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BRITISH MASS SPECTROMETRY SOCIETY

WWEM
2nd-3rd November 2016, Telford, England
Conference, Exhibition & Workshops
Water, Wastewater & Environmental Monitoring
7th International Conference and Exhibition on Water, Wastewater & Environmental Monitoring

10.15 **Keynote**: Professors Peter Tranchida & Luigi Mondello, Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Polo Annunziata, Università degli Studi di Messina, Messina, Italia
GCxGC/MS and LCxLC/MS for the Analysis of Environmental and Food Matrices.

Session 1. Aspects of Comprehensive Chromatography Mass Spectrometry

10.45. Bob Green, SepSolv, *Comprehensive insights into tobacco smoke using flow-modulated GCxGC-TOF MS*

Bob Green[1].

11.05. Chris Hopley, LGC, *Multidimensional chromatography for the certification of environmental reference materials*

11.25 – 11.45 Coffee Break

11.45. David Smith, SAL, *The Application of GCxGC-FID to Environmental Hydrocarbon Analysis*

12.05. Leon Barron, Kings College, London, *Suspect screening of emerging contaminants using liquid chromatography-high resolution mass spectrometry and in-silico methods*

12. 30 – 13.30 h Lunch & Exhibition

Session 2. Aspects of the applications of chromatography mass spectrometry to water and environmental matrices including the involvement of Ion Mobility Mass Spectrometry

13.30. Roberto Sommariva, University of Leicester. *Real-Time Mass Spectrometric Analysis of Hydrocarbons from Crushed Shales*

13.50. John Thompson and Daniel Blenkhorn, University of Birmingham, *Using refillable diffusion tubes for*

VOCs, SVOCs and oxygen-sensitive VOCs for calibration ***of PTR TOF MS***

14.10. Ashley Sage, SCIEX *Screening and Quantitation of Emerging Environmental Pollutants in Drinking and Waste Water using Targeted and Non-Targeted LC-MS/MS Workflows*

14.30. Eimear McCall, Waters Corporation. *Environmental Screening of Water Samples Utilising Ion Mobility Enabled High Resolution Mass Spectrometry*

14.50. Mark Barrow, University of Warwick, *Analytical Methods for Profiling of Water from the Athabasca Oil Sands Region*

15.10 -15.30 Tea Break

15.30 - 16.30 **Discussion Session**
Subject Area/Contributors

1. ***Aspects of Analytical Method Validation.*** John Thompson.
2. ***Increased Peak Capacity: Is it a question for conventional comprehensive chromatography and chromatography mass spectrometry?***
   Contributors: Prof. Peter Tranchida, Bob Green, Chris Hopley, David Smith, Eimear McCall.

Keynote Presentation

Comprehensive Gas Chromatography (GC×GC) coupled to MS/MS and Comprehensive Liquid Chromatography (LC×LC) for the Analysis of Food and Environmental Samples.

Professors Peter Tranchida & Luigi Mondello

Dipartimento di Scienze del Farmaco e Prodotti per la Salute (SCIFAR), University of Messina, Viale Annunziata, 98168 Messina, Italy.

The present lecture is focused on the hyphenation of comprehensive 2D chromatography methods with MS/MS instrumentation, and the application of such powerful analytical devices to the field of food and environmental analysis. Comprehensive 2D chromatography separations are performed on two independent columns, with a different selectivity. A transfer system (defined as modulator), located between the two dimensions, enables the continuous and sequential transfer of primary-column effluent bands onto the second column. Consequently, the entire initial sample is subjected to a multidimensional separation. Comprehensive 2D chromatography technologies produce very high capacities because analytes are distributed across a bidimensional separation space. In an ideal comprehensive 2D chromatography separation the resulting peak capacity becomes the product of the peak capacities relative to each dimension. The comprehensive 2D chromatography technologies, which will be the object of discussion, are based on liquid (LC×LC) and gas (GC×GC) mobile phases.

