Why frag table?
Why HR families?
Why HR frag table?

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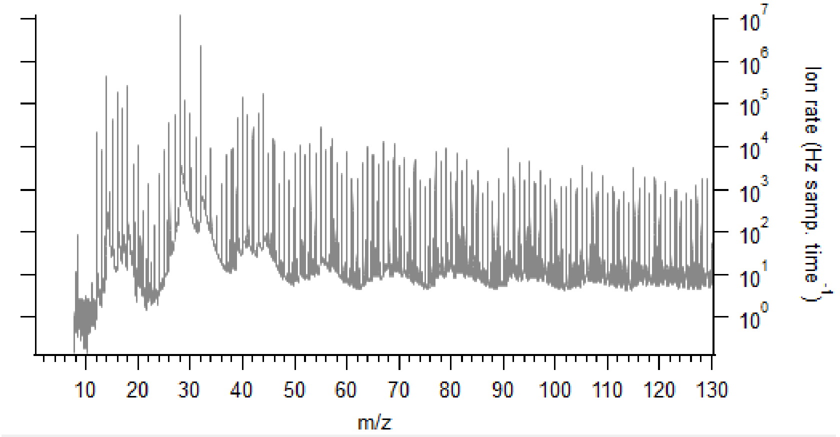
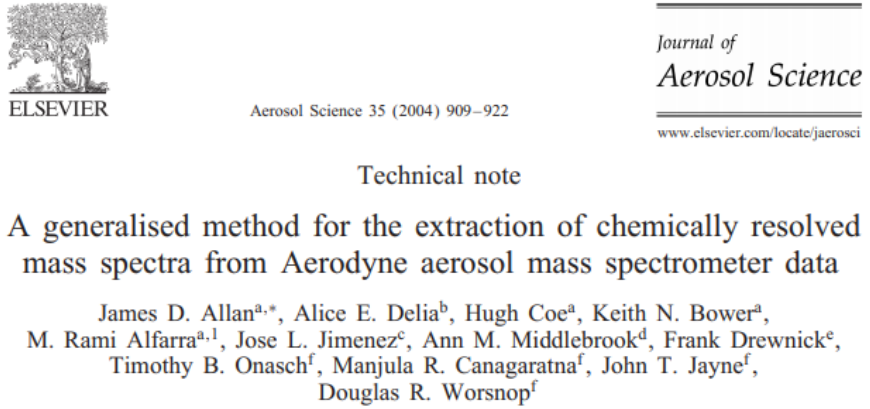
UMR frag table Origins





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Aerosol Science 35 (2004) 909–922

Journal of Aerosol Science

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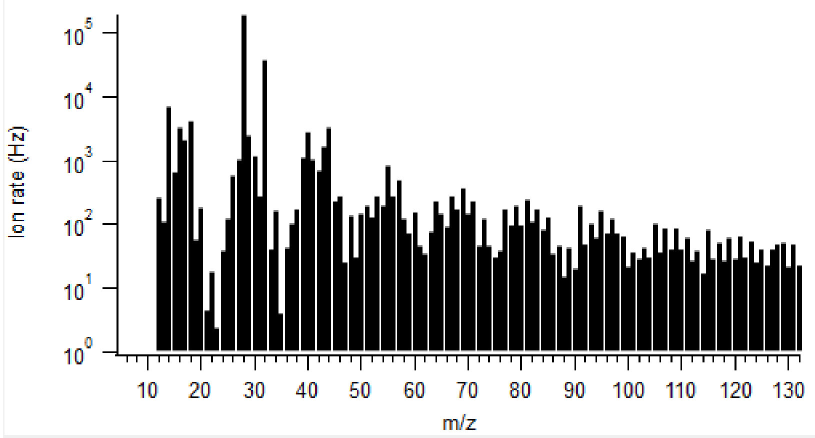
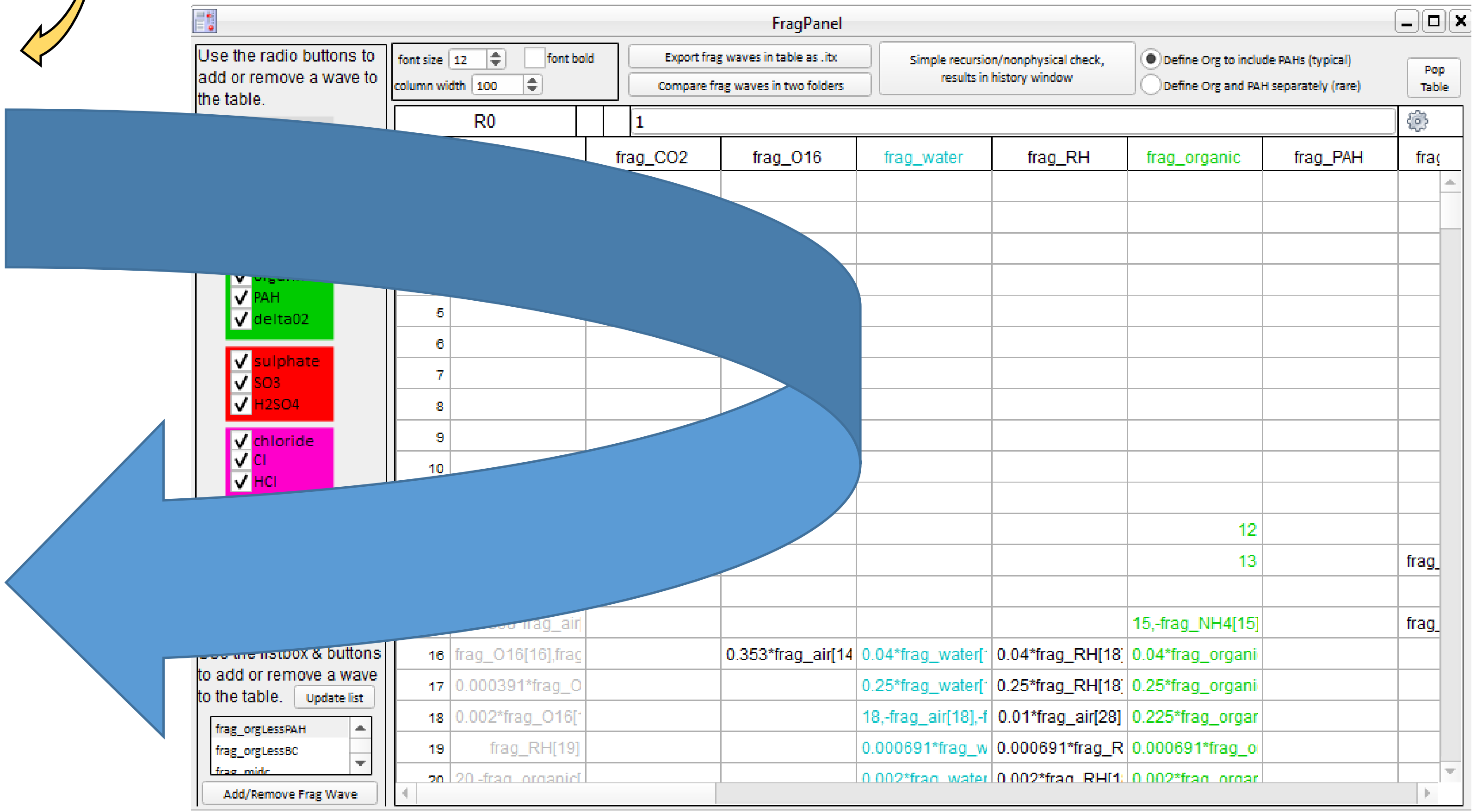
Technical note

