadvantages included the complexity of the flow path and the high elution temperatures attributed to fast temperature programming. He said that future work would be focused on mitigating these disadvantages and on further improvements to the flexibility of the instrument by investigation of additional micro-fluidic and inlet/detector technology.

Paul Zavitsanos from Agilent Technologies in Wilmington then spoke on "GCQQQ the next level of Detection".

He said that the modern bench-top single quadruple GC-MS system is a very sensitive instrument, capable of acquiring data in synchronous SIM-Scan mode and detecting target analytes down to levels at, or below, parts per billion (ppb).

However, as regulatory methods continue to drive detection limits ever lower, the interferent effects of the sample matrix can hinder the identification, confirmation and subsequent quantitation of analytes. Were a single quadrupole GC-MS may have problems in this regard, a tandem quadrupole GC-MS system (often referred to as a 'Triple Quadrupole GC-MS' or GC-QQQ) has both the selectivity and sensitivity to provide both confirmation and low detection limits in the most demanding of sample types such as those found in Food, Environmental, Clinical and Forensic Toxicology applications. Designing a tandem quadrupole mass spectrometer specifically for coupling to a GC requires different considerations than those required for LC-MS/MS systems.

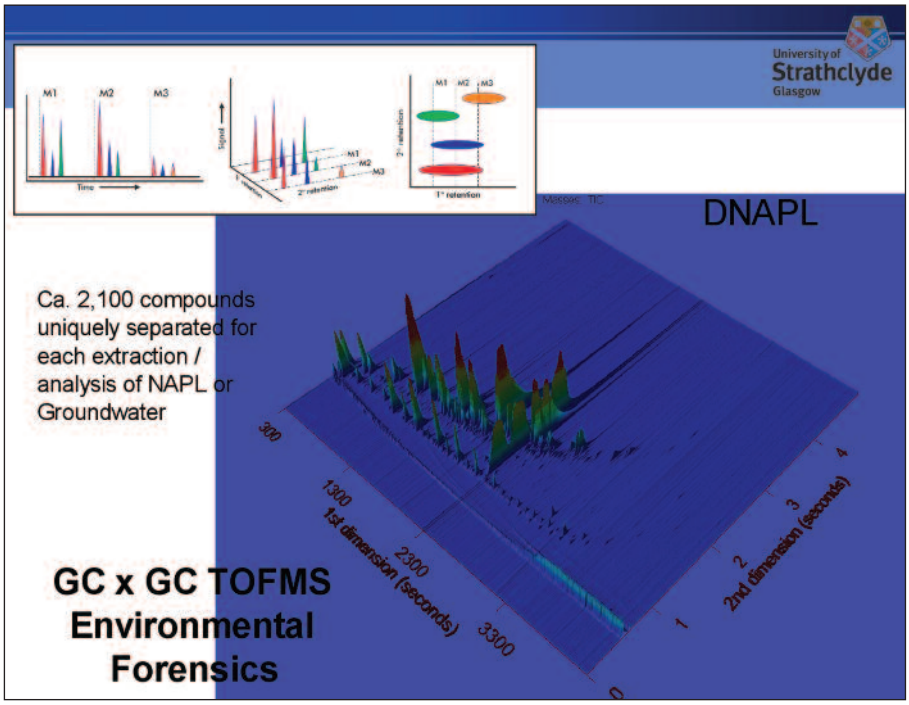
The talk reviewed the many innovations and design features unique to the Agilent 7000 Series GC-QQQ , these he said have resulted in a highly sensitive and selective instrument with the robustness required for use in routine, high through- put GC laboratories.

Results obtainable from GC-MS SIM mode to GC-MS/MS MRM mode where compared and discussed along with the productivity gains provided by the "Mass Hunter" qualitative and quantitative software packages.

For more information contact ian_clothier@agilent.com

The use of GC in the up and coming area of Environmental Forensics was discussed by Professor Robert Kalin from the Department of Civil Engineering, University of Strathclyde in his talk "GC x GC TOFMS Applications for Environmental Forensics and Environmental Metabolomics"

Hybrid GC techniques have been used for over a decade to elucidate complex mixtures of organic compounds in the environment. Recent advances in GCxGC TOFMS now allows detailed qualification and quantification of compounds previously unresolved with traditional GC-MS. At the Department of Civil Engineering, University of Strathclyde Glasgow, the technique has proved valuable for Environmental Forensics,



determination of source(s) and apportionment of responsibility for contaminants in the environment. Additionally, the technique is also being used at Strathclyde to evaluate the biodegradative fate of contaminants in soil and groundwater through cutting edge research into Environmental Metabolomics, the study of complex mixtures of extracellular metabolites and their relationship to the dominant biogeochemical in soil and groundwater. He said that this exciting new area of research opens the door for a whole new generation of mass spectrometry experts to data mine the complex relationships between contaminants and elucidate what novel biochemical transformations are responsible for the 1000's of unknown (yet to be identified) metabolites found in contaminated soil and groundwater.

For more information contact: robert.kalin@strath.ac.uk.

The final talk of the day was from Falko Drijfhout from the School of Physical and Geographical Sciences, Keele University who described the use of GC and sample preparation in the Forensic Science area in a talk titled "GCMS and MEP Solutions for Drugs of Abuse" .

He said the analysis of chemicals with very small concentrations has always been a challenge and method development in trace analysis tends to focus on the enrichment of the chemical of interest through trapping on a solid adsorbent. However if concentrations are very low, the volume of the sample (air or aqueous) can be increased in order to increase the final concentration of the analyte. Whilst you can use of specific detectors to increase the detection limit, the main disadvantage is that often the sample size is quite small and hence increasing the volume is problematic.

Micro Extraction by Packed Sorbent (MEPS) in contrast reduces the need for increased volume size of the sample to be analyzed and can be used with any chromatographic technique. Analysis with MEPS can be carried out off-line, but its real advantage is when it is used on-line with either gas chromatography or liquid chromatography. It reduces sample preparation time as well as the volume of solvent needed. In addition it allows analysis of samples as low as 5µl.

In his presentation the he described the benefits of MEPS in the trace analysis of two benzodiazepines: diazepam and oxazepam. Concentrations as low as 50 ppt could be detected in a single run. The reliability and limit of detection of MEPS was discussed as well as the techniques further use in the analysis of a wide range of controlled substances such as cannabis.

For more information contact: f.drijfhout@chem.keele.ac.uk

Alan Handley closed the meeting summarizing that whilst GC is often considered a mature technology the considerable interest in the meeting and the excellent developments presented suggested that it is still a very active and developing area.

Copies of the presentations will be available on the Chromatographic Societies Website, www.chromsoc.com and also the RSC North West Region Analytical Division website http://www.nwad.org.