EMERGING POLLUTANTS PUSHING THE SKILLS OF THE ANALYST

A report on the 4th National Conference on Environmental Mass Spectrometry, Chester, England

Since the last meeting in 2006 the pressure on Analysts to monitor ever-increasing numbers of compounds, which are suspected (or convicted) of causing health problems to humans and wildlife is increasing. Some of the compounds that were of academic interest in terms of methodology design are now subject to legislation in terms of specific maximum levels, which may be tolerated. New emerging environmentally pollutants (EEP) originate from a variety of sources thus making the task for the analyst more difficult. The practitioners, in tandem with the Instrument manufacturers have risen to meet the challenge and this meeting gave a fascinating overview of where we currently are and, having a vested interest in our environment, in seeing progress on all fronts.

Over 70 delegates *(Figure 1)* convened at the University of Chester to hear the Plenary Lecture, Keynote lectures and stimulating presentations and viewpoints given in oral presentations by both eminent Scientists active in the field *(Figure 2)*, plus post graduate students and view posters relating to the use of Mass Spectrometry and associated techniques applied to Environmental and Food/Flavour applications.

To complement the meeting over 12 commercial companies formed a trade show, which ran through the day to give an overview of commercially available products and solutions.

Prof. Darmia Barcelo from IIQAB-CSIC, Department of Environmental Chemistry, Barcelona, Spain gave the Plenary lecture entitled 'Novel Strategies for the identification and determination of pharamaceuticals, illicit drugs and their degredation products in the environment by LC hybrid tandem MS systems (Q Trap and Q Tof)'.

Prof. Barcelo spoke about the fact that Pharmaceutically active substances and illicit drugs are two classes of 'emerging' contaminants that are raising concerns in the last few years in environmental circles. Pharmaceuticals along with their metabolites, which can be more harmful than their parent compound, are continuously released into the environment, mainly through excreta, disposal of unused or expired drugs, or directly from Pharmaceutical discharges. Therefore, the adequate monitoring of their presence and elucidation of the (bio) degradable pathways and identification of transformation products is of crucial importance in understanding their fate in the aquatic environment. Furthermore the estimation of the concentration of illicit drugs in environmental samples such as river and wastewater has been recently proposed as a means of estimating drug consumption by the populous. Consequently, adequate analytical methodologies are needed for their determination in both surface and wastewaters.

The general trend observed in recent years, governed by the need for increased capabilities in environmental analysis is the development and application of generic methods that allow simultaneous analysis of multi-class compounds.

In this context, more recent approaches in LC-MS are hybrid instruments, such as quadruple time of flight (Aqua-TOF) and quadruple linear ion trap (Aqua-LIT), both of which are gaining widespread use and acceptance in several application areas.

Due to its unique characteristic of generating full-scan product ion spectra with exact masses Aqua-TOF-MS yields results with a much higher degree of certainty, which secures reliable identification of hitherto unknown compounds and avoids interpretation ambiguities.

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Figure 1. Delegates to the Symposium

On the other hand by using Aqua-LIT the same mass analyser can be run in two different modes, retaining the classical QqQ scan functions, such as selected reaction monitoring (SRM), product ion, neutral loss and precursor ion whilst providing access to sensitive ion trap (IT) experiments (MSn).

His presentation gave several practical examples on the application of LC-QqTOF and LC-QqLIT to the determination of multiclass pharmaceuticals and illicit drugs in both wastewater and rivers.

A screening method for the simultaneous determination of 80 pharmaceuticals using LC-QqLIT MS operating in both SRM and Information Dependent Acquisition (IDA) mode as well as multi class LC QqLIT MS/MS method (SRM mode) for the analysis of 17 drugs of abuse in waste and surface water was presented. Specific issues such as matrix effects, selectivity and sensitivity related to the number of SRM transitions monitored as well as the criteria for positive identification in terms of identification points (IP) were also discussed.

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Following the Plenary lecture, highly topical areas of interest were discussed in oral presentations some of which were preceded by Keynote lectures.

Session I following the Plenary lecture concentrating upon 'Recent Advances in the Methodology for Environmental Matrix Analysis'.

Here we heard from Dr Richard Robinson from Varian who spoke on 'Rapid Environmental Screening with Intelligent Data Systems for Confirmation'.

This was followed by Dr Chris Wright from the Safety and Environmental Assurance Centre of Unilever who spoke on' Challenges in the Analysis of Volatile Siloxanes in Environmental Samples'

Zoe Hall from LGC (formerly the Laboratory of the Government Chemist) spoke on 'High Accuracy Determination of Malachite Green in Salmon by exact Isotope Dilution MS'

Finally Dr Alan Herod from Imperial College presented on ' Advances in the estimation of Mass Ranges of Petroleum Asphaltenes for Environmental Reasons by LD-MS'

The Keynote speaker who started **Session II** was Dr Ramesh Kanda from Severn Trent Laboratories who spoke on the subject of 'Recent Advances in Analysis in the Water Industry'.

