# Squirrel and Pika Error Estimates

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Pika version 1.13/Squirrel version 1.54

UMR error concepts and math derivations by James Allan,
http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg11/JDAerrorpresentation.pdf

# Preamble

The purpose of this document is to provide clarity about signal (sticks) and error calculations performed in Squirrel and Pika.  A lengthy review of established practice within the UMR is first presented to demonstrate concepts and details. Next, a demonstration of the calculations of two HR errors ('Old'='TotCountErr' and 'New'='TotSigErr') is presented.

The purpose is not to provide a thorough examination of all possible AMS error contributions and their mathematical derivations.

# Glossary

<u>ToF</u> : time of flight

<u>UMR</u> : unit mass resolution, i.e. m/z 116

<u>HR</u> : high resolution; AMS signal that has been assigned a chemical formula, i.e. C3H4O3

<u>Raw spectra</u> : spectra that has not been integrated in the ToF or m/z dimension

<u>Stick or area of signal</u> : an integrated value, either UMR or HR, derived from raw spectra; in squirrel and pika the native units are Hz and always has the ToF duty cycle correction applied

<u>Peak width</u> : a user defined formula as a function of m/z of a parameter similar to the width parameter of a gauss formula.

<u>Peak shape</u> : a user defined formula which describes the average arrival signal in ToF space of an isolated HR ion

<u>Peak height</u> : visually, the vertical magnitude of a peak; the peak height, along with the peak width and shape, defines a peak; it is centered on an identified HR ion and is similar to the height parameter of a gauss formula

<u>ToF duty cycle correction</u> : a correction made to AMS ToF data to account for the non-linear response of ions with larger mass moving more slowly than ions of smaller mass when the ions are 'pushed' into the mass spectrometer; also called m/z duty cycle in the AMS panel. It is a sqrt(28/mz) multiplicative factor.

<u>AB</u> : airbeam

# Maths - we use the root sum square as a basis for all calculations.

From the Allan document, the UMR 1 sigma precision error is

$$\Delta I_{Hz} = \sqrt{(1+\beta^2)I_{Hz}^{*} + \alpha^2 t_s}$$

| | |
|---|---|
| $1+\beta_{SI}^{2}$ | Single ion relative error. This is the standard deviation of recorded single ion strengths divided by the mean strength. |
| $I_{Hz}^{*}$ | Number of ions measured; sticks; Integrated ion signal in Hz; see below. |
| $\alpha^2$ | Uncertainty due to electronic noise; see below. |
| $t_s$ | DAQ sampling time in seconds for a measurement. Note that depending on DAQ settings this is a different value in MS open mode than in MS closed mode. |

The values saved in squirrel as sticks, $I_{Hz}^{*}$, is modified by the following:
(i) $I_{Hz}^{*}$ has the ToF m/z duty cycle correction applied; this needs to be 'undone' to estimate actual ions counted.
(ii) The AB correction factor needs to be applied to to estimate actual ions counted due to MCP degradation etc.
(iii) $I_{Hz}^{*}$ is calculated separately above and below the baseline for MS open and MS closed spectra.
Thus:

$$I_{Hz}^{*} = \frac{I_{Hz}}{CF_t} \cdot \sqrt{\frac{28}{m/z}}$$

| | |
|---|---|
| $I_{Hz}^{*}$ | Sticks as they are saved in squirrel/pika. |
| $CF_t$ | Correction factor as a function of time. This is the correction factor as derived by the AB correction function within squirrel; it is unitless. |
| $m/z$ | Mass-to-charge ratio of the ion signal. |

The electronic noise term is estimated by:

$$\alpha^2 = \frac{Q^2 IW_{ITOF}}{SI^2 F_p} \cdot \frac{28}{m/z}$$

| | |
|---|---|
| $Q$ | Electronic noise factor. This is the standard deviation of signal-free data recorded at 1GHz. Units are bits root nanoseconds. |
| $IW_{ITOF}$ | Integration width in ion ToF space, in nanoseconds. This is derived using the squirrel m/z calibration and baseline resolution functions. |
| $SI$ | Single ion strength, in bit nanoseconds. |
| $F_p$ | ToF pulser frequency, in Hz. |

Replacing all the terms gives Equation 1:

$$\Delta I_{Hz} = \frac{1}{\sqrt{t_s}} \sqrt{\left(1+\beta_{SI}^{2}\right) \cdot \frac{I_{Hz}}{CF_t} \cdot \sqrt{\frac{28}{m/z}} + \frac{Q^2 IW_{ITOF}}{SI^2 F_p} \cdot \frac{28}{m/z}}$$

In practice, we always use the squared term; Equation 2:
$$\Delta I_{Hz}^{2} = \frac{1}{t_s}\left[\left(1+\beta_{SI}^{2}\right) \cdot \frac{I_{Hz}}{CF_t} \cdot \sqrt{\frac{28}{m/z}} + \frac{Q^2 IW_{ITOF}}{SI^2 F_p} \cdot \frac{28}{m/z}\right]$$

