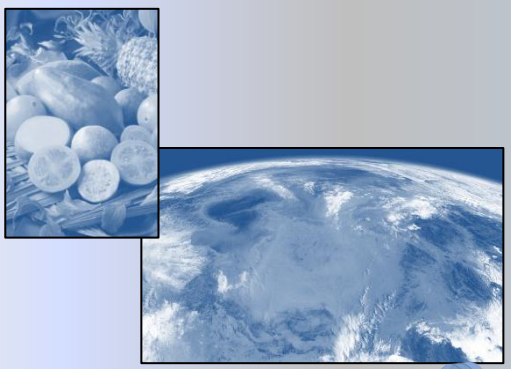
University of Leicester

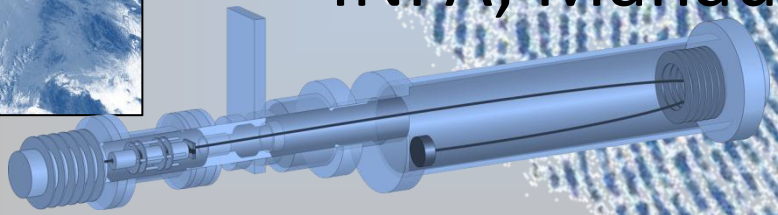
15th February, 2012

PTR-MS OVOC Measurements: Fingerprinting Air



BUNIAACIC

INPA, Manaus



Iain White

Kevin Wyche

Paul S. Monks

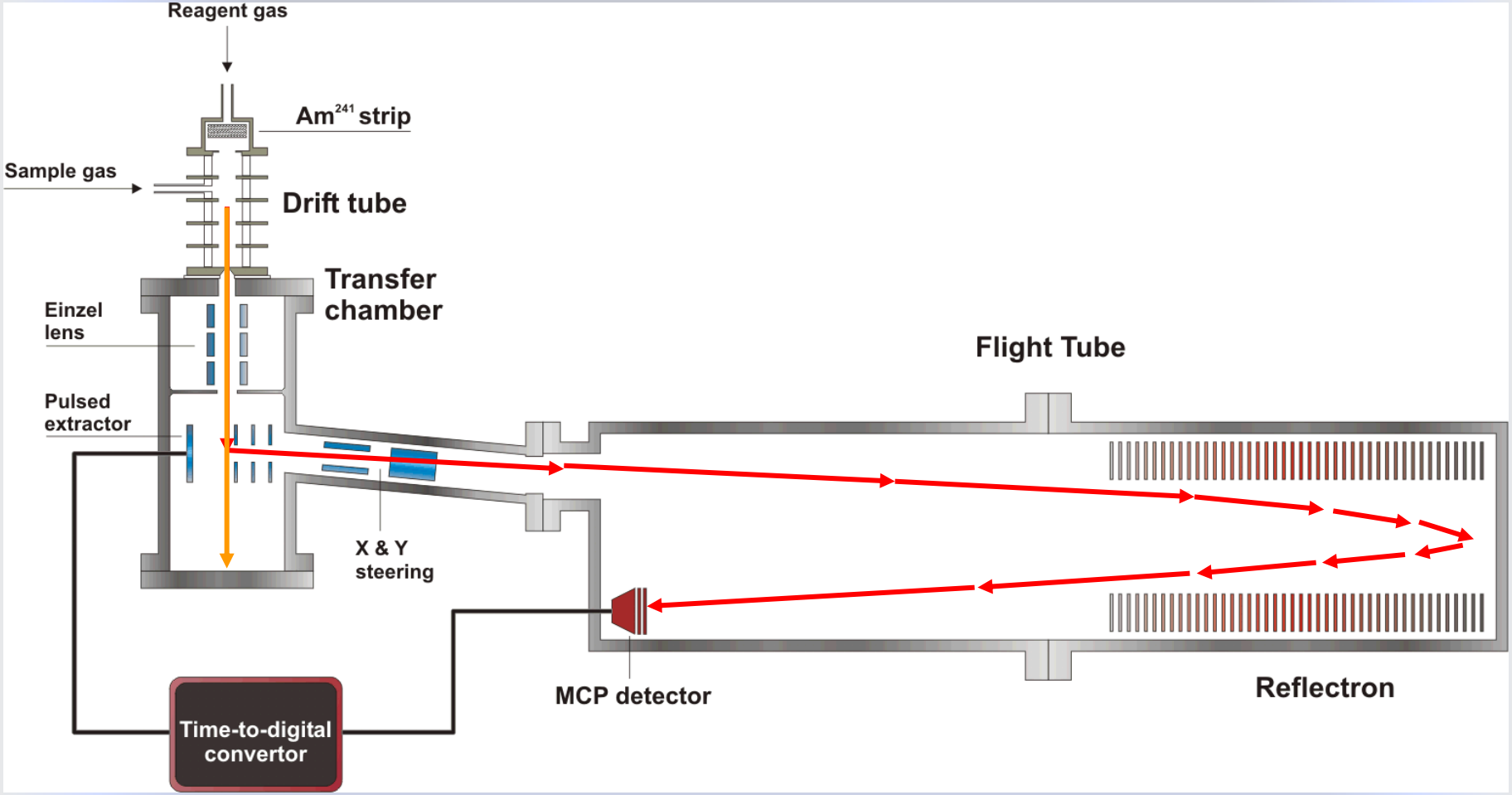
OVERVIEW

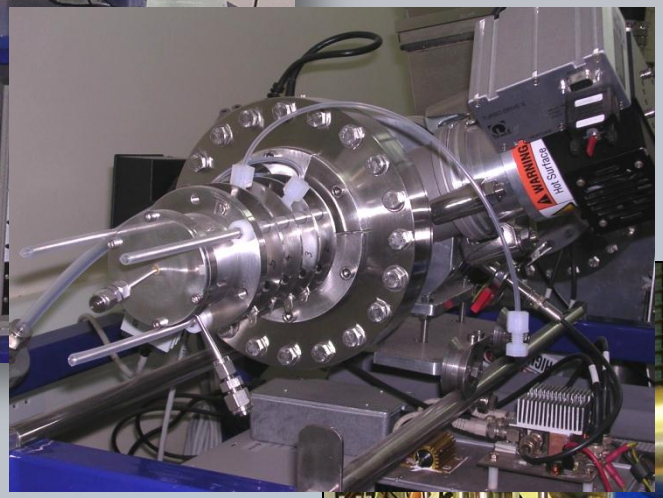
- Overview of the Work at UoL
- Case studies and examples
- Technology developments
  - Sensitivity
  - Semivolatiles

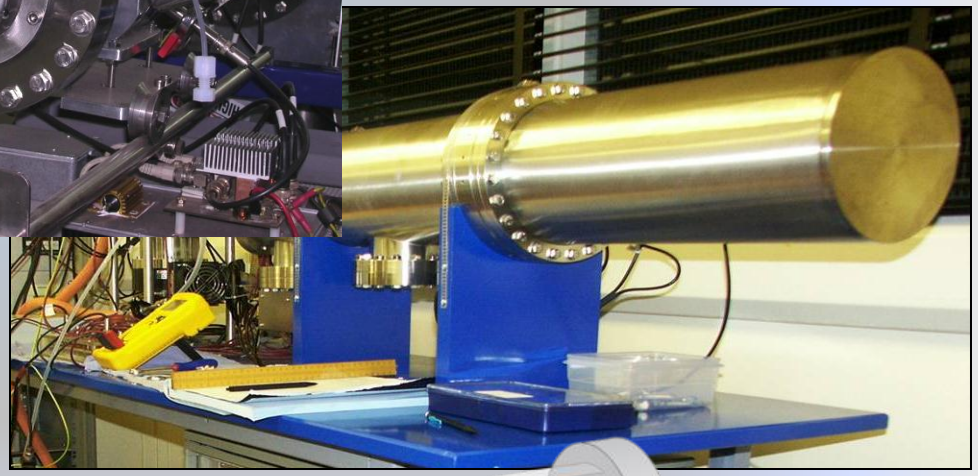
Fingerprinting Air

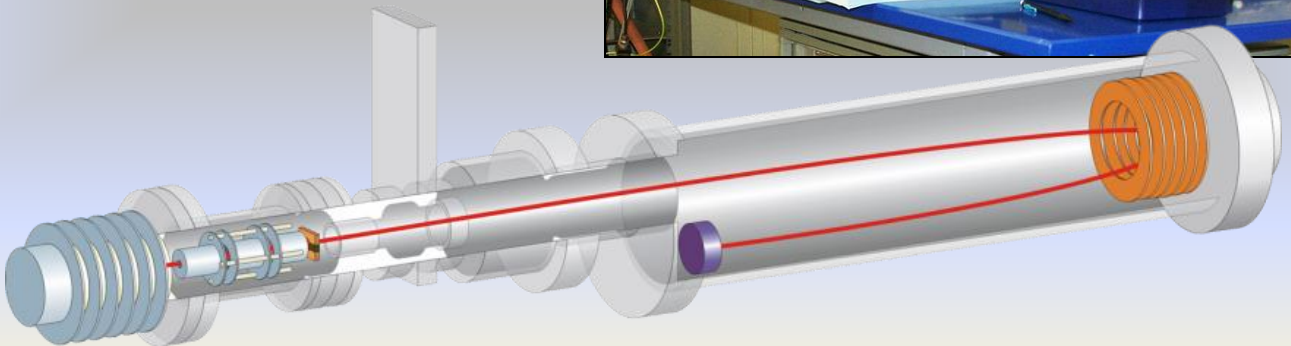
- Measuring in real-time the trace composition (VOC/OVOC) of complex mixtures of gases
- Developed CIRMS for real-time measurement of VOCs
  - Fast
  - Sensitive
  - Quantitative
  - Measure real-time change in large number of VOCs

CIR-TOF-MS


Reagent gas
Am^{241} strip
Sample gas
Drift tube
Transfer chamber
Einzel lens
Flight Tube
Pulsed extractor
X & Y steering
MCP detector
Reflectron
Time-to-digital convertor


