ToF-CIMS
Reagent ion chemistry &
Data analysis

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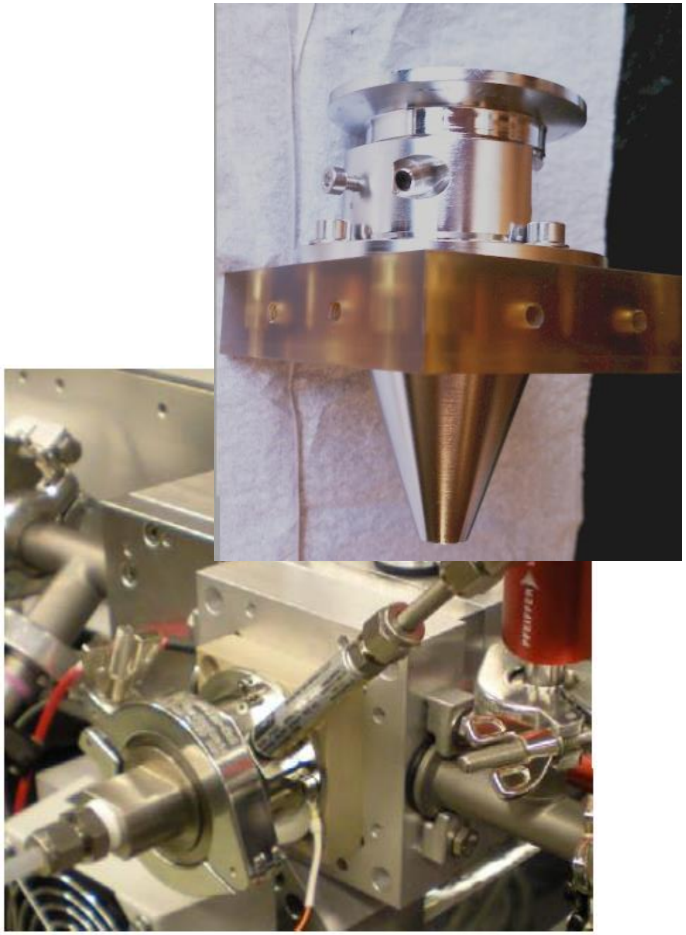
Two different ion sources, easily interchanged



All methods result in hundreds (thousands) of ion signals when sampling organic composition

Low Pressure Flow Tube (IMR)

Reagent: Acetate, I-, H30(H2O)n, …
Fast switching between reagent ions

Atm Pressure Drift Tube

Reagent: Nitrate
Supplied by Airmodus

ToF-CIMS compared to AMS

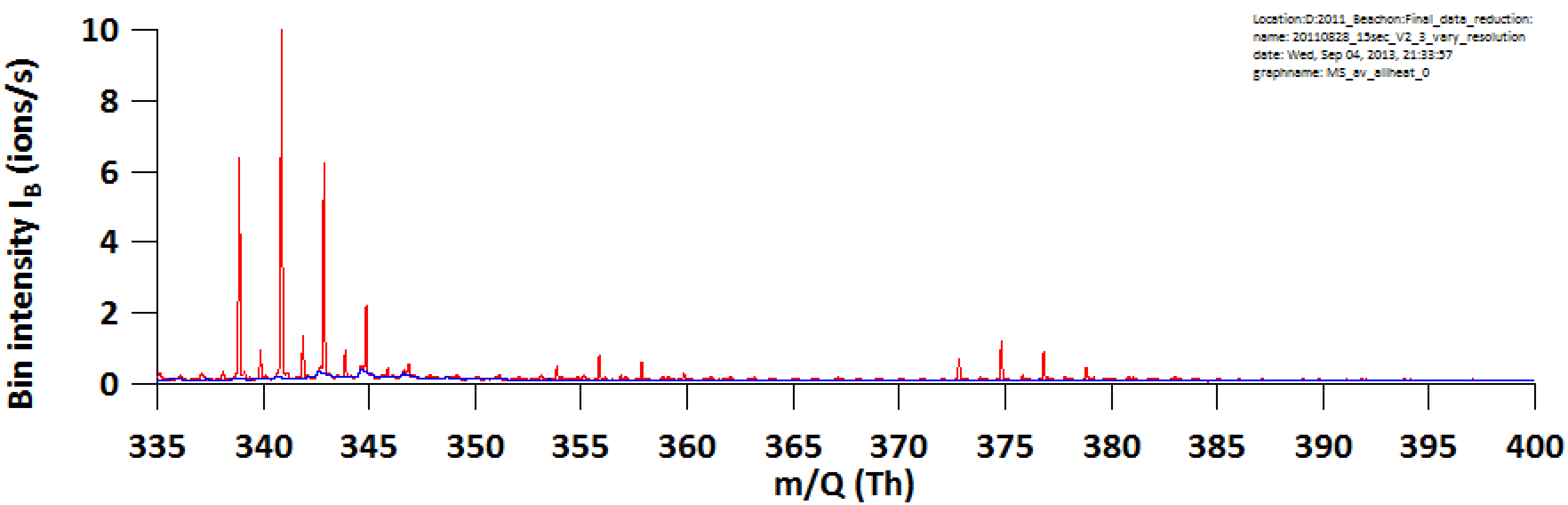
- Entering the well-developed field of CIMS (*~1969)
- Moving towards molecular identification
- Real-time, simultaneous measurements of hundreds (thousands?) of ions (compounds?)
- Measuring gas-phase and aerosol (FIGAERO)
- Opportunity to vary ionization method
- New data analysis tools required
- Use of “m/Q” with unit Thomson (Th) for mass-to-charge ratio