# What are the UMR errors that have been calculated in the squirrel corrections tab?
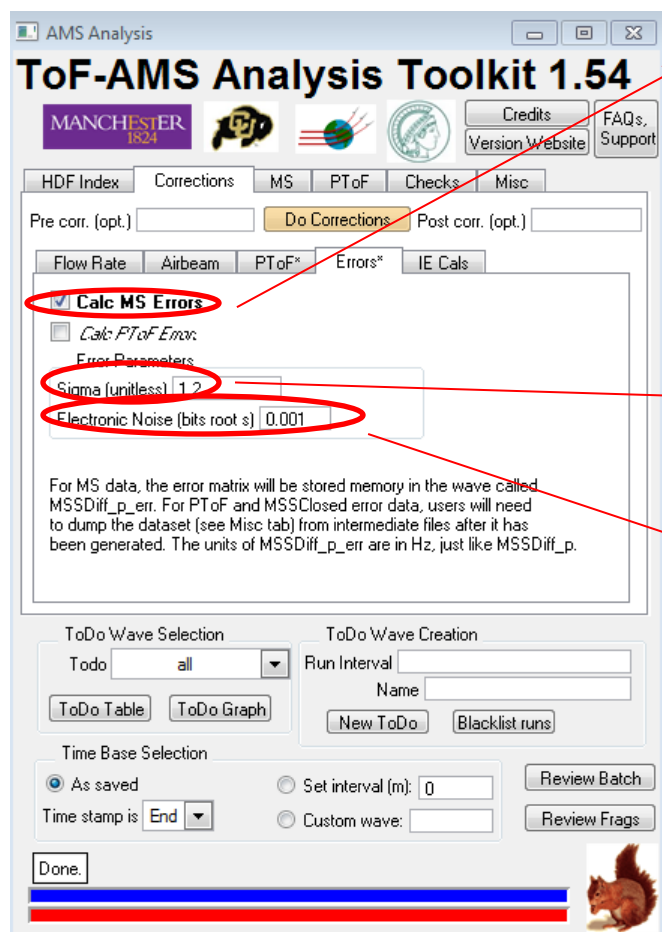


1$\sigma$ precision errors are calculated and saved in intermediate files via the gold "Do Corrections" button and the "Calc MS Errors" checkbox. Errors are calculated and saved for open MS spectra, closed MS spectra and the difference spectra, which is the square root of the sum of the squares of the open and closed.

Sigma is the estimate of the ion-to-ion measurement variability. It is the $1 + \beta^2$ term in the Allan presentation.

This is a factor of the estimate of electronic noise; it is the Q term of the previous slide.
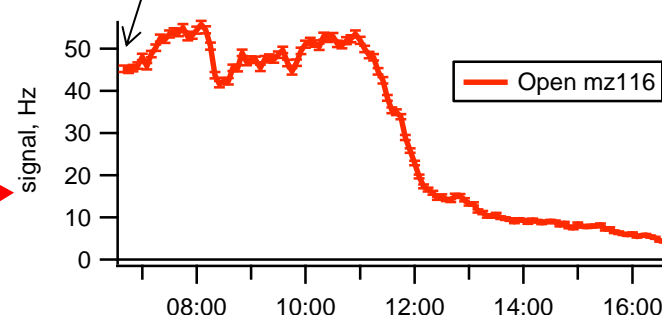
It is unusual for users to alter these two default parameters in the calculation of UMR errors.