A WARNING
High Surface

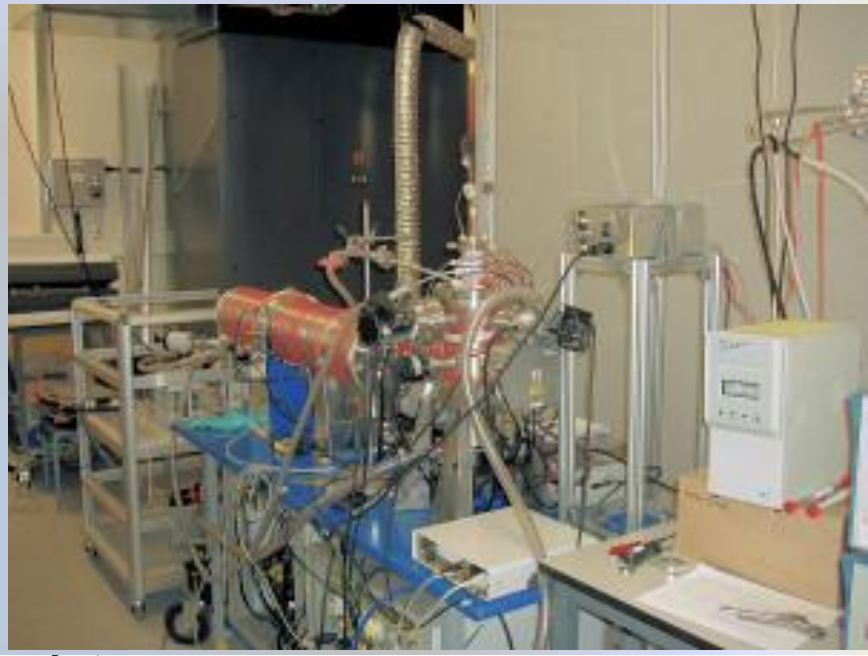


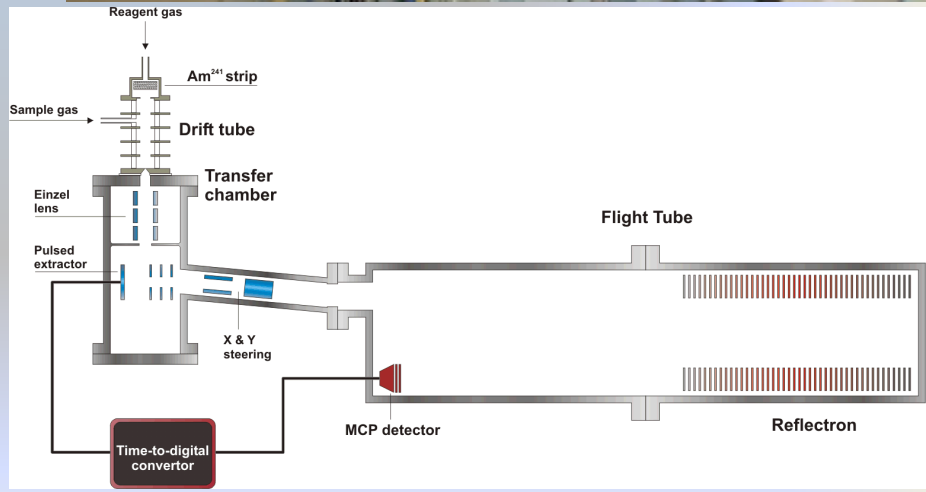


Why CIR-TOF-MS?

- Mass range: theoretically unlimited
- Mass resolution (m/Δm): ~3000
- Frequency: 10^4 Hz for 0 – 300 amu scan
- Detection limit: ~ 0.1 cps ppbV^{-1}

  (~1 ppbV min^{-1} Hydronium)
- Sensitivity: 20 – 200 ncps ppbV^{-1}
- High '*real-time*' accuracy and precision (~10%) across entire mass spectrum
- CI reagents: H_3O^+, NH_4^+, NO^+ and O_2^+

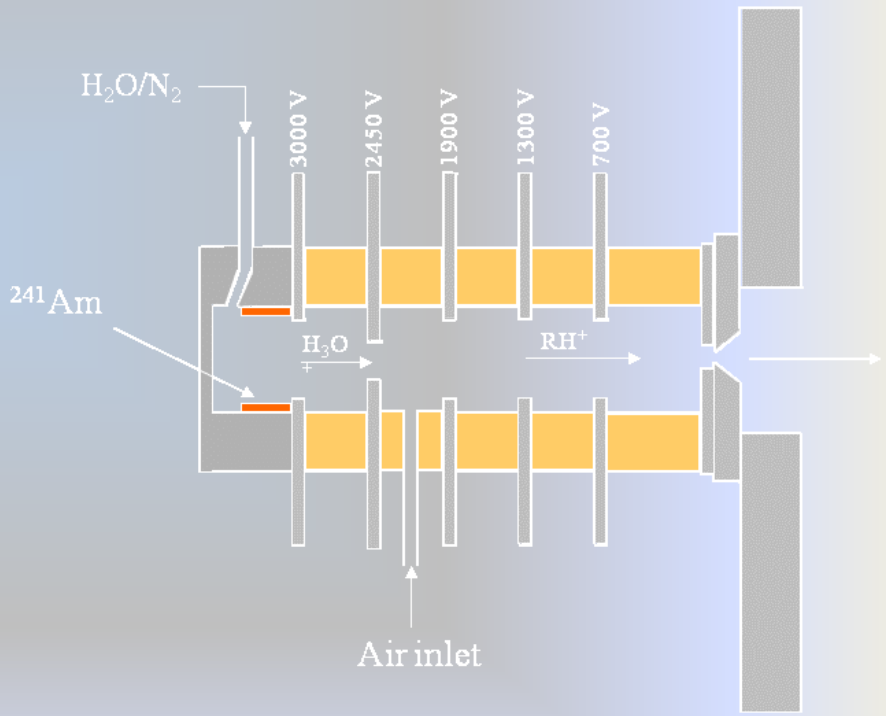




System Design and Method Development

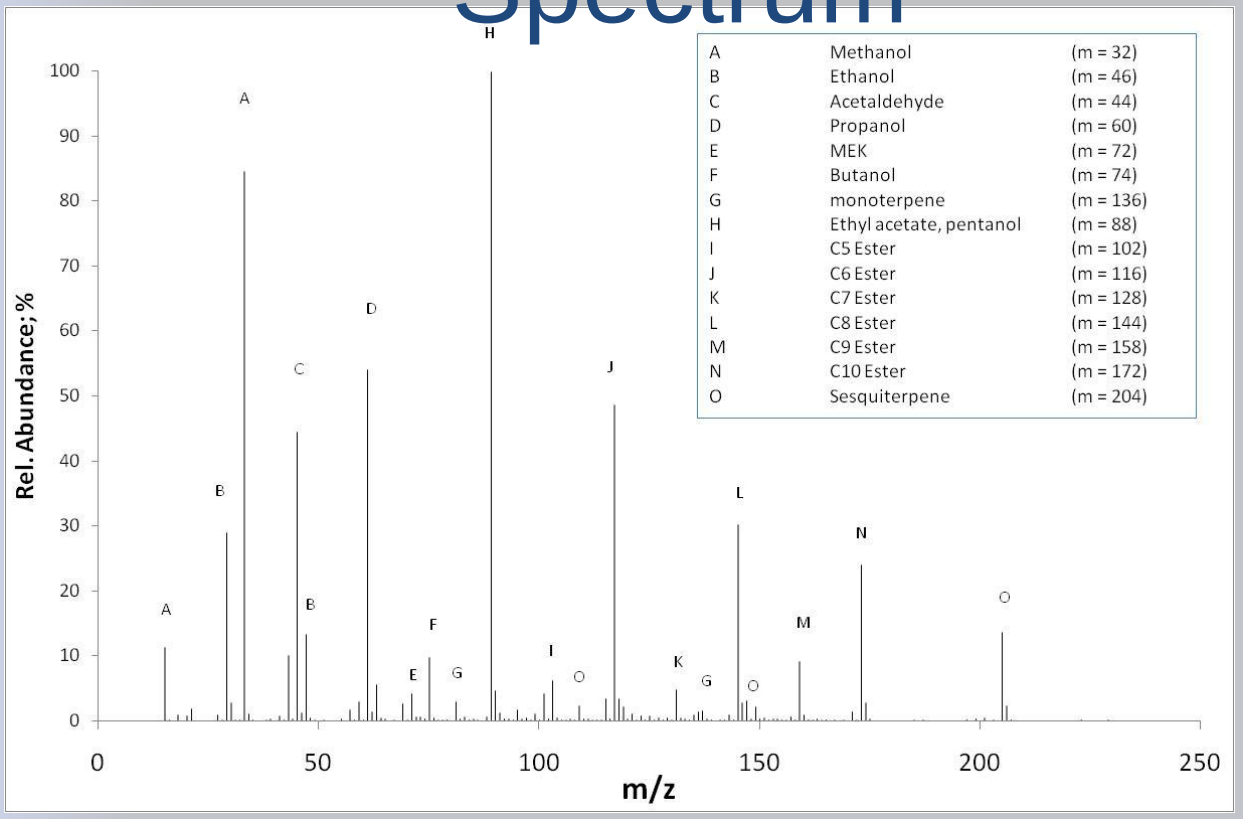
- Am Source gives clean spectrum
- Low E/N (Soft Ionisation – 80 Td)
  (high P, low Voltage)
- Minimise clustering by using
- H_2O bubbler and CID region (180 Td)

- Calibrate using Pressurized cylinders,
  Permeation tubes, Tedlar bags
- Estimate sensitivity based upon PA

