

# 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. C<sub>2</sub>H<sub>2</sub>O → CHO<sub>1</sub> 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 be 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, NO<sub>3</sub>, etc)

Current HR families:

Cx  
CH  
CHO<sub>1</sub>  
CHOgt<sub>1</sub>  
CHN  
CHO<sub>1</sub>N  
CHOgt<sub>1</sub>N  
CS  
HO  
NH  
Cl  
NO  
SO  
Air  
Tungsten  
Other

Current HRSpecies:

HRAir  
HROrg  
HRChloride  
HRSulphate  
HRNitrate

**ToF-AMS HR Analysis 1.08**  
PIKA module for SQUIRREL 1.49 or higher

Version Website  
FAQs, Website  
Upgrade Pika

Fit raw spectra with SQ baseline subtracted in Peak Width/Peak Shape, multi-peak fitting

Set Up HR Fits | HR Ion Groups | HR Fits One Spectra | HR Fits for Many Runs | HR Results

**Step 3: Choose HR masses to fit.**

**Modify/Choose HR ions to fit**  
(Optional, rare) Import new waves of all HR ions  
All HR ions table | Set HR ions to fit to default

Point	HR ion	Mass	Fit Mask
0	H4	4.031300	0 D
1	N2inV	7.001637	0 N
2	Li	7.016004	0 P
3	O2inV	7.997469	0 O
4	Be	9.012182	0 D
5	j10B	10.012940	0 D
6	B	11.009310	0 D
7	C	12.000000	1
8	j13C	13.003360	1

HR family table (editable) | Choose HR ions to fit & assign to families | HR family color legend

**View Subsets of Chosen HR Ions**  
Chosen HR ions table

Point	HR ion	Mass	Family	Cx
0	C	12.000000	Cx	1
1	j13C	13.003360	Cx	1
2	CH	13.007820	CH	
3	N	14.003070	Air	

Isotopes table | Check feasibility

Point	HR ion	Mass	Const	Isotop
0	j13C	13.0034	1	0.0
1	j13CH	14.0112	1	0.0
2	j15N	15.0001	1	0.0C

Initialize | < This HR family's table of HR ions | HR ion chemical formula query tool

**HR\_ChosenMasses Table**

Point	HR ion	Mass	Family	Cx	CH	CHO1	CHOg	CHN	CHO1	CHOg	CS	HO	NH	Cl	NO	SO	Air	Tungs	Other
0	C	12.000000	Cx	1															
1	j13C	13.003360	Cx	1															
2	CH	13.007820	CH		1														
3	N	14.003070	Air														1		

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 sensitive (unlike everything else we do in Igor).

The HR batch table defines the list of HR species.

Point	HR_specname_list	HR_spec_list	HR_specFrag_list	HR_spec	HR_sp	HR_specFamilyBase	HR_specF	HR_specCalFac	HR_specCalH
0	HRair	HRair	HR_frag_air	1	1	familyAir			1
1	HRPwater	HRPwater	HR_frag_Pwater	1	1	familyHO			1
2	HRammonium	HRNH4	HR_frag_ammonium	4	1	familyNH			0.25
3	HRnitrate	HRNO3	HR_frag_nitrate	1.1	1	familyNO			0.909091
4	HRsulphate	HRSO4	HR_frag_sulphate	1.2	1	familySO			0.833333
5	HRorganic	HROrg	HR_frag_organic	1.4	1	familyCx;familyCH,fam			0.714286
6	HRchloride	HRCl	HR_frag_chloride	1.3	1	familyCl			0.769231
7	HRPco2	HRPCO2	HR_frag_pco2	1.4	1				0.714286
8									

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

HR_specid	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.

HR_specid	HR	HR_frag_nitrate	HR_frag_organic	HR_frag_pco2
N	{N}	0.04*HR_frag_nitrate[{NO}],0.04*HR_frag_nitrate[{NO2}]		
j15N	0.00	0.00369359*HR_frag_nitrate[{N}]		
O	0.35	0.04	0.04*HR_frag_organic[{H2O}]	
HO	0.00	0.25	0.25*HR_frag_organic[{H2O}]	
j18O	0.00	0.00	0.00205000*HR_frag_organic[{O}]	
H2O	0.01	0.25	0.225*HR_frag_organic[{CO2}]	
Hj18O	0.00	0.00	0.00205000*HR_frag_organic[{HO}]	
H2j18O	0.00	0.00	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			0.00	
j34S			0.00	
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 HRCl 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

Pos	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[[H2SO4]]
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						

**HR\_Analysis\_Panel**

**ToF-AMS HR Analysis 1.08**  
PIKA module for SQUIRREL 1.49 or higher

Version WebSite  
FAQs Website  
Upgrade PIKA

Todo waves: allw

Fit raw spectra with SQ baseline subtracted in Peak Width, Peak Shape, multi-peak fitting

Set Up HR Fits | HR Ion Groups | HR Fits One Spectra | HR Fits for Many Runs | HR Results

**Step 6: View results of HR fits as time series or average mass spectra.**

HR ions, families, and/or species (e.g. j15N, familyNH, HRAir) | NO, j15NO, j18O, NO2, j15NO2

Set list to all HR species | Set list to aerosol HR species | Set list to all HR families | Clear list

\* The RIE and CE for HR ions and HR families is 1 (Nitrate Equiv.  $\mu\text{g}/\text{m}^3$ )

Data: OMinusC | Graph output: Plot single |  Convert to  $\mu\text{g}/\text{m}^3$  \* |  Ask for wave name suffix  
 Calc. plot err. | Initialize |  Use MS AB correction |  Convert neg. sticks to 0  
 For diurnal plots only, whiskers | Initialize |  For avg. mass spec only, sum to UMR

Time Series  
Integer m/z: 40 | Append to list all chosen HR ions at this m/z  
family: NO | Append to list all HR ions of this family  
Diurnal Time Series  
Calculate | Calc diurnal trends

Average Mass Spectrum  
 Stack sticks in display | Export for AMS HR database  
Calculate | Calculate 5-axis family summary

2-d Time Series Mass Spectra (input for PMF)  
Calc time series spectra (2d matrix, not plotted, leave list blank for all HR ions)

Sq vs PK species  
Calc & display  
Sq vs PK panel

**Elem. Anal. of HROrg (APES)**  
All calculations are done in Hz.  
Calibration factors:  
H/C: 0.910 | N/C: 0.960  
O/C: 0.750 | S/C\*: 1.000  
\*\*Not measured/published. Caution!

HROrg Atomic Mass Fraction Table  
Elemental Ratios, Time Series  
Calculate | Diurnal

Elemental Average Mass Spec  
 Normalize spectra (sum=1)  
 Separate y axes for each elem. (only for 'plot single' option)  
Calculate

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  $\mu\text{g}/\text{m}^3$  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.  
 $0.00037 * 1.36 * 1.28 * \text{HR\_frag\_air}\{\{\text{N2}\}\}$  is correct, but  
 $0.00037 * 1.36 * 1.28 * \text{frag\_air}\{\{\text{N2}\}\}$  would be nonsensical.

$\text{HR\_frag\_air}\{\{\text{CHO}\}\}$  and not  $\text{xx} * \text{HR\_frag\_air}\{\{\text{COH}\}\}$