A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data

James D. Allan[a,*], Alice E. Delia[b], Hugh Coe[a], Keith N. Bower[a], M. Rami Alfarra[a,1], Jose L. Jimenez[c], Ann M. Middlebrook[d], Frank Drewnick[e], Timothy B. Onasch[f], Manjula R. Canagaratna[f], John T. Jayne[f], Douglas R. Worsnop[f]

Raw spectra -> UMR ‘sticks’





FragPanel

Use the radio buttons to add or remove a wave to the table.

font size 12 ☐ font bold

column width 100

● Define Org to include PAHs (typical)

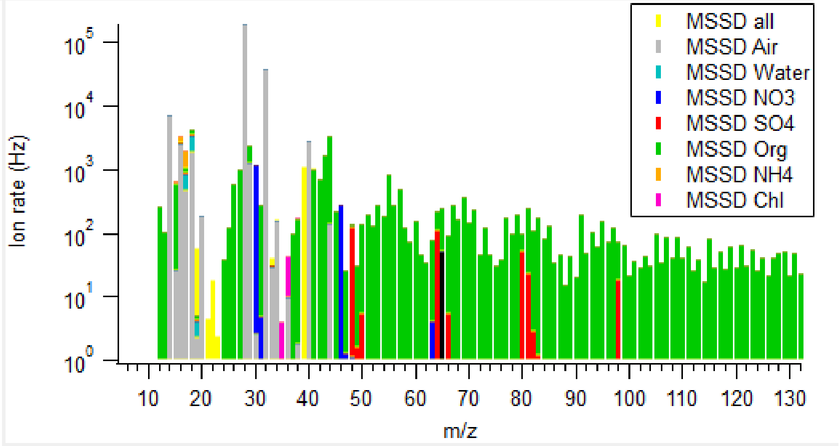
○ Define Org and PAH separately (rare)

R0 | 1

☑ PAH
☑ delta02
☑ sulphate
☑ SO3
☑ H2SO4
☑ chloride
☑ Cl
☑ HCl

		frag_CO2	frag_O16	frag_water	frag_RH	frag_organic	frag_PAH	frag
						12		
						13		frag_
	frag_air					15,-frag_NH4[15]		frag_
16	frag_O16[16],frag		0.353*frag_air[14	0.04*frag_water[	0.04*frag_RH[18]	0.04*frag_organi		
17	0.000391*frag_O			0.25*frag_water[	0.25*frag_RH[18]	0.25*frag_organi		
18	0.002*frag_O16[			18,-frag_air[18],-f	0.01*frag_air[28]	0.225*frag_orgar		
19	frag_RH[19]			0.000691*frag_w	0.000691*frag_R	0.000691*frag_o		

to add or remove a wave to the table.



UMR frag considerations

UMR frag entries come from:

- Multiple ions at the same UMR

i.e. m/z 30 ions can be attributed to NO^+, CH_2O^+, $C_2H_6^+$, ….