Reagent ions give different chemical views

- Low pressure (10s of mbar) reagent ions
  - Acetate (CH_3COO^-)
    - Proton abstraction $HX + CH_3COO^- \rightarrow X^- + CH_3COO$
    - Specific for acids
  - Iodide (I^-)
    - Clustering (ligand switching): $I^-(H_2O)_x + R \rightarrow I(H_2O)_yR^- + z\ H_2O$
    - Wide sensitivity range to many organics
  - Water-H_3O^+ clusters ($H_3O(H_2O)_x{}^+$)
    - Proton transfer: $H_3O(H_2O)_x{}^+ + RH \rightarrow RH_2{}^+ + (x+1)\ H_2O$
    - Complex chemistry due to clusters
- High pressure (1atm) reagent ion(s)
  - Nitrate (NO_3^-), different ion production hardware (airmodus)
    - Clustering (and proton abstraction) $NO_3(HNO_3)_n{}^- + RO_x \rightarrow (NO_3)RO_x{}^- + n\ HNO_3$; $NO_3(HNO_3)_n + H_2SO_4 \rightarrow HSO_4{}^- + (n+1)\ HNO_3$
    - Sensitive to (highly?) oxidized organics and sulfuric acid

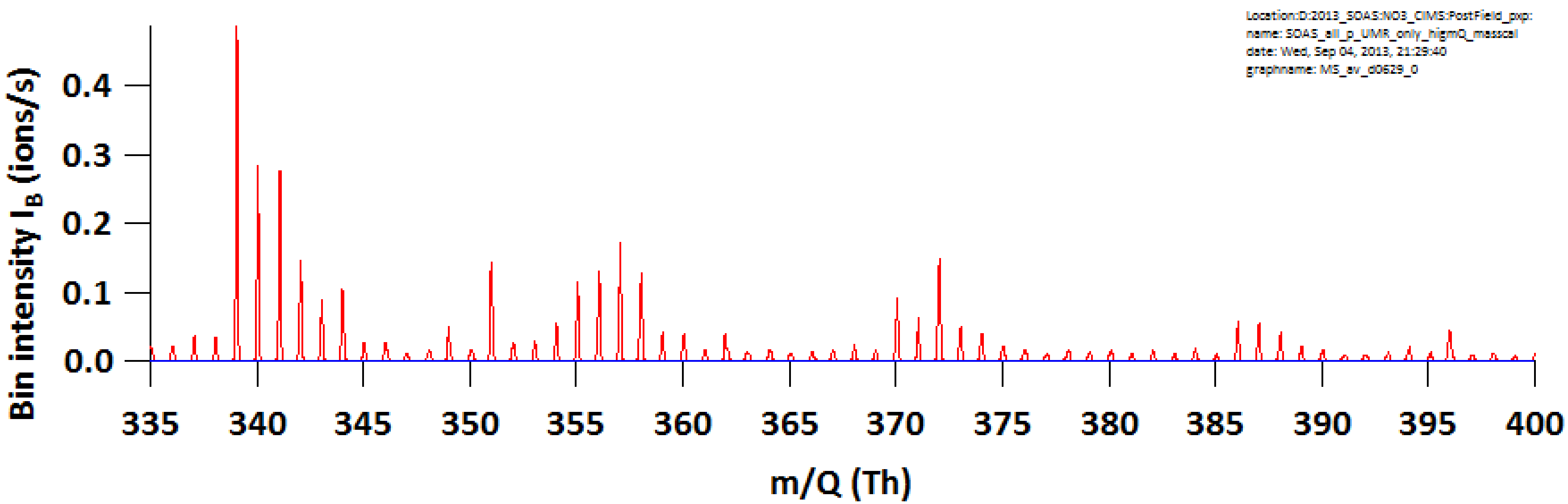
Acetate

- Selective for acids (e.g. HCOOH, HNCO, Pinic acid, ...)
- Demonstrated by Veres&Roberts et al. (2008)
- Fast switch e.g. with iodide possible
- High signal levels at many m/Q up to about 500 Th
- Used with FIGAERO



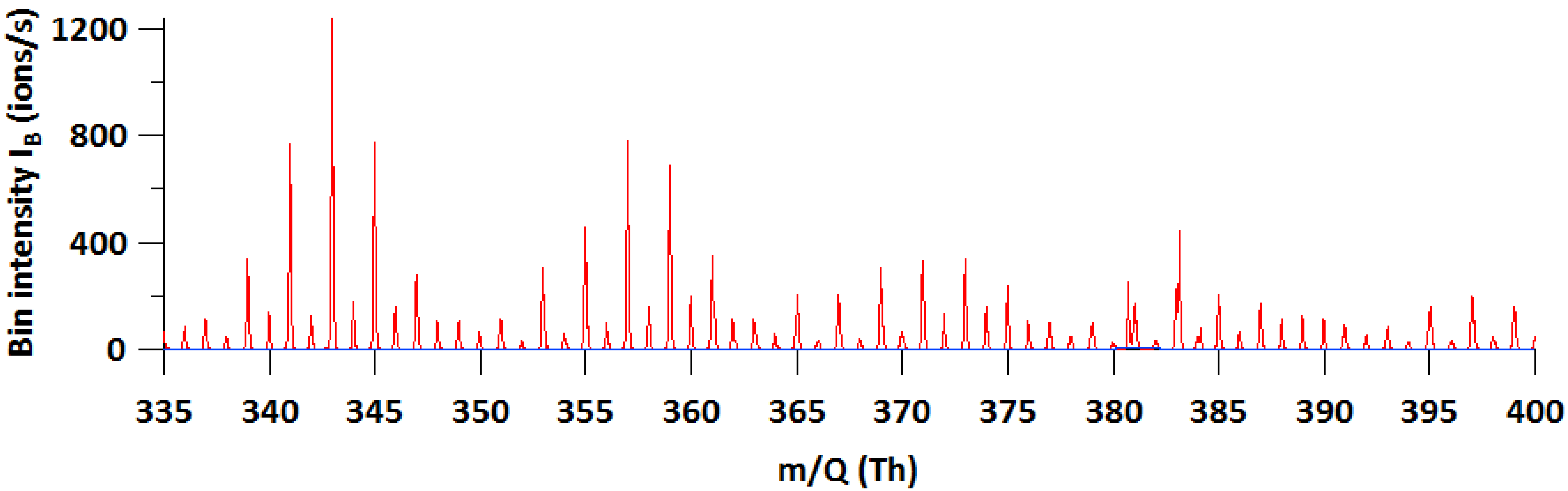
Nitrate

- Selective for highly oxidized organics
- Developed by Eisele (mainly for H_2SO_4, $OH+^{34}SO_2$)
- Coupled to ToF-CIMS by Univ. of Helsinki (Airmodus) for organics
- Sampled at atmospheric pressure
- Sulfuric acid clusters up to 2500 Th
- Organics up to 1200 Th



