HR frag table discussion

More advanced HR frag table entries for Pika 1.10H

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Preamble:
The purpose of the ppt is to demonstrate HR frag syntax and options.

While this ppt provides details for an m/z 29 HR organic correction, the approach and methods used herein are applicable to other HR corrections.

Sample graph data is V mode, ambient conditions, Org < 1ug/m3. Typical peak fitting settings were used:
All isotopes were constrained. There was one peak width and peak shape setting for all runs. All default HR ions were fit.

The m/z calibration and the peak shape were not optimized for this data set.

The ppt is organized into two sections. The first section demonstrates the problem with various graphs. The second section details how the issue was addressed.

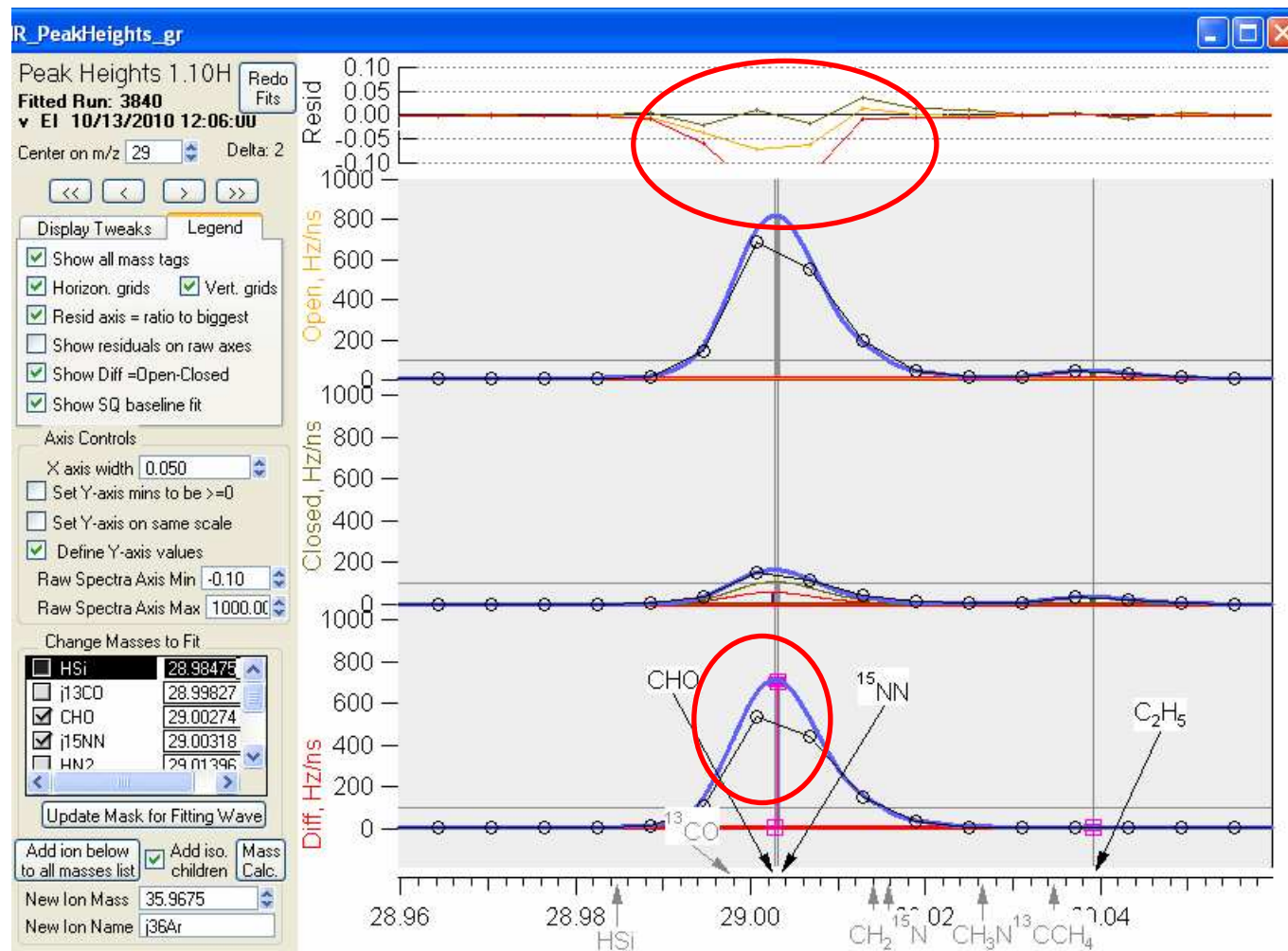HR peak fitting for m/z 28 using the default choice of HR ions: N2
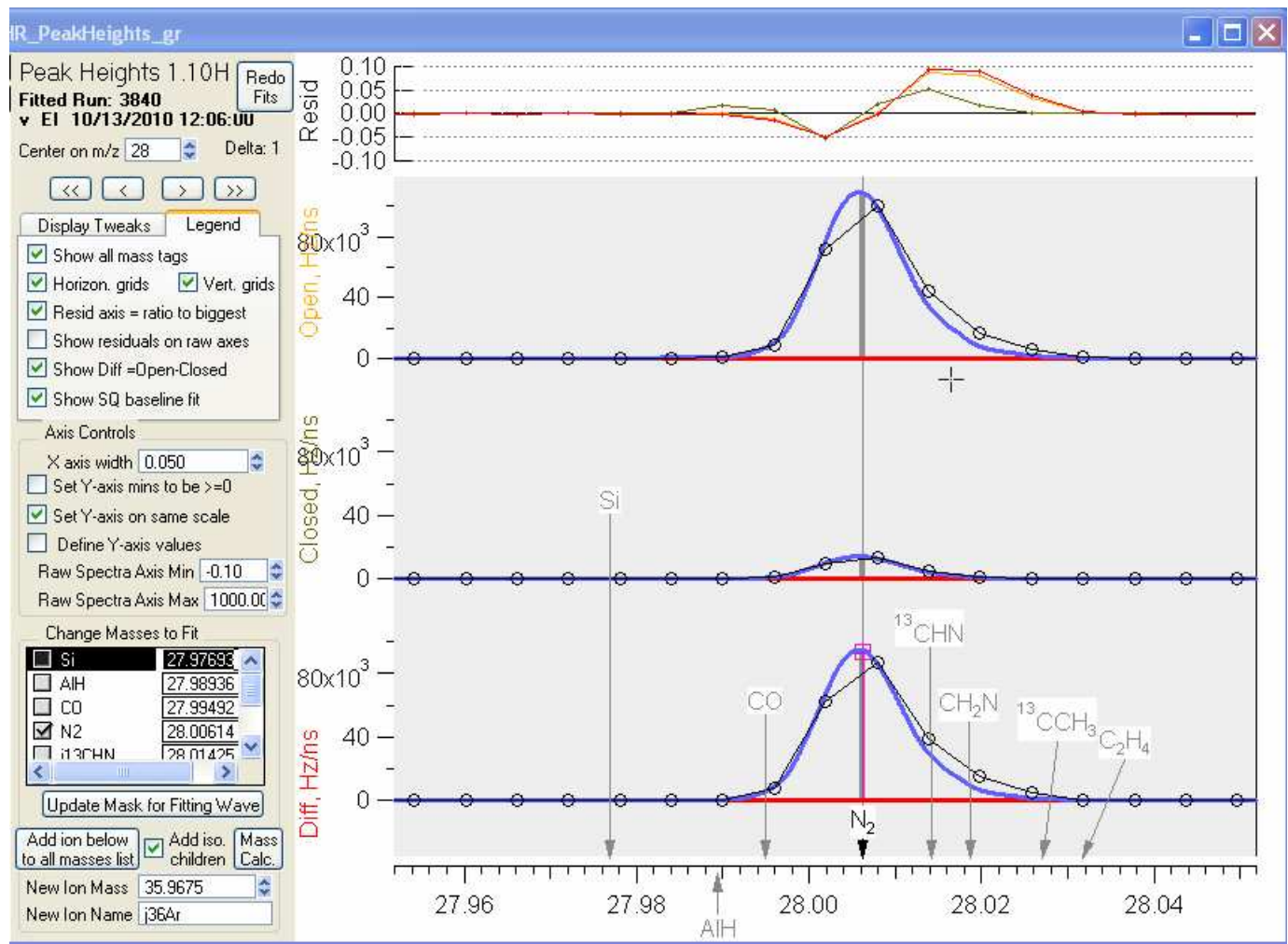
The residuals indicate that the peak shape and the m/z calibration may not be optimized.

