High Resolution ToF AMS Clinic

Re-introduction to Pika

Coding ideas, tools from many!
Pete, Jose, Allison, Manula, Doug, Jesse, Tim,
Qi, Sally, Samara, Manuel, Mike, Puneet, ....
too!

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ToF AMS Unit Resolution Analysis - Squirrel

Raw Spectra
At integer m/z

I_m = area under curve in Hz
Area due to A = frag_{m,sA} \cdot I_m
Area due to B = frag_{m,sB} \cdot I_m
Area due to C = frag_{m,sC} \cdot I_m
Area due to D = frag_{m,sD} \cdot I_m

frag_{m,sX} is the numerical frag table entry at mass m/z of species s that contains X

Also, A may arise for two different species, i.e. OH from water, acids
ToF AMS Unit Resolution Analysis - Squirrel

**Raw Spectra**
At integer m/z m

**Conditions for good Unit Mass Resolution (UMR) analysis:**

1. We have good sticks
   - 1A We have a ‘reasonable’ handle on the m/z calibration for each run
     “Accurate to several datapoints”
   - 1B The integration regions for all m/z are reasonable
   - 1C We have reasonable estimates of baselines

2. Fragmentation values correctly identify/account for species.

3. General AMS issues, i.e. airbeam correction, CE, have been identified and corrections applied.

Raw Spectra
At integer m/z m
4 chemical fragments, A,B,C,D are possible at m

**Squirrel**
I_m = area under curve in Hz
Area due to A = frag_{m,SA} * I_m
Area due to B = frag_{m,SB} * I_m
...

**Pika**
Peaks at A,B,C,D have same ‘shape’ only different heights. At a peak height of 1, area under shape = α
Area due to A = PeakHeightA * α
Area due to B = PeakHeightB * α
Area due to C = PeakHeightC * α
Area due to D = PeakHeightD * α
As a check, Σ areas A,B,C,D = I_m
Raw Spectra

At integer m/z m
4 chemical fragments, A, B, C, D are possible at m/z

Squirrel

Im = area under curve in Hz
Area due to A = fragm,sA * Im
Area due to B = fragm,sB * Im
…

Peaks at A, B, C, D have same ‘shape’ only different heights. At a peak height of 1, area under shape = α
Area due to A = PeakHeightA * α
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Area due to D = PeakHeightD * α

As a check, Σ areas A, B, C, D = I_m

Conditions for good High Resolution (HR) analysis:

We must know or x-axis values very well
m/z calibration
feasible set of fragments A, B

We must know our y-axis values very well
baseline
area under canonical peak shape, α known very well

** However, the fitted HR peaks by themselves won’t handle the
apportionment of HR to different species (i.e. OH from water, acids).
There will still be a need for an HR frag table.

ToF AMS High Resolution Analysis - Pika

Conditions for a good HR analysis:

(0) General AMS issues (i.e. airbeam correction) have been identified in Squirrel.

(1) We can subtract baselines well.

(2) Very good m/z calibration.
The x-axis points, the m/z of species A, B, C, D are fixed.
Very good ≈ “Accurate to 1/10 point”

(3) The peak shape is well characterized for all runs in todo wave.
3A We have a correct parameterization of the peak width from gaussian fits.
3B We have a correct look-up table describing true peak shape (using 3A).

(4) Because 1 – 3 may be imperfect, we often need to be judicious about which peaks we choose to fit.
At higher m/zs (>60) the number of feasible fragments increases exponentially.

(5) The few, but important, HR frag table entries are identified.
What are we trying to do in Squirrel?

\[ C_{s,t} = \frac{10^{12} MW_{NO_3}}{CE_{s,t} RIE_s IE_{NO_3} Q_t N_A} \sum_{m=1}^{\text{max m/z}} f_{s,m,t} I_{m,t} \]

- \( MW_{NO_3} \) is the molecular weight of nitrate in g/mol
- \( CE_{s,t} \) is the collection efficiency of species s (unitless)
- \( RIE_s \) is the relative ionization efficiency of species s relative to nitrate (unitless)
- \( IE_{NO_3} \) is the ionization efficiency of nitrate
- \( Q_t \) is the volumetric sample flow rate in cm\(^3\)/s
- \( N_A \) is Avogadro’s number
- \( f_{s,m,t} \) is the fractional amount of m/z m attributable to species s
- \( I_{m,t} \) is the integrated amount of detected ions at m/z in Hz
- \( 10^{12} \) is a factor needed for unit conversion
- The summation is over all measured m/z

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- The summation is over all measured m/z HR ions in species s
How to get HR sticks correct?

\[ HRI_{hrm,t} = \text{PeakHeight} \times \text{PeakWidth} \times A \]

- **A** is a scalar indicating the area under the parameterized peak shape for peak height=1 and peak width =1
- **Peak Width** = \( f(m/z) \). In versions of Pika prior to 1.05, \( f \) was a linear function, \( PW = a + b \times (m/z) \). But in 1.05 \( f \) is generalized to a power law function, \( PW = a + b \times (m/z)^c \).
- **Peak Height** is the only parameter that is found during a multi-peak Pika fit.

*Everything else has been pre-determined!*
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