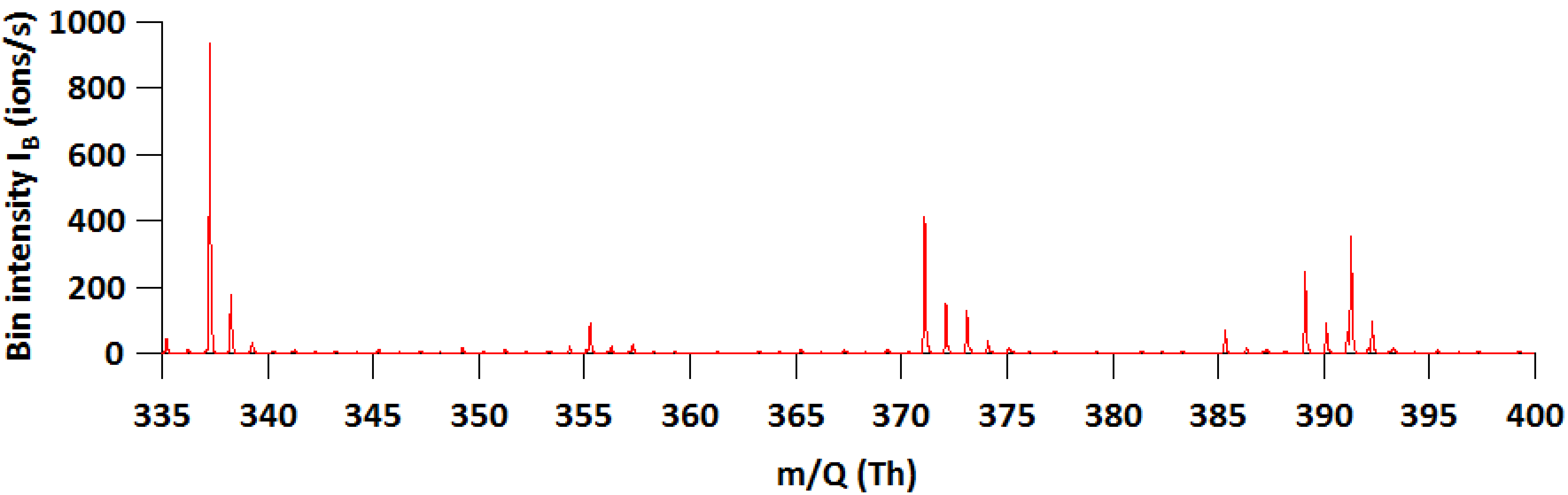
Iodide

- Selective for high polarizability organics
- Fast switching with acetate possible
- Hanson & Ravishankara (1991), Abbatt&Thornton (~2000)
- Used with FIGAERO (see Claudia Mohr's talk)

