Landmarks in the last 50 years of British Mass Spectrometry

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BMSS Annual Meeting
Alderley Park, April 2014
Acknowledgements

- Martin Elliott
- Gareth Brenton
- Frank Pullen
- Alison Ashcroft
- John Monaghan

.....and the surviving Aston Medal recipients.....
Overview

- Origins of BMSS

- A reflection of landmarks through the Aston Medal winners
Origins of BMSS

- Institute of Petroleum
- MS Discussion Group
- Mass Spectroscopy Group
  - 13th May 1964
  - Maccoll & Elliott
- British Mass Spectroscopy Group
  - 1974
- BMSS
  - 1981
Meetings aren't what they used to be....

- AEI MS Users Meeting - 1967?
the fifth meeting of the

MASS
SPECTROSCOPY
GROUP

chemistry department
university of bristol
july 13 - 15 1971
IMSC 1985 - Swansea

ORGANIZING COMMITTEE

J H Beynon (Chairman)
D E Games (Vice-chairman)
G M Harris (Secretary)
A G Brenton (Treasurer)

E Clayton
C Eckers
S Evans
S J Gaskell
Y Hoppliardi
J C James
K R Jennings
T R Kemp
A Marshall
A McCormick
W L Mead

University College of Swansea
University College of Cardiff
University College of Swansea
University College of Swansea
ICl Pharmaceuticals Division
Hewlett-Packard
Finnigan MAT
Tenovus Institute for Cancer Research
Ecole Polytechnique, Palaiseau, France
University College of Swansea
University of Warwick
Kratos Analytical Instruments
University College London
Ministry of Defence
The British Petroleum Company

Advances in Mass Spectrometry 1985

PART A

EDITED BY J. F. J. TODD
F W Aston

- University of Birmingham
  - Studies of discharge tubes

- Cavendish Laboratory
  - Worked with Thomson
  - Sector instrumentation
    - Momentum AND Energy Focusing
  - Accurate masses of natural isotopes
    - Whole number rule

- Nobel Prize for Chemistry 1922
Citation for the Aston Medal

- to be given to individuals deserving special recognition by reason of their outstanding contributions to knowledge in the biological, chemical, engineering, mathematical, medical, or physical sciences relating directly to mass spectrometry.
### Aston Medal Winners

<table>
<thead>
<tr>
<th>Name</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alan MacColl</td>
<td>18th Annual Conference, Nottingham 1989</td>
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<tr>
<td>John Beynon</td>
<td>19th Annual Conference, UCL, 1990</td>
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<tr>
<td>Brian Green</td>
<td>22nd Annual Conference, Swansea 1996</td>
</tr>
<tr>
<td>Keith Jennings</td>
<td>23rd Annual Conference, Warwick 1998</td>
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<tr>
<td>Dai Games</td>
<td>LC-MS Meeting, Cambridge 2000</td>
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<tr>
<td>Colin Pillinger</td>
<td>IMSC, Edinburgh 2003</td>
</tr>
<tr>
<td>Tom Preston</td>
<td>28th Annual Conference, York 2005</td>
</tr>
<tr>
<td>John Todd</td>
<td>IMSC, Prague 2006</td>
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<tr>
<td>Robert Bateman</td>
<td>30th Annual Conference, York 2008</td>
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<tr>
<td>Richard Evershed</td>
<td>31st Annual Conference, Cardiff 2010</td>
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<tr>
<td>Carol Robinson</td>
<td>32nd Annual Conference, Cardiff 2011</td>
</tr>
<tr>
<td>Tony Stace</td>
<td>34th Annual Conference, Eastbourne 2013</td>
</tr>
</tbody>
</table>
1989 - Allan Maccoll

- University College, London
  - Lecturer (1947)
  - Reader (1953)
  - Professor (1963)
  - Emeritus Professor (1981)

- Founding Editor - Organic Mass Spectrometry

- Founding Editor - European Mass Spectrometry
Organic Mass Spectrometry

Founded 1968
Founded 1995
1990 - John Beynon

- ICI Blackley
  - MS8 (Robert Craig)

- Purdue University
  - RMH2
  - MS9

- Royal Society Research Unit, Swansea
  - ZAB

- Founding Editor - Rapid Communications in Mass Spectrometry

- IMSF Thomson Medal 1985
Molecular Formula Determination

- '(mass spectrometers) can also be used for qualitative analysis of unknown substances'
- 'Since the mass spectrometer can handle milligram quantities of material…'
- 'from an analytical point of view, the molecular weight is perhaps the most useful single item of information obtainable by mass spectrometry…'
- '…if the mass of any ion is measured with sufficient precision, its elemental composition can immediately be deduced…'
Ion Kinetic Energy Spectroscopy

- Metastable peak from loss of CO from phenol molecular ion
1996 - Brian Green

- Metropolitan Vickers / AEI (1958)
  - MS9
    - First unit - Shell Amsterdam
    - Maccoll
    - Yale
Sabbatical.....
1996 - Brian Green

- Metropolitan Vickers / AEI (1958)
  - MS9
    - First unit - Shell Amsterdam
    - Maccoll
    - Yale

- VG Micromass (1972)
  - First scanning accurate mass measurements into data systems.
  - Laminated magnets
  - Dioxin methodologies
  - ESI of haemoglobins
Laminated Magnets

- Higher mass range
  - Less saturation

- Lower hysteresis
  - 4x less than solid core
  - Faster scanning
  - No degradation in mass resolution

- Lower stray fields
  - 8x less than solid core
  - Less interference
Haemoglobinopathies

- Determination of amino acid sequence in variant haemoglobins.