# Blow-up of HR peak fitting for m/z 28 using the default choice of HR ions
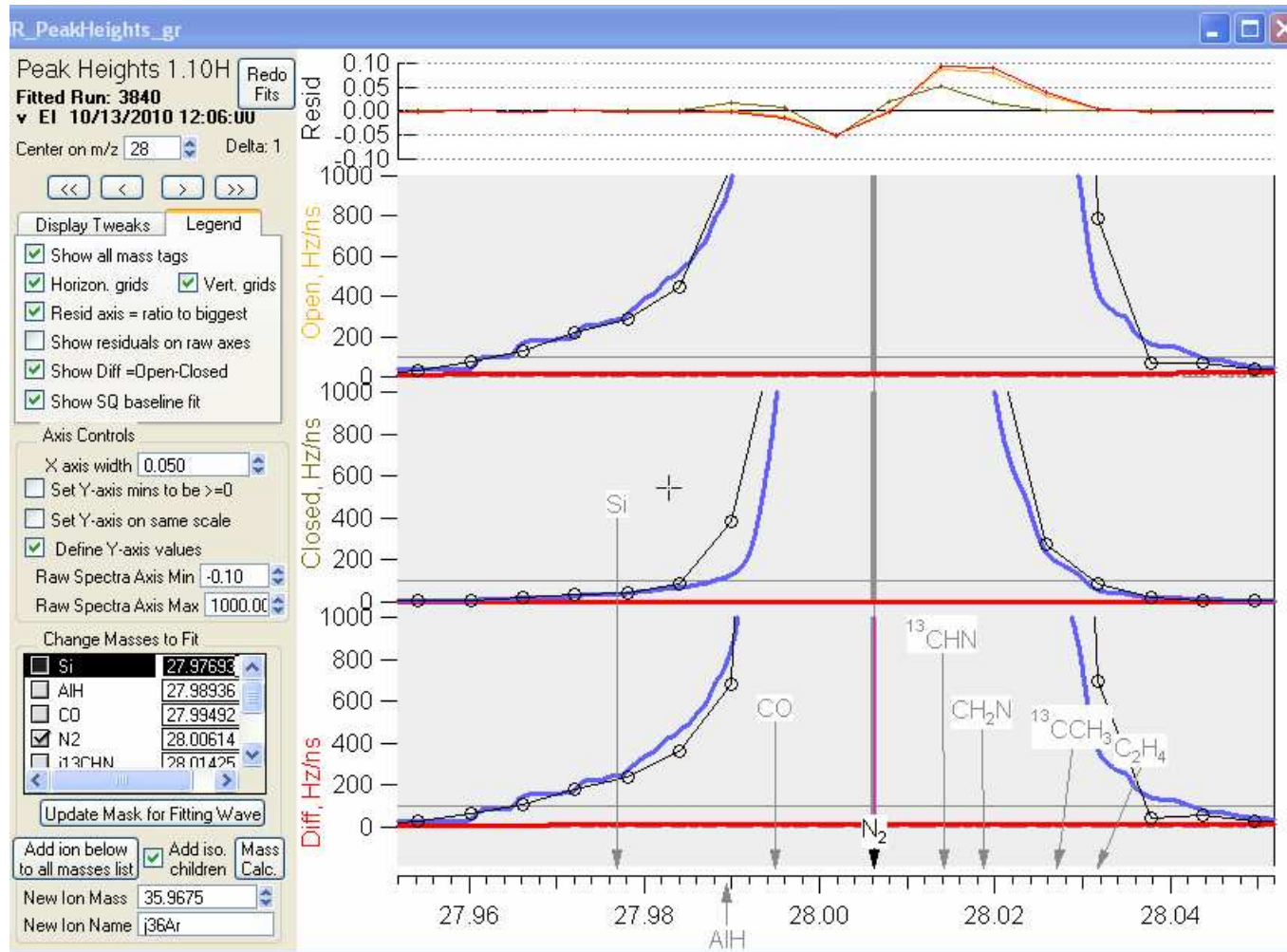
On this scale the overall peak fitting doesn't do too bad. The lumpy peak shape should eventually be addressed, but won't interfere with the purpose of this discussion

HR peak fitting for m/z 29 using the default choice of HR ions: CHO, j15NN, C2H5


The constrained value for j15NN results in an overestimation of 15NN. It is not clear from this data if and to what extent CHO may be present.

