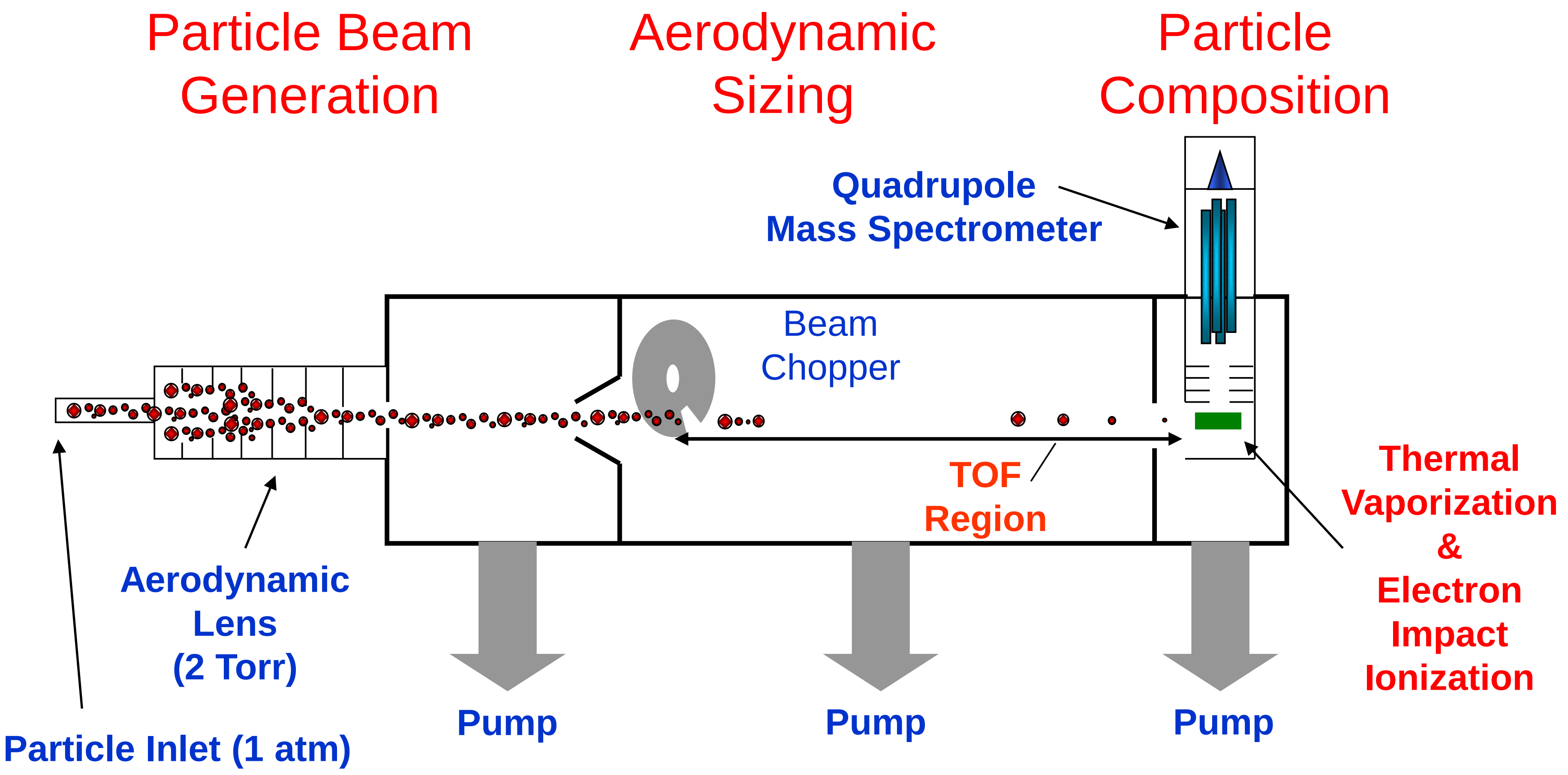
epToF Update

AMS Users Meeting

8 September, 2018

Leah Williams, Donna Sueper, Mike Cubison

Aerosol Mass Spectrometer (AMS)



100% transmission (80-600 nm), aerodynamic sizing, linear mass signal.

Jayne et al., Aerosol Science and Technology 33:1-2(49-70), 2000.