- Over 1,000 reported variants e.g. Sickle (β6 Glu→Val, Δm-30Da)

- Of the 4,550 samples analysed, 321 different variants have been analysed (151 α-chain, 162 β-chain, 1 δ-chain, 2Gγ chain, 5 hybrids)

- 73 novel mutations have been discovered since 1988 (44 α-chain, 29 β-chain).
1998 - Keith Jennings

- NRC Ottawa

- University of Sheffield
  - Metastable studies
  - Collision-induced dissociation

- University of Warwick
  - CID
  - Metastable studies
  - MS/MS

- ACS Field & Franklin Award
- ASMS Distinguished Contributions
- IMSF Thomson Medal 1985
Fragmentation and Metastable Ion Studies

- Studies of fragmentation - AEI MS10 & MS9 (early 1960s)
  - Metastable fragmentation
  - $m^* = m_2^2/m_1$
  - Increase fragmentation through introduction of gas

- CID & SID - Four sector instruments (1980s)

- Application of mass spectrometry in Life Sciences (from 1994)
An unlikely collection of characters......
2000 - Dai Games

- King's College, London
- McMaster University, Hamilton
- University of Wales, Cardiff
- Swansea University

- Editor-in-Chief - Biomedical and Environmental Mass Spectrometry

- IMSF Thomson Medal 1997
Field Desorption & Field Ionisation

- Low-energy ionisation techniques

- Promote molecular ion formation

The Field Ionization Spectra of some Natural Coumarins

D. E. Games, A. H. Jackson, D. S. Millington and M. Roosier
Department of Chemistry, University College, P.O. Box 78, Cardiff CF1 1XL, Wales

(Received 24 September 1973)

Abstract: The field ionisation and electron impact mass spectra of eleven coumarins have been compared. In the field ion spectra, the molecular ions were the base peaks and structurally diagnostic fragment ions formed by direct cleavage were present, whereas the molecular ions were weak in the electron impact spectra and fragment ions formed by rearrangement were dominant. Crude coumarin mixtures obtained from natural sources have been successfully examined using field ionization and gas chromatography + field ionization mass spectrometry.
Hyphentaed MS

- Coupling of chromatography and mass spectrometry
  - LC
  - SFC
  - CEC
  - HSCC

- Finnigan moving belt interface (Bill McFadden)
  - EI
  - Library-searchable spectra

- BMSS LC-MS courses
Proudest achievement??

- The students!
2003 - Colin Pillinger

- University of Bristol
- University of Cambridge
- Open University
Martian Meteorites

- Studies of astronomical samples

- Confirmation of the presence of martian meteorites on earth
  - Sensitivity
  - Isotope ratio measurements
Beagle 2

- Consortium Leader & Lead Scientist

- Communication lost - Christmas Day 2003
Rosetta
2005 - Tom Preston

- Stable Isotope Biochemistry Laboratory, SUERC
- Professor of Stable Isotope Biochemistry, University of Glasgow
- Adjunct Professor, St John’s Research Institute, Bangalore, India
EA-IRMS: the first CF-IRMS instrument

Aquatic biogeochemistry
Terrestrial productivity
Agriculture/soils
Ecology
Forensics
Fisheries Management
Plant water use efficiency
etc…

Nick Owens and Tom Preston about to hoist the first commercial EA-IRMS (Europa Scientific) onto the RRS Challenger, Troon, July 1987.
Non-invasive $^{13}$C breath tests

- Urea Breath test
- Gastric emptying
- Liver function
- Oro-caecal transit
- Small bowel overgrowth
- Fat digestion
- Starch digestion etc

Raw Data and Seigel Curve Fit

AP2003 $^{13}$C breath test IRMS, Analytical Precision, UK
GC-C-IRMS of short chain fatty acid production from dietary fibre
Volatiles in a helium carrier are separated by GC and combusted on line to CO$_2$

In-house GC-combustion interface, 20-20 IRMS, SerCon, Crewe, UK
Body composition and total energy expenditure

Obesity and type II diabetes

Thermo Fisher Delta V Advantage, IAEA Collaborating Centre for Nutrition, St John’s Research Institute, Bangalore
2006 - John Todd

- Leeds University
- Yale University
- University of Kent at Canterbury

- IMSF Thomson Medal 1997
Ion Traps
Rosetta

- Conceived 1994
- Launched 02-Mar-2004
  - Dormant for 2.5 years
  - Woke up in January 2014
  - Now switching on instruments
- Scheduled comet landing November 2014