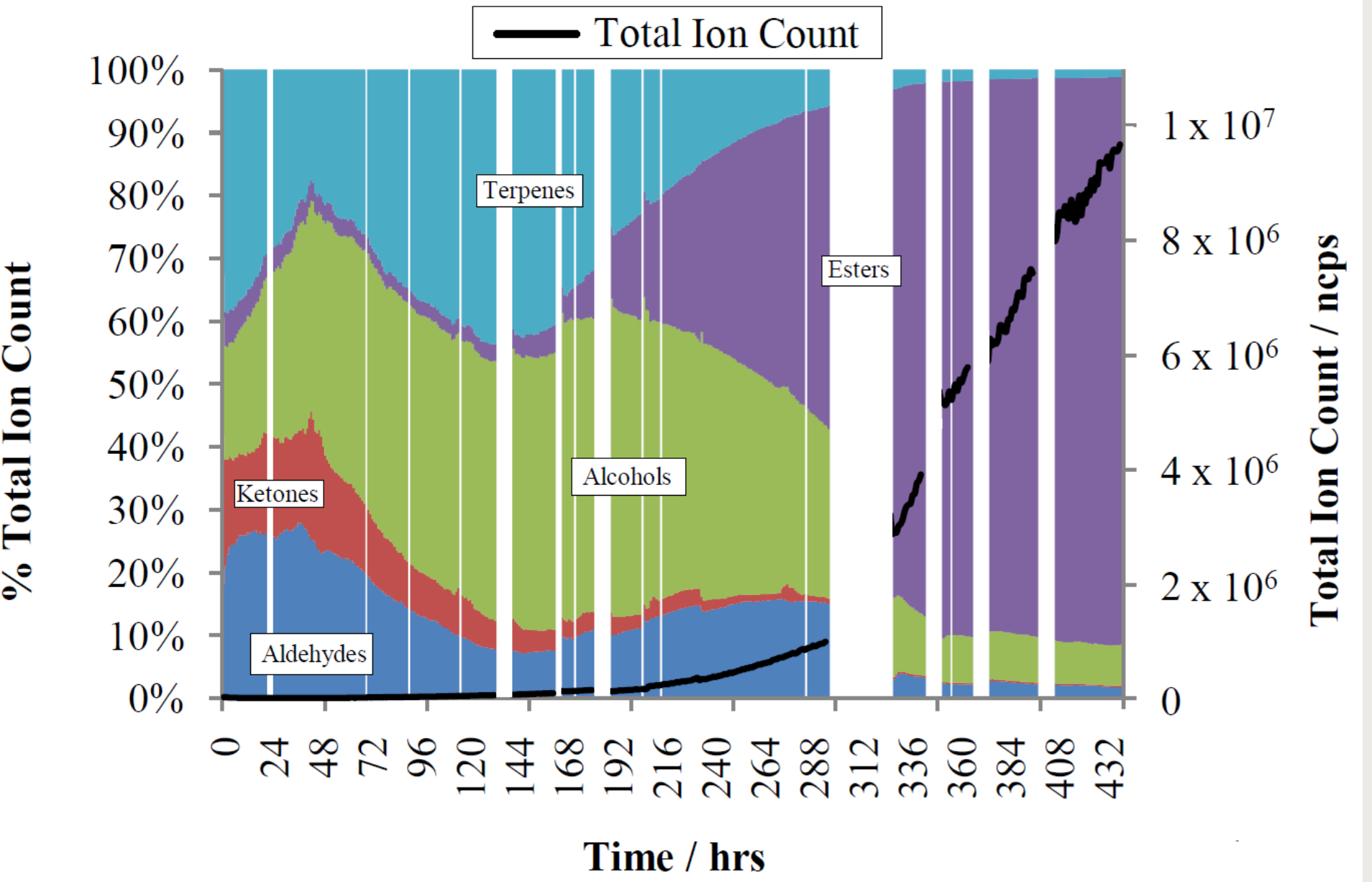


If $[H_3O^+] >> [RH^+]$ then $[R] = \{i(RH^+)/i(H_3O^+)\}/kt$

Case Study: Typical Mango Headspace Real-time Mass Spectrum



- Each peak potentially represents an aroma compound produced during ripening

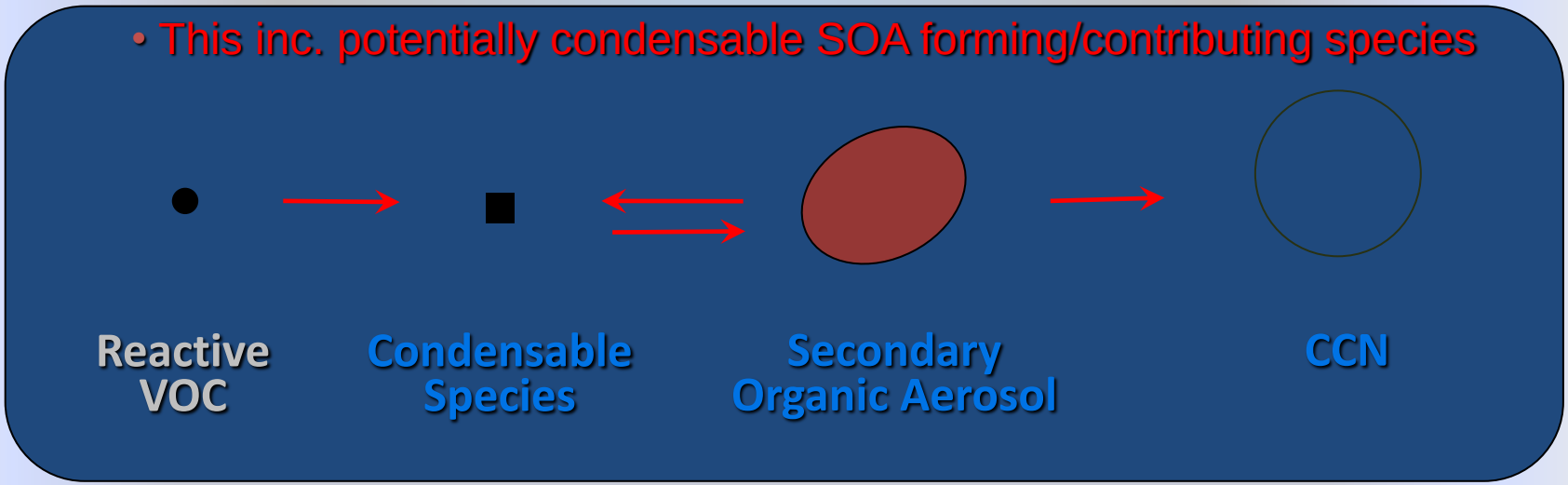

Total Ion Count
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% Total Ion Count
1 x 10^7
8 x 10^6
6 x 10^6
4 x 10^6
2 x 10^6
0
Total Ion Count / ncps
Terpenes
Esters
Alcohols
Ketones
Aldehydes
0
24
48
72
96
120
144
168
192
216
240
264
288
312
336
360
384
408
432
Time / hrs

ACES Introduction

What do we do?

– *Examine the fundamental formation of (organic) aerosol*

ACES Goals: To observe and quantify the gas phase VOC SOA precursor species and their oxidation products



Experiments

ACES I

13 Basic photo-ox / nucleation exps,
high (250 ppbV) and low (50 ppbV) concentration,
with NO_x (VOC:NOx ~ 2:1)
4 monoterpenes, 1 sesquiterpene:
α-pinene, limonene, α-terpinene, ocimene,
β-caryophyllene

ACES II

5 Basic photo-ox / nucleation exps:
α-pinene, myrcene, linalool
2 photo-ox / inorganic seed exps:
isoprene, limonene
6 photo-ox / organic seed exp:
isoprene, limonene on β-caryophyllene

ACES III

6 mesocosm photo-ox / nucleation exps.
5 mesocosm photo-ox / inorganic seed exps.
2 different fig species and 1 birch

ACES IV

Ensemble experiments:
Isoprene:monoterpenes ratio varied to see affect on
aersol formation

ACES

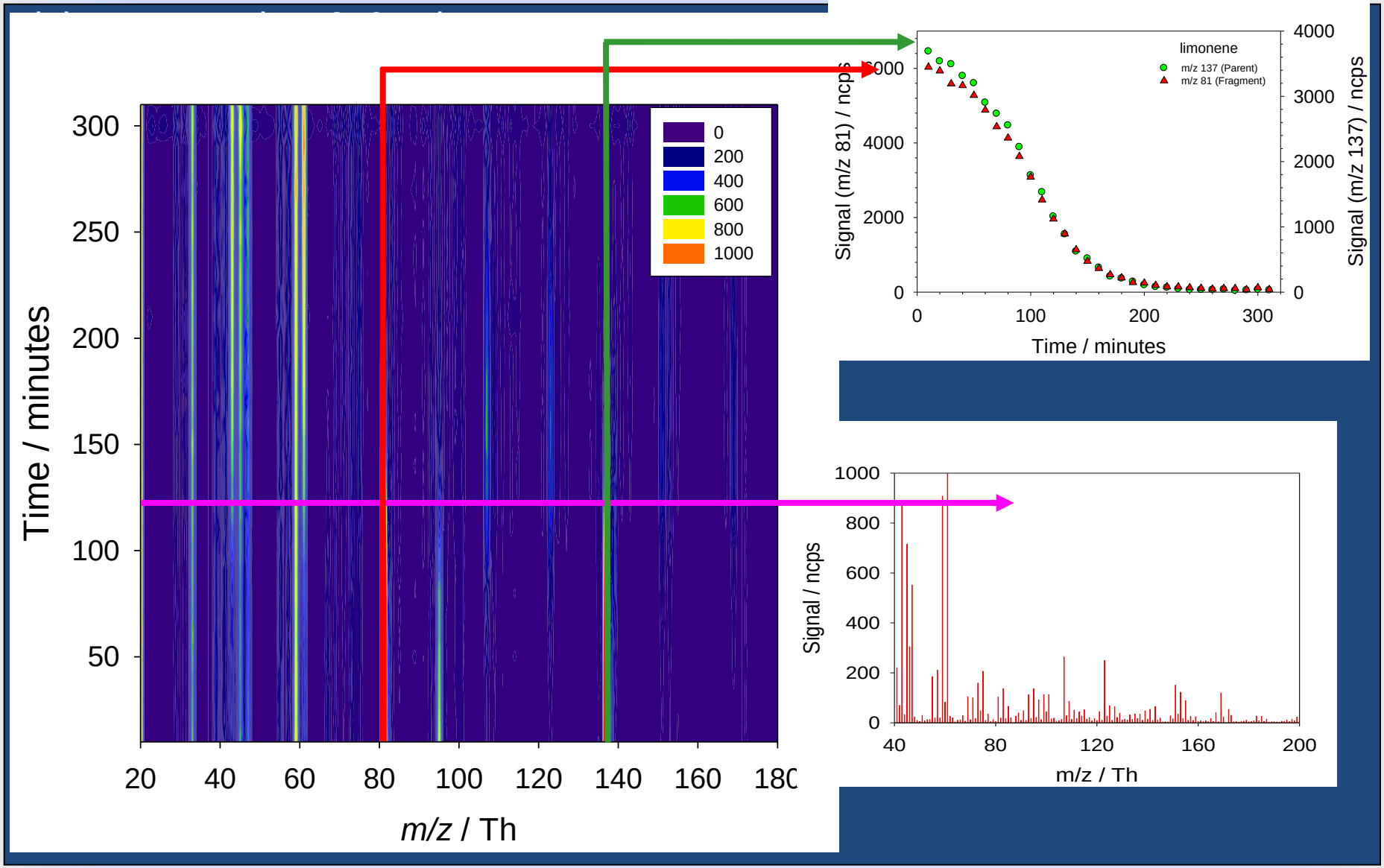
- Successfully measured a wide array of gas phase oxidation products in *real-time* using CIR-TOF-MS, from a total of 8 different SOA precursors over 4 intensive campaigns: α-pinene, β-caryophyllene, α-terpinene, limonene, ocimene, myrcene, linalool and isoprene

- Conducted gas phase analysis of mesocosm system over 11 experiments for two different fig species and one birch species

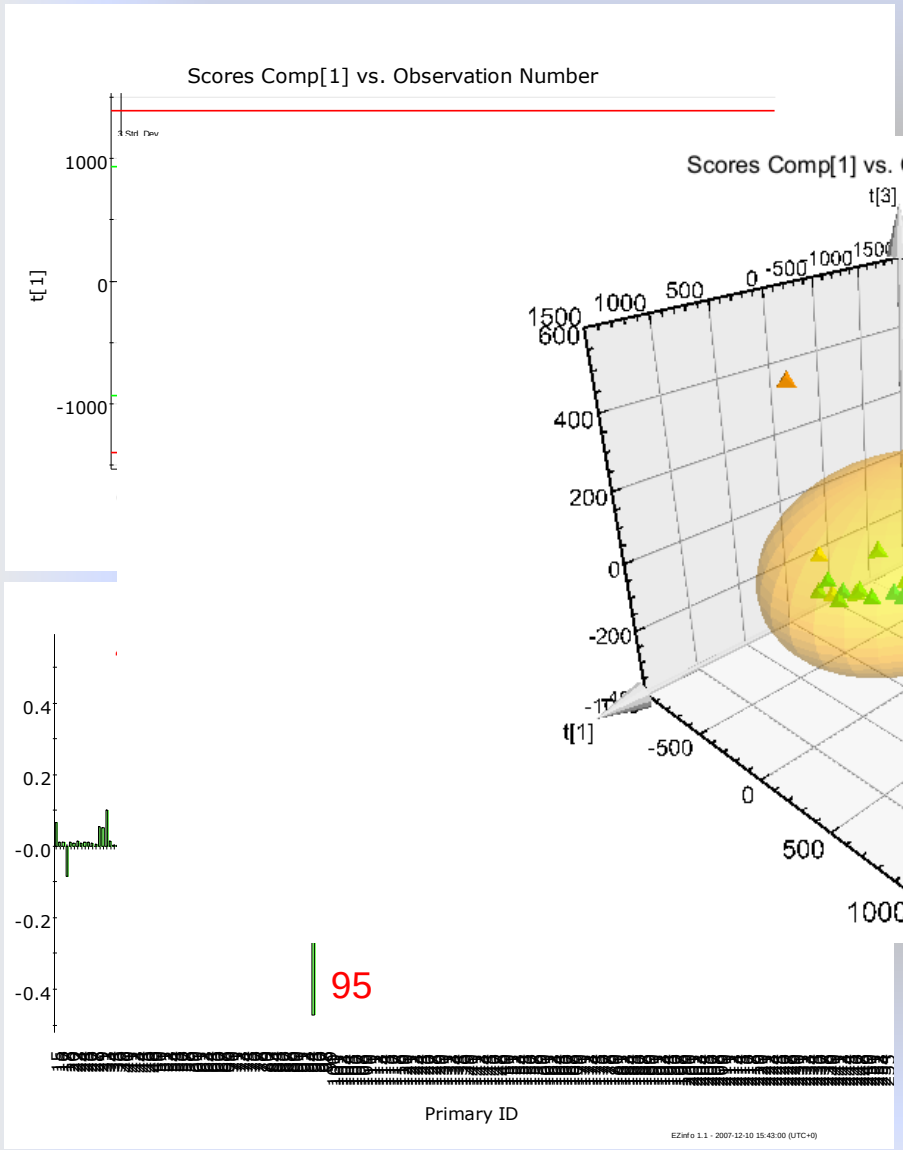
- Developed method to measure Terpenoids in real time