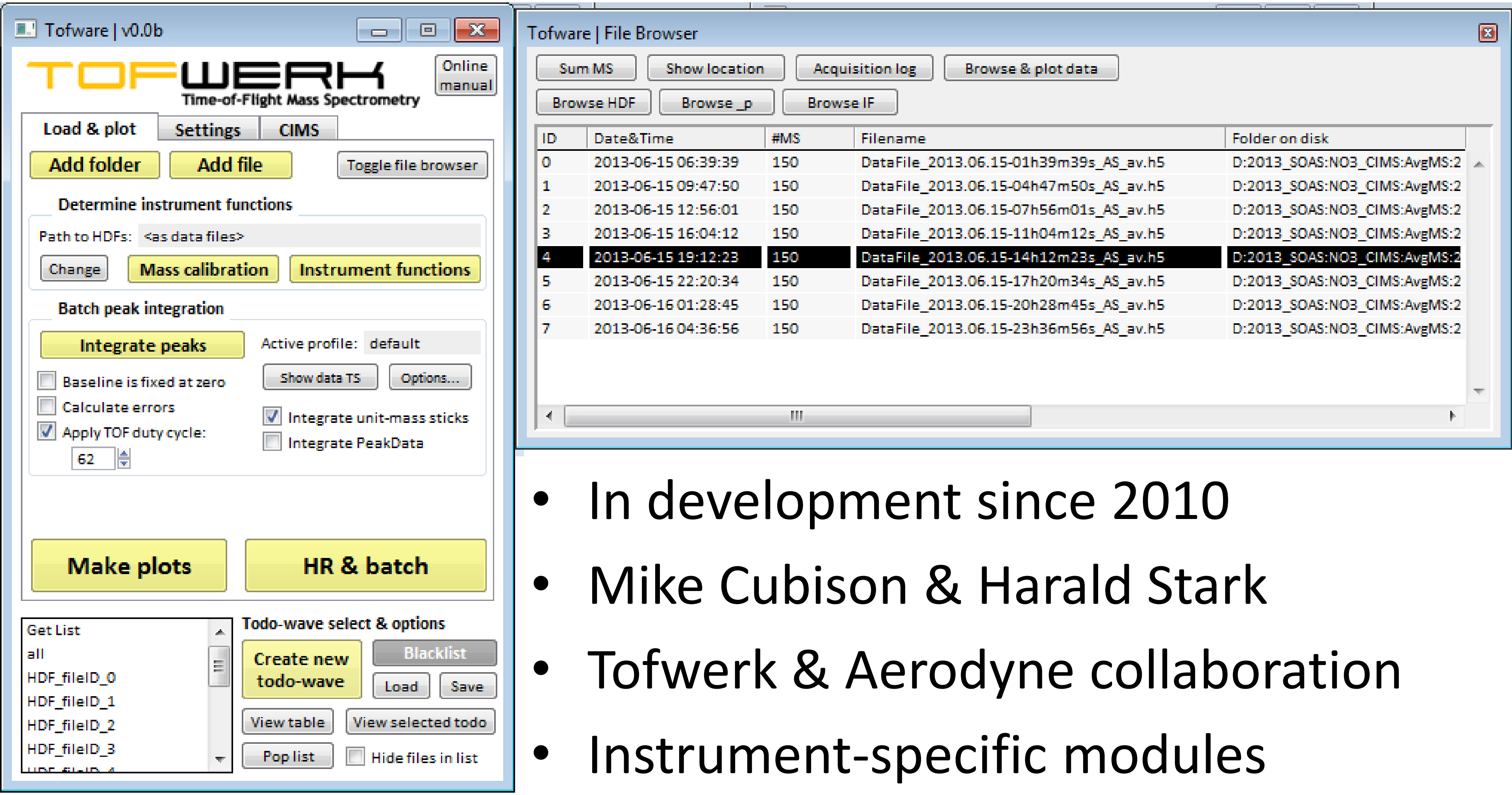


H_3O-Water clusters

- Unclustered H_3O^+: with specially designed drift tube) PTR-MS technique, developed by Lindinger, de Gouw
- Clustered H_3O^+: advanced by Bertram, Thornton, Hildebrandt
- Varying sensitivity due to rel. humidity makes quantitative detection difficult



