IMS-MS for on- and offline analysis of atmospheric gas and aerosol compounds


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Background

- Ion Source (ESI, CI)
- TOF

**IMS**

- Add in pre-separation of ions BEFORE they enter TOF
- Provide more chemical information about ions than possible with TOF alone

NOTE: Analogous to if you had LC or GC before TOF, but IMS-TOF has many advantages over these techniques
Chemical Ionization + Ion Mobility Spectrometry (CI-IMS-TOF)

- Ions move through electric field while colliding with buffer gas (pressure = 1 atm)
- Separates ions according to differences in ion mobility

W.C. Röntgen, Nature v. 53, p. 274 (1895)
**Ion Mobility Time of Flight Mass Spectrometry (IMS-TOF)**

### TOF-MS
- Mass accuracy ~ 2-7 ppm
- Resolution > 4000

### Low field Drift Tube
- \( P = 1 \text{ atm} \)
- \( T = 50 – 150 \text{ °C} \)
- Resolution > 100

### Multiplexing

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**Diagram:**
- Pressure-controlled enclosure
- Interface
- ESI Source
- Desolvation Region
- Ion Gate
- IMS Drift Tube
- Extractor
- Detector
- 10\(^{-6}\) mbar
- Reflector TOF
1) Pulse of ions into the drift tube to set $t=0$ is multiplexed (high sensitivity)

2) Drift tube operated at atmospheric pressure (<150 ms drift times)

Resolution $= \frac{t}{\Delta t}$

(resolution of 150 compared to typical low pressure values of 40)
**Ion separation Mechanism**

- Based on Mass to Charge Ratio

  ![Flight Path](image)

  \[ t = \frac{L}{\sqrt{2U}} \sqrt{\frac{m}{q}} \]

- Based on Collision Cross Section

  ![Electric Field](image)

  \[ t = \frac{L^2}{KU} \]
Ion Mobility: what

Mobility depends on the ion and the drift gas.

Each ion/gas combination gives a characteristic mobility:

\[ \Omega = \frac{3ze}{16N} \left( \frac{2\pi}{k_B \mu T} \right)^{1/2} \frac{1}{K} \]

Cross section derived from measured mobility

Measured mobilities calibrated against standards
2D IMS spectrum
IMS separation of Isomers

2 uM peptides
m/z = 490.47
IMS separation of Isomers

IMS separation of Isobars and Isomers (CI-IMS)

CIMS Molecular-level identification limited by Isomeric and Isobaric species

$m/z$ 310

$m/z$ 339

HOMs in ambient environment (SOAS 2013)

Time-resolved isomer trends (CI-IMS)

Ambient environment (SOAS 2013)
Collision Induced Dissociation

• Increase kinetic energy of ions exiting drift tube such that bonds within ion are broken during ion-molecule collisions with buffer gas in interface region.

• Parent and fragment ions have same drift time (Advantage over MS/MS)
CID for molecular structure (ESI-IMS)

sulfate ester of 2-methylglyeric acid

CID for detecting oligomers (ESI-IMS)
2D Trends for biomolecules

From Ion Mobility Mass Spectrometry, By Eiceman and Karpas
2D Trends for small molecules

Clear separation in space according to molecular functionality

Conclusions

- IMS-MS provides 2D (cross section vs. \( m/z \)) characterization of chemical composition.
- Can be used for gas (CIMS) and particle (ESI) characterization. Demonstrated for ambient real-time operation.
- Separates isobaric and isomeric species that correspond to an elemental formula.
- CID allows for identification of molecules and for detection of oligomers.
- Species with different chemical functionalities separate from each other in 2D space.
Thank you for listening!

References with more information


- Zhang X. et al., Highly Oxygenated Multifunctional Compounds in α-pinene Secondary Organic Aerosol, Env. Science and Technology, 2017