Visiting the 13th International Symposium on Hyphenated Techniques in Chromatography and Hyphenated Chromatographic Analysers (HTC-13) and the 3rd International Symposium on Hyphenated Techniques for Sample Preparation (HTSP-3)

Trevor Hopkins, Editor Chromatography Today, trevor@intlabmate.com

The 13th International Symposium on Hyphenated Techniques in Chromatography and Hyphenated Chromatographic Analysers (HTC-13) was held in Bruges, Belgium from 29th to 31st January 2014. For the third time the HTC conference was organised in conjunction with the HTSP symposium (International symposium on Hyphenated Techniques for Sample Preparation). HTSP-3 started the day before HTC-13 on 28th January and shared a common day on Wednesday 29th January. The symposia were organised jointly by the Royal Flemish Chemical Society (KVCV) and the Separation Science Group of the Royal Society of Chemistry (RSC).

Bruges a beautiful small town in Western Belgium has a rich history and exhibits it well with its medieval churches and official buildings, squares and cobbled streets, all of which are pristine in appearance after renovations. The oldest habitation of the city dates from the 1st century AD. Today Bruges is a modern shopping town with an extensive selection of fast-food stands, bars, bistros and starred restaurants.

The symposia took place in the Congress Centre Oud Sint-Jan, the large renovated complex of the medieval St. John's hospital dating from 1188 AD, which was until 1978 when it closed one of the oldest hospitals in Europe. The site is very compact but still housed three parallel sessions, provided ample space for posters and an exhibition with 21 exhibitors on the top level where the cocktail reception, coffee breaks and lunches were located.

As usual, academia, industry and government were all well represented among the speakers and over 306 delegates from 32 different countries were in attendance. The events were again accompanied by a one day short course on 28th January which featured two sessions on strategies for hyphenated techniques:

- Mass spectrometry: fundamental developments and hyphenation strategies Instructor: Professor E. De Pauw (ULiege) and
- Strategies for efficient hyphenations of (U) HPLC with MS Instructor: Dr G. Rozing

Picture of Oud-Sint-Jan from the bridge by Church of our Lady.

The aims of HTSP-3 were to 'highlight the prominent place which sample preparation techniques have taken in 21st century chemical analysis and emphasis will be set on the hyphenation with chromatography and with separation techniques in general'. Focus areas for the two day symposium were speed, automation, cost saving and green approaches in sample preparation.

Sample preparation techniques covered during the two day symposium included extraction techniques - solid-phase extraction (SPE), solid-phase micro-extraction (SPME), molecular imprinted polymers (MIPs), liquid-phase micro-extraction (LPME), sample introduction strategies (e.g. headspace methods; pyrolysis, derivatisation methods) and multi-column methods.

The opening plenary lecture of HTSP-3 was given by Professor Alois Jungbauer (AT) speaking on the subject of 'Separation of large biomolecular assemblies, viruses, VLP, and protein superstructures' and was

by his own admission off topic and had no real relevance to hyphenated techniques. He was followed by Janusz Pawliszyn (CA) whose topic was 'SPME for on-site and lab quantification in complex systems – advantages and limitations' and then by Valerie Pichon (FR) who talked about 'Biological and biomimetic approach for selective sample pretreatmen'. These plenary lectures were in a session titled Novel techniques and materials for sample preparation and separation which was chaired by Hernan Cortes.

After a short break the day resumed with a session on sorptive sampling techniques chaired by Valerie Pichon. Speakers in this session included Patrick Dirinck (BE) who talked on 'GC-MS and mass fingerprinting for understanding and measuring aroma characteristics in food products', discussing how the use of GC-MS was superior to the technique of GC–Olfactory detection and answered questions such as 'why do my food, orange juice and wine taste different' and the growing use of mass fingerprinting in determining flavours and odours in foodstuffs. Roland Meesters (CO) followed with a talk on the 'Evaluation of peripheral blood microsampling techniques in combination with LC-HRMS for drug pharmacokinetics in clinical studies'.

A break for lunch and ample time to review posters and the exhibits were followed in the afternoon with sessions on 'Advances in sample prep and hyphenation' chaired by Alois Jungbauer and 'life-science and biological samples' chaired by Janus Pawliszyn.

Keynote lectures by Nobuo Ochiai (JP) – 'Multi-stir bar sorptive extraction (SBSE): a new approach for SBSE using non-polar and polar coatings' which really was a commercial presentation dressed up to be a keynote lecture and Monika Wortberg (DE) 'Use of laboratory chromatographs as online instruments for waste water monitoring' who showed how BASF in Germany deal with waste water treatment by using online Full Evaporation Headspace Gas Chromatography (FE-HSGC) as a monitoring tool.

Oral presentations followed by:

- Audrey Combes (FR), a student of Valerie Pichon discussed the 'Synthesis and evaluation of a MIP for selective extraction of β-methylamino-L-alanine'.
- Beate Gruber (DE) discussed 'Needle trap microextraction combined with GCxGC-TOF for the analysis of breath gas' .
- Krzysztof Gorynski (CA) 'Development of SPME-LC-MS method: application to pharmakinetic study'.
- A tutorial session given by Tuulia Hyotylainen (FI), the HTC-12 award recipient, on 'Sample preparation for metabolomics and for biological samples'.

