HR frag in Pika

A review of concepts, defaults

What is most confusing/difficult concept about Pika?

A. Thinking about Errors (in preparation for input to PMF)

B. Deciding which ions to fit

C. Getting good m/z parameters

D. Understanding where all the results are & how to access results

E. The utility and implementation of families and HR species

Pika review – clicker question!

What issues are *not* important when performing a pika fit (multipeak fitting routine)?

A. Using good baseline parameters via the squirrel baseline panel

B. Using good m/z parameters

C. Getting the Single Ion value correct

D. Going through all the m/z values for at least one run (or average of runs)

E. They are all important

Families are groups of HR masses, and should be thought of as an accounting tool.

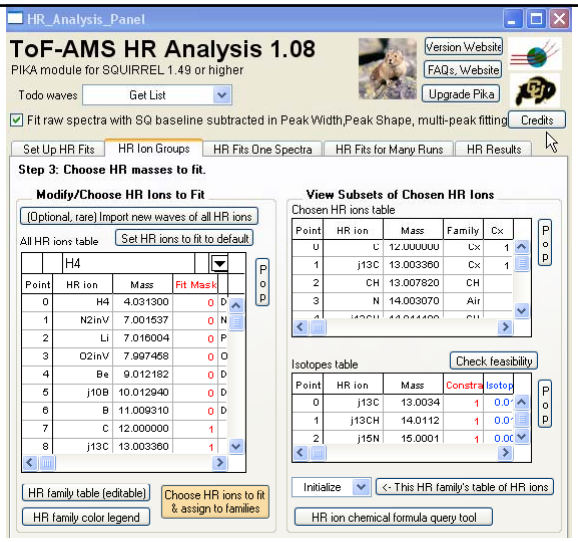
- **Every HR mass is a member of one and only one family.**
- Most masses are assigned a family based on a good (but not perfect) algorithm which tries to decode the chemical formula. I.e. C2HO -> CHO1 family.
- Some families are explicitly defined, users can add families explicitly.
- The HR mass family sorting algorithm can be changed to add more families, but this should not be done by the user.

HR Species are groups of HR masses and possible portions of the more highly fragmented HR masses.

- **HRSpecies more accurately reflect chemically related aerosol components.** I.e. the HR mass OH should apportioned to atmospheric gas phase water and particulate water due to carboxylic acids, etc.
- HR species are intended to mimic and possibly extend the common list of AMS species (Org, NO3, etc)

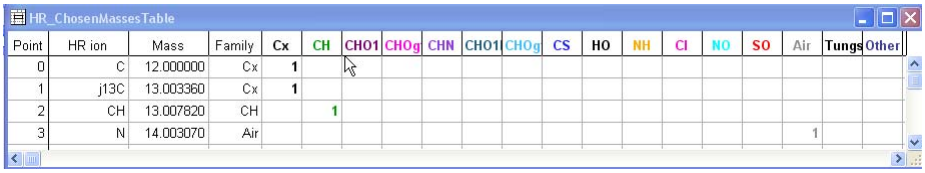
Current HR families:
Cx
CH
CHO1
CHOgt1
CHN
CHO1N
CHOgt1N
CS
HO
NH
Cl
NO
SO
Air
Tungsten
Other

Current HRSpecies:
HRAir
HROrg
HRChloride
HRSulphate
HRNitrate

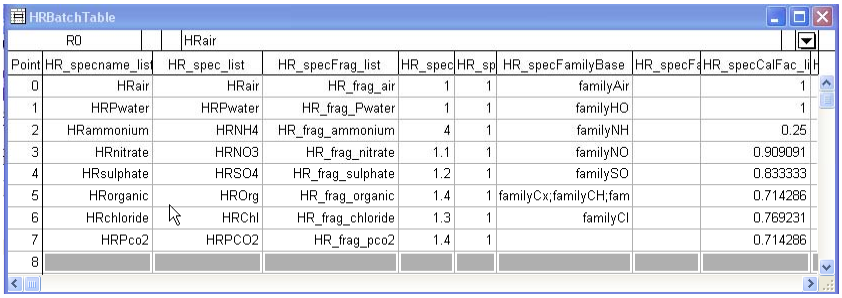


Once you select the HR ions to fit every ion gets assigned a family based on the chemical formula name (i.e. C4H4O2)

The chemical formula names of HR ions *ARE* case sensitve (unlike everything else we do in Igor).



