

# HR sticks for PMF

A look at what tools are currently available

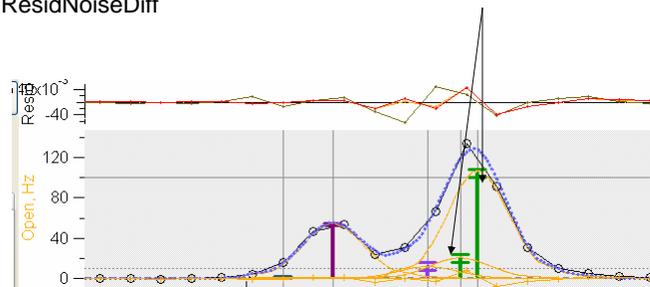
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## Within Pika, the compilation of uncertainties in stick calculation is under development

There are two uncertainty estimates that are somewhat easily accessible for you (as soon as you have done Pika peak fitting on a todo wave).

### Uncertainty #1 "Residuals"

Uncertainties as viewed in Open, Closed, Diff from the HR\_PeakHeights\_gr are saved in a data set called HRResidNoiseOpen, HRResidNoiseClosed, HRResidNoiseDiff



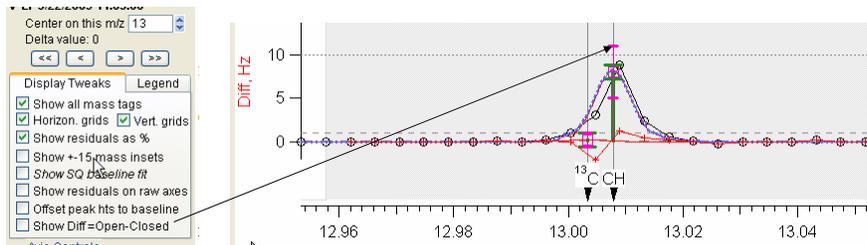
HRResidNoiseDiff = mean (absolute value of residuals at 4 peak widths distance)

## Within Pika, the compilation of uncertainties in stick calculation is under development

### Uncertainty #2 "Counting"

Uncertainties as optionally viewed in Diff from the HR\_PeakHeights\_gr are called HRCountErrorDiff

Formula for calculating this error is the same as for unit resolution sticks (sum of squares...)



For the difference spectra, one run, IF you have found multiplex fits for the raw difference spectra MSD, then the peak height values as calculated by the peak height of the open – peak height of closed (and it's 'error') can be displayed.

## To get the HR sticks for all runs (that were fit) in memory:

Go to the Pika panel, HR Results tab, Time Series Spectra section.

Leave the Mass list blank, Choose a todo wave (usually choosing all is easier in the long run, because rows = t\_series).

Press the "Export Matrices" button

A 2D wave called HRmxD\_sticks is put in memory

HRMxD\_sticks: rows = runs, columns = chosen HR fragment

For HR Clinic sample data set (Helsinki) I only found HR sticks for my V mode data, and the instrument was in V/W switching mode. So every other run is blank.

Row	HRMxD_sticks[[0]	HRMxD_sticks[[1]	HRMxD_sticks[[2]	HRMxD_sticks[[3]	HRMxD_sticks[[4]	HRMxD_sticks[[5]
0						
1	0.0522735	0.000568043	0.0156114	7.08387	-2.57587e-19	0.0257191
2						
3	0.0485004	0.000527041	0.0091795	7.11869	-2.43845e-18	0.0258455
4						
5	0.0406192	0.000441398	0.0126655	7.05077	0.0190185	0.0255989

Point	ExactMassT	ExactMassV	dutyCycleCo	CH	CHO1	CHOg	CHN	CHO1	CHOg	CS	HO	NH	CI
0	C	12.000000	1.52753	1									
1	j13C	13.003355	1.46741	1									
2	CH	13.007825	1.46716	1									
3	N	14.003074	1.41406										
4	CH2	14.015650	1.41342	1									
5	j15N	15.000108	1.36626										
6	NH	15.010899	1.36576									1	
7	CH3	15.023475	1.36519	1									

### To get the 'Residual' uncertainties for all runs (that were fit) in memory:

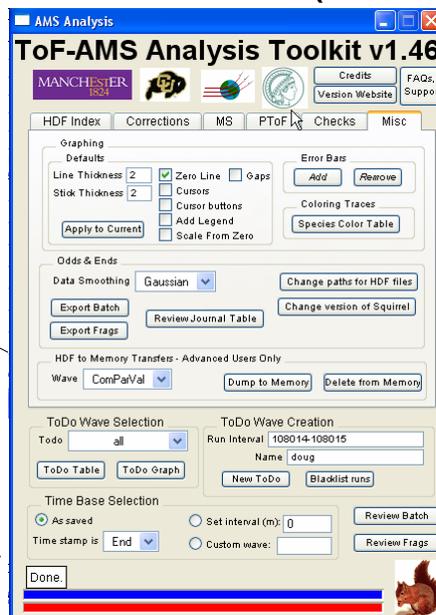
Go to the Squirrel panel, Misc tab, HDF to Memory Transfer section.