With regard to MS/MS instrumentation, a great deal of evolution has occurred over the last 10 years; in fact, ultimate generation MS/MS systems can be employed for both untargeted and highly-selective/sensitive targeted analyses. These mass spectrometric devices can now meet the requisites of both LC×LC and GC×GC separations, with such a combination creating highly powerful and flexible four-dimensional analytical tools.

Comprehensive 2D GC investigations related to environmental analysis will be directed to experiments involving the analysis of phytosanitary compounds in drinking water, and the determination of harmful sulphur constituents in heavy petroleum fractions, namely coal tar and heavy gas oil. In particular, coal tar was subjected to analysis by using a novel LC-GC×GC-MS/MS instrument, while heavy gas oil was investigated by using a GC×GC-MS/MS system, with a low-costing, cryogen-free modulator. Apart from MS/MS, space will be also given to the use of rapid-scanning single quadrupole and high-resolution time-of-flight MS in GC×GC-based environmental studies.

The number of possible combination of stationary phases is higher in LC×LC, with respect to GC×GC, in order to maximize the gain in peak capacity, through the coupling of independent separation modes. When a class-type separation is to be achieved in the first dimension, orthogonality may be obtained by using normal-phase LC, coupled to reversed-phase (RP) LC; this approach was applied for the characterization of the lipidic fraction of sea organisms. An RPLC×RPLC method will be also illustrated, in which the use of segmented gradients allowed to increase the 2D separation space for the analysis of biomasses. Whatever the front-end separation, the use of MS/MS brings in added dimensions in terms of selectivity, specificity, and structural information.

Presentation 1

SepSolve

MARKES international

Comprehensive insights into tobacco smoke using flow-modulated GCxGC-TOF MS

Bob Green[1], Stefan Koschinski[2], Matthew Edwards[1] and Laura McGregor[2]
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The hazardous constituents of cigarette smoke have attracted considerable attention lately, especially with increasing regulation around the world limiting or banning smoking in public places – and even in private cars if children are present.

From an analytical perspective, however, there is much that remains to be learnt about the composition of cigarette smoke, because of its high degree of complexity – tobacco smoke is thought to contain thousands of components across multiple chemical classes and wide concentration ranges.

Comprehensive two-dimensional gas chromatography (GC×GC), when coupled with time-of-flight mass spectrometry (TOF MS), has been shown to provide improved chemical fingerprinting of complex samples in areas of study as diverse as petrochemical analysis and fragrance profiling. However, commonly-used thermal modulation devices are unable to successfully modulate the most volatile components.

In this study, we use thermal desorption (TD) for collection and analysis of whole cigarette emissions, and couple it with flow-modulated GC×GC–TOF MS, to enable the constituents of whole smoke to be routinely and confidently sampled, separated and identified.

Presentation 2

LGC
Setting standards
in analytical science

Multidimensional chromatography for the certification of environmental reference materials

Chris Hopley, LGC, Teddington

The certification of environmental reference materials pose many challenges, in terms of both the low levels of the analytes and maintaining the traceability of the assigned values to the SI units. Multidimensional chromatography coupled to mass spectrometry has the potential to allow the unambiguous identification and certification of analytes at the trace level, without interfrences and with increased sensitivity. This allows the production of relevant materials that users can have confidence in to demonstrate the effectiveness of their own methods.

The specific application of both fully comprehensive GCxGC and heart cut GCxGC for the certification of materials for environmental matrix certification will be discussed, specifically for the measurement of PCBs and PBDEs, including optimisation of the chromatography and MS conditions to achieve traceable results. The system utilised is a Zoex ZX2 system or a Deans switch system on an Agilent single quadrupole GC-MS. The use of this system for quantification is challenging due to the speed and resolution of the ZX-2 2D separation, however with careful optimisation good data is achieved for a number of analytes in a single run. The heart cut system is also discussed as an alternative to fully comprehensive GCxGC. Recently we have also had the opportunity to evaluate and develop a 2D LC system coupled to mass spectrometry, both QTOF and QQQ systems. A brief comparison of the systems will be presented, with a discussion on the relative merits of the different approaches available for reference material certification.