The HR batch table defines the list of HR species.



The HRspecies names have an ‘HR’ prefix to distinguish between non-HR species

The HRspecies use the already established family designation as a base set for inclusion.

This prevents a lengthy, cumbersome list/table of all fitted masses.

Prevents the resorting of items when new masses are fit or old masses are chosen not to fit.

This scheme still allows complete flexibility to the user, while hiding tedious details.

The HR frag table defines each HR species.

Defaults for HRair and HRPwater

HRFragTable

17R X 1C

Poi	HR_spec	HR_frag_air	HR_frag_Pwater
0	N	{N},-HR_frag_nitrate[{N}]	
1	j15N	0.00369359*HR_frag_air[{N}]	
2	O	0.353*HR_frag_air[{N}],0.04*HR_frag_air[{H2O}]	0.04*HR_frag_Pwater[{H2O}]
3	HO	0.000391*0.353*HR_frag_air[{N}],0.25*HR_frag_air[{H2O}]	0.25*HR_frag_Pwater[{H2O}]
4	j18O	0.00205000*HR_frag_air[{O}]	0.00205000*HR_frag_Pwater[{O}]
5	H2O	0.01*HR_frag_air[{N2}]	{H2O},-HR_frag_air[{H2O}],-HR_frag_sulphate[{H2O}],-HR_frag_organic[{H2O}]
6	Hj18O	0.00205000*HR_frag_air[{HO}],0.000691*HR_frag_air[{H2O}]	0.00205000*HR_frag_PWater[{HO}]
7	H2j18O	0.00205000*HR_frag_air[{H2O}]	0.00205000*HR_frag_PWater[{H2O}]
8	CO2plus		
9	CO		
10	Cj18O	0.00205000*HR_frag_air[{CO}]	
11	S		
12	j33S		
13	j34S		
14	CO2	0.00037*1.36*1.28*1.14*HR_frag_air[{N2}]	
15	j13CO2	0.01081570*HR_frag_air[{CO2}]	
16	Cj18OO	0.00410998*HR_frag_air[{CO2}]	
17			

The HR frag table defines each HR species.

Defaults for HROrg, HRNO3, HRpCO2.

HRFragTable

17R X 1C

HR_specM	HR_	HR_	HR_f	HR_frag_nitrate	HR_	HR_frag_organic	HR_f	HR_frag_pco2
N	{N},			0.04*HR_frag_nitrate[{NO}],0.04*frag_nitrate[{NO2}]				
j15N	0.00			0.00369359*HR_frag_nitrate[{N}]				
O	0.35	0.04			0.0	0.04*HR_frag_organic[{H2O}]		
HO	0.00	0.25			0.2	0.25*HR_frag_organic[{H2O}]		
j18O	0.00	0.00			0.0	0.00205000*HR_frag_organic[{O}]		
H2O	0.01	{H2			0.6	0.225*HR_frag_organic[{CO2}]		
Hj18O	0.00	0.00			0.0	0.00205000*HR_frag_organic[{HO}]		
H2j18O	0.00	0.00			0.0	0.00205000*HR_frag_organic[{H2O}]		
CO2plus2						{CO2plus2}		
CO						HR_frag_organic[{CO2}]		
Cj18O	0.00					0.00205000*HR_frag_organic[{CO}]		
S					0.2			
j33S					0.0			
j34S					0.0			
CO2	0.00					HR_frag_pco2[{CO2}]		{CO2},-HR_frag_air[{CO2}]
j13CO2	0.01					HR_frag_pco2[{j13CO2}]		0.01112*HR_frag_pco2[{CO2
Cj18OO	0.00					HR_frag_pco2[{Cj18OO}]		0.004*HR_frag_pco2[{CO2}]

Note that HRNH4 and HRChl are blank. This means that we just use the family designations to define what HR ions are in these HR species.

