

High Resolution ToF AMS Clinic

Re-introduction to Pika

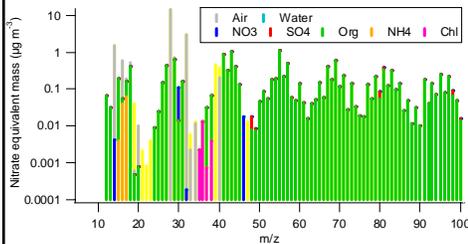
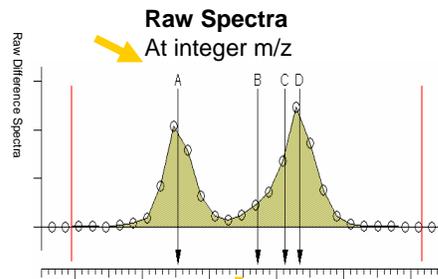
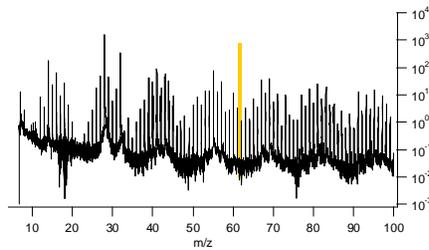
Coding ideas, tools from many!
 Pete, Jose, Allison, Manula, Doug, Jesse, Tim,
 Qi, Sally, Samara, Manuel, Mike, Puneet,



too!

Donna Sueper
 June 6, 2009

ToF AMS Unit Resolution Analysis - Squirrel



I_m = area under curve in Hz

Area due to A = $\text{frag}_{m,SA} * I_m$

Area due to B = $\text{frag}_{m,SB} * I_m$

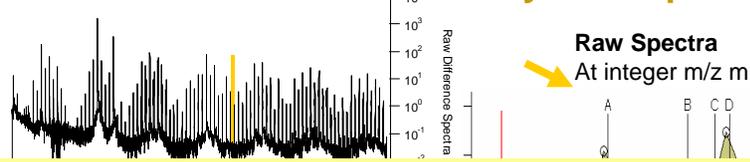
Area due to C = $\text{frag}_{m,SC} * I_m$

Area due to D = $\text{frag}_{m,SD} * I_m$

frag_{mSX} 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

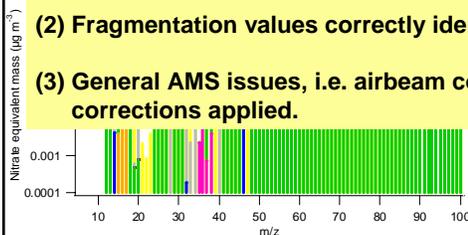


Conditions for good Unit Mass Resolution (UMR) analysis:

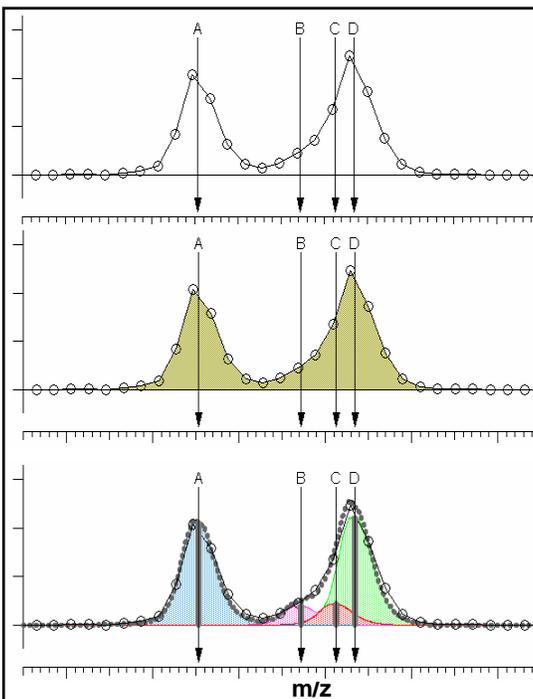
- (1) We have good sticks
 - 1A We have a 'reasonable' handle on the m/z calibration for each run
"Accurate to several datapoints"
 - 1B The integration regions for all m/z are reasonable
 - 1C We have reasonable estimates of baselines

(2) Fragmentation values correctly identify/account for species.