Presentation 3

The Application of GCxGC-FID to Environmental Hydrocarbon Analysis

David Smith Technical Director Scientific Analysis Laboratories Ltd

When refined oil products leak into the environment, biomarkers which are extensively used for 'crude oil' source identification may be absent in these products, and alternative approaches need considering to identify the potential sources. Petrol, kerosene and diesel have very little or none of these biomarkers. High resolution chromatographic techniques can be employed to look at very minor differences in components to try to discriminate between them in some way, which is extremely difficult in similar hydrocarbon fractions due to the total number of compounds they contain. Over time hydrocarbon profiles will change considerably in the environment, and this will further complicate identification. Example of this is shown appended (figure-2). The best efforts to increase the resolving powers of chromatographic systems to try to overcome the problems above have focused recently on two-dimensional gas chromatography (GCxGC). As the title suggests GCxGC produces a two-dimensional analysis that is much better for component identification than the traditional single dimensional analysis. A component separation is now dependent on two independent fundamental properties; volatility & polarity. The fundamental properties needed to separate all components of a mixture by chromatography. Each are known as a dimension and are optimised individually to get the best resolution. Using GCxGC, compounds of similar structure are grouped together in the chromatogram. These properties are used to interpret the total chromatogram in both dimensions which has far more combined information than a single dimension GC trace. A typical chromatogram is shown appended (figure-1) It is normal practice for environmental laboratories to employ GC-FID for the identification and quantification of hydrocarbons. GC-MS is very good at identifying target compounds within a complex mixture, but MS is less useful for this application where compounds are required to be grouped by carbon number and type before quantification. There is an increasing number of isomers for aliphatic hydrocarbons as the carbon number increases (and to a similar extent for aromatics). This creates a problem with the number of characteristic ions that increase as well. This makes ion extraction impractical for resolving these types of mixtures. The information required is chain length groups separated into aliphatic/aromatic bands. This is tackled far more efficiently and simply by FID. This presentation will focus on the application of GCxGC-FID, giving real life examples of where SAL have used this technology to solve customers analytical problems, and show how this technique can open up new ways of looking at hydrocarbon analysis in all environmental applications.

Presentation 4

Suspect screening of emerging contaminants using liquid chromatography-high resolution mass spectrometry and in-silico methods

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Characterising the breadth of emerging contaminants in the environment has been a dynamic challenge for decades. Recent attention has focussed on liquid chromatography coupled to full-scan high resolution, accurate mass spectrometry (LC-HRMS) as a means to capture large and retrospectively mineable datasets. Influent wastewaters, as well as being a major source of contaminants, have also been used to estimate community-wide consumption of illicit drugs. Other activity, such as manufacture or usage of explosives may also be possible. Herein, the development and application of LC-HRMS-based methods are presented for screening of 166 pharmaceuticals, illicit drugs and metabolites as well as 57 explosives, their pre-cursors and transformation products in influent wastewater from a major London sewage treatment works serving 3.5 m people. Solid phase extraction, LC stationary phases and the performance of atmospheric pressure ionisation sources for HRMS are discussed. Quantitative performance was investigated using a sub-selection of ~50 physico-chemically diverse compounds. Following chemical analysis, the use of automated search tools for compound identification via retention time and/or accurate m/z and isotopic abundance profiles from a commercially available reference library of >1400 compounds was assessed. For new compounds, and especially were reference standards were lacking, a novel quantitative structure retention relationship (QSRR) model was developed and validated using artificial neural networks for retention time prediction coupled with calculated m/z and isotopic profile data [1, 2]. The value of this QSRR approach facilitated ~50 % of HRMS data to be rapidly discarded and retention times could be predicted to within 1.30 min of measured values in most cases. Case examples of new drugs in influent are presented as well as a preliminary application to explosives. For pharmaceuticals in particular, and on any one day in London, ~30-40 additional compounds could be identified in 24-hour composite wastewater samples [3]. The value of LC-HRMS for targeted and suspect screening applications was clear, but particularly so when used in combination with in silico modelling tools to direct analytical standard synthesis for confirmatory purposes.