Oral presentations followed by Stig Pedersen-Bjergaard (NO) talking about '"Liquid-phase microextraction – Implementation in micro-chips and 96-well technology', whose presentation focused on the very recent development of Parallel Artificial Liquid Membrane Extraction (PALME) [4]. PALME is a modification of hollow fibre liquid-phase microextraction (HF-LPME) where the hollow fibres are replaced by flat membranes in a commercially available 96-well plate sandwich format. Benjamin L'homme (BE) gave the last oral presentation of the day on 'Analysis of Persistent Organic Pollutants in 20 µL blood by MEPS-GC-MS/MS' looking at the isolation and quantitation of the 'Dirty Dozen' pollutants listed by the Stockholm Convention.

This was followed by a novel concept introduced for the first time – Flash Posters - where a poster can be presented in a 5 minute time slot to a wider audience in a lecture theatre setting.

Taking place in parallel during the first day of HTSP-3 were the two short HTC courses with titles of 'Mass spectrometry: fundamental developments and hyphenation strategies' with Professor E. De Pauw (ULiege) as the instructor and 'Strategies for efficient hyphenations of (U)HPLC with MS' Instructed by Dr G. Rozing

Starting the second day the aims of the three day HTC-13 meeting were to 'cover all fundamental aspects, instrumental developments and applications of hyphenated chromatographic techniques'. These include hyphenation between chromatography and detection systems (with a focus on mass spectrometry), multi-column (multi-dimensional) chromatography, and the coupling between sample-preparation and separation techniques. Many aspects of chromatography were addressed, including automation and the use of robots, miniaturisation and microfabricated analytical devices, high-pressure and high-temperature LC, and new detection techniques.

HTC-13 covered many innovative applications based on hyphenated techniques, taking place in 3 parallel sessions which for at least the Wednesday included HTSP-3 in parallel, making it difficult and a little frustrating attempting to participate in the multitude of interesting discussions.

This review will now focus on a selection of the presentations given during the HTC-13 meeting. However an overview of the main topics covered during the symposium is given here:

- Fundamental strategies for the hyphenation of contemporary chromatographic and other separation techniques with sample preparation and advanced detection systems.
- Emerging detection strategies compatible with current separation techniques.
- The marriage of hyphenated techniques with process analytical technology.
- New developments in column technology.
- Applications in life sciences, including pharmaceutical analysis, biosystems research, and bio-analysis.
- Relevance in food science, including the analysis of contaminants and residues.
- Environmental science.
- Clinical and forensic applications.
- Combination with chemometrics and data-analysis.
- Applications in the chemical and petrochemical industry.
- Hyphenated techniques for natural products, flavours and fragrance analysis.
- Applicability in 'omics' (metabolomics, proteomics, lipidomics, etc.).
- Hyphenated techniques and polymers analysis.

The opening session of HTC-13 chaired by Hernan Cortes, Pat Sandra and Freddy Adams consisted of two plenary lectures, first Gert Desmet (BE) discussed the 'Instrument influences on observed column performance' and expressed the opinion that instrumentation needs to change from the 'hifi tower' construction of today to an injection-column-detection system which has no interconnecting tubing. Hans-Gerd Janssen (NL) then discussed 'From good multi-dimensional data to great multi-dimensional information'.

The closing of this session on the Wednesday, saw a lifetime-achievement-award presented to Milton Lee from the Department of Chemistry and Biochemistry, Brigham Young University, Provo, USA. The

Milton Lee in receiving the award

criteria for this award are 'for outstanding achievements in hyphenated techniques in chromatography and for distinguished service to the international chromatographic community'. The award was presented by Hernan Cortes, president of the selection committee.

Milton Lee in receiving the award discussed Thermal gradient gas chromatography (TGGC) and how it is differentiated from temperature programmed gas chromatography (TPGC), showing how high resolution separations of complex mixtures can be accomplished using short (i.e., less than 1-m) columns. Both theoretical and practical comparisons of TGGC and TPGC demonstrated that innovations in GC and its associated hyphenated techniques are far from over. Milton promised more exciting work on this subject in the future.

After the break two keynote lectures in the session LC^n and GC^n chaired by Aviv Amirav saw Andre De Villiers (SA) discuss the 'Systematic optimisation and evaluation of LC×LC separation of phenolics: Fundamental aspects and selected applications' and Professor Luigi Mondello (IT), the chairman of the 38th ISCC and 11th GCxGC to be held in Riva del Garda in May, discuss the 'Rapid collection of high solute amounts by using an on-line four-dimensional LC-GC-GC-GC preparative instrument'.

The afternoon session selected for review was on "Column technology for sample preparation and HPLC" chaired by Gert Desmet featured three oral presentations and two keynote lectures. The oral presentations were given by Szabolcs Fekete (CH) on the 'Possibilities and limitations of current state-of-the-art column technology' who discussed the optimum solid core particle size arriving at the conclusion that 1.3µm was optimal, and optimal column lengths for routine analysis of 5cm, high resolution separations of 8cm and 16cm for peptide analysis.

