Characterization of Organic Aerosol Using Electrospray Ionization Coupled to Ion Mobility Spectrometry High-Resolution Time-of-Flight Mass Spectrometry (ESI-IMS-HR-TOFMS)

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Motivation for Study

• ~10–30% of total organic aerosol mass is identified at the molecular level with existing techniques (e.g., GC/MS or LC/MS) [Hallquist et al., 2009]

• Existing methods typically limited in ability to resolve exact species in WSOC fraction – contribute greatly to OA mass [Weber et al., 2007]

• Molecular-level characterization requires filter/impactor collection & preparative steps (e.g., derivatization) – poor time resolution & costly

• **Goal of Work:** Assess separation & identification capabilities of ESI-IMS-HRTOFMS by re-analyzing archived laboratory-generated & ambient aerosol samples that have been chemically characterized with existing techniques (i.e., LC/MS) – potential alternative online technique
ESI-IMS-HRTOFMS: Multidimensional Separations

Current Instrument Configuration:

- Parent ions produced by ESI separated in IMS – rather than by GC or LC – before MS
- IMS separates ions by their size/charge ratios and interactions with buffer gas ($N_2$) – millisecond timescales
- Alternative buffer gases easily interchangeable with ambient IMS – similar to changing type of LC column
- Voltages at skimmer electrode can be increased (1 to 20 V) to fragment mobility-separated ions – MS/MS analyses
- HRTOFMS same as in Aerodyne ToF-AMS and chemical ionization TOFMS instruments – sufficient mass resolution/accuracy for elemental composition info.
LC/ESI-MS Analysis of Summer 2010 PM$_{2.5}$ from Yorkville, GA

Base Peak Chromatogram (BPC) – Negative Ion Mode, [M – H]$^-$:

- **Sulfate:** $m/z$ 97
- **Isoprene SOA:** $m/z$ 215, 139, 260
- **Monoterpene SOA:** $m/z$ 157, 183, 187, 255, 281, 294

Isoprene-derived SOA constituents contributes significantly to OA mass fraction (~12-33%):

* See Sri Hapsari Budisulistiorini [Thursday, 9SA.2]
* See Ying-Hsuan Lin [Friday, 11RA.1]
ESI-IMS-HR-TOFMS Analysis: Yorkville, GA PM$_{2.5}$

- Ions separated by drift time (mobility)
- Same ions observed by LC/MS, but many more ions are now resolved
- $m/z$ 215 also most abundant signal
ESI-IMS-HR-TOFMS Analysis: Yorkville, GA PM$_{2.5}$

2D-Plot:

At 1 m/z several isomers/isobars are resolved in drift time.

Trendlines could be used for helping to resolve certain organic classes [Kanu et al., 2008]
LC/ESI-MS Has Difficulty Resolving WSOC Species

Summer 2010 PM$_{2.5}$ from Yorkville, GA:
Another Example of LC/ESI-MS Having Difficulty in Resolving WSOC Species

Toluene SOA Generated under High-NO$_x$ Conditions:
ESI-IMS-HRTOFMS Can Resolve WSOC Fraction

WSOC species separated on millisecond timescales – none of the ions have exact same drift indicating likely not ESI clusters
Example of Isomer Separation for WSOC Fraction Using ESI-IMS-HR-TOFMS

$m/z$ 215 (i.e., IEPOX-derived Organosulfates):

Yorkville, GA PM$_{2.5}$
Example of Tandem MS (MS/MS) Analysis

PM$_{2.5}$ from Yorkville, GA:

Fragment-ion (MS/MS) spectra for individual compounds in mixture are separated in 2D spectra by drift times of parent ions.
Conclusions and Implications

• Advantages of ESI-IMS-HR-TOFMS:
  - Separation of isomeric & isobaric species
  - Improved chromatographic resolution relative to LC
  - Identification of WSOC species not resolved by LC
  - Controlled fragmentation of all parent ions for structural analysis
  - Molecular identification of OA constituents via accurate mass analysis in the high-resolution 2D spectra

• These advantages demonstrate potential of ESI-IMS-HR-TOFMS for online chemical characterization of lab-generated and field OA

• Issues to be resolved in future work:
  - Examine potential of PMF to resolve complexity of data
  - Examine if trendlines exists for different functional groups
  - Examine potential of quantification – for example, can we use internal standards of different surface activities for correcting for various ionization efficiencies