Data Analysis: Tofware



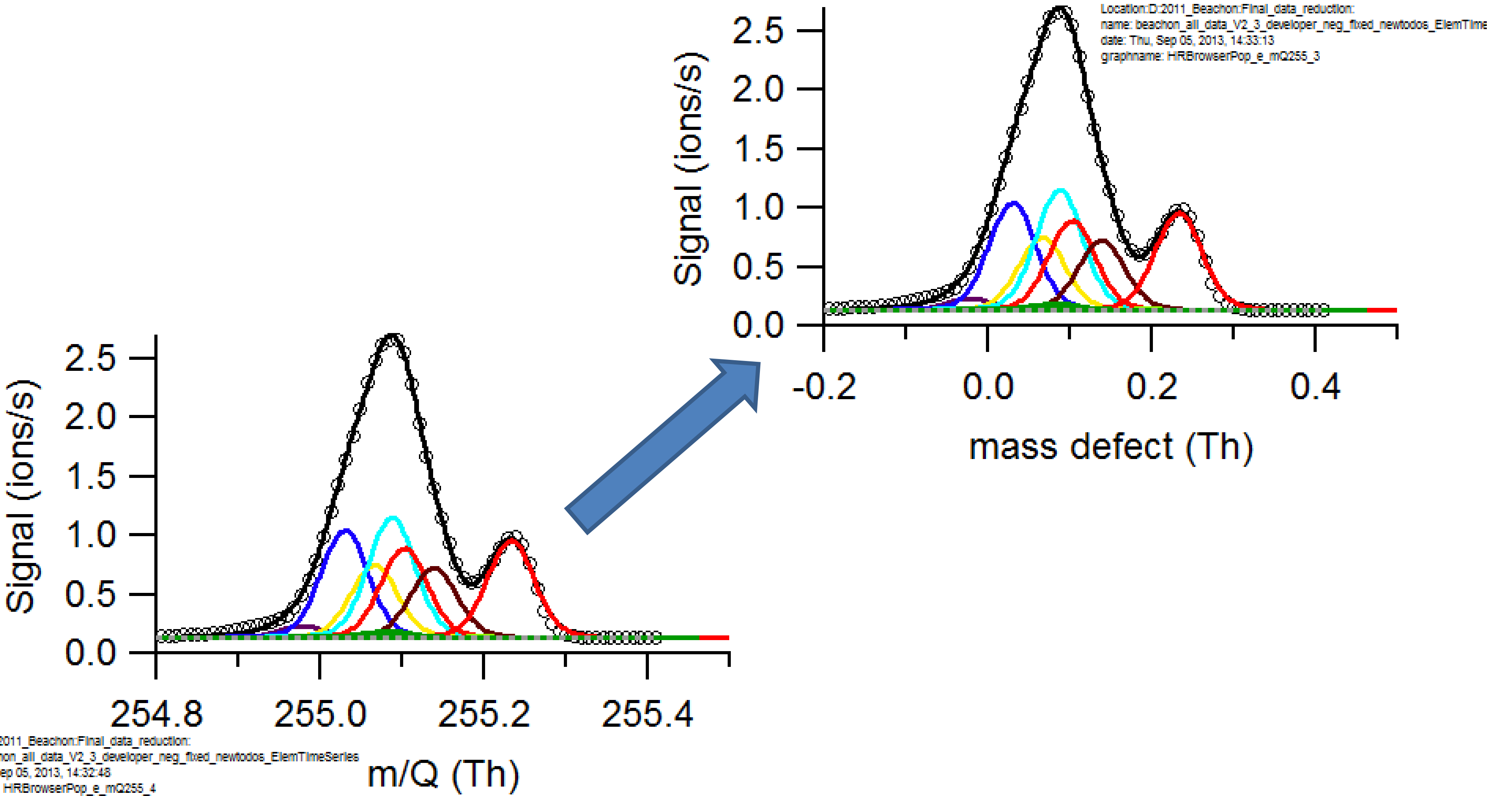
- In development since 2010
- Mike Cubison & Harald Stark
- Tofwerk & Aerodyne collaboration
- Instrument-specific modules
  - CIMS, ACSM, IMS, …
- Advanced diagrams
  - Mass defect (tile), “Kroll”, van Krevelen