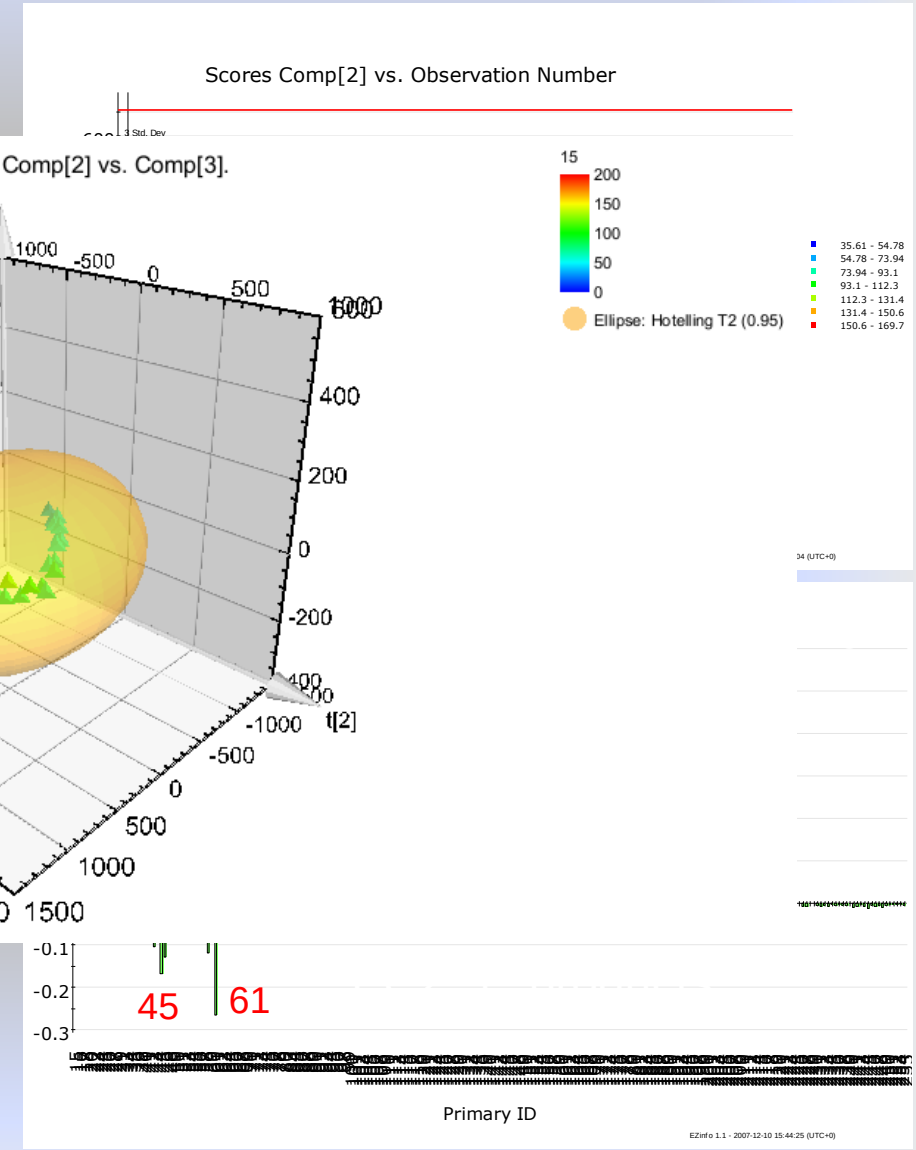
- Over all experiments this equated to ~ 86 million data points to analyse
- CIR-TOF-MS ACES data currently being used to help us:
  - Understand, test and improve VOC oxidation mechanisms
  - elucidate the mechanisms behind SOA formation by precursor species
  - understand SOA composition by precursor species
  - move our simulation experiments towards “the real world” (organic seed, mesocosm and ensemble experiments)

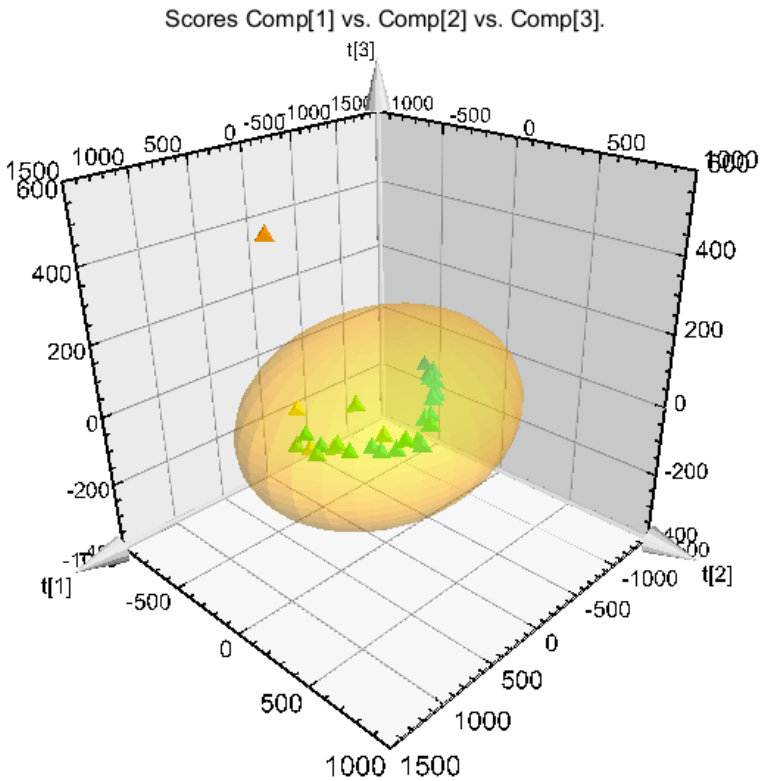
Limonene Photo-oxidation



Limonene PCA







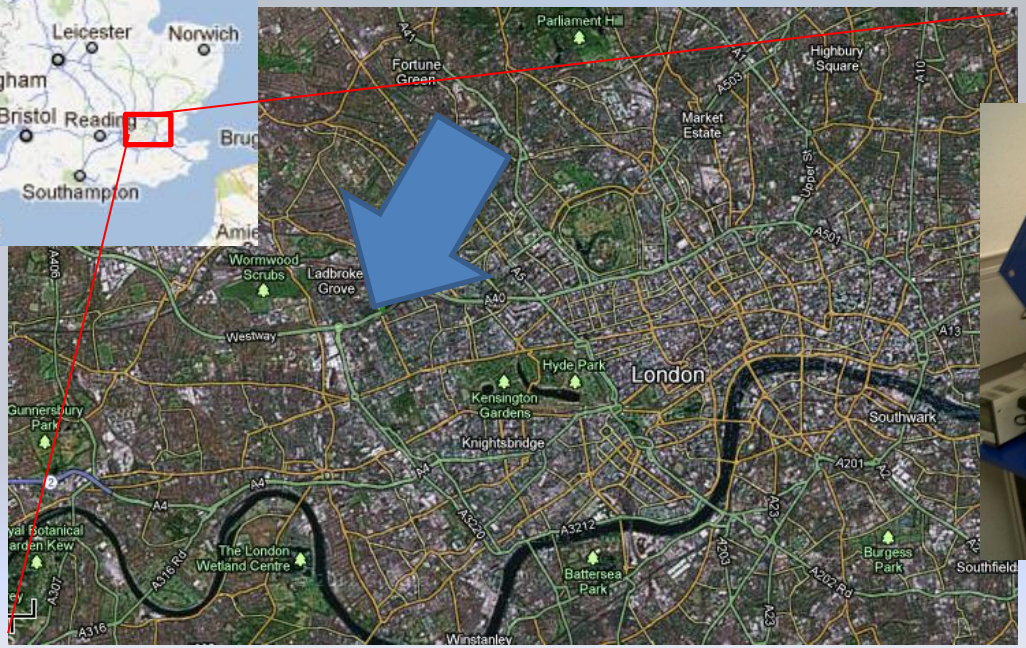
- Deconvolute and **speciate** complex spectra produced from mixtures of gases representing biogenic and anthropogenic systems using multivariate statistical techniques

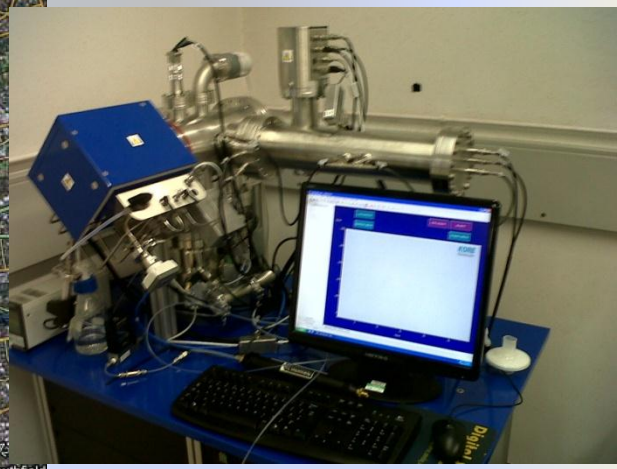
- **Identify** and **Quantify** OVOC products invoking knowledge of PTR ion chemistry using values obtained from DFT and through intercomparison with atmospheric chemistry models