[1] L. Barron, G. McEneff, Gradient liquid chromatographic retention time prediction for suspect screening applications: A critical assessment of a generalised artificial neural network-based approach across 10 multi-residue reversed-phase analytical methods, Talanta, 147, 2016, 261-270.
[2] R. Bade, L. Bijlsma, T. Miller, L. Barron, J. Sancho, F. Hernández, Suspect screening of large numbers of emerging contaminants in environmental waters using artificial neural networks for chromatographic retention time prediction and high resolution mass spectrometry data analysis, Sci. Total Environ. 538, 2015, 934-941.
[3] K. Munro, T. Miller, C. Martins, A. Edge, D. Cowan, L. Barron, Artificial neural network modelling of pharmaceutical residue retention times in wastewater extracts using gradient liquid chromatography-high resolution mass spectrometry data, J Chromatogr A. 1396, 2015, 34-44.

Presentation 5

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LEICESTER

Real-Time Mass Spectrometric Analysis of Hydrocarbons from Crushed Shales

R. Sommariva (1), R.S. Blake (1), R.J. Cuss (2), R.L. Cordell (1), I.C.A. Goodall (1), J.F. Harrington (2), M.T. Ortega (1), S. Ouheda (1), P.S. Monks (1)

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Organic-rich shales are a type of sedimentary rock which contain significant quantities of organic matter (up to 8% by weight). In the past few years they have become an important alternative source of hydrocarbons, thanks to the development of the hydraulic fracturing technique ("fracking"). Knowledge of the abundance of methane and speciated non-methane hydrocarbons, and how that relates to the geological characteristics of shale is important to understand both the source rock potential and the potential pollutants from "fracking" activity.

We present real-time observations of the release of non-methane hydrocarbons from crushed shale samples taken from the Bowland-Hodder formation (North-Western England). The measurements were taken with a Proton-Transfer-Reaction Time-Of-Flight Mass Spectrometer (PTR-TOF-MS). Using different reagent ions (H3O+, CF3+), it was possibile to observe a wide range of hydrocarbons, mostly alkanes and aromatics, and examine how their release from the crushed rock varies with time and temperature.

The real-time analysis was complemented by full speciation by Solid Phase Micro-Extraction Gas-Chromatography Mass Spectrometer (SPME-GC-MS). We discuss the implications of these findings for the environment and for the industrial and commercial exploitation of shales.

Presentation 6

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Tracer
Measurement
Systems Ltd.

Using refillable diffusion tubes for VOCs, SVOCs and oxygen-sensitive VOCs for calibration of PTR TOF MS

John M. Thompson and Daniel J Blenkhorn. Tracer Measurement Systems Ltd., Institute of Research and Development, Birmingham Research Park, Edgbaston, Birmingham B15 2SQ & Molecular Physics Group, School of Physics and Astronomy, University of Birmingham, Edgbaston, Birmingham B15 2TT

It is important to calibrate any mass spectral method used for reliable and meaningful trace analyses of VOCs and SVOCs in both internal and external environments. In ISO 6145-8-2005 “Gas Analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 8: Diffusion Methods”, the illustrated designs of diffusion tubes are not at all easy to use for VOCs but impossible to use with viscous or solid

SVOCs. Using permeation tubes as an alternative is especially problematic with oxygen-sensitive VOCs.
Tracer Measurement Systems uniquely identifiable, laser-engraved, refillable and re-useable diffusion tubes offer the capability to produce trace gas calibration mixtures over a wide range of concentrations of VVOCs, VOCs, SVOCs and oxygen-sensitive compounds as well as inorganic elements and compounds of environmental importance.
The ways in which they may be used is illustrated with some of our recent applications research and development work on methyl vinyl ketone, an environmentally significant oxygen-sensitive VOC being monitored using PTR TOF MS in a forest in the West Midlands. Work is also presented on the SVOCs siloxane D5 and BHT and on trace formaldehyde generated by the thermal decomposition of paraformaldehyde.