Blow-up of HR peak fitting for m/z 29 using the default choice of HR ions
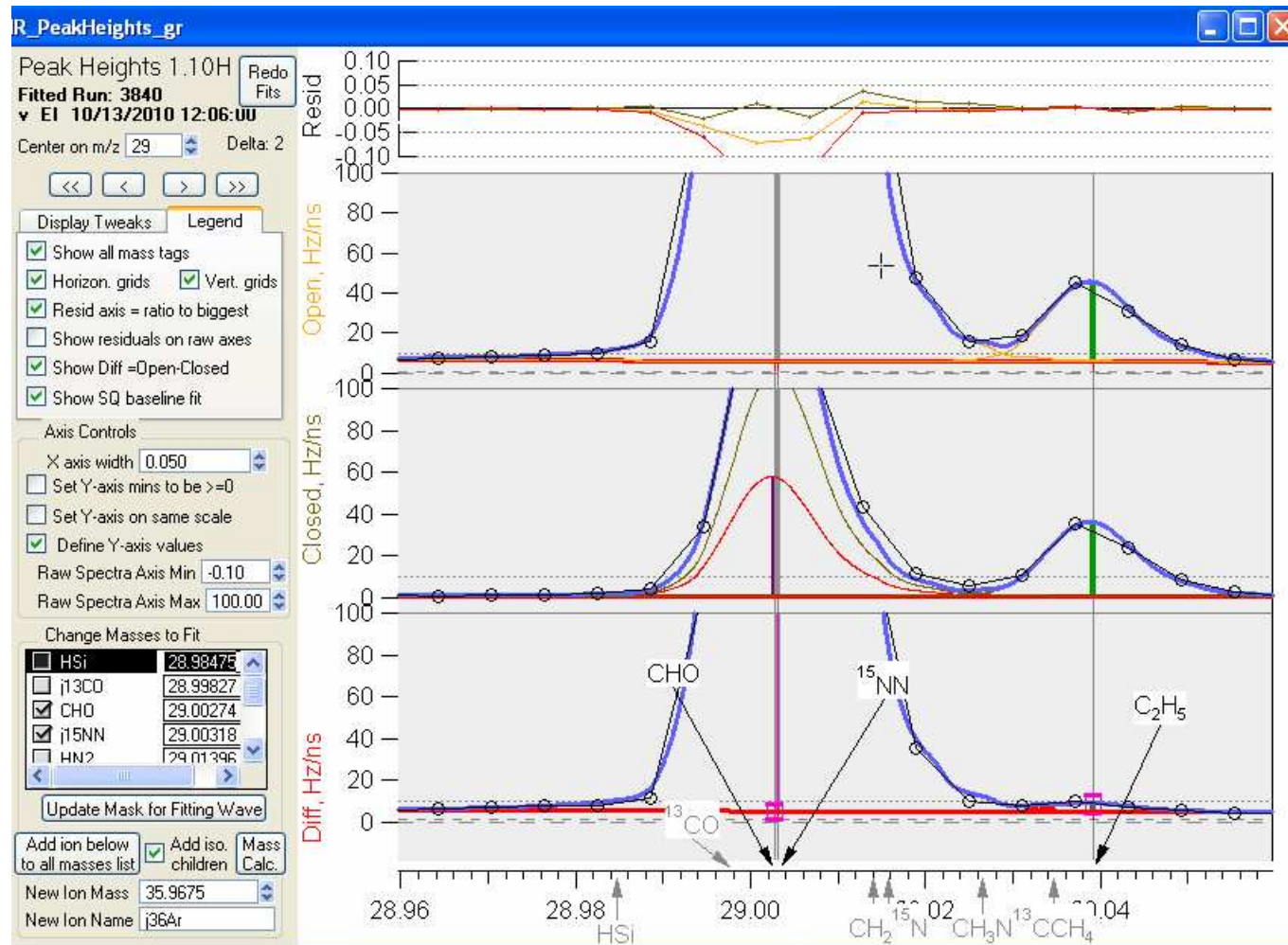
We can successfully fit C2H5 – it is not in the tail of the j15NN/CHO peak. The fit for Open and Diff at CHO is essentially zero, whereas for Closed, it is a positive value. When we examine OMinusC, for CHO we will get a negative value.