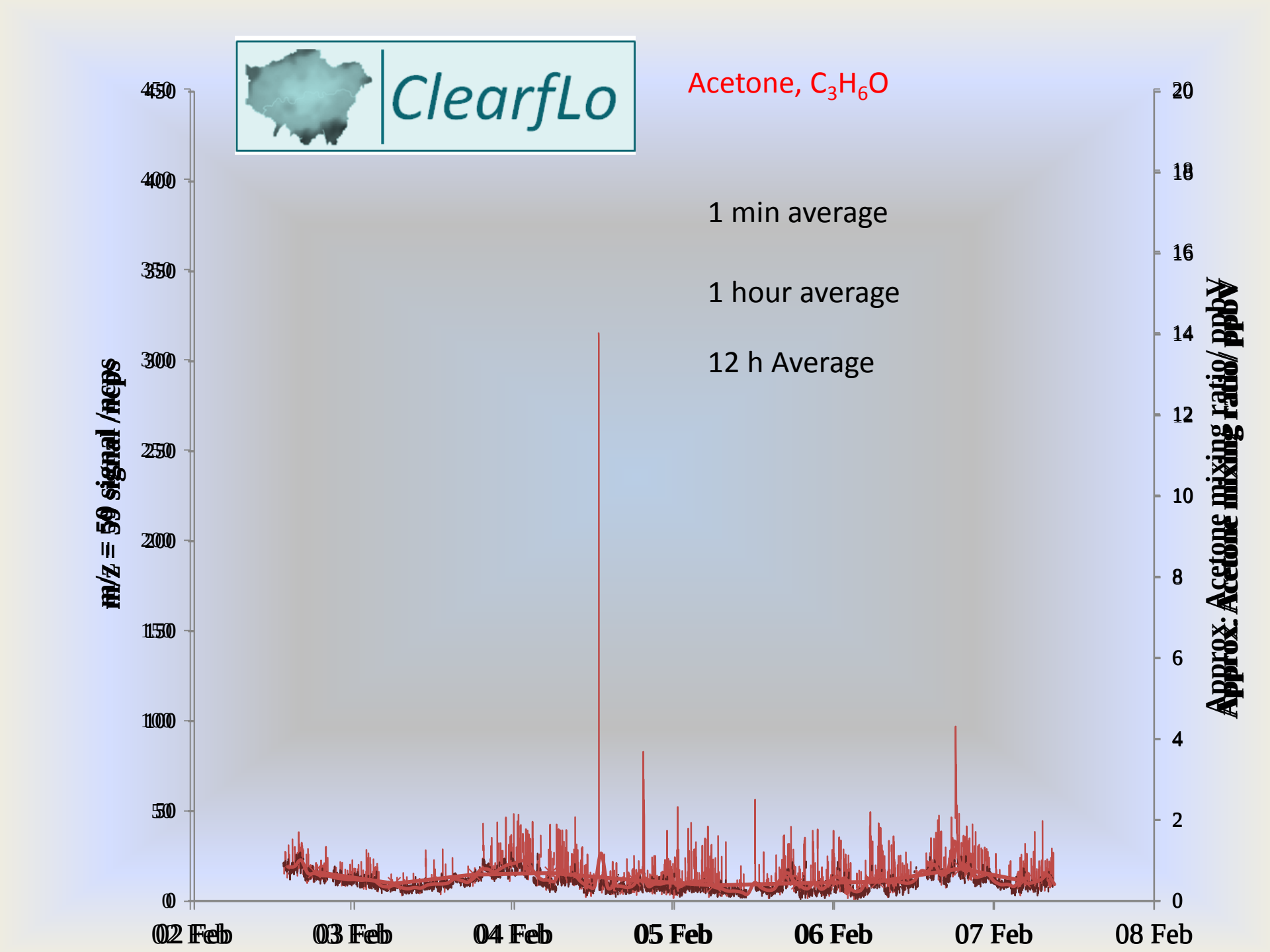
ClearfLo

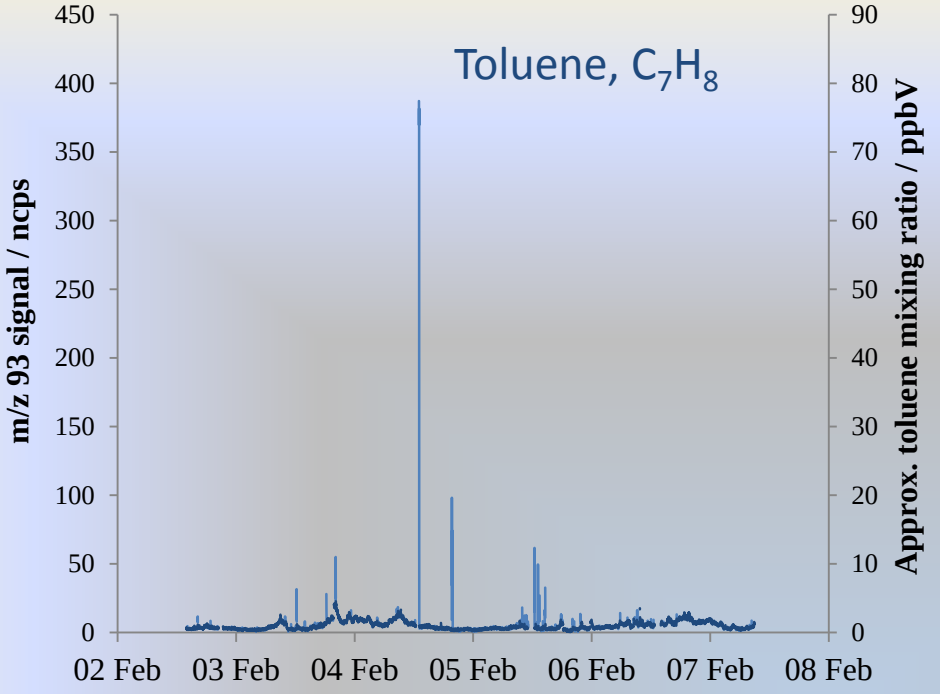
- PTR-ToF-MS deployed in central London as part of the *ClearfLo* project.

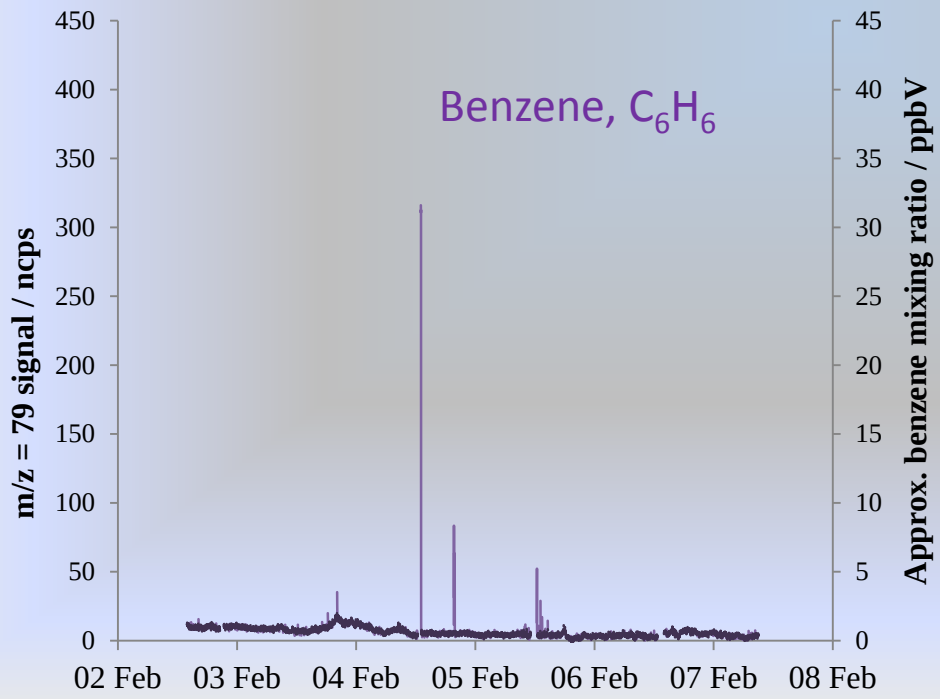
- VOCs measured in near real-time over a 5 week period between January and February 2012



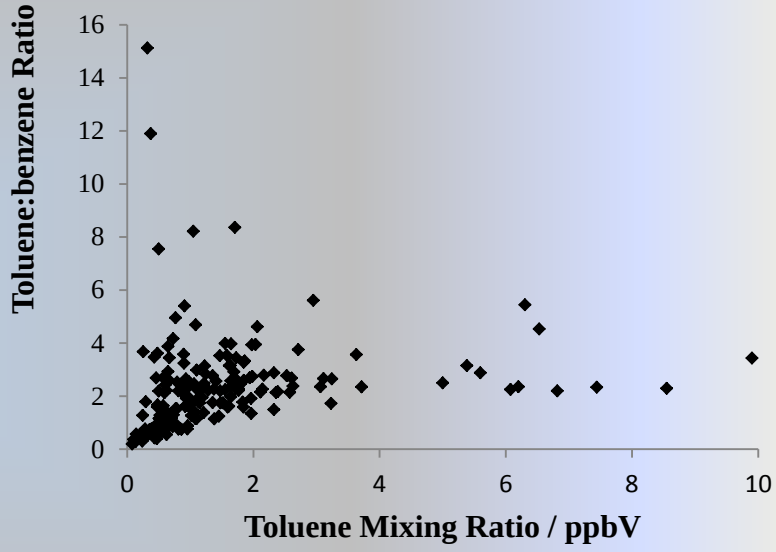



ClearfLo
Acetone, C_3H_6O
1 min average
1 hour average
12 h Average
m/z = 59 signal /ncps
Approx. Acetone mixing ratio/ ppbV
450
400
350
300
250
200
150
100
50
0
20
18
16
14
12
10
8
6
4
2
0
02 Feb
03 Feb
04 Feb
05 Feb
06 Feb
07 Feb
08 Feb


Toluene, C_7H_8
m/z 93 signal / ncps
Approx. toluene mixing ratio / ppbV
0
50
100
150
200
250
300
350
400
450
0
10
20
30
40
50
60
70
80
90
02 Feb
03 Feb
04 Feb
05 Feb
06 Feb
07 Feb
08 Feb

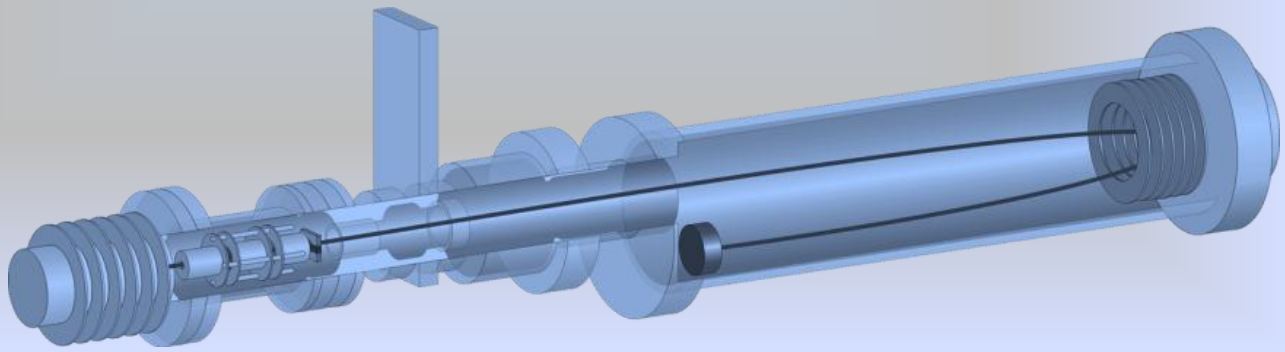

Benzene, C_6H_6
m/z = 79 signal / ncps
Approx. benzene mixing ratio / ppbV
0
50
100
150
200
250
300
350
400
450
0
5
10
15
20
25
30
35
40
45
02 Feb
03 Feb
04 Feb
05 Feb
06 Feb
07 Feb
08 Feb