SOAS comparison of different reagent ions

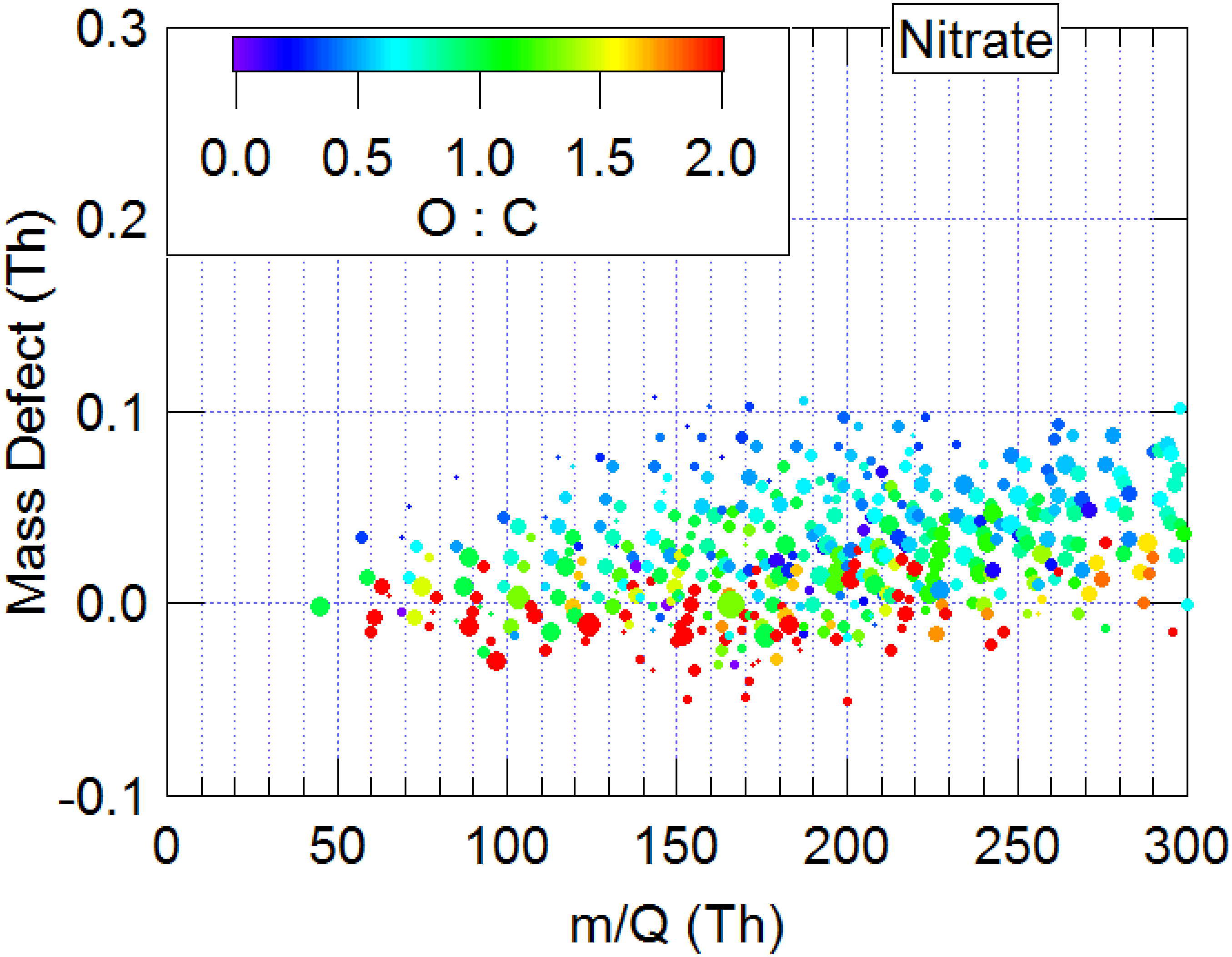
- “Southern Oxidants Aerosol Study”
- June-July, 2013
- Rural Alabama, US
- Biogenic emissions (isoprene) + anthropogenic influence
- Example plots
  - Mass defect
  - Kroll diagram
  - Mass defect tile plot? If time allows…