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# How do I view the UMR errors that have been calculated in the corrections tab? …. One method
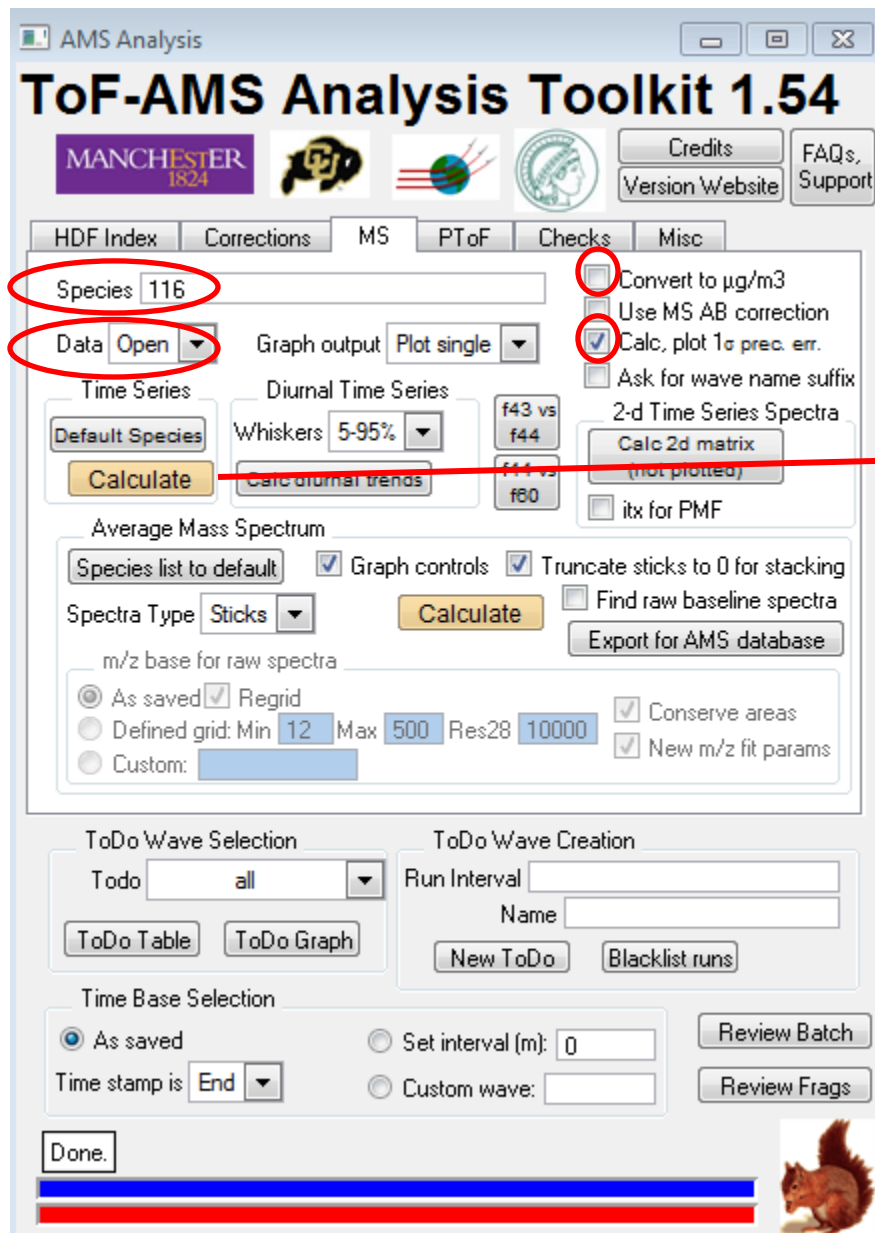
For simplicity, focus on
- one run (the first run)
- one m/z, 116
- Hz units



In this example m/z 116 signal for the first run for MSOpen is **45.245** Hz; the error is **0.770** Hz.

The next slides will explicitly show how the **0.770** Hz error for the open spectra was calculated.

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# Detailed example of UMR 1σ precision error calculation for MS at single run, single m/z, part 1

To generate errors, we need the number of ions counted above and below the baseline of the open spectra,

$$I_{OpenAboveBaselineHz} \quad \text{and}$$

To the right are graphs taken from the MS baseline panel for this run, shown at two y-axis ranges at the m/z 116 region. The pink region indicates the UMR peak integration region.

Technical detail: Raw spectra data points saved with the AP240 cards (this case) are 1ns apart. New ADQ cards can sample at faster than a 1GHz rate. For the ADQ cards the familiar single ion value, used to converted integrated area, are saved in bits/sampling interval (i.e. bits*0.625ns). By integrating data in points space (not m/z space) and using the single ion value the raw spectra sampling interval units cancel out to generate stick data in Hz.





For the open stick (area of signal) above baseline:

OpenSignal_a = area(DAQ raw spectra-calculated baseline, mz116 integration start point , mz116 integration start point )
OpenSignal_a = area(blue-red, left pink side , right pink side)  for visual learners
OpenSignal_a = area(blue-red data in bits, 13393, 13445 (or 52.294ns) integrating in point space = 6.041e-2 (bits*ns)
OpenSignal_b = (OpenSignal_a /single ion)*ToF pulsers = (6.041e-2 /16.4)*25000          = 92.093 (Hz)
OpenSignal_c = OpenSignal_b /ToF duty cycle corr = 92.093 *sqrt(28/116)          = 45.245 (Hz) = $I_{OpenAboveBaselineHz}$

For the open stick  (area of signal) below baseline:

OpenBase_a = area(calculated baseline, mz116 integration start point , mz116 integration start point )
OpenBase_a = area(red data, left pink side , right pink side)  for visual learners
OpenBase_a = area(red data in bits, 13393, 13445) integrating in point space          = 3.966e-3 (bits*ns)
OpenBase_b = (OpenBase_a /single ion)*ToF pulsers = (3.966e-3/16.4)*25000          = 6.045 (Hz)
OpenBase_c = OpenBase_b /ToF duty cycle corr = 6.045 *sqrt(28/116)          = 2.970 (Hz) = $I_{OpenBelowBaselineHz}$          6

# Detailed example of UMR 1σ precision error calculation for MS at single run, single m/z, part 2

For this run we spent 63.5 s in MS open; the AB correction factor at this run is 0.911 (unitless); single ion strength is 16.4 (bits*ns); ToF pulsers were at 25000 (Hz); UMR integration width is 52.294 (ns); the open stick above baseline of mz116 is 45.245 Hz (see previous slide); the open stick below the baseline m/z 116 is 2.970 Hz (see previous slide). From the AMS panel, error tab, sigma is 1.2 (unitless) and electronic noise is 0.001 bits*sqrt(ns). The ToF duty cycle correction is sqrt(28/mz of interest). Below we generate terms in Eq. 2.