Two Operating Modes

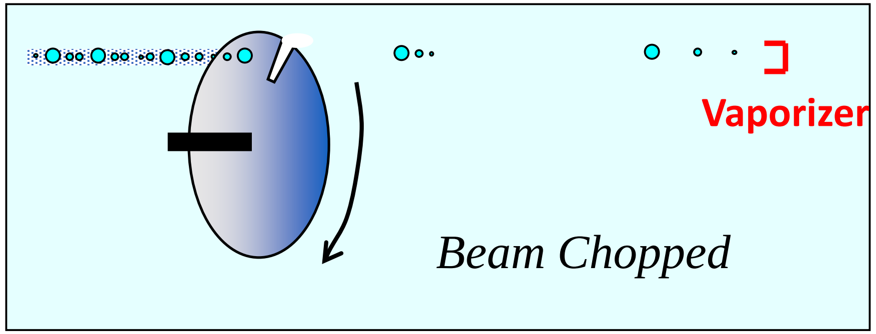
Size Distribution (pToF)

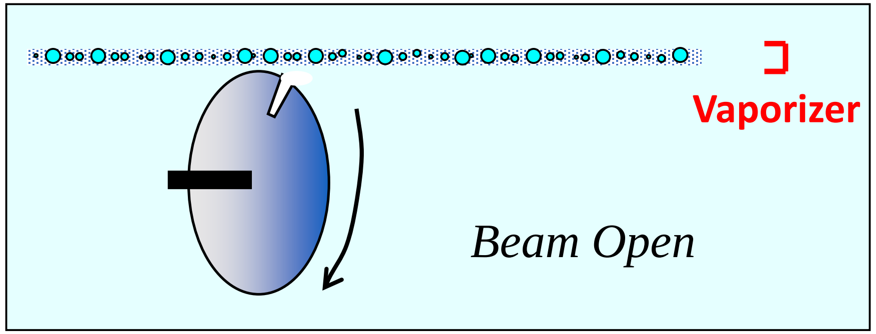
(2% duty cycle)

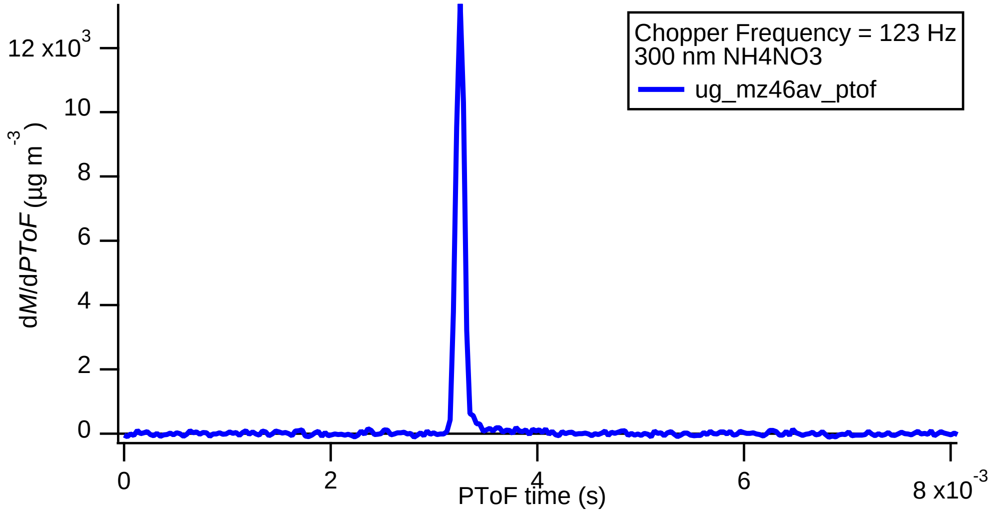
Average Composition (MS)