- Isotopic abundances

i.e. ^{15}NO estimated from NO abundance

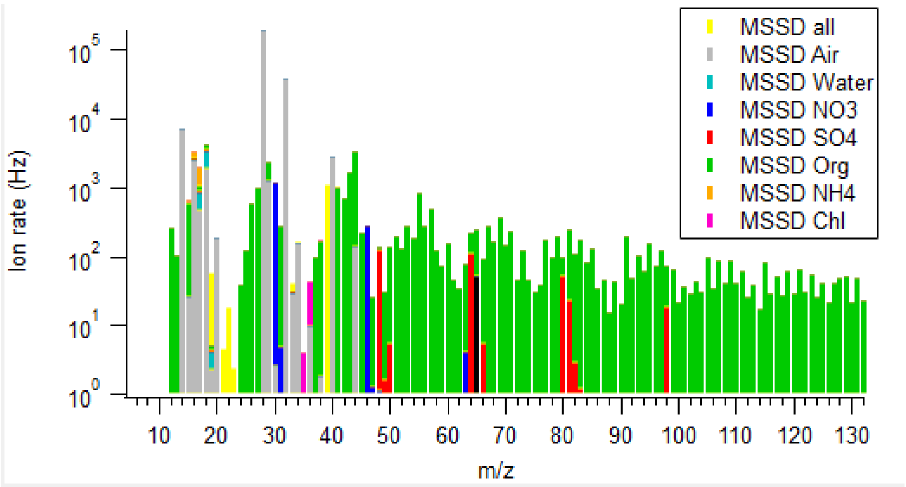
- Contribution of different species to the same ion

i.e. CO_2^+ fragment can be from both air molecule or from a larger organic aerosol molecul

Care must be taken to ensure

✓ signal is not undercounted
✓ signal is not overcounted

➢ Squirrel frag check panel

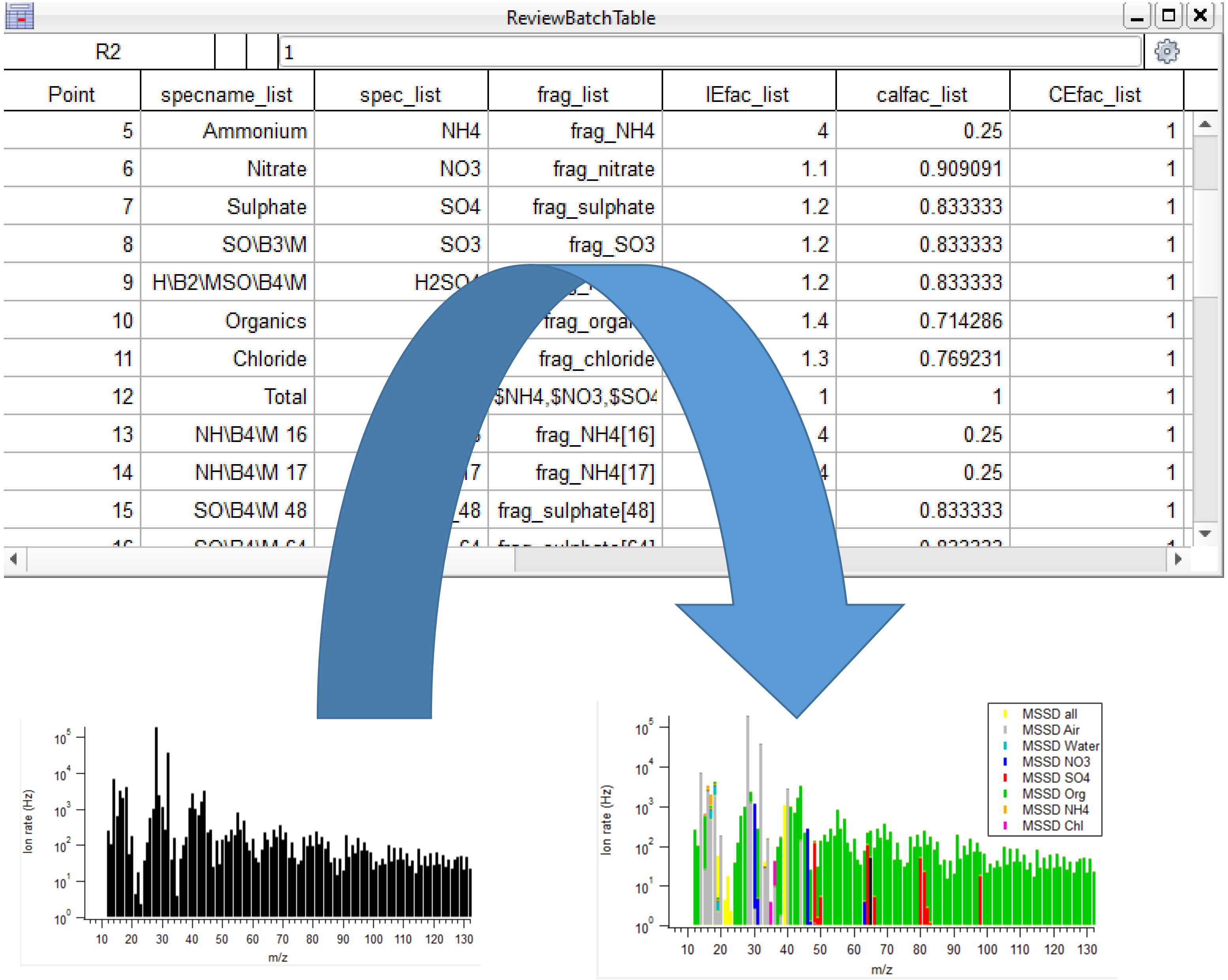


How are species defined in Squirrel?