Error for the open signal above baseline:
OpenErr_a = abs(Open stick above baseline) = abs(45.245)       = 45.245 (Hz)
OpenErr_b = OpenErr_a/sampling time in s= 45.245/63.5     = 0.713 (Hz^2)
OpenErr_c = OpenErr_b*sigma^2 = 0.713*(1.2^2)      = 1.026 (Hz^2)
OpenErr_d = OpenErr_c/AB correction factor = 1.026/0.911   = 1.126 (Hz^2)
OpenErr_e = OpenErr_d/ToF duty cycle corr = 1.126*sqrt(28/116) = 0.553 (Hz^2)

Error for the open signal below baseline (do just as we did for signal above baseline):
OpenBaseErr_a = abs(Open stick below baseline) = abs(2 .970)    = 2 .970 (Hz)
OpenBaseErr_b =OpenBaseErr_a/sampling time in s= 2.970/63.5  = 4.678e-2 (Hz^2)
OpenBaseErr_c = OpenBaseErr_b*sigma^2 = 4.678e-2 *(1.2^2)  = 6.736e-2 (Hz^2)
OpenBaseErr_d = OpenBaseErr_c /AB correction factor at this run = 6.736e-2 /0.911 = 7.390e-2 (Hz^2)
OpenBaseErr_e = OpenBaseErr_d /ToF duty cycle corr = 7.390e-2/sqrt(28/116) = 3.631e-3 (Hz^2)

Error for the electronic noise (not dependent on open/closed spectra):
ElecNoise_err_a = ElecNoise^2 = 0.001^2         = 1e-6 (bits^2*ns)
ElecNoise_err_b = ElecNoise_err_a /(single ion^2) = 1e-6/(16.4^2)  = 3.718e-9 (1/ns)
ElecNoise_err_c = ElecNoise_err_b*UMR integration width = 3.718e-9* 52.294 = 1.944e-11 (unitless)
ElecNoise_err_d = ElecNoise_err_c /ToF pulsers = 1.944e-11 / 25000  = 7.777e-12 (s)
ElecNoise_err_e = ElecNoise_err_d*ToF duty cycle corr^2 = 7.777 e-12 *(28 /116) = 1.877e-12 (s)

**Total Open error** = sqrt((OpenErr_e + ElecNoise_err_e) + (OpenBaseErr_e + ElecNoise_err_e))
= sqrt (0.553 + 1.877e-12 + 3.631e-3 + 1.877e-12 )    **= 0.770 (Hz) for UMR m/z 116 Open; signal =45.245 Hz**

Similar calculations for m/z 116 for the closed signal for this same run (using different sampling time in MS Closed mode) gives ClosedErr_e= 2.896e-1, ClosedBaseErr= 2.512e-3 Note: diff signal for this run is open-closed = 45.245-2.332=42.913 Hz Diff signal.

**Total Diff Error = sqrt(sum all squared terms)**
= sqrt((OpenErr_e+ElecNoise_err_e)+(OpenBaseErr_e+ElecNoise_err_e)+(ClosedErr_e+ElecNoise_err_e)+(ClosedBaseErr_e+ ElecNoise_err_e) )
= sqrt((0.553 + 0 1.877*e-12 ) + (0.256 + 0 1.877*e-12 )+ (0.256 + 0 1.877*e-12) +( 0.256 + 0 1.877*e-12)**= 0.788 (Hz) for UMR m/z 116 Diff ; signal= 42.913 (Hz)**

Ugh! That was painful... what have I learned?

* A good estimate (when the open is much larger than the closed) is to divide the UMR Hz signal by the time spent measuring and then find the square root.

For the previous calculation of MS open for this m/z and this run this is
~ sqrt(45/63) ~= sqrt(1) = 1 (est) ~= .8 (actual)

For the previous calculation of MS diff for this m/z and this run this is
~ sqrt (  (45/63)^2 + (2/63)^2 ) ~= sqrt(1) = 1 (est) ~= .8 (actual)

* If you change your AB correction you really should recalculate your errors.

