Aerodyne’s Chemical Ionization Mass Spectrometers

AMS User Meeting
Lund, Sweden
Aug 24-25, 2019
Chemical Ionization Mass Spectrometry (CIMS)

- “Soft” ionization → Detect parent molecule instead of fragments
- Selective sensitivity to species in contrast to electron ionization
- Range of ionization schemes needed to cover oxidation range of atmospheric organic species

Proton Transfer (PTR-MS), Benzene

Gas-phase VOC emissions

Semi-volatile products

- Acetate and Iodide
- Flow tube IMR Source

Low volatility products

- Nitrate
- (O/C > 0.7, ELVOC)
- Drift Tube Source

Oxidation Level (O/C)
Volatility
Schematic of API TOF MS

Collaboration with Tofwerk
Add an Ion Source to get ‘CIMS’

IONSOURCE

Collaboration with Tofwerk
Flow Tube IMR  
(50 - 500 mbar, Flow Tube, Po-210 or X-ray ionizer, Acetate, H30(H2O)n, I-, Compatible w/ FIGAERO inlet) 
Chemical formulas and volatilities of Gas + Particle phase molecules

Nitrate Source (Jokinen et al., ACP, 2014)  
(1000 mbar, Drift tube, X-ray ionizer, NO3- clusters w/ Analyte, Not compatible w/ FIGAERO)  
• Chemical Formulas of low and extremely low volatility aerosol precursors

Easily Exchange Ion Sources for Different Reagent Ions

Oxidation Level (O/C)

LVOCs

ELVOCs
FIGAERO: Filter Inlet for Gas and Aerosol

Two separate inlets for gas and aerosol sampling,
• Mounts to KF40 flange on IMR source
• Controlled by EyeOn system

Molecular Information & Volatility (Particle and Gas)
The EESI Source

On-line molecular information of particle phase species w/o thermal decomposition

Gallimore and Kalberer 2013

Figure 1. Schematic of the EESI-TOF inlet and ion source, including connection to TOF-MS.

Lopez-Hilfiker et al., Atmos. Meas. Tech. Discuss., 2019
EESI Performance

Lopez-Hilfiker et al., Atmos. Meas. Tech. Discuss., 2019
Vocus PTR-TOF from Aerodyne / Tofwerk

Vocus PTR Reaction Cell
- High ion transmission due to RF focusing
- Efficient sample introduction
- Extremely bright reagent ion source

Same field-proven API-TOF platform as ToF-CIMS

*Not interchangeable with IMR and Nitrate

Tofware data analysis software

Particle Phase Species w/ Vocus PTR

* VIA – Vocus Interface for Aerosol sampling (Denuder + Heated inlet for evaporating aerosols)
PTR ionization depends on proton affinity

\[
\begin{align*}
\text{H}_3\text{O}^+ + M & \rightarrow \text{MH}^+ + \text{H}_2\text{O} \\
\text{(H}_2\text{O})\text{H}^+ + M & \rightarrow \text{MH}^+ + 2\text{H}_2\text{O}
\end{align*}
\]

- **Transfer proton to** \( M \)
- **Detect** \( \text{MH}^+ \)
- **Reaction occurs** if \( M \) has higher proton affinity than reagent ion \([\text{H}_3\text{O}^+ \text{ or (H}_2\text{O})\text{H}_3\text{O}^+]\)
- **Exothermic and fast for**
  - Most alkenes
  - Aromatics
  - Most functional groups
Highest Available PTR-MS Sensitivity and Resolution

1-sec LOD: 5 to 10 ppt
1-min LODs: < 1 ppt
Sensitivity to wide range of chemical species

Example: α-Pinene Ozonolysis products

Riva et al., AMT, 2019
ARI Modular GC system
lightweight, compact and customizable.

Adaptable to:
• EI-TOF MS
• Vocus PTR-TOF MS
• CI-ToF-MS
• Other detectors

Max. heating rate: 130 C/min
Max cooling rate: 190 C/min
Size: 55H x 55W x 30D (cm)
Weight: 24 kg (52 lbs)
Power: ~250W
Vocus mass spectrum at m/Q 69, shows four separate peaks.

C$_5$H$_9^+$ is 6 different isomers

Chromatographic retention time separates the compounds

Brian Lerner, Megan Claflin, Joost de Gouw
IMS-TOF

- Ion mobility spectrometer (IMS) + API-TOF
- IMS separates ions by collision cross section (CCS)
  - 2D separation increases peak capacity and improved identification
  - Isomer Resolution
- Optional collision induced dissociation (CID) for structural analysis

Beyond Molecular Formulas

Krechmer et al., AMT, 2016
Zhang, X. et al., ACP, 2016
Applications: Lab Photooxidation of 1,3,5 TMB
Applications: Source Apportionment

AMS

EESI: Increased information about SOA

Stefenelli et al., ACP, 2019
Applications: Mass Accommodation

$\alpha$ for dihydroxynitrates (DHNs), trihydroxynitrates (THNs), and carbonyl dihydroxynitrates (CDHNs).

Near-unity mass accommodation coefficients during G/P partitioning for representative types of aerosol that is at atmospherically relevant mass loadings (several to tens of $\mu$g m$^{-3}$).
Aerodyne ToF-CIMS

More than 90 instruments worldwide
US, Europe, Asia
Lab, ground sites, aircraft, research vessels
100+ publications

Diverse applications
Sensitive, high resolution mass spectrometer (HTOF or LTOF)
Standard Inlet -> Real-time trace gas measurement
Change Ion chemistry -> Different classes of compounds
  Vocus PTR -> sub ppt VOCs
FIGAERO Inlet -> Simultaneous aerosol and gas-phase
EESI Ion source -> Molecular Aerosol Analysis
Modular GC, IMS -> Isomer separation and molecular identification

Advanced analysis software
“Tofware” led by Harald Stark

Collaborative user community
60+ attendees at 2019 ToF-CIMS users meeting in Boulder
Acknowledgements:

Jordan Krechmer, Francesca Majluf, Phil Croteau, Andy Lambe, Harald Stark
Brian Lerner, Megan Claflin
John Jayne, Doug Worsnop

Thank you for your attention!