Mass defect

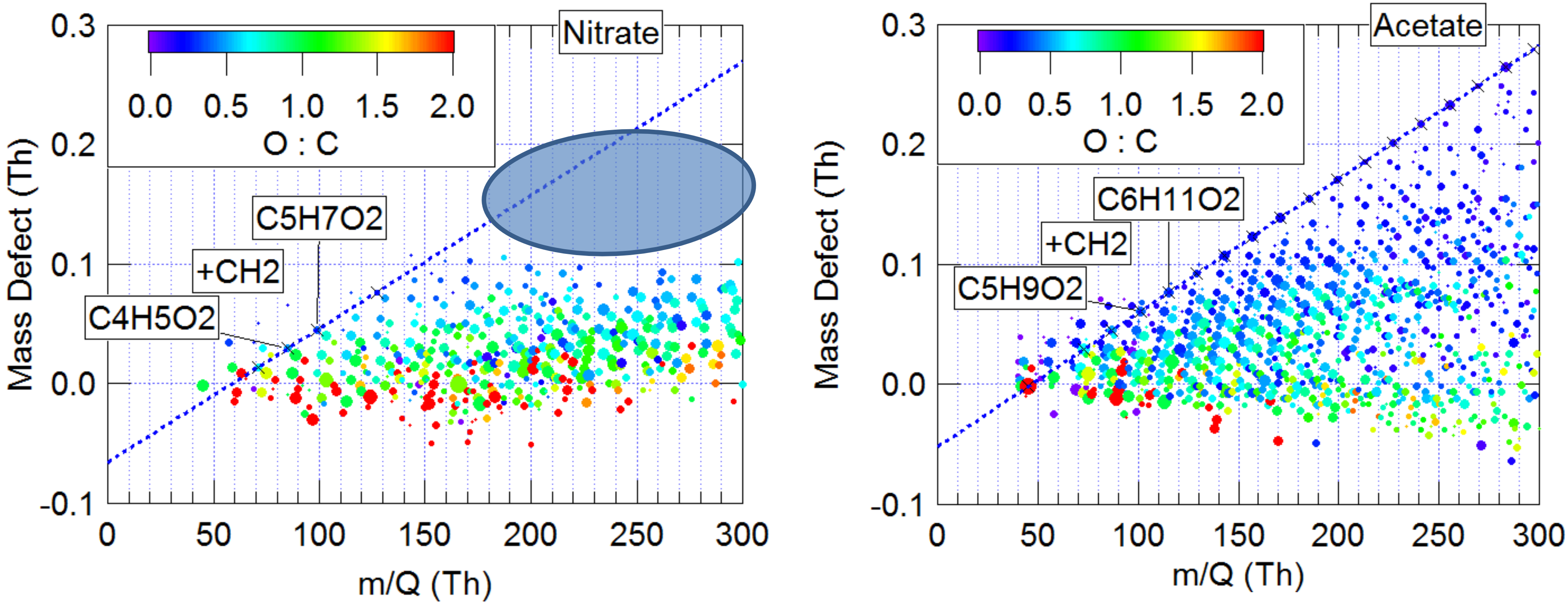
- Mass defect = $m/Q_{exact} - m/Q_{unit}$