<u>A species is a row in the batch table!</u>

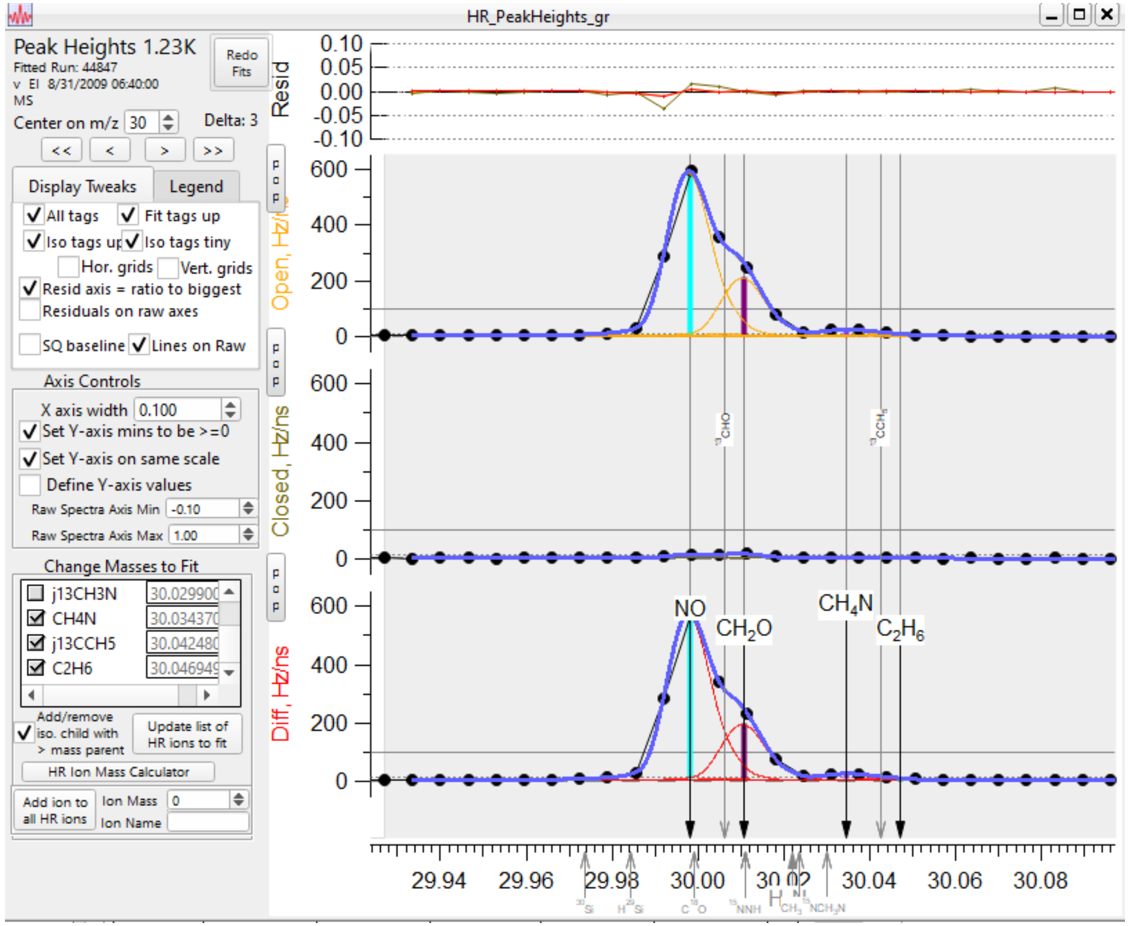
- long name
- short name
- frag wave
- RIE, CE
- Color in RGB

A UMR is not a species!
m/z 30 is not a species,
but NO3_30 is a species



Point	specname_list	spec_list	frag_list	IEfac_list	calfac_list	CEfac_list
5	Ammonium	NH4	frag_NH4	4	0.25	1
6	Nitrate	NO3	frag_nitrate	1.1	0.909091	1
7	Sulphate	SO4	frag_sulphate	1.2	0.833333	1
8	SO\B3\M	SO3	frag_SO3	1.2	0.833333	1
9	H\B2\MSO\B4\M	H2SO		1.2	0.833333	1
10	Organics		frag_orga	1.4	0.714286	1
11	Chloride		frag_chloride	1.3	0.769231	1
12	Total		$NH4,$NO3,$SO	1	1	1
13	NH\B4\M 16		frag_NH4[16]	4	0.25	1
14	NH\B4\M 17	17	frag_NH4[17]	4	0.25	1
15	SO\B4\M 48	48	frag_sulphate[48]		0.833333	1

Why do we need an HR frag table?



Peak Heights 1.23K
Fitted Run: 44847
v EI 8/31/2009 06:40:00
MS
Center on m/z 30
Delta: 3

☑ All tags ☑ Fit tags up
☑ Iso tags up ☑ Iso tags tiny
☐ Hor. grids ☐ Vert. grids
☑ Resid axis = ratio to biggest
☐ Residuals on raw axes
☐ SQ baseline ☑ Lines on Raw

Axis Controls
X axis width 0.100
☑ Set Y-axis mins to be >=0
☑ Set Y-axis on same scale
☐ Define Y-axis values
Raw Spectra Axis Min -0.10
Raw Spectra Axis Max 1.00

Change Masses to Fit

☐	j13CH3N	30.029900
☑	CH4N	30.034370
☑	j13CCH5	30.042480
☑	C2H6	30.046949

☑ Add/remove iso. child with > mass parent
Update list of HR ions to fit
HR Ion Mass Calculator
Add ion to all HR ions
Ion Mass 0
Ion Name

UMR Frag entries come from:

