Topics discussed here

I) Effect of particle bounce on Closed (Filter) measurements in AMS vs ACSM

II) ACSM closed measurements with filter switching measurements

III) Thoughts on f44 variability

Acknowledgements (PSI Group, Andy Lambe)
AMS Vaporization Scheme

MS open/closed detection timescales: 5s (AMS), 30s (ACSM)
pTOF detection timescale: 2 ms, 50 μs (Single Particle)
Open and Closed Signals: MS mode

Fast MS 1-10 Hz Data (From Andy Lambe)

Less volatile species have larger $\tau$ and residual signal in MS closed. Ideally closed measurement needs closed dwell time $>> \tau$
I: Slow Vaporization

Slow Vaporization is observed for species that:

1) Are refractory at oven temperature of 600 Deg C

2) Bounce off vaporizer and undergo subsequent vaporization off other surfaces
   - Cooler surfaces in ionizer cage (250 deg C) -- increased decomposition/fragmentation due to slow timescale or decreased decomposition/fragmentation due to lower temperature? LS-AMS Single particle data suggest latter.
   - Particles bouncing off ionizer are vaporized at higher temperatures
     (1600 deg C) -- increased decomposition/fragmentation
Significant SO4 (20%) and chloride (60%) mass detected in AMS Closed mode

Closed Mass at ambient T is > Closed Mass at 250 deg C  (Detection of Bounced particles not as efficient as TD for same Temperature)

Huffman et al.

Atmos. Chem. Phys., 9, 7161–7182, 2009
Closed Mass is significant for organic (20%). Results similar across Milagro and SOAR.

This is important since it allows for standardization across instruments (CE correction factor, mass spectra)
Variability in closed signal from bounce

1) Particle Composition/ Phase

2) Alignment of particle beam with oven *

3) Oven temperature *

4) Dwell time spent while acquiring in closed needs to be monitored and reported (closed dwell time $>> \tau$)

5) Size of the ionizer cage
   ACSM cage is smaller and so bounce may have larger effect than in AMS. This is consistent with some ACSM observations:
   - RIE of SO4 is more variable than in AMS systems
     - Observation that ion chamber in ACSM is dirtier
   - CE of 0.5 for ACSM sometimes over estimates mass

Work in progress to understand ACSM variability.
II: “Closed” measurement

• Chopper Position Moved(AMS)
• Filter Switched(ACSM)
  - Is there a difference in quality of “closed measurement?"
NH₄NO₃ filter/bypass switching

30 second filter switches, Fast MS, C-ToF

mz30

mz46

mz28

mz44
Glutaric acid filter/bypass switching

30 second filter switches, Fast MS, C-ToF

mz86

mz114

mz44

[Graphs showing data for mz86, mz114, and mz44 over time, with peaks at specific times]
All Airbeam signals (44,28,14,40 (exp done in Ar)) appear to experience slow re-equilibration after switch. f44 will depend on where on decay and rise it is scanned. Typically, it would be around 6-7 seconds after switch when the curvature is still very steep. Could be a source of the ACSM f44 differences.
III. The f44 Issue(s)
There may be more than one effect

- Bounced particles that land on the ion chamber
  - Could be particularly important in ACSM systems which have a smaller ion chamber than AMS systems

- Filter switching used for the ACSM may result in slow re-equilibration of air peaks on timescale of open/closed switches. Exact timing with scanning may result in high variability for f44

- Catalytic production of CO2 via NO from NH4NO3
  - Simone’s work at PSI, (High NO$_3$/Organic)
  - Porous W vaporizer may be a bad surface
  - Can this chemistry be happening on the ion chamber?