Initially he outlined the problems that face analysts in that an increasingly diverse range of contaminants are finding their way into potable water supplies such as pharmaceuticals, personal care products, endocrine disrupting products and other persistent organic pollutants. Some of these compounds, especially those with the potential to cause significant ecotoxicological damage to wildlife and humans have become subject to regulation. Therefore the analyst and in particular the mass spectrometrist must devise methods to monitor the extremely low concentration of these compounds in a variety of sample matrices.

The 3 main groups of compounds specific to this presentation were;

Endocrine disrupting compounds (EDC), which is the subject of major studies worldwide. Research during the 1990`s showed that the occurrence of intersex in male roach was widespread in UK rivers and this was partly due to treated sewage effluent.

Toxicity identification and evaluation (TIE) studies in the UK have found that the naturally occurring steroid oestestrogens: oestrone (E1) and 17β-oestestradiol (E2) and the synthetic oestrogen, 17α-ethynyloestestradiol (EE2) is responsible for most of the oestrogenic activity of domestic sewage effluent.

Extraction, followed by concentration and multistage cleanup using Gel Permeation Chromatography and analysis-using LCMSMS allows the detection of these oestrogens with limits of detection less than 0.1ng/l.

Perchlorate, which can occur both naturally and due to anthropogenic contamination. Potential health effects such as Thyroid dysfunction in humans caused the US EPA to recommend a maximum level in drinking water of 1ppb. Existing methods of analysis using ion chromatography and conductivity detection allows determination to ppb levels. Coupling the IC to tandem MS with API allows levels down to low ppt levels.

Haloacetic acids (HAA) are produced during the treatment of water with chlorine. Existing methods of detection involve extraction, concentration, derivitisation and analysis by GC using electron capture detection or MS. Ion Chromatography with MS or ICMSMS does not require any sample preparation. Analysis using eluent suppression systems and a matrix diversion valve to divert the matrix to waste is employed. Detection of the acids is carried out using –ve ion electrospray technology with MSMS after mixing the IC flow with acetontrile.

A series of presentations around the same Environmental Analysis Protocol theme were then given as follows:

'Rapid and Sensitive Approach for the Direct Measurement of Trace Organic Contaminants in Surface and Potable Waters by LC/MS/MS' by Dr Pamela Smith from Applied Biosystems.

'Analysis of Organophosphorous Pesticides and Organonitrogen Herbicides using GC-Ion Trap/MS in fs mode' by Ray Thomas from EHS Northern Ireland and,

'Multicomponent target compound GCMS Analysis with High Selectivity in Complex Environmental Matrices' by Dr Hans-Jurgen Heubschmann, Thermo Fisher Scientific.

The second Keynote speaker was Deborah Hudson from UKAS who spoke on 'Accreditation in Environmental Analysis –MCERTS and Beyond'

The general requirements for the competence of testing laboratories seeking accreditation are laid out in the European and International standard ISO/IEC 17025. The document is applicable to a variety of laboratories involved in a diverse range of testing.

The Environment Agency set up their MCERTS to provide a framework of standards to be used to monitor factors affecting the environment. During this coming year a new set of MCERTS standards will be published for the chemical testing of environmental and waste waters. These standards will provide additional requirements above those already in place. This presentation outlined the proposed new legislation to the delegates.

Session III then followed with an interactive discussion forum featuring a series of topical presentations, the first of which involved a description of an LC/MS/MS based solution incorporating a high throughput screen (3000 compounds/Hour, 50 Compounds/min) for the detection and confirmation of organic contaminants that have been inadvertently, or deliberately, introduced into the domestic water supply given by Tony Drury of Applied Biosystems.

Figure 2. Plenary Speaker and other presenters (Left to right) Damia Barcelo, Pamela Smith, Tony Drury, Alan Herod, Chris Wright, Zoe Hall, Rakesh Kanda, Tasneem Muharib

The second topic was titled ' Imaging Uranium Particles' led by Mark Soames from AWE, Aldermaston and focussed on the combination of SEM, SIMS, and TIMS to identify Uranium particles.

Finally Tasneem Muhrib of Sheffield Hallam University offered thoughts on

'Quantitative Aspects of the Determination of Isocyanates on Air Sampling filters by Image-Matrix Assisted Laser Desorption Ionisation-Mass Spectroscopy (i- MALDI-MS)'.

Several of the presentations were also presented as posters along with 'UHPLC Analysis of Phenol Pollutants in Water' by Charlotte Blythe and Monica Dolci from Thermo Fisher Scientific and 'An LC-MS/MS Method for the Determination of Species of Blood-based Meat Binders in Food Processing' by Helen Grundy et al. of the Central Science Laboratory.

All in all the meeting gave an opportunity for some in-depth discussions amongst practioners of the art of running Mass Spectrometers to those whose need is more focussed on the application of the data produced and its relevance to the environment and dietary habits of the general public.

The meeting was organised by the Chester Centre for Science Communication and the University of Chester in conjunction with the Environmental Mass Spectrometry special interests group (EMSSIG) and formed part of the BMSS promoted meetings series. The local organising committee consisted of Dr Peter Baugh, Prof. Graham Bonwick, and Prof. Chris Smith.

Following the meeting it was decided that there should be a similar meeting in 2010.

More details can be obtained at www.analyticalmethodologycentre.co.uk