ClearfLo


Toluene:benzene Ratio
0
2
4
6
8
10
12
14
16
0
2
4
6
8
10
Toluene Mixing Ratio / ppbV

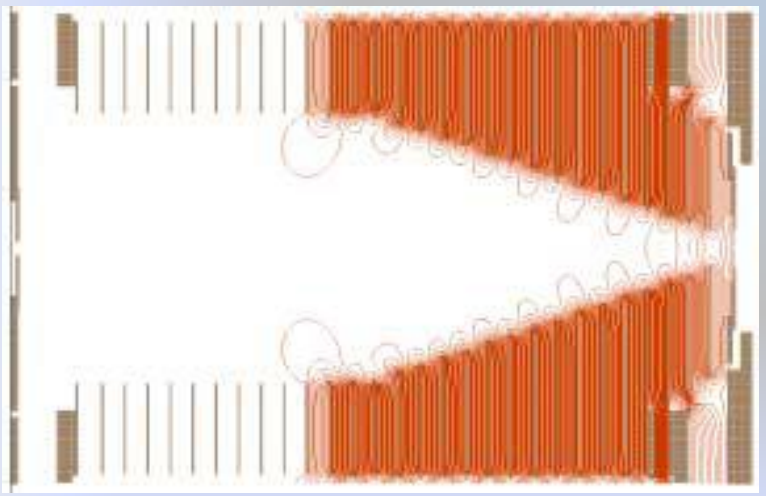
TECHNOLOGICAL DEVELOPMENTS

- The drive for increased sensitivity



RF Funnel

- The funnel consists of a series of ring electrodes where the internal diameter tapers down to an exit
- The RF and DC electric potentials are applied to these electrodes and the ions are ‘guided’ into the flight tube
- 2 orders of magnitude improvement on sensitivity



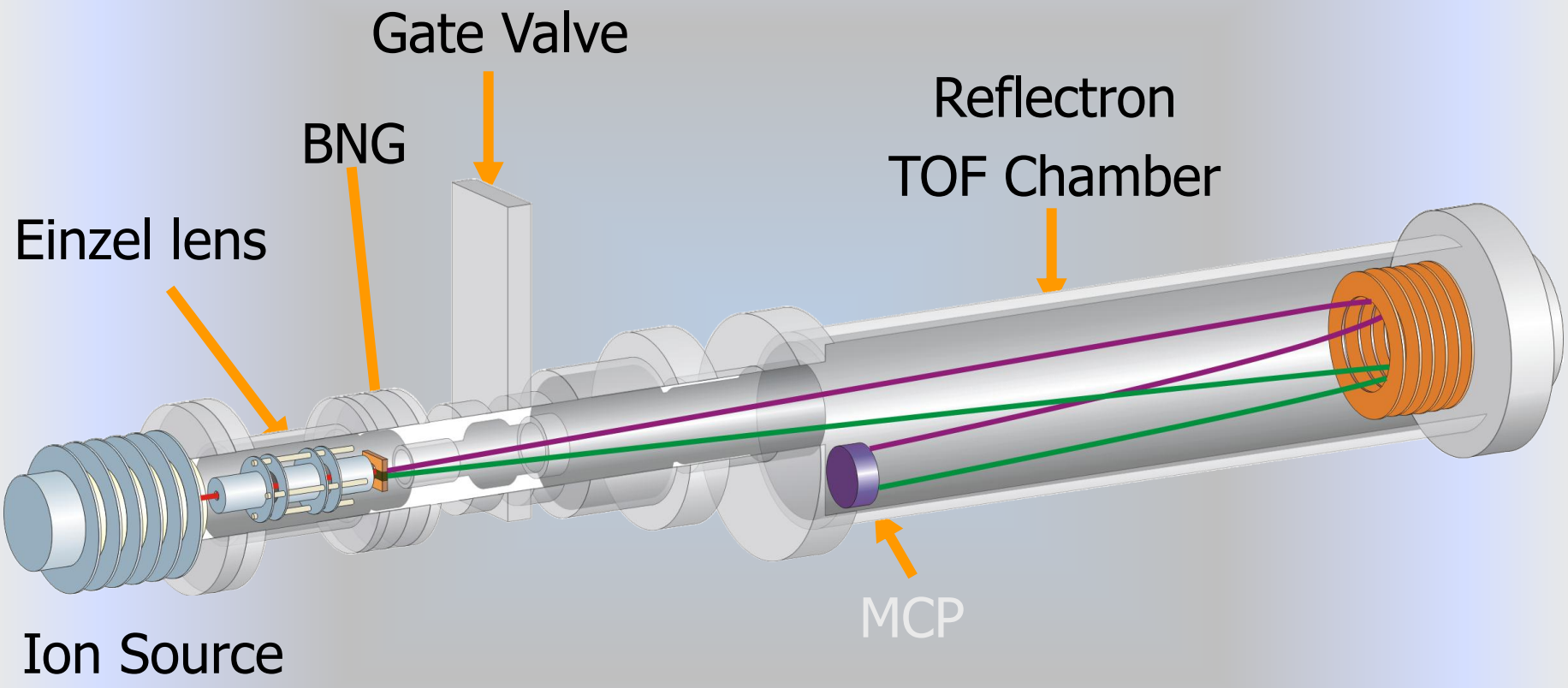
RF component modelled

RF Funnel attached to instrument

Improving the Duty Cycle

- Duty cycle can be improved through the application of a multiplexing technique
- Instead of analysing a single discrete ion packet, we rapidly pulse multiple ion packets into the TOF-MS for analysis, according to a pre-determined sequence
- The instrument subsequently records a superposition of multiple, overlapping time-of-flight spectra
- How can we do this in the TOF-MS?

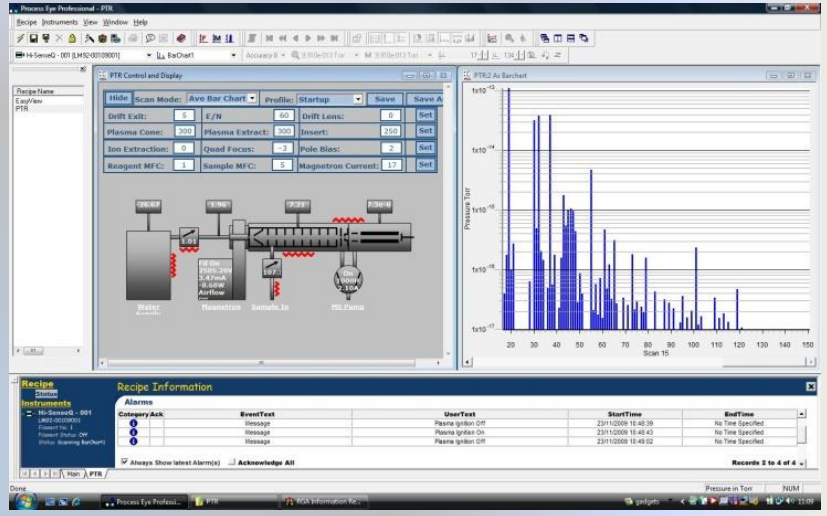
The Instrument

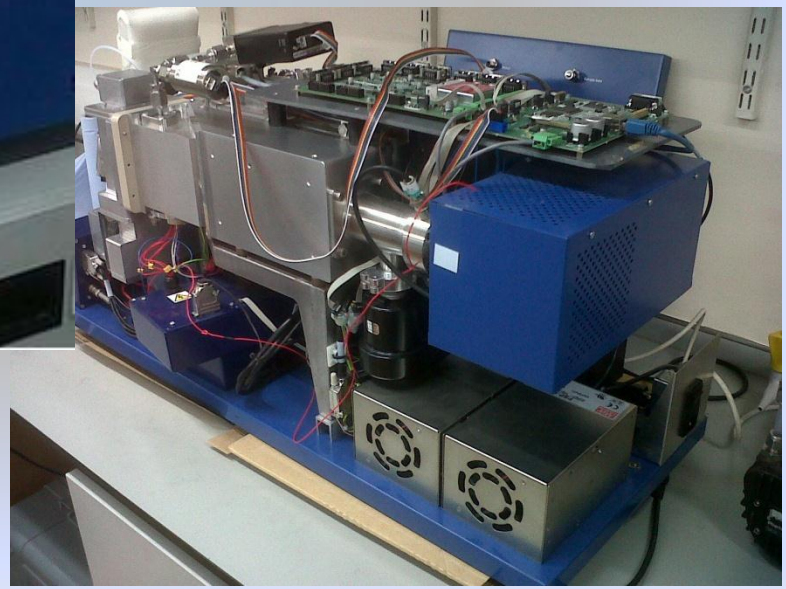


Inside the system

Hi-Sense^{Q}


Hi-Sense^{Q}
Online Trace VOC Analysis


Process Eye Professional - PTR
PTR Control and Display
Recipe Information
Alarms



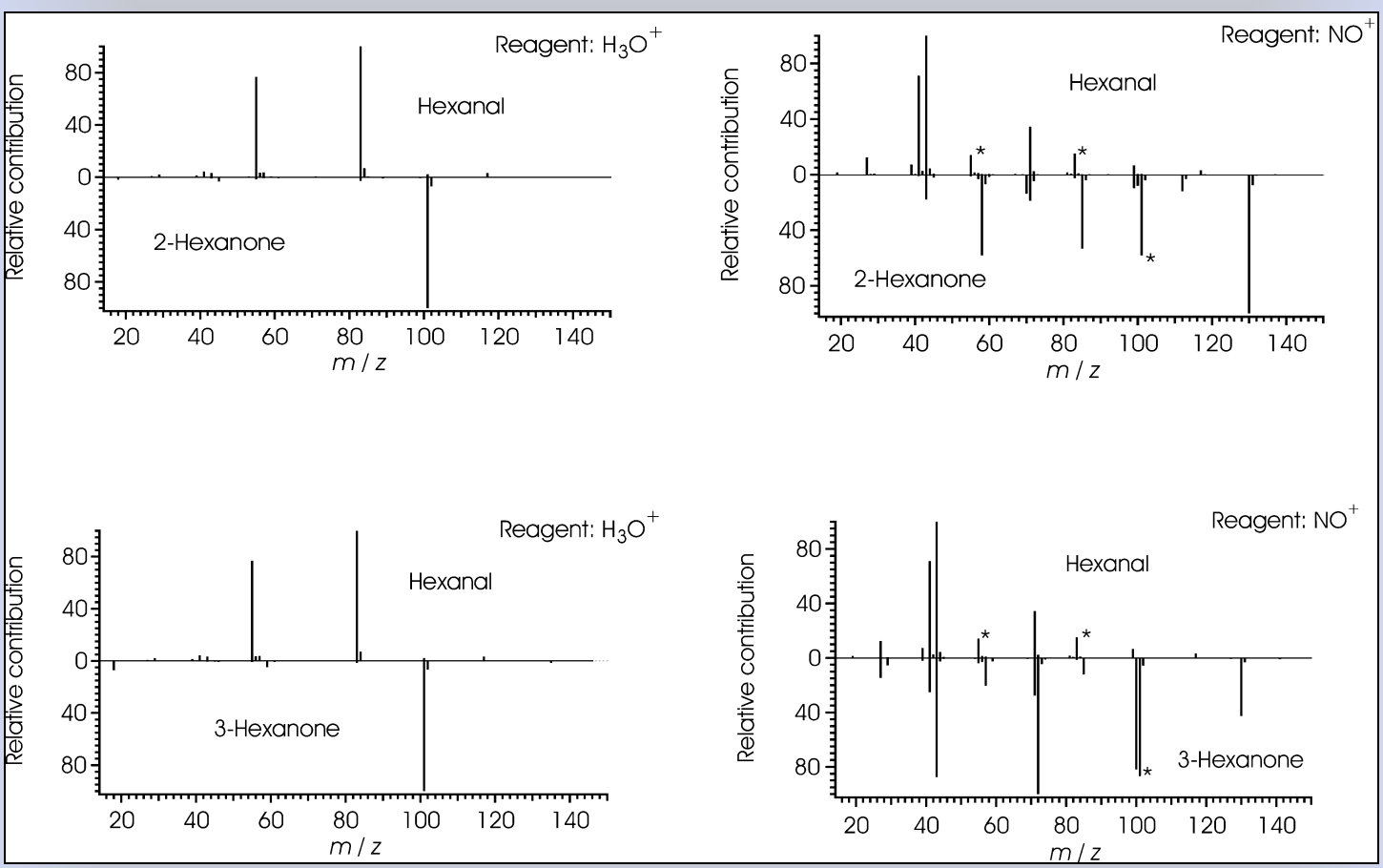
TECHNOLOGICAL DEVELOPMENTS

- Semivolatiles: High temperature PTR-MS
  Trapping technology
  Thermal desorption

