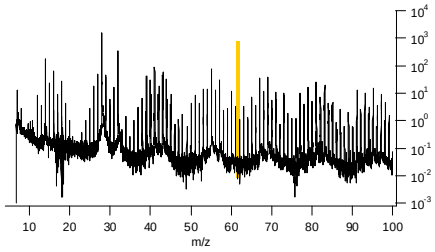
Pika
How does it work?

High Resolution ToF-AMS Analysis

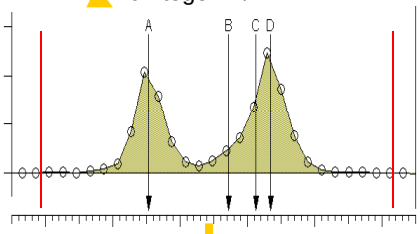
Nov. 1, 2009
AMS User's Meeting, Toronto

Donna Sueper
Aerodyne, University of Colorado, Boulder

ToF AMS Unit Resolution Analysis - Squirrel



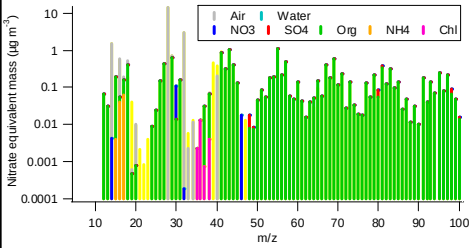
Raw Spectra
At integer m/z



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

$frag_{mSX}$ 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



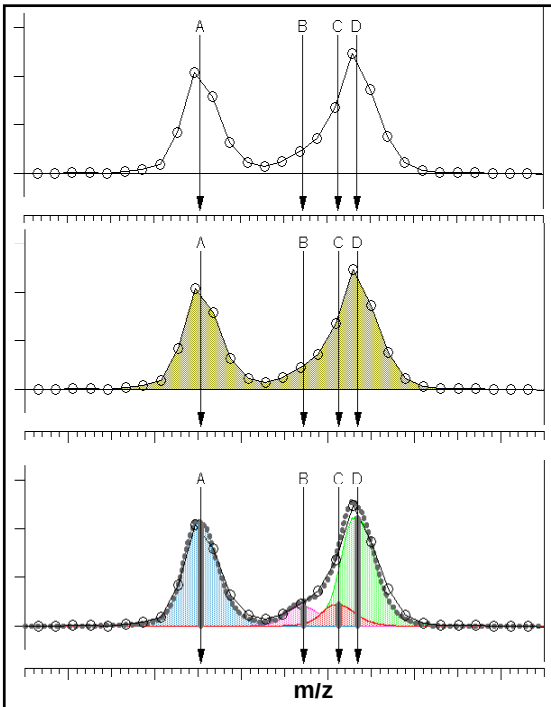
ToF AMS Unit Resolution Analysis - Squirrel

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

(1) We have good sticks
- **1A We have a 'reasonable' handle on the m/z calibration for each run "Accurate to several data points"**
- **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

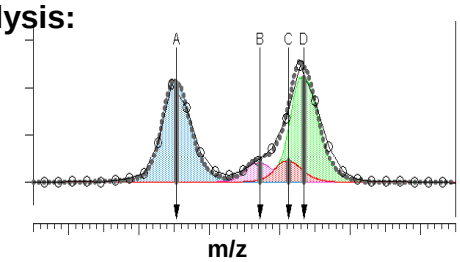
Squirrel
I_m = area under curve in Hz
Area due to A = $frag_{m,sA} * I_m$
Area due to B = $frag_{m,sB} * I_m$
…

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

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.

How to get HR sticks correct?

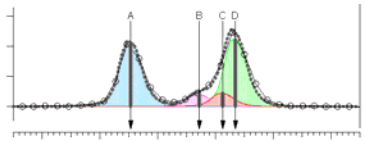
$$HRI_{hrm,t} = PeakHeight * PeakWidth * A$$

• 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.