- Multiple ions at the same UMR

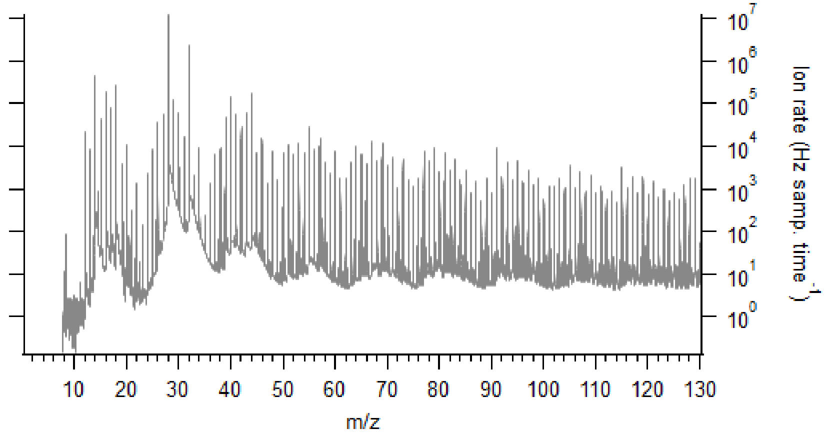
For HR tofs, largely irrelevant for m/z < 100

- Isotopic abundances

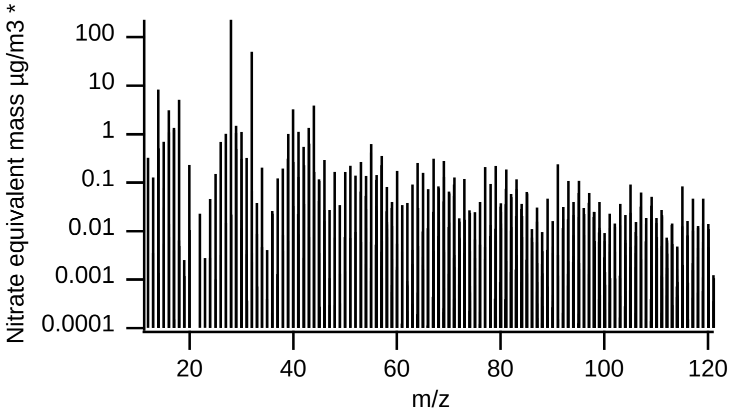
For HR tofs, largely irrelevant (Pika constrain option is used by default)

- Contribution to different species from the same ion

For HR tofs, this issue remains but there are very few issues (CO2)



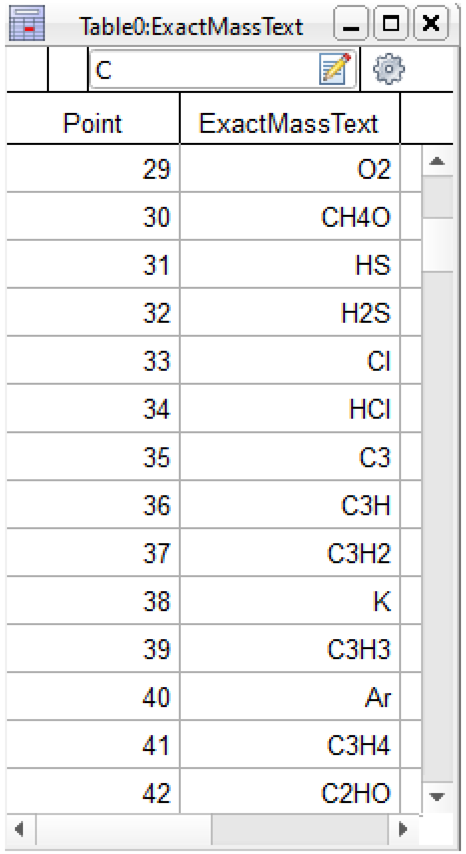
Raw spectra -> HR ‘sticks’



Why do we need HR families?

For a typical HR spectra we have >400 ions (not isotopes) we fit.
We need a grouping mechanism!

Use the chemical formula to group these ions!
Cx (only has Cs)
CH (only has Cs and Hs)
CHO1 (only has Cs and Hs and one O)
CHOgt1 (only has Cs and Hs and more than one O)
CHN
CHO1N
CHOgt1N
CS
HO
NH
Cl
NO
SO
Air
Tungsten
CSi
Other
Any user defined list of HR ions



Point	ExactMassText
29	O2
30	CH4O
31	HS
32	H2S
33	Cl
34	HCl
35	C3
36	C3H
37	C3H2
38	K
39	C3H3
40	Ar
41	C3H4
42	C2HO

Families allow easy grouping of any fitted HR ion
Each HR ion is assigned one and only one family

We can then use families to begin to assemble species

We still need an HR frag table!