# Time series for HR ions m/z 29, and for CHO Open, Closed, Diff, OMinusC
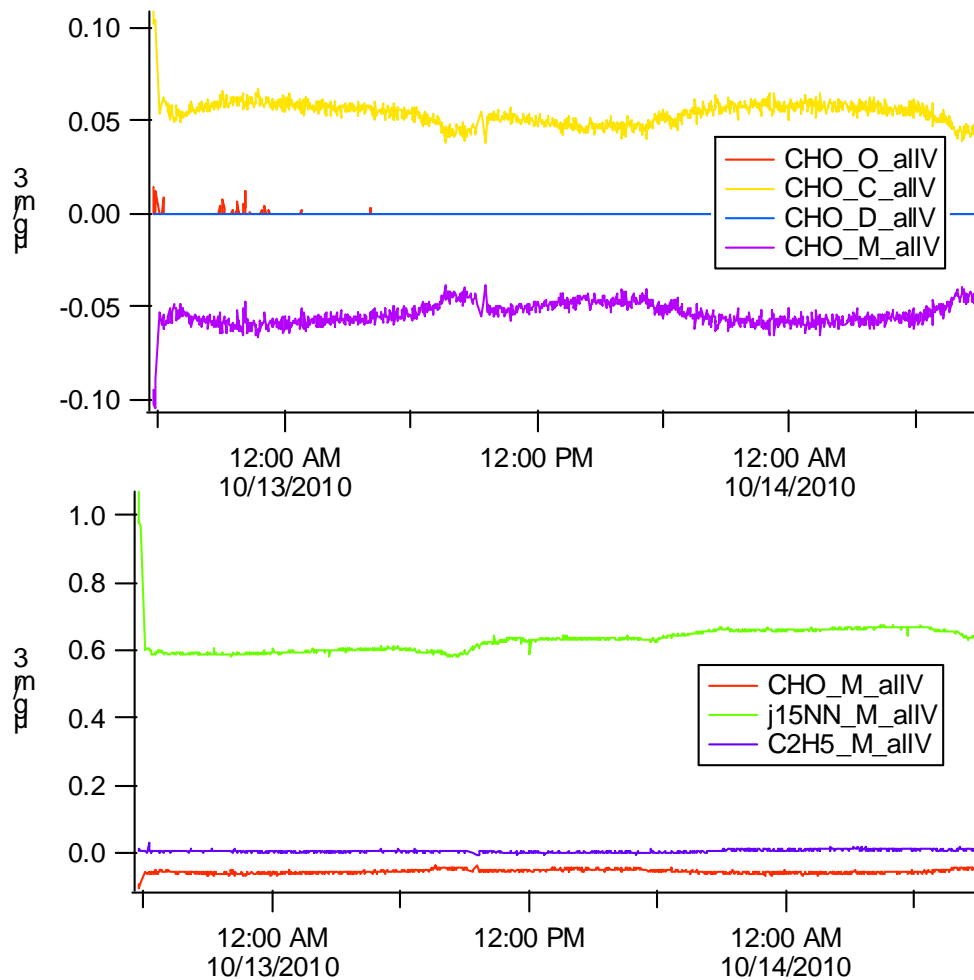
Recall:
The peak fitting for Open, Closed and Diff spectra is such that the peak heights are constrained to be >=0.

OMinusC is the value of Open HR sticks – Closed HR sticks. OMinusC can result in negative values (when Closed > Open). HR time series of Open, Closed and Diff are helpful diagnostics, but OMinusC is the data set of primary interest.