Mass defect plots



Mass defect plots

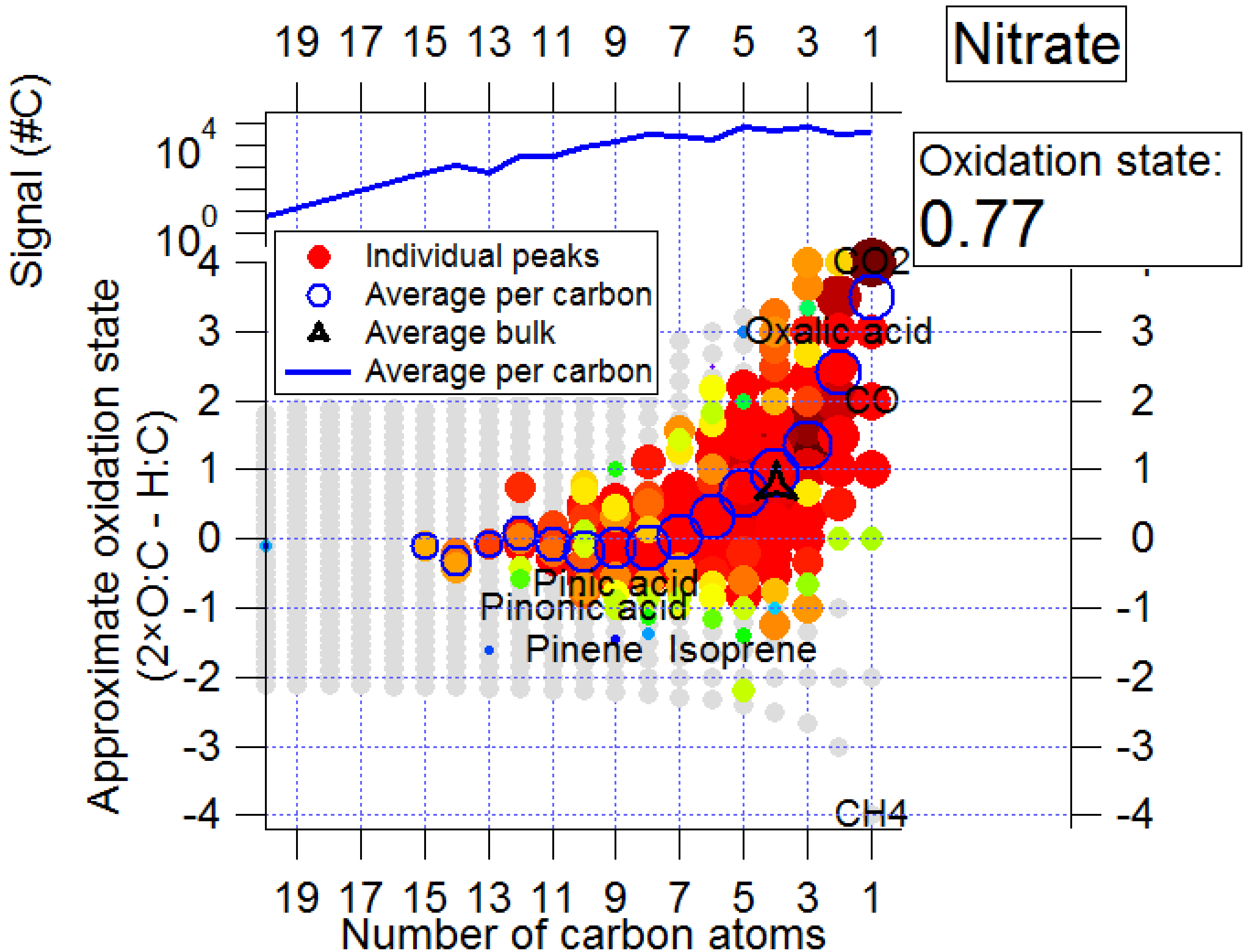


- Nitrate: detects more oxidized compounds
- Slightly lower peak density

Oxidation state

- Approximate oxidation state (carbon):
  - OSC = 2×O:C – H:C (Kroll et al., 2011)
  - Example: $C_4H_8O_6$
    - 2×6:4 – 8:4 = 3-2 = 1

Kroll Diagram (Oxidation State vs. Number of Carbon)



Kroll Diagram (Oxidation State vs. Number of Carbon)

- 2 Kroll diagrams: nitrate and acetate from SOAS
- Nitrate: higher oxidation state & carbon number