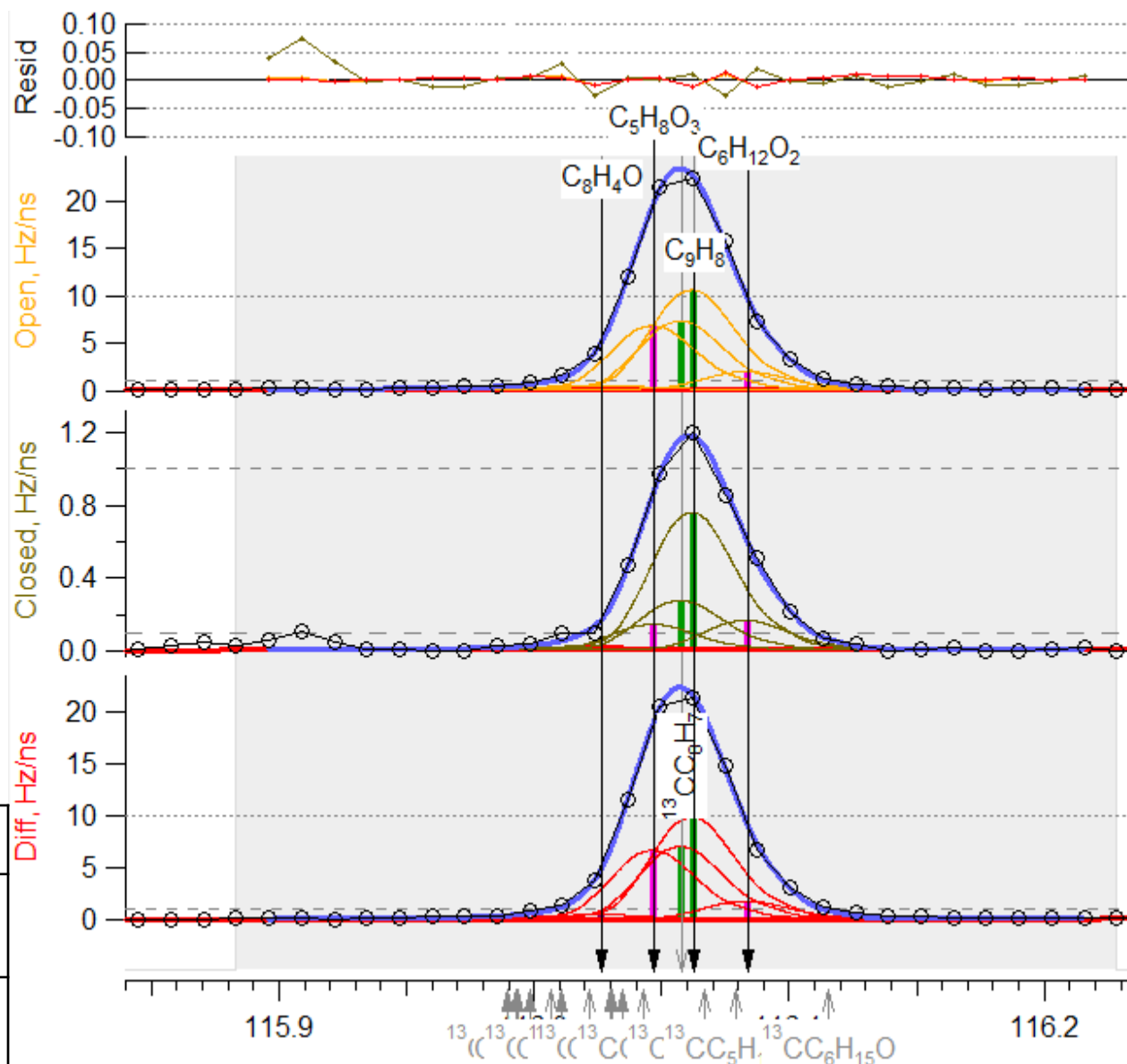# How are HR sticks different from UMR?   part 1

This is the 'pika' graph for the same run and same m/z as in previous slides.

As an aside, this is V mode data with aerosol loadings of ~40 ug/m3.

The HR peak height is what is fit.  To convert to signal we convert from peak height to area. The formula for converting peak height to peak area is:

$$I_x = PH_x \cdot PW_x \cdot PSS \cdot \sqrt{\pi}$$

| | |
|---|---|
| $PH_x$ | Peak height of HR ion x, units of Hz/ns |
| $PW_x$ | Peak width of HR ion x, is empirically determined before the fit, units of ns |
| $PSS$ | Peak shape scalar, is empirically determined before the HR fit, unitless |



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# How are HR sticks different from UMR?   part 2

The HR stick calculation is heavily dependent on
(a) the m/z calibration, which directly affects
           (ai) HR ion identification and
           (aii) fitting
(b)           relative proximity and heights (fit results) of selected HR ions
and in general, to a somewhat lesser extent,
(c)           the peak width,
(d)           peak shape and
(e)           the baseline estimate
(x)           various other subtleties

To address a–e a good check is to sum all the HR sticks for one integer m/z and compare to the UMR value. (See the previous slide and the Sq vs Pk button in the pika panel). The examination of isolated HR ions is also most useful.

For low m/zs (<80 m/z) the list of possible HR ion formulas is small enough and the m/z distance between chosen adjacent HR ions is wide enough that typically (ai) is not an issue.

For high m/zs (120-150 m/z) use of the W mode signal can instruct the selection of ions, but this must be balanced with the amount of new information these high m/zs may contain.

# Detailed example of HR stick calculation for MS open at single run, single HR ion, C5H8O3

<u>For the open stick (area of signal) above baseline:</u>
Perform a linear least squares fit of the peak heights of baseline-subtracted spectra with user-defined peak shapes of set of HR ions chosen at m/z 116 (in this case C8H4O C5H8O3, j13CC8H7, C9H8, C6H12O2), where the isotopes is constrained (j13CC8H7 is not fit, the signal is determined by the C9H7 'parent').