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



$frag_{m,sX}$ is the numerical frag table entry at mass m of species s that contains A



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

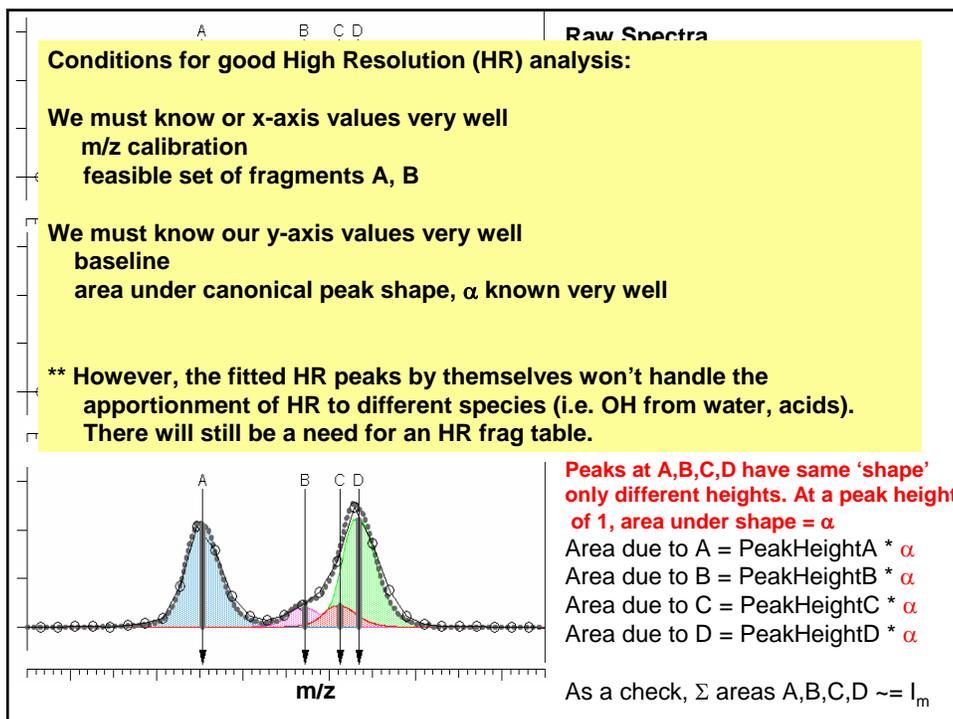
Area due to A = $PeakHeightA * \alpha$

Area due to B = $PeakHeightB * \alpha$

Area due to C = $PeakHeightC * \alpha$

Area due to D = $PeakHeightD * \alpha$

As a check, \sum areas A,B,C,D $\approx I_m$



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 \sim "Accurate to 1/10 point"

(3) The peak shape is well characterized for all runs in todo wave .

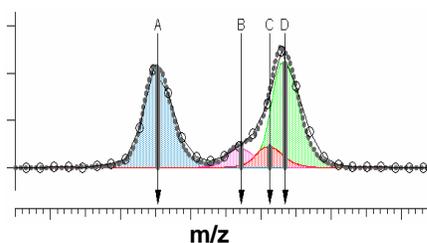
3A We have a correct parameterization of the peak width from gaussian fits.

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?

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

- 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 amt 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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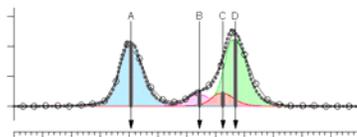
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- The summation is over all measured ~~m/z~~ ^{fragment hrm} HR ions in species s

How to get HR sticks correct?

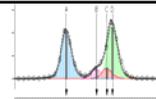
$$HRI_{hrm,t} = PeakHeight * PeakWidth * A$$

- 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, $PW = a + b*(m/z)$. But in 1.05 f is generalized to a power law function, $PW = a + b*(m/z)^c$.
- Peak Height is the only parameter that is found during a multi-peak Pika fit.

Everything else has been pre-determined!



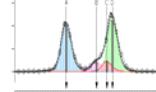
ToF AMS High Resolution Analysis - Pika



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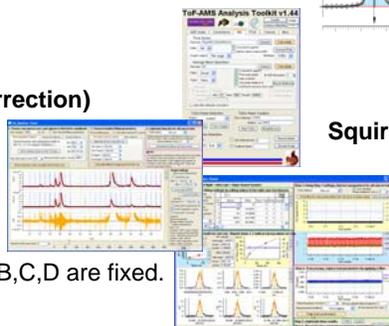
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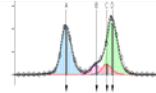
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Squirrel!



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