- Jirka Urban (CZ) 'Hypercrosslinking modification of organic polymer-based monoliths'.
- Fabien Brothier (FR) 'Miniaturization of selective sorbents: antibody/aptamer-modified monoliths'.

The keynote lectures were by:

- Michael Laemmerhofer (DE) 'Tailoring chromatographic selectivity'.
- Deirdre Cabooter (BE) on 'Detailed characterization of the kinetic performance of first and second generation silica monolithic columns'.

On Thursday morning, to honour individuals deserving special recognition of their innovation or influential work in the field of Separation Science, the John Knox award was presented by John Langley (RSC) to Peter Schoenmakers from the University of Amsterdam, NL who captivated the packed auditorium with a fascinating plenary lecture on selective LCxLC hyphenation. Peter made reference to his history in LC and to the Poppe, Giddings, Knox plot which he jokingly referred to as the 'IQ 500 plot'. Several other humorous comments including his definition of UHPLC as 'Ultra high patience liquid chromatography' when showing a separation which took 30 hours and commenting that 'with 4 injections a week this was just what PhD students needed'. His wit, interspersed with his deep intellect, had the audience in raptures and produced a solid lecture on the practice and theory of two dimensional liquid chromatography.

During the subsequent two RSC sessions chaired by Ian Wilson, LC-MS and human health and in particular phenotyping were discussed by various protagonists in the field including:

- Jeremy Nicholson (GB) on 'Large scale metabolic phenotyping of populations and patients'.
- Matthew Lewis (GB) on 'Mapping the metabolome - large scale phenotyping of human populations'.
- Nicola Gray (GB) on 'Targeted methods for metabolic phenotyping'.
- Elizabeth Want (GB) on 'Metabolic phenotyping: training the next generation'.
- Robert Plumb (GB) on 'Advancing Micro LC/MS and SFC-MS for metabolic phenotyping'.

The final award presented during the closing session, the HTC award, was presented to Dr Frank David, Research Institute for Chromatography, Kortrijk and University of Gent (Belgium). The nomination was based on the lecture 'New hyphenated techniques for aroma analysis', the most valuable and innovative contribution of the conference.

Poster prizes were also presented, the first and second of which were awarded to Jelle De Vos, Vrije Universiteit Brussel, Brussels (Belgium) and Piotr Alvarez, Ghent University, Ghent (Belgium) for their posters titled, 'A fundamental study of post-column focusing in liquid chromatography' and 'Combining multiplexed gel capillary electrophoresis with liquid chromatography for offline comprehensive analysis of complex oligonucleotide samples' respectively. The third prize was awarded to Thorsten Teutenberg, Institut für Energie- und Umwelttechnik e.V., Duisburg (Germany) for the poster titled 'Evaluation of a concept hyphenating flame ionization detection with nano- and capillary liquid chromatography'.

The Conference Chair, Professor Frederic Lynen Separation Sciences Group University of Gent, summarised the meeting saying, "The ongoing success of the HTC symposium series is closely related to the impressive evolution of both high-end separation techniques and mass spectrometry in the last two decades. Each instrumental or methodological improvement presents new hyphenation challenges which are ideally addressed during the HTC and HTSP conference series".

A week long instrument and supplies exhibition created the ideal forum to assess the state-of-the-art of modern instrumentation. Furthermore, during 7 product seminars, various sponsoring companies (FMS and Campro Scientific, Shimadzu, Waters Corporation, Gerstel, Peak Scientific, Markes International, and Sigma Aldrich) had the opportunity to go into detail about their new developments and products.

There was a full and lively social program, covering every evening, including two welcome receptions (one for each symposia)

HTC-13 and HTSP-3 in Bruges

a reception in the 14th century city hall, beer tasting in a local brewery, a banquet in the provincial governments hall and a closing reception at the symposium venue.

After the successful 13th edition of the symposium on Hyphenated Techniques in Chromatography and Hyphenated Chromatographic Analyzers the next and 14th edition will be organised in January 2016. Dates were not available from the organisers at press time. When asked what the focus would be for 2016 Professor Lynen answered, "I'm looking forward to incorporating sessions on hyphenated microfluidic techniques in 2016. We will also try to offer more contributions in the field of bio-therapeutics as this is a particular field of interest where there is a need for improved transfer of know how of the most recent hyphenation strategies".

These extremely valuable meetings covered everything from basic principles to fundamental aspects, method developments and applications of the various hyphenated chromatographic techniques and analyses. The high quality of the poster contributions and the novelty of the scientific content of the presentations, describing all aspects of hyphenated separation techniques, were of tremendous value for both novices and experts. Of particular note and interest to the author were the following areas: sample preparation for metabolomics, biological samples and biopharmaceuticals, the role of hyphenated techniques in the petroleum industry, metabolomics and the continuing evolution of chromatography and chemometrics and what can each one do for the other. A critical evaluation of HILIC and HILIC-MS was also a great summary of the power of HILIC, all making this a meeting that should not be missed for analysts involved in Hyphenated Techniques in Chromatography.