For this run and at this m/z the peak width, PW, is 1.858 (ns), the peak shape scalar, PSS, is 1.034 (unitless).
The spectra being fit has already been converted to Hz/ns units and the baseline subtracted. Specifically,
RawSpectra_Hz = DAQRawSpectra * (1/Single ion)*Tof Pulsers = Raw spectra signal * (1/16.4)*25000  = data in Hz/ns
RawSpectraLessBaseline_Hz = RawSpectra_Hz - baseline in RawSpectra_Hz  = data in Hz/ns

Signal_C5H8O3_a = peak height fit found centered at point at C5H8O3 of RawSpectraLessBaseline_Hz  = 6.685 (Hz/ns)
Signal_C5H8O3_b = Signal_C5H8O3_a*PW*PSS*sqrt(pi) = 6.685*1.858*1.034*sqrt(pi)  = 22.523 (Hz)
Signal_C5H8O3_c = Signal_C5H8O3_b /ToF duty cycle corr = 22.794*sqrt(28/116.047)  = 11.064 (Hz)

As  check with the UMR, the sum of all the HR ions at m/z 116 above baseline is 44.06, which is 97.4%  of the UMR value of 45.245.

$$I_{m/z=116Hz} \approx I_{C8H4OHz} + I_{C5H8O3Hz} + I_{j13CC8H7Hz} + I_{C9H8Hz} + I_{C6H12OHz}$$

By pressing the gold "Table of HR sticks from step 4 fit" button in the pika panel we get a display of peak height and peak signal values of C5H8O3 and other HR ions at m/z 116:

OneRunHRSticksTable

590R X 1C          424.630

| ExactMassWave | ExactMassText | ExactI | ExactMas | OneRunStickOpe | OneRunPeakHeightO | |
|---|---|---|---|---|---|---|
| 116.026 | C8H4O | | | 0.744 | 0.449 | |
| 116.047 | C5H8O3 | | | 11.064 | 6.685 | |
| 116.058 | j13CC8H7 | C9H7 | 0.097341 | 11.884 | 7.181 | |
| 116.063 | C9H8 | | | 17.294 | 10.451 | |
| 116.084 | C6H12O2 | | | 3.074 | 1.858 | |

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# What is the HR error named HR*TotCountErr?

* is O, C, or OMinusC for Open, etc

These are the errors one gets by considering only the signal attributed to each HR ion.

The HROTotCountErr for C5H8O3 is calculated by its signal in Hz, which in turn is a linear multiple of the peak height. This peak height dependence is emphasized by the dark circles and gold traces in the graph.
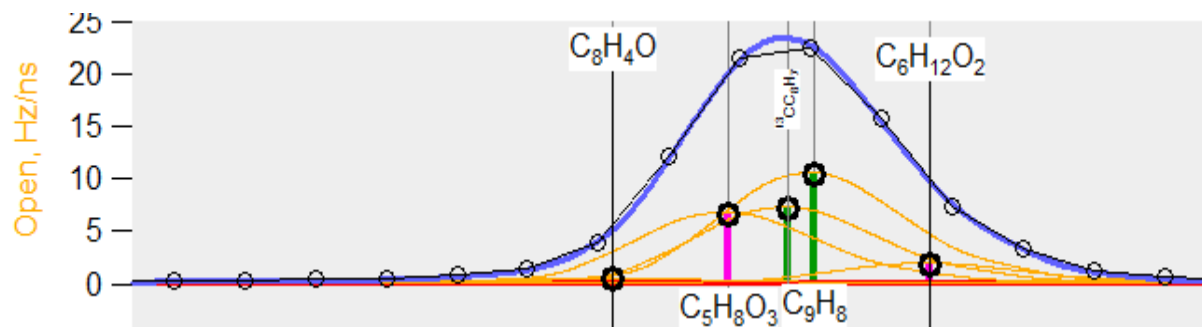


All of the terms in of the UMR error calculation of equation 2 are applicable; $I_{Hz}$ is simply replaced with $I_{C5H8O3 \text{ (Hz)}}$.

Most of the time the HROTotCountErrr is an <u>underestimation</u> due to overlapping HR ion signals. In general, greater HR ion signal overlap should result in greater error.

However signal for j13CC8H7 is constrained and not 'fit'. Its error is predetermined by the signal of the parent ion and the relative isotopic abundance. Colloquially, "it doesn't matter what the raw data at m/z 116 is."

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# Detailed example of HROTotCountErr calculation for MS at single run, single HR ion (C5H8O3), part 1

<u>For the open stick (area of signal) below baseline:</u>
If we want to consider only the signal 'below' the HR peak at C5H8O3 we consider only a fraction of the area of the UMR signal below the baseline. How big a fraction? We use the peak width found at m/z 116 and consider +/-4 peak widths of the average baseline value. The use of +/- 4 peak widths is an estimate. For this data +/- 4 peak widths encompasses 99.5% of a peak shape.