<u>HR Frag entries come from:</u>

- Multiple ions at the same UMR

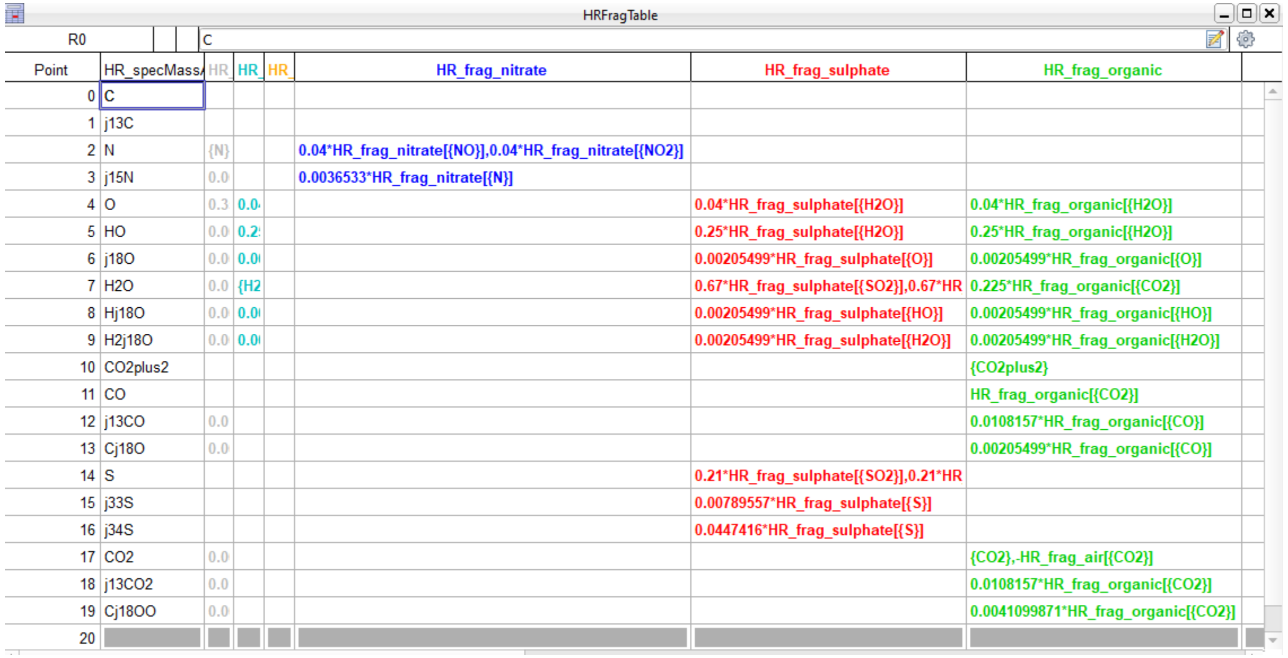
S at 32 (buried in O2), CO at 28 (buried in N2)

- Isotopic abundances

Rare but sometimes needed if dominant m/z HR ion has > m/z than nondominant isotope or dominant ion ‘buried’ in another peak