Because j15NN was overestimated, CHO for OMinusC is negative. This needs to be fixed.
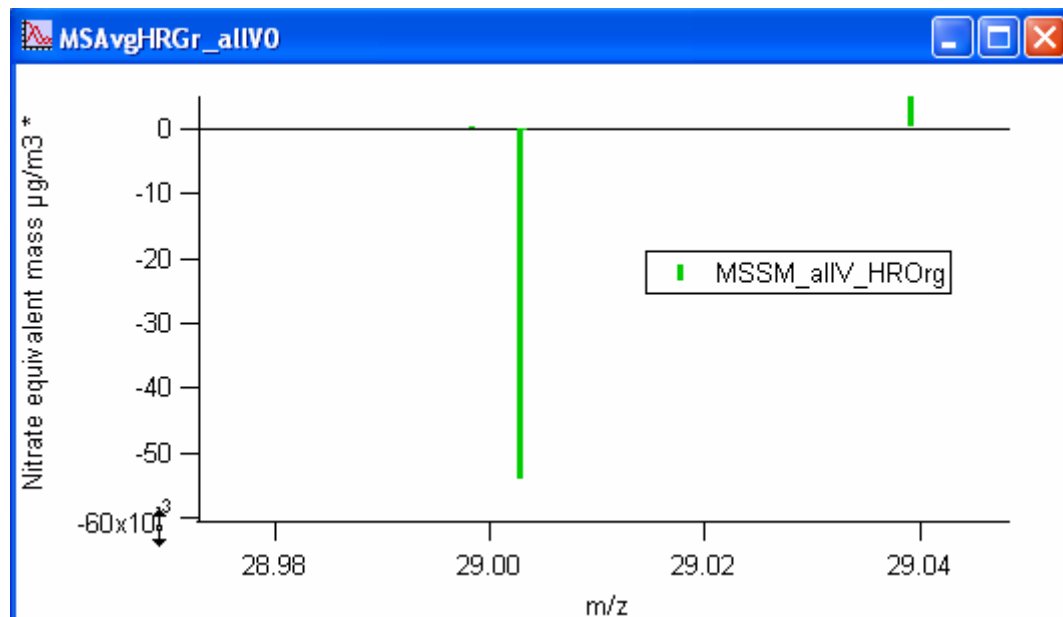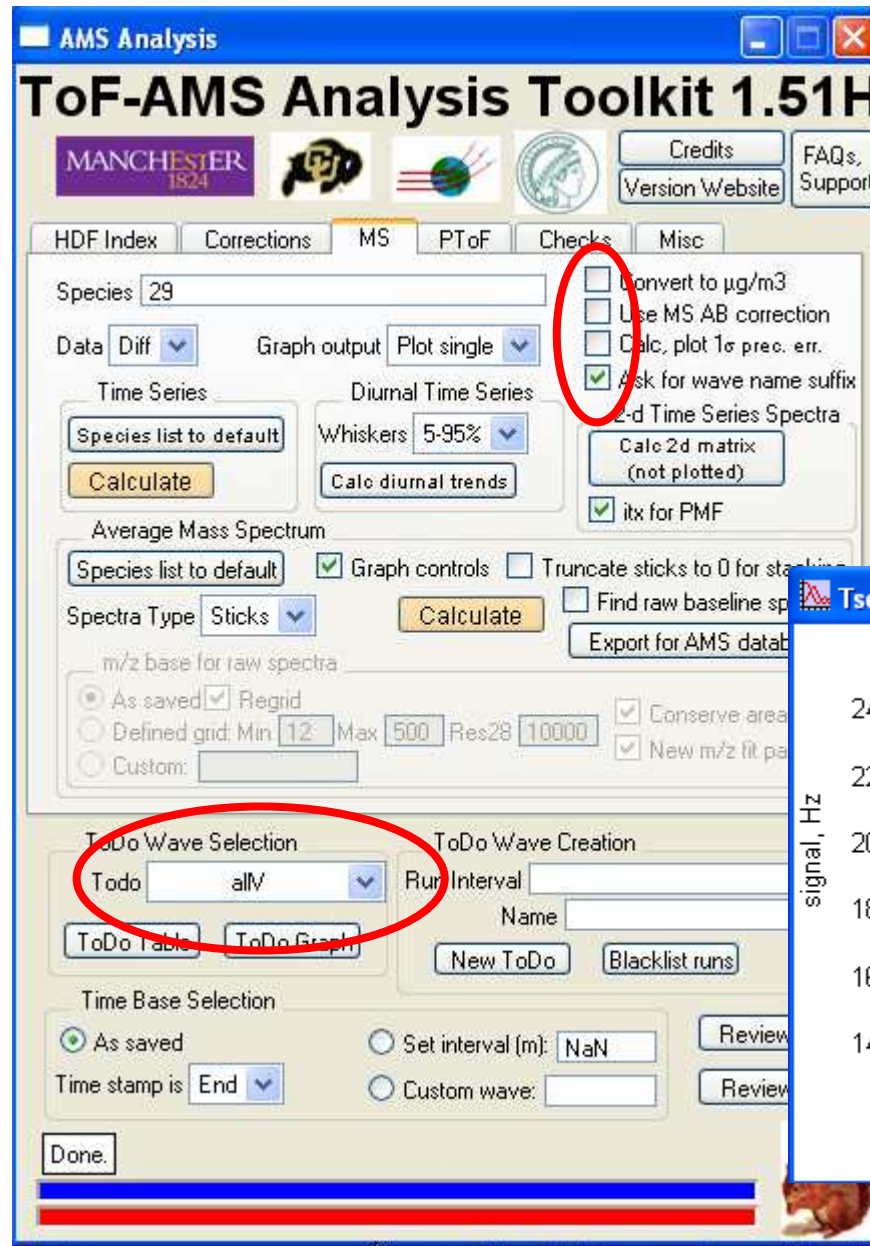
HR mass spectra of HROrg, NOT summed to UMR