The pink rectangle in the graph indicates pictorially the amount of open signal below the baseline signal we are attributing to the C4H8O3 HR ion.
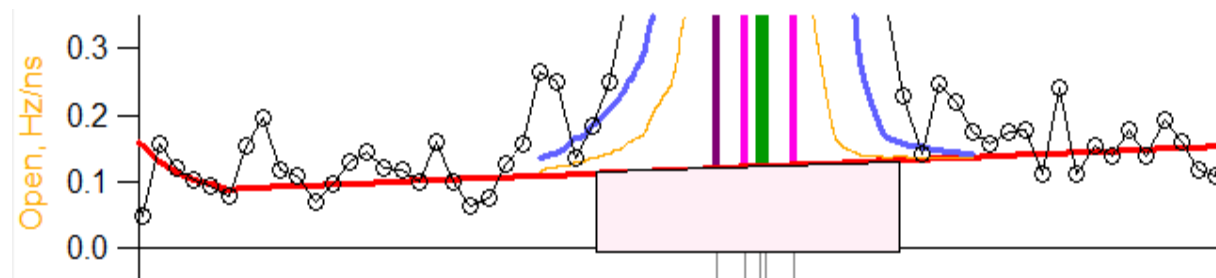


HROpenBase_stick = (OpenBaseErr_e/UMRwidth in ns)*8*PW in ns = (2.970/52.294)*8*1.858          = 0.831 Hz

# Detailed example of HROTotCountErr calculation for MS at single run, single HR ion ($C_5H_8O_3$),  part 2

Error for the open signal of $C_5H_8O_3$ above baseline:

HROpenErr_a = abs(signal) = abs(11.064 )                                   = 11.064 (Hz)

HROpenErr_b = HROpenErr_a/sampling time in s= 11.064/63.5         = 0.174 (Hz^2)

HROpenErr_c = HROpenErr_b*sigma^2 = 0.174*(1.2^2)                   = 0.251 (Hz^2)

HROpenErr_d = HROpenErr_c/AB correction factor = 0.251/0.911        = 0.276 (Hz^2)

HROpenErr_e =HROpenErr_d/ToFdutycyclecorr = 0.276*sqrt(28/116.047)   = 0.135 (Hz^2)

Error for the open signal of $C_5H_8O_3$ below baseline (do just as we did for signal above baseline):

HROpenBaseErr_a = abs(HROpenBase_stick ) = abs(0.831)                    = 0.831 (Hz)

HROpenBaseErr_b = HROpenBaseErr_a/sampling time in s= 0.831 /63.5        = 1.309-2 (Hz^2)

HROpenBaseErr_c = HROpenBaseErr_b*sigma^2 = 1.309-2*(1.2^2)            = 1.885e-2 (Hz^2)

HROpenBaseErr_d = HROpenBaseErr_c /AB correction factor at this run = 1.885e-2/0.91 = 2.072e-2(Hz^2)

HROpenBaseErr_e = HROpenBaseErr_d /ToF duty cycle corr = 2.072e-2/sqrt(28/116.047) = 1.016e-2 (Hz^2)

Error for the electronic noise of $C_5H_8O_3$:

For simplicity, this value is estimated to be equal to the UMR electronic noise.  This is a slight overestimation, but the contribution is too small to bother.

We set HRElecNoise_err = ElecNoise_err_e = + 1.877e-12 (s)

**HROTotCountErr**  = sqrt((HROpenErr_e + HRElecNoise_err) + (HROpenBaseErr_e + HRElecNoise_err_e))

            = sqrt ((0.135 + 1.877e-12) + (1.016e-2 + 1.877e-12))                    **= 0.381 (Hz)**

# What is the HR error named HR*TotSigErr?

Briefly, these are the errors one gets by incorporating overlapping HR ion signals. In Pika 1.13 the exception is if the HR ion is a constrained isotope, then the TotSigErr is the same as the TotCountErr.

The HROTotCountErr for C5H8O3 is calculated by the fit of all signal for m/z 116 . The heavy blue trace indicates the sum of the HR fits at m/z 116. Thick black circles represent the estimated instantaneous signal at each HR ion of the sum of the fits; we use this as a surrogate for a peak height.  The teal traces outline an area in Hz which is used to calculate the errors for each HR ion.  The exception is the isotope, j13CC9H7; in this case we just the peak height of the signal (teal trace = gold trace in previous graph for j13CC9H7; ). Instead of using $I_{C5H8O3\ (Hz)}$ we generate an estimate of the 'total signal seen at C5H8O3', $I_{signal\ centered\ at C5H8O3\ (Hz}$
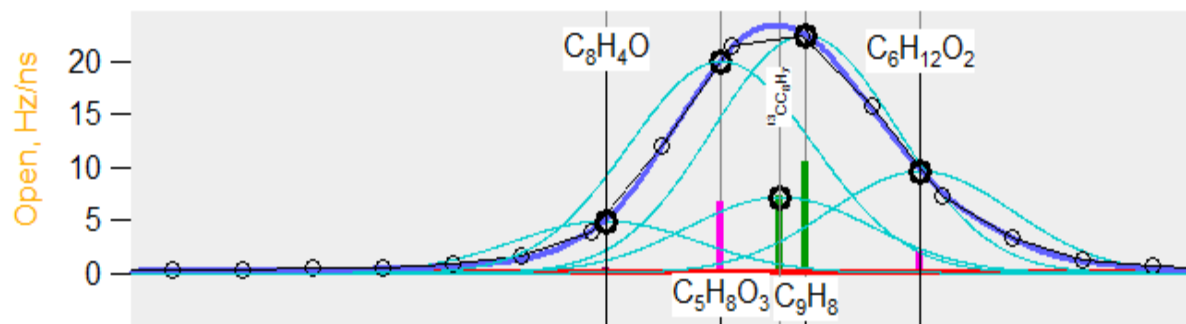