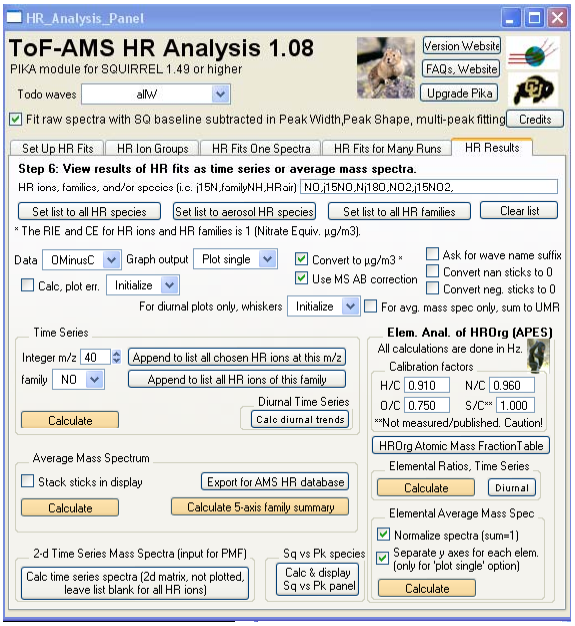
The HR frag table defines each HR species.

Defaults for HRSO4

HRFragTable

17R X 1C

Poi	HR_spec	HR_	HR_	HR_	HR_	HR_frag_sulphate
0	N	{N}			0.0	
1	j15N	0.0(			0.0(	
2	O	0.3	0.0			0.04*HR_frag_sulphate[{H2O}]
3	HO	0.0(	0.2			0.25*HR_frag_sulphate[{H2O}]
4	j18O	0.0(	0.0(			0.00205000*HR_frag_sulphate[{O}]
5	H2O	0.0	{H2			0.67*HR_frag_sulphate[{SO2}],0.67*HR_frag_sulphate[{SO}]
6	Hj18O	0.0(	0.0(			0.00205000*HR_frag_sulphate[{HO}]
7	H2j18O	0.0(	0.0(			0.00205000*HR_frag_sulphate[{H2O}]
8	CO2plus					
9	CO					
10	Cj18O	0.0(				
11	S					0.21*HR_frag_sulphate[{SO2}],0.21*HR_frag_sulphate[{SO}],0.068*HR_frag_sulphate[{HSO3}],0.068*HR_frag_sulphate[{H2S(
12	j33S					0.0080059*HR_frag_sulphate[{S}]
13	j34S					0.0451912*HR_frag_sulphate[{S}]
14	CO2	0.0(				
15	j13CO2	0.0				
16	Cj18OO	0.0(				
17						



For time series results, there are 3 categories:
HR masses (i.e. C3H4O)
HR families (i.e. familyCH)
HR species (i.e. HRAir)

For average mass spec results, there are 2 categories:
HR families (i.e. familyCH)
HR species (i.e. HRAir)

For elemental analysis we only look at HROrg

RIE and CE set to 1 for families and HR ions when Units of µg/m3 are used.

Some HR frag details to keep in mind

* We may need separate versions of the HR frag tables for V and W modes

* We still don't have a nice way for dealing with situations where two HR masses are 'too adjacent' or are 'too dominated by a tail of a major peak' to be fit accurately. (Mike Cubison to discuss.) We need to be clear about what the HR frag table does/does not do to address this issue. I.e. CO/N2 at 28, S/O2 at 32? Others?

when two adjacent are fit, but you don't want to trust them

when only one of two was fit but you want to use the frag table to 'artificially' partition these masses. Example: The current HR frag table allows the partitioning of the HR mass CO. We can base the partitioning of CO based on fitted elements like CO2, but how should this fold into the use of other masses at 28, like N2? Doug says "User's Responsibility!!"

* Current code doesn't complain when 'bad' entries exist. I.e.
0.00037*1.36*1.28*HR_frag_air[{N2}] is correct, but
0.00037*1.36*1.28*frag_air[{N2}] would be nonsensical.

HR_frag_air[{CHO}] and not xx*HR_frag_air[{COH}]