Conclusions

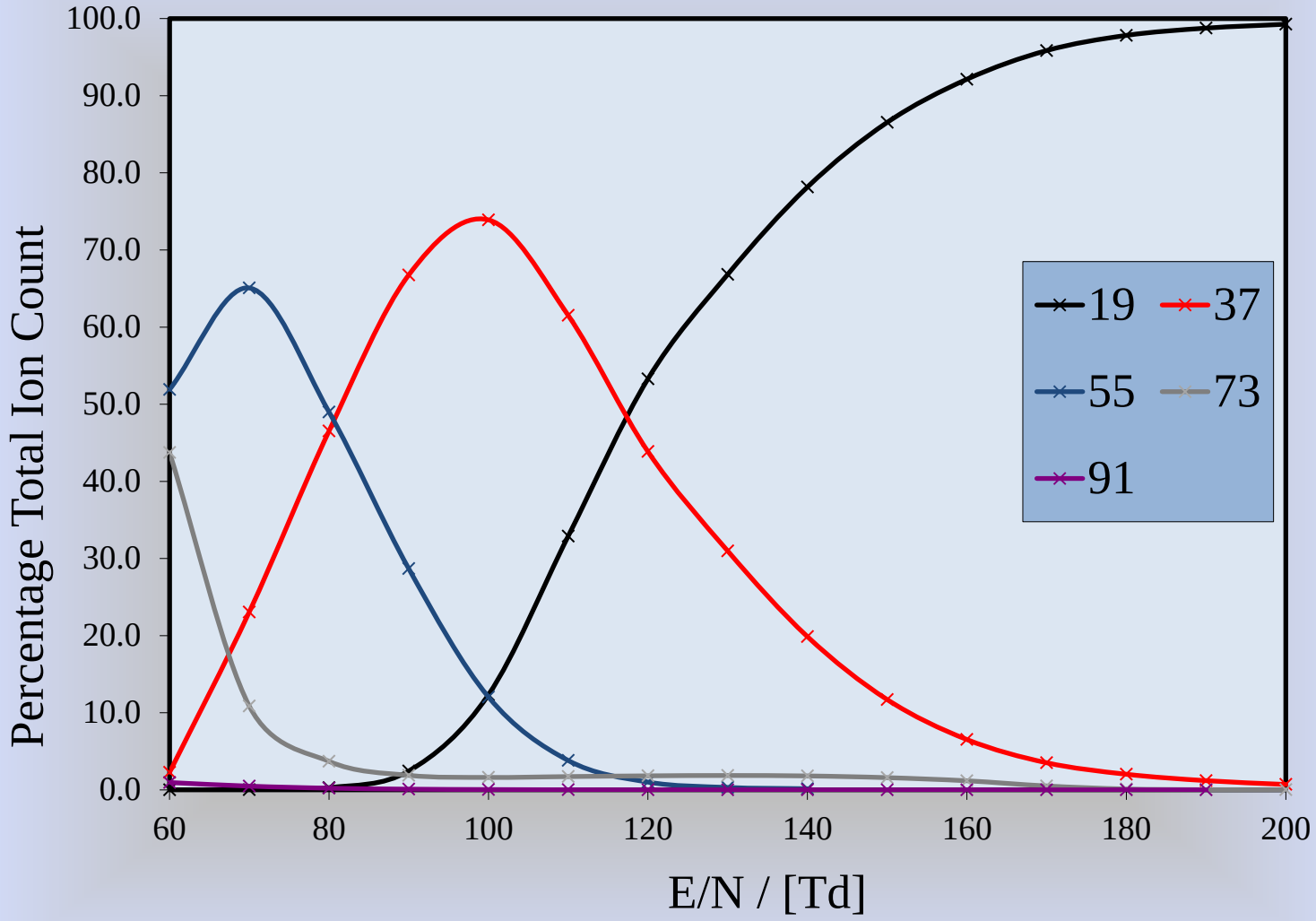
- Developed CIRMS system to measure terpenoids in real time
- Developed statistical methodology to deconvolute complex PTR-MS
- Technology developments
  - Increased sensitivity
  - Semivolatile VOC analysis

Distinguishing isobaric compounds using CIRMS

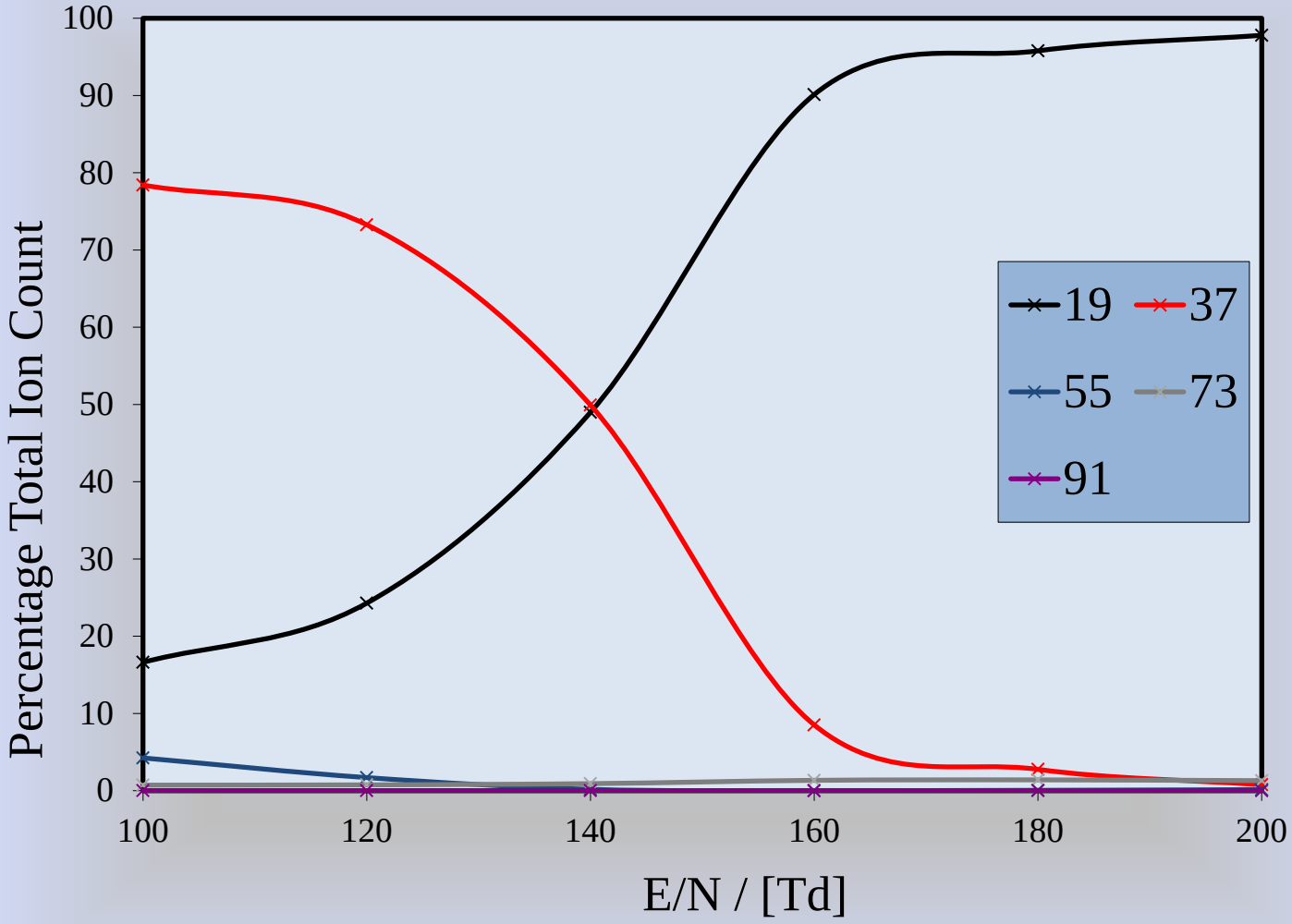


Rapid Comm. Mass Spectrom. 19, 3356 (2005)
Int. J. Mass Spectrom., 254, 85 (2006)