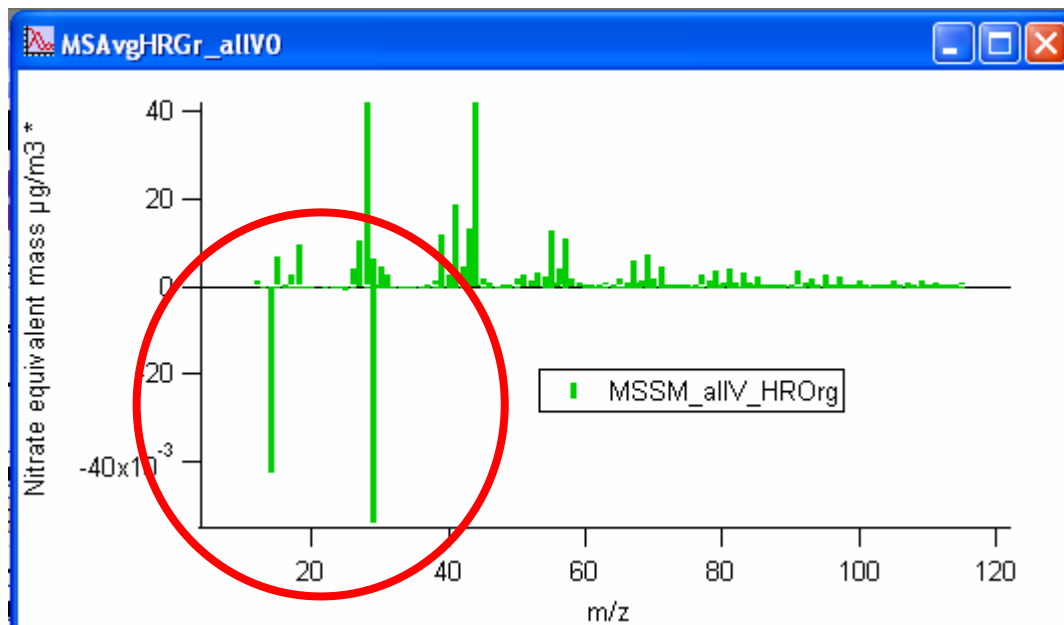
In this particular data set, there are issues at for HR ions at m/z 15 AND and m/z 29.
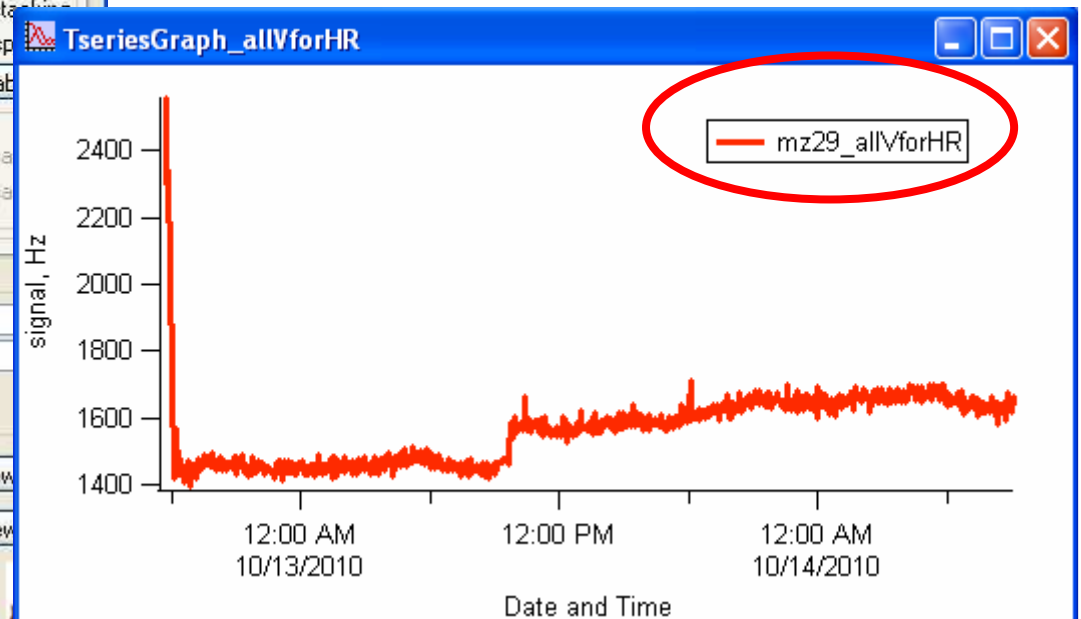
This ppt will give an example of fixing mz29.