Choose HRResidNoiseDiff in the Wave popup.

Choose a todo wave (usually choosing all is easier in the long run, because rows = t\_series).

Press the "Dump to Memory" button

A 2D wave called HRResidNoiseDiff\_d is put in memory



HRResidNoiseDiff\_d : rows = runs, columns = chosen HR fragment

For HR Clinic sample data set (Helsinki) I only found HR sticks for my V mode data, and the instrument was in V/W switching mode. So every other run is blank.

The top window, 'Table4:HRResidNoiseDiff\_d', displays a grid with 8 rows (0-7) and 8 columns (0-6). The data values are as follows:

Row	0	1	2	3	4	5	6
0							
1	1.59096	0.666635	0.813046	75.0342	29.3199	1.50386	3.10
2							
3	1.84284	0.284679	0.33553	100.47	54.2455	1.74338	2.55
4							
5	0.62712	0.27263	0.290838	40.8098	14.7183	0.922836	1.94
6							
7	1.94721	0.318418	0.410594	38.9361	18.0615	2.08007	2.76

The bottom window, 'ChosenMassTable:ExactMassText....', shows a table with 8 rows (0-7) and 13 columns. The data is as follows:

Point	ExactMassT	ExactMassV	dutyCycleCo	CH	CHO1	CHOg	CHN	CHO1	CHOg	CS	HO	NH	CI
0	C	12.000000	1.52753	1									
1	j13C	13.003355	1.46741	1									
2	CH	13.007825	1.46716	1									
3	N	14.003074	1.41406										
4	CH2	14.015650	1.41342	1									
5	j15N	15.000108	1.36626										
6	NH	15.010899	1.36576									1	
7	CH3	15.023475	1.36519	1									

## To get the 'Counting' uncertainties for all runs (that were fit) in memory:

Two Steps:

(1) From the command line run:  
`squirrel_fetch(all, pk_CountingErrors, "", "HROpenStick;HRClosedStick")`

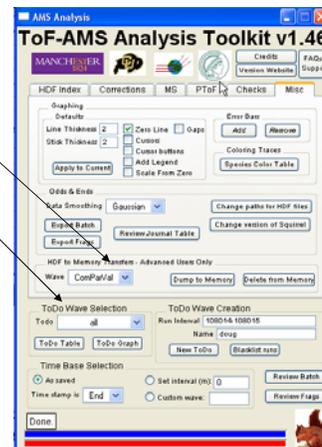
(2) Go to the Squirrel panel, Misc tab, HDF to Memory Transfer section.

Choose HRCCountErrorDiff in the Wave popup.

Choose a todo wave (usually choosing all is easier in the long run, because rows = t\_series).

Press the "Dump to Memory" button

A 2D wave called HRCCountErrorDiff\_d is put in memory



### What are 'Counting' uncertainties? In Squirrel:

Sigma is one value, is defined by user in squirrel panel, 'width of single ion'  
Noise is one value, is defined by user in squirrel panel, 'corresponds to electronic noise'  
IntegrationWidthNs is wave, is squirrel stick integration region for each m/z in ns units  
SI is single ion wave, in bits ns units, one value for each run  
ToFPulserInHz, is a wave, one value for each run, 99.99% will be constant value  
samptimeClosed is the time spent in closed for each run.

Take abs value of sticks, multiply by sigma, divide by stick integration region, undo duty cycle correction:

```
err_Closed =abs(MSSClosed)*sigma/samptimeClosed // for each run
err_Open=abs(MSSOpen)*sigma/samptimeOpen // for each run
if (waveexists(corr_fact)) // if airbeam correction factor exists, use it
    err_Closed/=corr_fact
    err_Open/=corr_fact
endif
err_Closed*=sqrt(28/(q+1))
err_Open*=sqrt(28/(q+1))
```

Calc a noise error estimate in Hz-type units:

```
err_tmp =noise*noise*IntegrationWidthNs*28/((SI)*ToFPulserInHz*m/z))
```

**Add noise errors to sticks errors, take square root of sum of squares**

```
err_Closed +=err_tmp
err_Open += err_tmp
err_Diff = sqrt(err_Open+err_Closed) = MSSDiff_p_err
```

### How are 'Counting' uncertainties applied? In Squirrel:

Multiply the sticks error matrix by square of frag coefficients:

```
MSSD_all_Mat_Org_err = MSSDiff_p_err *OrgFragMatrix^2 // cross product
```

### How are uncertainties applied? In Pika:

The 'Residual' nor the 'Counting' uncertainties do \*not\* incorporate an airbeam correction. Also, the 'Electronic Noise' and 'Sigma' are hard-coded, not user modifiable. Also, currently calculated Pika uncertainties do include the 'electronic noise' error.

There is no HR frag table yet, so there is no code that 'applies' it to species.