Presentation 7

Screening and Quantitation of Emerging Environmental Pollutants in Drinking and Waste Water using Targeted and Non-Targeted LC-MS/MS Workflows

Ashley Sage, Daniel McMillan & Claire Sanderson
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Pharmaceuticals and personal care products (PPCPs), illicit drugs, herbicides, pesticides and associated metabolites are environmental contaminants of growing concern. In order to properly assess the effects of such compounds on our environment, especially their disruption of endocrine function in mammals and fish, it is necessary to accurately monitor their presence in the environment. The diversity of chemical properties of these compounds makes method development challenging, requiring multiple analytical techniques to assess and profile the levels of such compounds. Even more difficult to assess are the compounds that are ‘unknown’ and we will highlight the development with LC-MS technology and associated workflows to determine the presence of these suspect compounds.

Here we present results of PPCPs, illicit drugs, steroids and pesticides analysed in water samples collected in different geographies and from different types of water, including drinking water, rivers, lakes, sea etc. All samples were analyzed by direct injection Liquid Chromatography coupled to tandem Mass Spectrometry (LC-MS/MS). We will present methods using hybrid quadrupole linear ion trap (QTRAP®) and high resolution accurate mass (QTOF) LC-MS/MS instrumentation, and highlight the benefits of both types of platform for targeted and non-targeted analysis.

Two analytical methods were used. A method which enables the quantitation of environmental at low ppt levels using Multiple Reaction Monitoring (MRM) and their identification using full scan MS/MS with mass spectral library searching using a hybrid triple quadrupole linear ion trap LC-MS/MS system (QTRAP®). In addition a high resolution and accurate mass LC-MS/MS system (TripleTOF™ 5600+ and X500R QTOF) was used to further explore collected samples for unexpected analytes. Data processing turned out to be the bottleneck of the general unknown screening methodology. New and advanced data processing tools where used to automatically identify unexpected and unknown pollutants. LODs and dynamic range will be discussed for both instrument types, along with the benefits of high resolution mass spectrometry.

Presentation 8

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Environmental Screening of Water Samples Utilising Ion Mobility Enabled High Resolution Mass Spectrometry

Eimear McCall, Lauren Mullin, Gareth Cleland, Adam Ladak
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Companies and environmental regulatory authorities are under pressure to develop screening methods capable of detecting a broad spectrum of environmental contaminants in a single analytical run. Many are turning to High Resolution Mass Spectrometry (HRMS) as part of the solution. Data collected using data independent acquisition of both high and low energy simultaneously with ion mobility separation was interrogated for a range of environmental contaminants, including legacy and emerging polyfluorinated compounds. The same instrument was operated in this mode coupled with a variety of chromatographic techniques and ionising methods (including ESI and API). By utilising the different chromatographic and ionisation techniques the range of compounds covered can be expanded. Using a fully integrated scientific information system, which performs data processing via Apex 3D peak picking and componentisation, a target list of compounds was screened against. In order to identify target compounds against a library mass error, isotopic fidelity and fragment matching was used. A unique measurement that is made via the mobility separation collisional cross section (CCS) giving an extra point of confirmation for known compounds. The mobility separation also allowed the spectral clean up in data allowing identification to be performed with more confidence. The same data was then used to isolate non-targeted compounds by using an array of comparison and discovery tools without the need to reprocess. Identification of these significant compounds of interest is also addressed by discussing elucidating techniques, such as a novel batch elucidation tool, available within the integrated scientific information system.