The HROTotSigErr incorporates HR ion signal of overlapping HR ions.

$$I_{\text{signal centered at C5H8O3, Hz}} = PH_{\text{signal centered at C5H8O3, Hz/ns}} \cdot PW_{m/z116,ns} \cdot PSS \cdot \sqrt{\pi}$$

For the open stick (area) above baseline:
Signal_C5H8O3_a = peak height of sum of all HR fits found centered at point at C5H8O3                    = 20.014 (Hz/ns)
Signal_C5H8O3_b = Signal_C5H8O3_a*PW*PSS*sqrt(pi) = 20.014 *1.858 * 1.034 *sqrt(pi)                    = 68.151 (Hz)
Signal_C5H8O3_c = Signal_C5H8O3_b/ToF duty cycle corr = 68.151 *sqrt(28/116.047)                    = 33.121 (Hz)

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# Detailed example of HROTotSigErr calculation for MS at single run, single HR ion (<u>C4H8O3</u>)

Error for the open signal of C5H8O3 above baseline:

| | | |
|---|---|---|
| HROpenErr_a = <u>abs</u>(signal of C5H8O3 above baseline) = abs(33.121) | | = 33.121 (Hz) |
| HROpenErr_b = HROpenErr_a /sampling time in s= 33.121/63.5 | | = 0.522 (Hz^2) |
| HROpenErr_c = HROpenErr_b*sigma^2 = 0 .522*(1.2^2) | | = 0.751 (Hz^2) |
| HROpenErr_d = HROpenErr_c / AB correction factor = 0.751/0.911 | | = 0.824 (Hz^2) |
| HROpenErr_e =HROpenErr_d/ToFdutycyclecorr = 0.824*sqrt(28/116.047) | | = 0.405 (Hz^2) |

Error for the open signal of C5H8O3 below baseline (do just as we did for HROTotCountErr):
HROpenBaseErr_a = abs(HROpenBase_stick ) = abs(0.831)           = 0.831 (Hz)
HROpenBaseErr_b = HROpenBaseErr_a/sampling time in s= 0.831 /63.5     = 1.309-2 (Hz^2)
HROpenBaseErr_c = HROpenBaseErr_b*sigma^2 = 1.309-2*(1.2^2)       = 1.885e-2 (Hz^2)
HROpenBaseErr_d = HROpenBaseErr_c /AB correction factor at this run = 1.885e-2/0.91 = 2.072e-2(Hz^2)
HROpenBaseErr_e = HROpenBaseErr_d /ToF duty cycle corr = 2.072e-2/sqrt(28/116.047) = 1.016e-2 (Hz^2)

Error for the electronic noise for C5H8O3 (do just as we did for HROTotCountErr) :
We set HRElecNoise_err = ElecNoise_err_e =  1.877e-12 (s)

**HROTotSigErr**  = sqrt(HROpenErr_e + HRElecNoise_err + HROpenBaseErr_e + HRElecNoise_err_e)
                     = sqrt (0.405 + 1.877e-12 + 1.016e-2 + 1.877e-12  ) **= 0.644 (Hz)**

## Below is a table or relevant parameters for the two HR error calculations.

| | HROTotCountErr | | | HROTotSigErr | | |
|---|---|---|---|---|---|---|
| | (slide 12 thick black circles) | | | (slide 15  thick black circles) | | |
| HR ion | Open signal (Hz/ns) | Open signal (Hz) | HROTotCountErr (Hz) | Open signal (Hz/ns) | Open Signal (Hz) | HROTotSigErr (Hz) |
| C8H4O | 0.449 | 0.744 | 0.139 | 4.916 | 8.136 | 0.331 |
| C5H8O3 | 6.685 | 11.064 | 0.381 | 20.014 | 33.121 | 0.644 |
| j13CC8H7 | 7.181 | 11.884 | 0.394 | 7.181 | 11.836 | 0.394 |
| C9H8 | 10.451 | 17.294 | 0.471 | 22.478 | 37.196 | 0.682 |
| C6H12O2 | 1.858 | 3.074 | 0.218 | 9.617 | 15.438 | 0.452 |

# Conclusions

You should use of HR*TotSigErr instead of HR*TotCountErr Errors.

HR*TotSigErr >= HR*TotCountErr for any HR ion.
HR*TotSigErr >> HR*TotCountErr for a tiny HR ion next to a large HR ion.
HR*TotSigErr = HR*TotCountErr when the HR ion is isolated.
HR*TotSigErr = HR*TotCountErr for HR isotopes that are constrained.

The HR*TotSigErr errors still do not account for many things such as uncertainty in m/z calibration, peak width, peak shape, baselines...
HR ions that are 'really close together' or 'buried' in the signal of an adjacent HR ion will have errors that are still currently underestimated.

A final graph:
Comparison of the two errors for all non constrained HR ions (n=304) which have been fit for this run. The black cross indicates the HR ion examined in previous slides, C5H8O3.



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