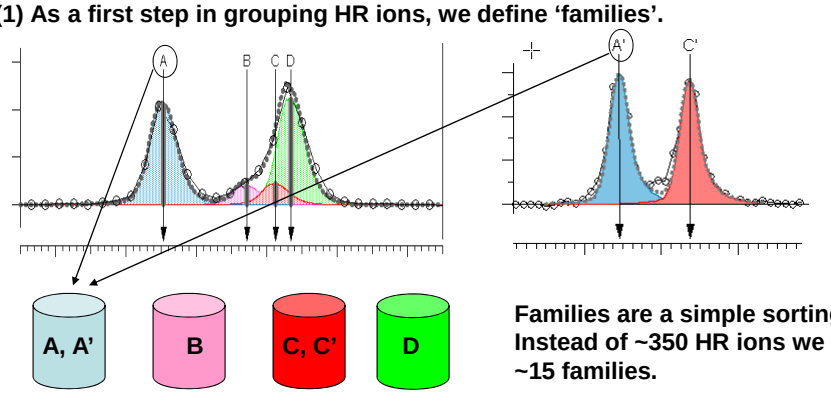
Everything else has been pre-determined!



After we get HR sticks correct, then what?

We need flexible ways to group HR ions. In particular, we want to be able to define "organic", "nitrate", etc.

(1) As a first step in grouping HR ions, we define 'families'.



Families are a simple sorting tool. Instead of ~350 HR ions we have ~15 families.

Every HR ion is a member of one and only one family.
Each HR ion gets put into a family based on it's chemical formula.

After we get HR sticks correct, then what?

(1) continued. Current HR families & the rules for family groupings:

Air (Oz where z>=1, Nw where w>=1, or Ara where a>=1)
Cx (**new in 1.07**, Cx where x>=1 These HR ions used be belong to the CH family)
CH (CxHy where x>=1 and y>=1)
CHO1 (CxHyOz where x>=1, y>=0, z=1 CO is currently a member of this family, as is C2O, other oddballs)
CHOgt1 (CxHyOz where x>=1, y>=0, z>1 CO2 is currently a member of this family, as is C2O2, other oddballs)
CHN (CxHyNw where x>=1, y>=0, w>=1)
CHO1N (CxHyOzNw where x>=1, y>=0, z=1, w>=1)
CHOgt1N (CxHyOzNw where x>=1, y>=0, z>1, w>=1)
CS (CxSr where x>=1, v>=1)
HO (HyOz where x>=1, y>=0 Includes some non-water oddballs such as HO2)
NH (NwHy where w>=1, y>=1)
Cl (Clu where u>=1)
NO (NwOz where w>=1, z>=1 Includes some oddballs such as N2O3)
SO (**changed in 1.06J** SrOz where r>=1, z>=0 In 1.06G S, HS now belong to this family. They used to be in the Other family)
Tungsten (By default this family is explicitly defined. Ws where s>=1. This family was defined as an example to users to make other, new families explicitly)
Other (Anything that doesn't fit into any other family. These end up being mostly metals, potassium)

After we get HR sticks correct, then what?

(2) We can group families and/or portions of HR ions into familiar species ("organic", "nitrate"!)

In some cases, such as Cl and NH, the family IS the species.
In other cases, we need to apportion ('frag') special HR ions.

HRBatchTable

R0 HRair

HR_specname_list	HR_spec_list	HR_specFrag_list	HR_specFamilyBase	HR_specIE	Hf
HRair	HRair	HR_frag_air	familyAir	1	
HRPwater	HRPwater	HR_frag_Pwater	familyHO	1	
HRammonium	HRNH4	HR_frag_ammonium	familyNH	4	
HRnitrate	HRNO3	HR_frag_nitrate	familyNO	1.1	
HRsulphate	HRSO4	HR_frag_sulphate	familySO	1.2	
HRorganic	HROrg	HR_frag_organic	familyCx;familyCH;fam	1.4	
HRchloride	HRChl	HR_frag_chloride	familyCl	1.3	
HRPco2	HRPCO2	HR_frag_pco2		1.4	

HRFragTable

N

Poin	HR_specMa	HR_frag_organic
0	N	
1	j15N	
2	O	0.04*HR_frag_organic[{H2O}]
3	OH	0.25*HR_frag_organic[{H2O}]
4	j18O	0.002*HR_frag_organic[{O}]
5	H2O	1*HR_frag_organic[{CO2}]
6	j18OH	0.002*HR_frag_organic[{OH}]
7	H2j18O	0.002*HR_frag_organic[{H2O}]
8	CO2plus2	{CO2plus2}
9	CO	HR_frag_organic[{CO2}]
10	Cj18O	0.002*HR_frag_organic[{CO}]
11	S	

What is different between Squirrel & Pika?