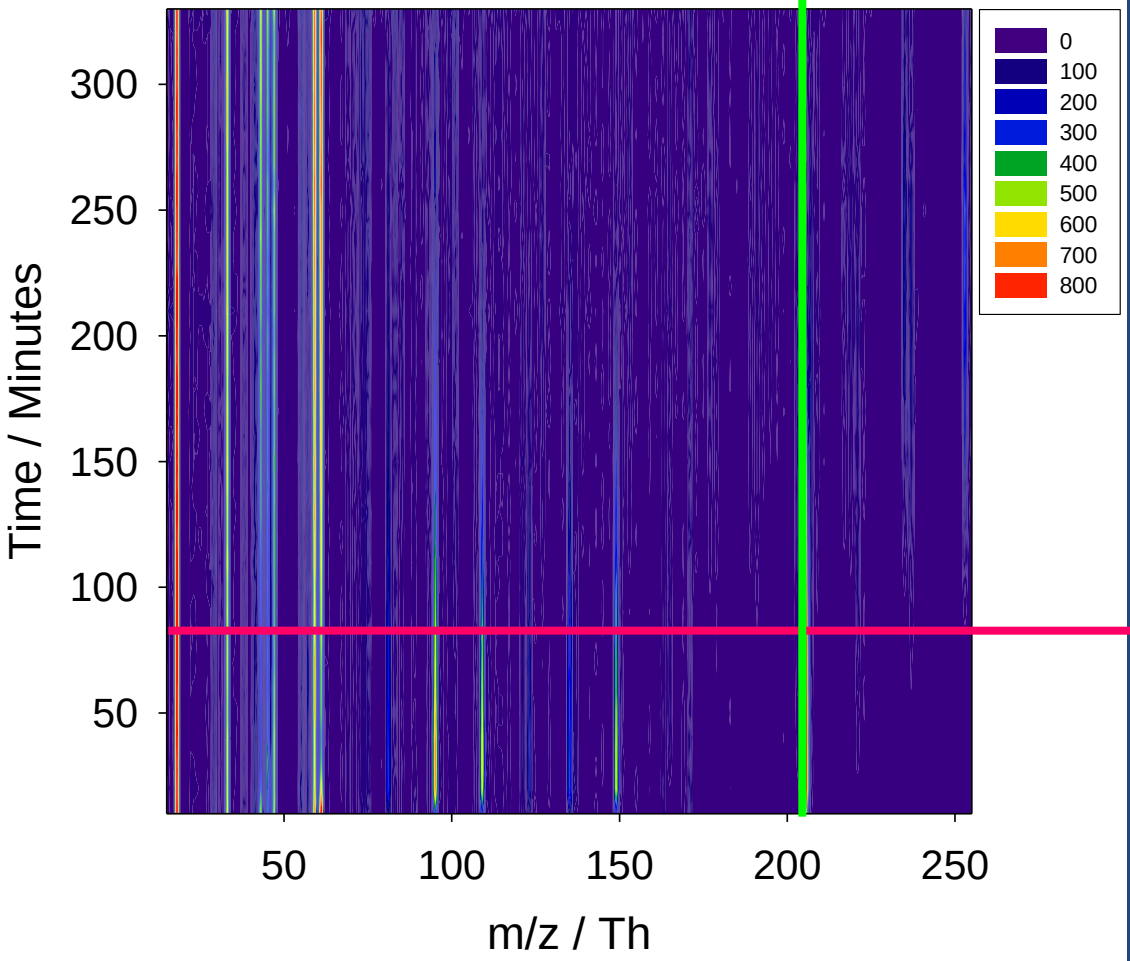
Water clusters vs E/N

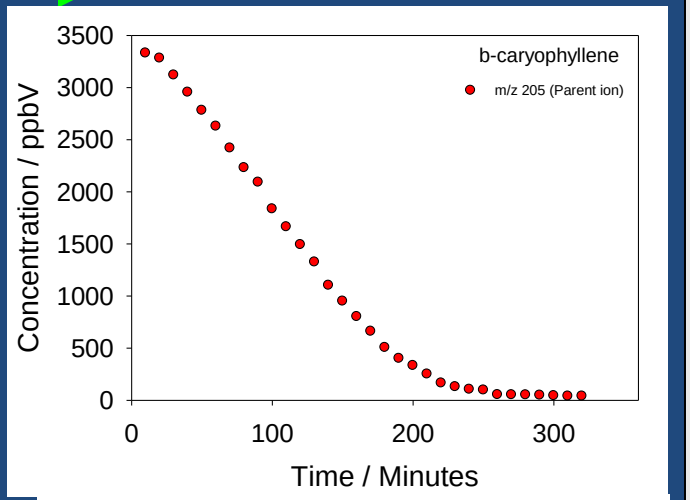


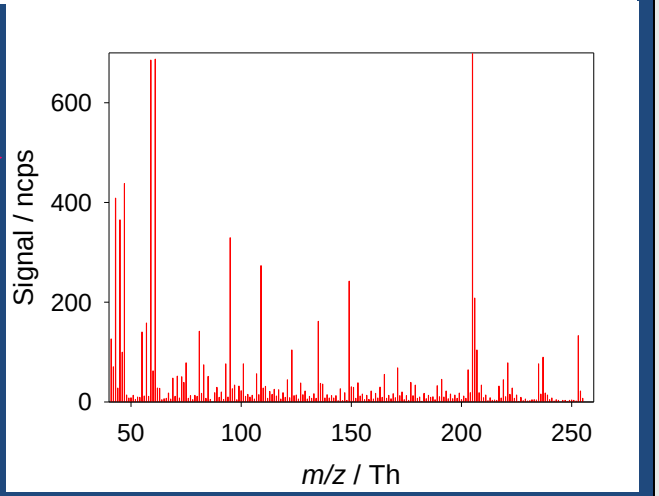
Water clusters with CID



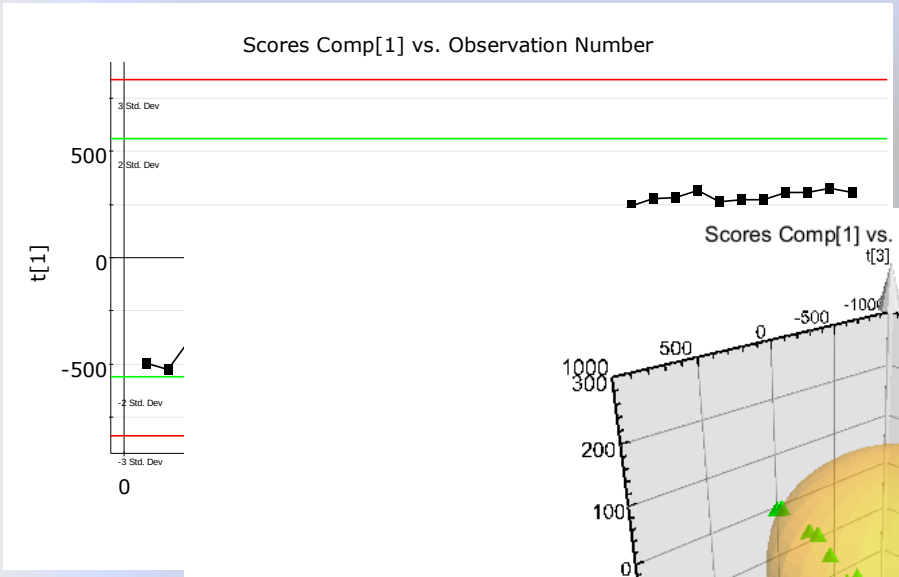
β-caryophyllene Oxidation

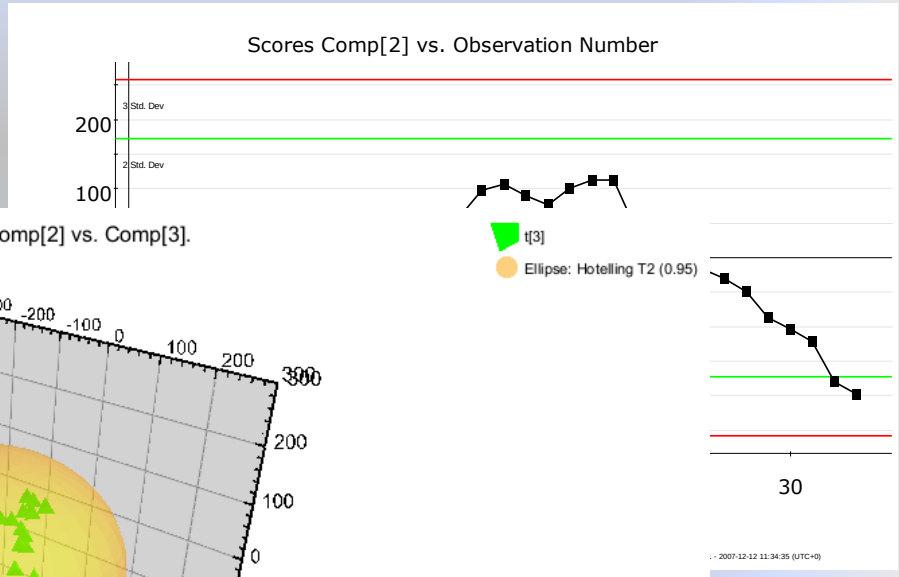


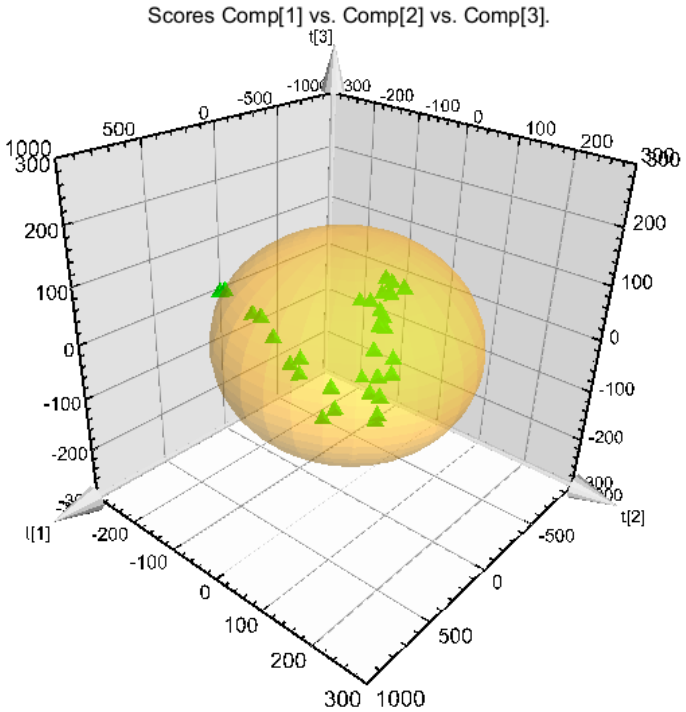


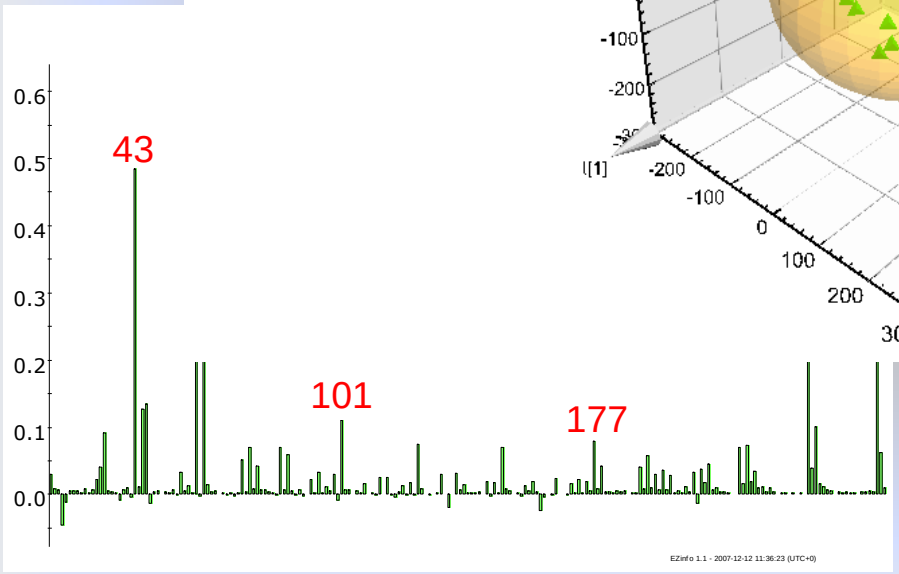


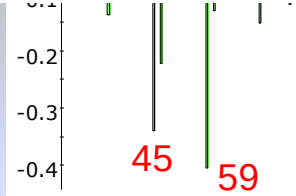
β-caryophyllene PCA

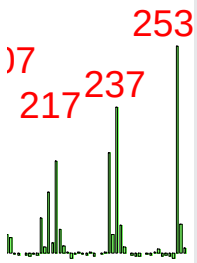












β-caryophyllene Oxidation Products