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MODULUS Ptolemy Experiment

- Methods of Determining and Understanding Light elements from Unequivocal Stable isotope compositions
- Accurate isotope measurement for Th

- 250x330x110mm
- 4.5kg
- <10W power consumption
2008 - Bob Bateman

- Cambridge University
- AEI (1969)
- VG Micromass (1973)
VG ZAB 2F

- Reverse geometry - collision cell for ion activation
Non-normal entry into same magnet
- Half angle, double radius, increase mass range 4x
Tri-sector EBE configuration

16 bit ADC at 400 kHz sampling rate

(16 bit ADC at 500 kHz sampling rate)
Autospec 6F
oaTOF

Sensitivity
Speed
Size
Simplicity

AutoSpec-TOF
Synapt HDMS
IMS-MS
2010 - Richard Evershed

- Ph.D. Keele
- University of Bristol (1981)
- University of Liverpool (1984)
- University of Bristol (1993) — Chair of Biogeochemistry
2010 - Richard Evershed

- Ph.D. Keele
- University of Bristol (1981)
- University of Liverpool (1984)
- University of Bristol (1993) — Chair of Biogeochemistry

“Pioneered the development and application of molecular and isotopic techniques to study environments of the past and present”
Analytical chemistry of molecules past and present

**BIOGEOCHEMISTRY**
Role of microbes and invertebrates in soil organic matter cycling

**CHROMATOGRAPHY**
- **ORGANIC GEOCHEMISTRY**
  - Reconstructing past climate and environments (peat bogs and lakes)

**BIOMOLECULAR PALAEONTOLOGY**
Fossilisation processes and palaeoenvironmental information

**BIOMOLECULAR ARCHAEOLOGY**
Reconstructing human activity in the past

**CHROMATOGRAPHY**
Molecular and stable isotopic compositions
Organic Chemistry Archaeology

- Pistacia resin
- Frankincense
- Birch bark products
- Coniferous resin
- Heated resin product
- Widely occurring sterol
- Manure indicators in soils
- Petroleum bitumen
- Plant epicuticular waxes
- Beeswax
- Isoprenoid fatty acid
- Common fatty acid
- Natural dyes
- Oxidised fatty acid
- Thermally altered fatty acids
- Macromolecule building blocks: collagen, aDNA, carbohydrates, etc.
Bronze Age soil

Mummies

Mary Rose

Roman cosmetic

Bog body

Resins, tars, pitches and bitumen

Plant remains

Organic pigments

Art objects

Skeletal remains

Neolithic pottery
Synergies in structures and isotopic compositions

Compound-specific isotopes and biomolecular archaeology

\(^{12}\text{C},^{13}\text{C}\) (metabolism/biochemical pathways)*****
\(^{14}\text{C}\) (radiocarbon dating)*
\(^{1}\text{H},^{2}\text{H}\) (temperature/precipitation)*
\(^{16}\text{O},^{18}\text{O}\) (temperature/precipitation)
\(^{14}\text{N},^{15}\text{N}\) (trophic interactions/metabolism)*
University Research Centre & NERC Facility for molecular and light stable isotope MS analyses

- 3 x GC/MS
- 6 x GC-C-IRMS
- LC/MS/MS
- LC-IRMS
- HRMS

New accelerator mass spectrometer for UK science for 2015
2011 - Carol Robinson

- M.Sc. Swansea (Beynon)
- Ph.D. Cambridge (Williams)
- Oxford University (1991)
- Cambridge University (2001)
- Oxford University (2009)
- Biemann Medal (2003)
- DBE (2013)
Intact GroEL_{14-mer} survives

Ion mobility separation of protein complexes

$t = 5 \text{ ms}$

$t = 15 \text{ ms}$

$t = 30 \text{ ms}$

Ruotolo, Science 2005
First mass spectrum of a membrane complex

Mass spectrum of intact ATPase from *Thermus thermophilus*

Zhou et al. 334,380 Science 2011
2013 - Tony Stace

- Ph.D. Essex
- Sussex University (1974)
- Southampton University (1977)
- Sussex University (1983)
- Nottingham University (2004)
Cluster studies

- Cluster fragmentation patterns
  - Solvation of protons in solvent
  - Formation of proton hydrates in ionosphere

- Metal multi-cation complexes in the gas phase

- Coulomb fission from multiple-charged cations
  - Applications in cloud formation to nebuliser delivery
Cold trap techniques
  - Visible / UV laser spectroscopy metal dication complexes
Most newcomers to mass spectrometry in the last 10 years will have little concept of the difficulties faced in obtaining the mass spectra of four solid samples during a working day......

Keith Jennings, 2012
Concluding thoughts

- Mass spectrometry has changed enormously in the last half century
- Now in routine use, touching many aspects of our daily lives
- Where will we be 50 years from now?
Thank you for your attention