- Contribution to different species from the same ion

CO2, H2O, OH, O, N

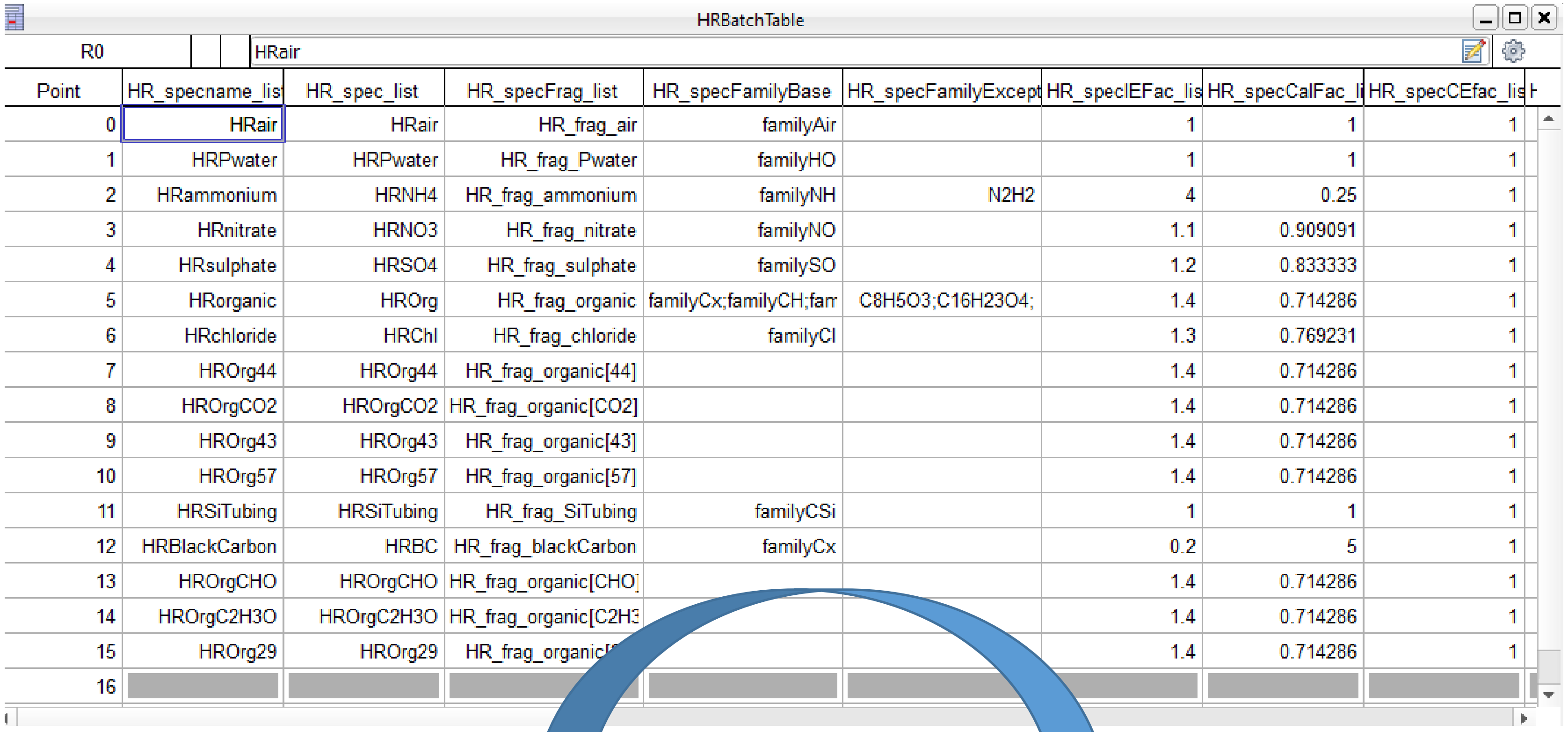


Point	HR_specMass	HR_	HR_	HR_	HR_frag_nitrate	HR_frag_sulphate	HR_frag_organic
0	C						
1	j13C						
2	N	{N}			0.04*HR_frag_nitrate[{NO}],0.04*HR_frag_nitrate[{NO2}]		
3	j15N	0.0			0.0036533*HR_frag_nitrate[{N}]		
4	O	0.3	0.0			0.04*HR_frag_sulphate[{H2O}]	0.04*HR_frag_organic[{H2O}]
5	HO	0.0	0.2			0.25*HR_frag_sulphate[{H2O}]	0.25*HR_frag_organic[{H2O}]
6	j18O	0.0	0.0			0.00205499*HR_frag_sulphate[{O}]	0.00205499*HR_frag_organic[{O}]
7	H2O	0.0	{H2			0.67*HR_frag_sulphate[{SO2}],0.67*HR	0.225*HR_frag_organic[{CO2}]
8	Hj18O	0.0	0.0			0.00205499*HR_frag_sulphate[{HO}]	0.00205499*HR_frag_organic[{HO}]
9	H2j18O	0.0	0.0			0.00205499*HR_frag_sulphate[{H2O}]	0.00205499*HR_frag_organic[{H2O}]
10	CO2plus2						{CO2plus2}
11	CO						HR_frag_organic[{CO2}]
12	j13CO	0.0					0.0108157*HR_frag_organic[{CO}]
13	Cj18O	0.0					0.00205499*HR_frag_organic[{CO}]
14	S					0.21*HR_frag_sulphate[{SO2}],0.21*HR	
15	j33S					0.00789557*HR_frag_sulphate[{S}]	
16	j34S					0.0447416*HR_frag_sulphate[{S}]	
17	CO2	0.0					{CO2},-HR_frag_air[{CO2}]
18	j13CO2	0.0					0.0108157*HR_frag_organic[{CO2}]
19	Cj18OO	0.0					0.0041099871*HR_frag_organic[{CO2}]
20							

How are HR species defined in Pika?

<u>A species is a row in the HR batch table!</u>

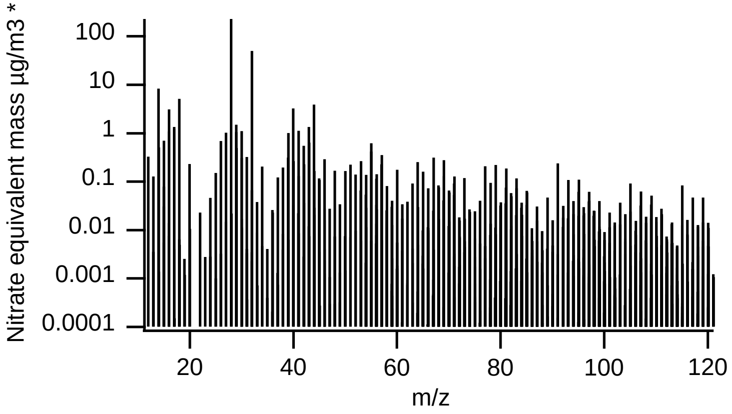
- long name
- short name
- HR frag wave
- *List of families*
- *HR exceptions to families*
- RIE, CE
- color in RGB
- *Must begin with 'HR'*