A blow up of the mz 29 region confirms that the issue is with the CHO HR ion.

Step 1: Create a UMR mz29 stick wave that we'll use for the HR frag table.

I gave this time series wave a unique name, so that I don't have to fear that it will be overwritten by mistake when performing other UMR actions. It is important this this wave is in units of Hz, NOT ug/m3.

Step 2: Create a time series wave that will be a multiplicative inverse of a HR ion

Due to the current syntax restrictions of the use of time dependent waves in UMR and HR frag entries, we need to create another time series wave. This wave needs to be a multiplicative inverse of an 'allowed' time-changing entity. For this demonstration I am choosing the HR ion CH2O, but it can be any HR ion that doesn't have any HR frag wave complications (perhaps the C HR ion would have been better – less chance of typos). Again, it is important that the units are Hz.

I then executed in the command line: C2HO_M_InverseForHR=1/C2HO_M_InverseForHR

Step 3: Create a new row in the HR frag table for CHO

It is important to add the HR ion in increasing mass order and to not have any typos in the frag wave. The 0.985 multiplier works for this data set. Users can tweak this number (as in UMR frag waves) as is appropriate. The 'C2HO_M_InverseForHR*{C2HO}' factor will always be equal to one.

Step 4 OPTIONAL: Create a new row in the HR batch table so I can see the time series of the values for HROrg : CHO

Point	HR_spec_list	HR_specFrag_list	HR_specB	HR_sp	HR_specFamilyBase	HR_specFamilyExceptio	HR_specCalFac_li	HR_s
0	HRair	HR_frag_air	1	1	familyAir		1	
1	HRPwater	HR_frag_Pwater	1	1	familyHO		1	
2	HRNH4	HR_frag_ammonium	4	1	familyNH	N2H2	0.25	
3	HRNO3	HR_frag_nitrate	1.1	1	familyNO		0.909091	
4	HRSO4	HR_frag_sulphate	1.2	1	familySO		0.833333	
5	HROrg	HR_frag_organic	1.4	1	familyCx;familyCH;fam	C8H5O3;C16H23O4;	0.714286	
6	HRChl	HR_frag_chloride	1.3	1	familyCl		0.769231	
7	HROrg44	HR_frag_organic[44]	1.4	1			0.714286	
8	HROrgCO2	HR_frag_organic[CO2]	1.4	1			0.714286	
9	HROrg43	HR_frag_organic[43]	1.4	1			0.714286	
10	HROrg57	HR_frag_organic[57]	1.4	1			0.714286	
11	HROrgCHO	HR_frag_organic[CHO]	1.4	1			0.714286	
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Step 5 : Confirm that this HR frag entry works: HROrg mass spec, HROrgCHO time series.
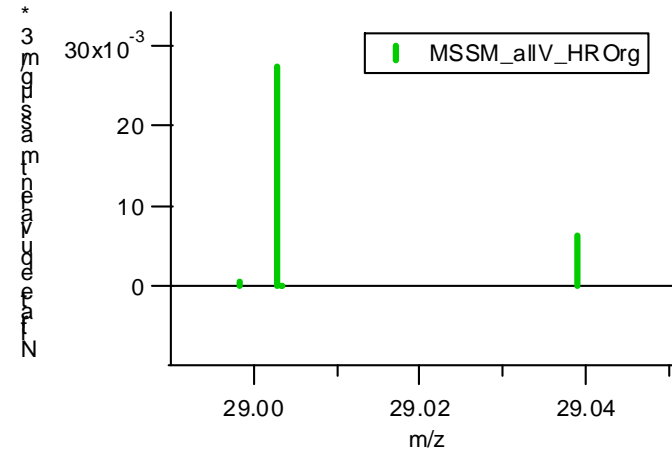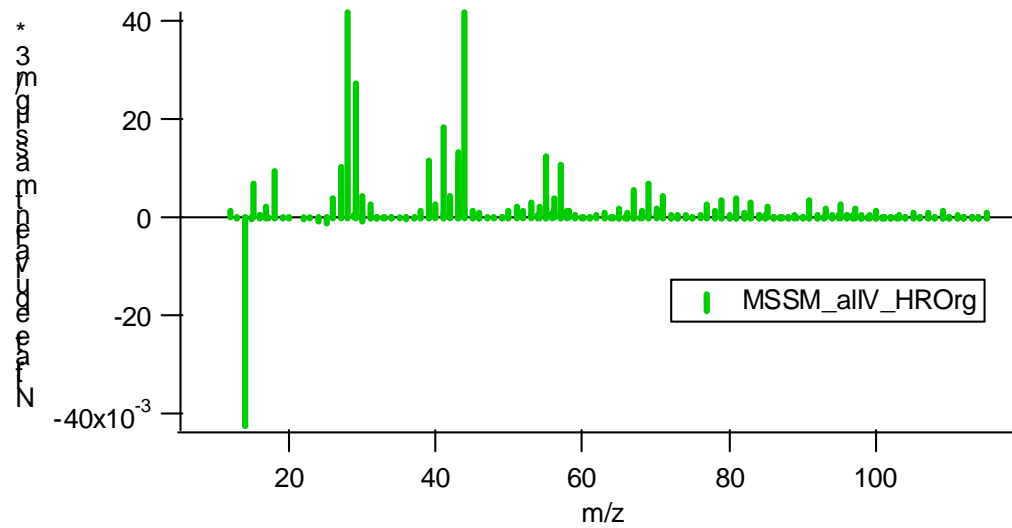
In this particular data set, I do not have a filter period. Optimally, a user would create a time series and avg mass spec of a filter so that the 0.985 coefficient is adjusted to make the CHO contribution to be zero at the filter(s).