Squirrel:

$$C_{s,t} = \frac{10^{12} MW_{NO_3}}{CE_{s,t} RIE_s IE_{NO3} Q_t N_A} \sum_{m=1}^{\max m/z} f_{s,m,t} I_{m,t}$$

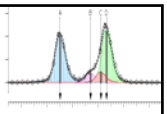
Pika:

$$C_{s,t} = \frac{10^{12} MW_{NO_3}}{CE_{s,t} RIE_s IE_{NO3} Q_t N_A} \sum_{hrm}^{hrm \text{ in } s} f' HRI_{hrm,t}$$

In squirrel, focus is on fragmentation less on UMR sticks: $f_{s,m,t} I_{m,t}$

In pika, focus is on HR sticks, less on fragmentation $f' HRI_{hrm,t}$

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) baselines well.

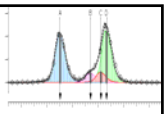
(2) Very good m/z calibration.
The x-axis points, the m/z of species A,B,C,D are fixed.
Very good ~= "Accurate to 1/10 point"

(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).

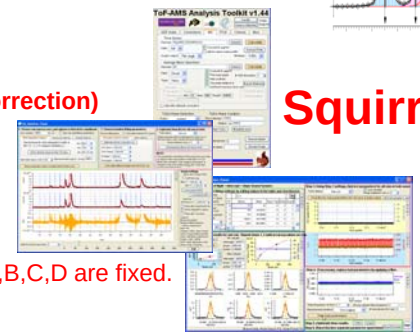
(4) Because 1 – 3 may be imperfect, we often need to be judicious about which peaks we choose to fit.
At higher m/zs (>60) the number of feasible fragments increases exponentially.

(5) The few, but important, HR frag table entries are identified.

ToF AMS High Resolution Analysis - Pika



Conditions for a good HR analysis:



Squirrel!

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

(1) We can subtract baselines well.

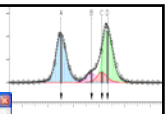
(2) Very good m/z calibration.
The x-axis points, the m/z of species A,B,C,D are fixed.
Very good ~= "Accurate to 1/10 point"

(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.

ToF AMS High Resolution Analysis - Pika

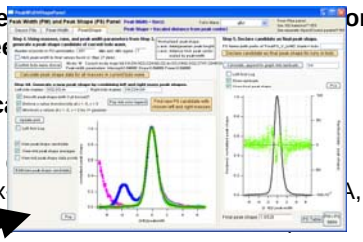


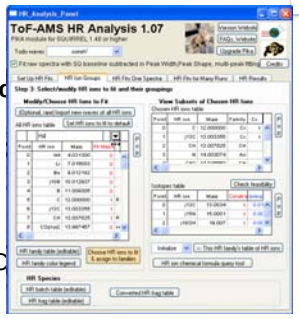
Conditions for a good HR analysis:

(0) Gene **orrec**
have bee

(1) We c

(2) Very
The x A,B,C
Very





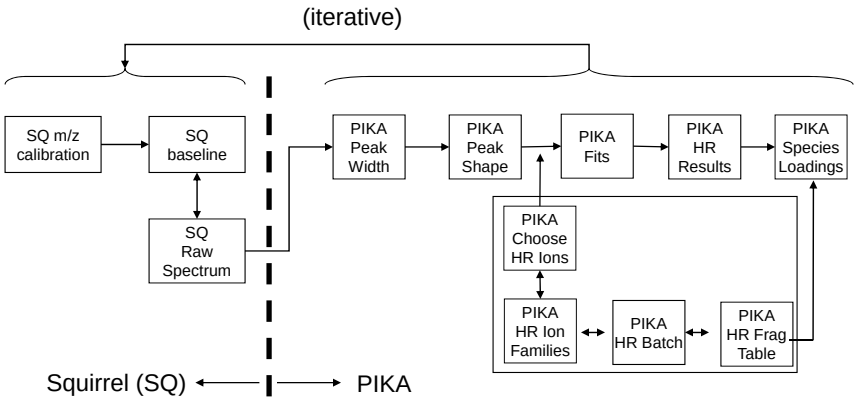
Pika!

(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.

HR flow chart



The end