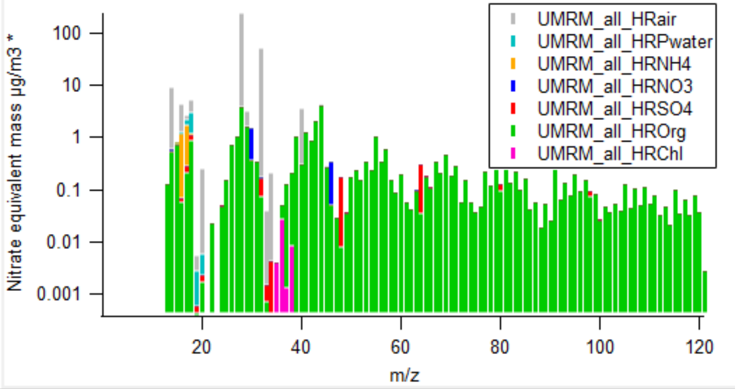


HRBatchTable

R0 | HRair

Point	HR_specname_list	HR_spec_list	HR_specFrag_list	HR_specFamilyBase	HR_specFamilyExcept	HR_specIEFac_lis	HR_specCalFac_li	HR_specCEfac_lis
0	HRair	HRair	HR_frag_air	familyAir		1	1	1
1	HRPwater	HRPwater	HR_frag_Pwater	familyHO		1	1	1
2	HRammonium	HRNH4	HR_frag_ammonium	familyNH	N2H2	4	0.25	1
3	HRnitrate	HRNO3	HR_frag_nitrate	familyNO		1.1	0.909091	1
4	HRsulphate	HRSO4	HR_frag_sulphate	familySO		1.2	0.833333	1
5	HRorganic	HROrg	HR_frag_organic	familyCx;familyCH;fam	C8H5O3;C16H23O4;	1.4	0.714286	1
6	HRchloride	HRChl	HR_frag_chloride	familyCl		1.3	0.769231	1
7	HROrg44	HROrg44	HR_frag_organic[44]			1.4	0.714286	1
8	HROrgCO2	HROrgCO2	HR_frag_organic[CO2]			1.4	0.714286	1
9	HROrg43	HROrg43	HR_frag_organic[43]			1.4	0.714286	1
10	HROrg57	HROrg57	HR_frag_organic[57]			1.4	0.714286	1
11	HRSiTubing	HRSiTubing	HR_frag_SiTubing	familyCSi		1	1	1
12	HRBlackCarbon	HRBC	HR_frag_blackCarbon	familyCx		0.2	5	1
13	HROrgCHO	HROrgCHO	HR_frag_organic[CHO]			1.4	0.714286	1
14	HROrgC2H3O	HROrgC2H3O	HR_frag_organic[C2H3			1.4	0.714286	1
15	HROrg29	HROrg29	HR_frag_organic[			1.4	0.714286	1
16								





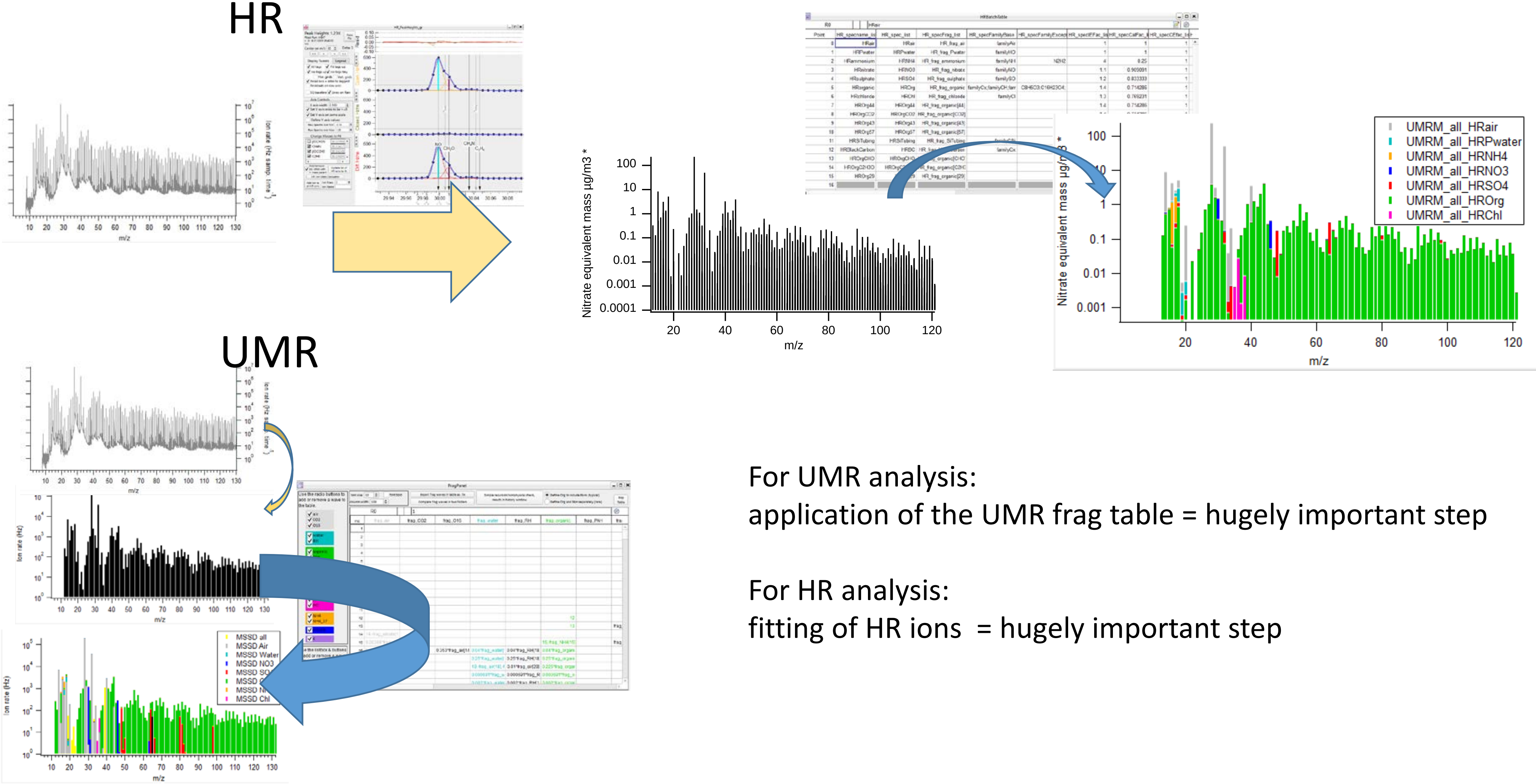
A HR ion is not a species!

i.e. C3H3O is not a species

Two answers to the same question: UMR & HR

HR

UMR



For UMR analysis:
application of the UMR frag table = hugely important step

For HR analysis:
fitting of HR ions = hugely important step