Presentation 9

Analytical Methods for Profiling of Water from the Athabasca Oil Sands Region

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The global demand for petroleum continues to increase, particularly due its value as a source of energy and as a precursor to compounds used in manufacturing, the food industry, medicine, and research. With the growing pressures upon the conventional supplies, it has become increasingly necessary to turn to alternative sources of petroleum, which are typically more expensive. One non-conventional source is the oil sands found in the Athabasca region of Alberta, Canada. The oil sands consist of clay, sand, water, and bitumen and it is possible to use an alkaline hot water extraction process to separate the bitumen, which can then be upgraded to synthetic oil. Approximately three barrels of water are consumed for every barrel of oil produced, but, due to environmental regulations, the water cannot be discharged into the environment after use. This oil sands process water (OSPW) must be stored in large tailings ponds and it is known that the OSPW contains a wide range of organic compounds. With the growing importance of the oil sands industry, there is an accompanying need to develop and utilize a wide range of analytical tools for environmental monitoring.

Due to the inherent ultrahigh resolution and mass accuracy, Fourier transform ion cyclotron resonance (FTICR) mass spectrometry (MS) has been playing a leading role in the characterization of petroleum and other complex mixtures. For many years, naphthenic acids have been targeted in oil sands-related samples but it has been shown that targeting of these components is not sufficient. Electrospray ionization (ESI) can be used for analysis of polar components, observing acidic species in negative-ion mode and basic species in positive-ion mode, while non-polar components must be ionized using a different method such as atmospheric pressure photoionization (APPI). For complex mixtures, sample preparation is also vital. When preparing samples for infusion into the mass spectrometer, the choice of solvents impacts upon the relative contributions of different compound classes to the data. Investigation of extraction methods, used to generate the organic extracts from water samples for characterization, has been shown to strongly influence the range of components observed.

Water samples were acquired from industrial sites and the environment in the Athabasca region of Alberta, Canada, and organic extracts were prepared. A 12 T FTICR mass spectrometer has been used for ultrahigh resolution characterization of these samples. Following assignment of molecular compositions, the components were categorized according to heteroatom content, carbon number, and double bond equivalents (DBE), and the data can then be visualized using a variety of methods. Ultrahigh resolution profiles of the organic components are important for advancing environmental monitoring of the Athabasca region, and the findings demonstrate the importance of using complementary analytical approaches for characterization of complex mixtures.

Discussion Session

Subject Area/Contributors

1. *Aspects of Analytical Method Validation*

Dr. John M. Thompson

The Eurachem Guide: "The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics" 2nd Edition, 2014 (ISBN 978-91-87461-59-0) deals with the statistical and experimental approaches to issues of analytical method validation in ways which are firmly rooted in approaches based on "classical" (Gaussian-based) parametric statistics.

These approaches have some significant weaknesses, especially as applied to both Environmental and Food Analyses, in particular relating to all forms of trace analyses. Ways of tackling these include robust nonparametric approaches which more reliably deal with typically left-truncated, non-Gaussian distributions of trace analytes and issues around non-detects, as well as more recent and novel approaches based on compositional data analytical methods. These areas will be briefly reviewed to initiate discussion on how these might be considered and adopted in practical ways, including appropriate hands-on training of environmental/food analysts to incorporate these into everyday use.

2. *Increased Peak Capacity: Is it a question for conventional comprehensive chromatography and chromatography mass spectrometry?*

Contributors: Prof. Peter Tranchida, Bob Green, Chris Hopley, David Smith, Eimear McCall

Summary

Comprehensive chromatography with conventional detectors, such as FID, is essential for the separation of individual target analytes in multi-component mixtures because of the increase in peak capacity, which assists greatly in identification and quantification. However, with mass spectrometry as the detection system by a process of deconvolution the problems of overlapping peaks can be largely overcome, particularly at high resolution. Comprehensive chromatography with mass spectrometry gives greater confidence in the separation, identification and quantification of analytes in a mixture while, alternatively, ion mobility mass spectrometry enhances the peak capacity through differences in drift time and the involvement of TWIM.