Vapors that grow particles

Ehn et al. Nature 2014
Calibration needs

- Reproducible, independently quantified, and transportable source of several multi-functional organics and some inorganics.

- Use to constrain instrument response as a function of molecular properties.

- The challenge is that:
  - We don’t know what the structures of most ELVOC and LVOC are.
  - Even if we knew the structures, unlikely commercial products exist and synthesis likely very dangerous and/or very expensive.
  - Likely hundreds of individual compounds – can’t calibrate to them all.

Pinic acid (SVOC), sort of commercially available?

A possible HOM?
Iodide Adduct Chemical Ionization

\[ \text{I}^- (\text{H}_2\text{O}) + \text{X} \rightarrow \text{I}^- (\text{X}) + \text{H}_2\text{O} \]

Ion chemistry

\[
\frac{\text{Signal}_{iX}}{[X]} \propto \left[ \int_0^t k_f [I^-] dt \right] T_{iX} \left( \frac{m}{Q}, \varepsilon, B_{iX} \right)
\]

- \( I^- (H_2O) + X \rightarrow I^- (X) + H_2O \) net forward rate
  - no faster than collision limit

- \( I^- (X) \rightarrow I^- + X \) decomposition
  - function of binding energy and instrument settings

Lopez-Hilfiker et al, AMT 2016
Sensitivity, collision limit, binding enthalpy

Huey, et al JPCA 1996
Iyer, et al JPCA under review
Key standards allow determination of collision limit

Huey, et al JPCA 1996
Iyer, et al JPCA under review
Field strength, binding energy, transmission

Chemical Ionization Atmospheric Pressure Interface

Shift together towards (-dV)
All other voltages remain constant

Diagram showing field strength, binding energy, and transmission with data points and lines representing different chemical structures and their responses to varying voltages.
Calibration needs

- Reproducible, independently quantified, and transportable source of several multi-functional organics and some inorganics

- Likely does not need to be many (some even very simple) to allow quantification of a broad suite of components

- Span a range of binding energies, molecular weight, and functional groups
Chemical complexity (functionality)

Sensitivity or Mass Concentration

Collision limit – high priority ("easy")

Lower Priority

Higher Priority
Ozone - Or OH → HOM Products

All peaks detected as clusters with $^{15}\text{NO}_3^-$

- **Monomers**: $\text{C}_{8-10}\text{H}_{14-16}\text{O}_{7-11}$
- **Dimers**: $\text{C}_{18-20}\text{H}_{28-32}\text{O}_{10-18}$

Ehn et al, Nature 2014
Berndt et al, Nat. Comm 2016
Mechanism: Organic peroxy radical (RO$_2^\cdot$) autoxidation

Crounse et al JPC 2011
Ehn et al Nature 2014
More chemistry
Field strength, binding energy, transmission

Iyer et al, JPCA 2016
UW FIGAERO HR-ToF-CIMS

Ionization

ToF-MS

Filter

UHP N₂ heater

Monocarboxylic acids only

Lopez-Hilfiker et al AMT 2014