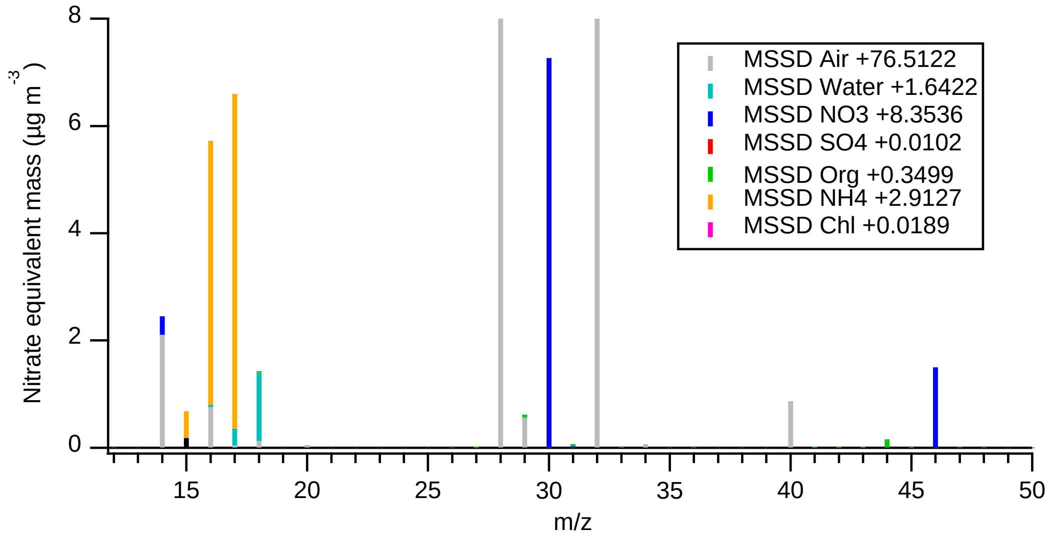
Diff = Open - Closed

(no size info)



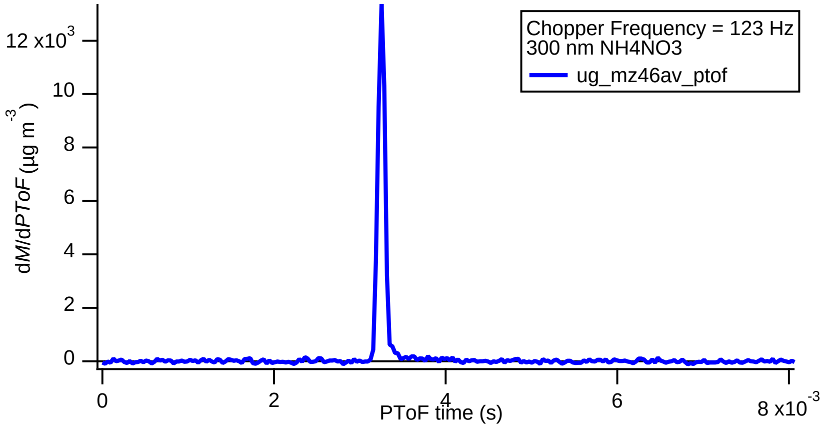


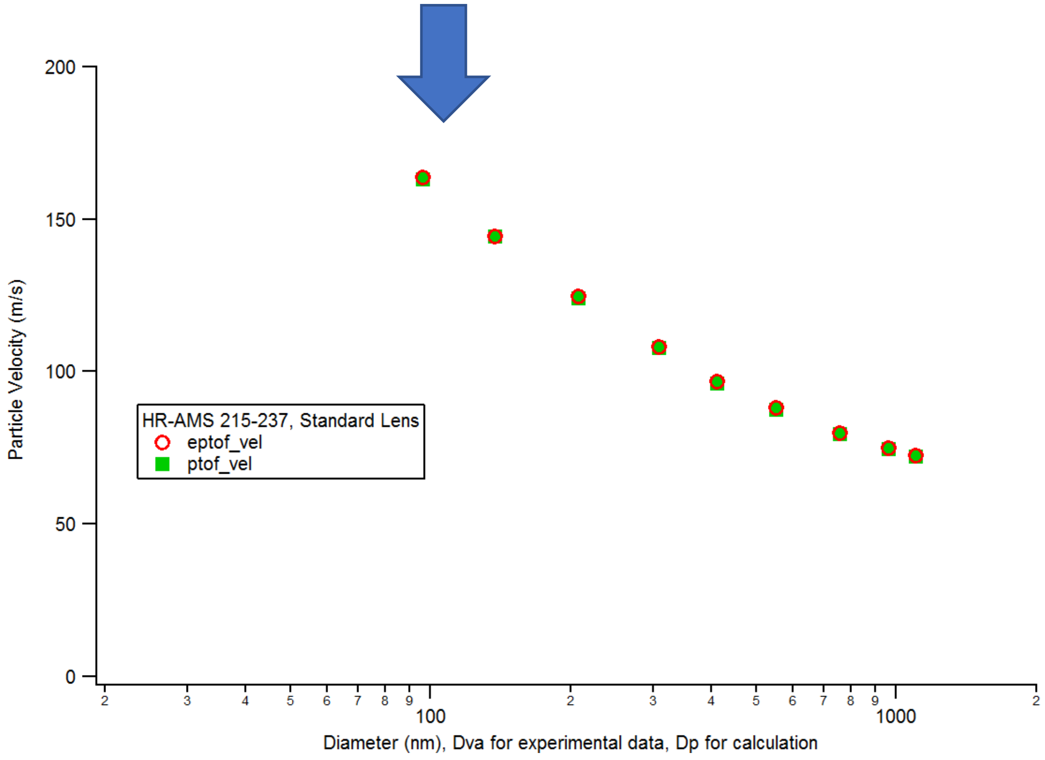


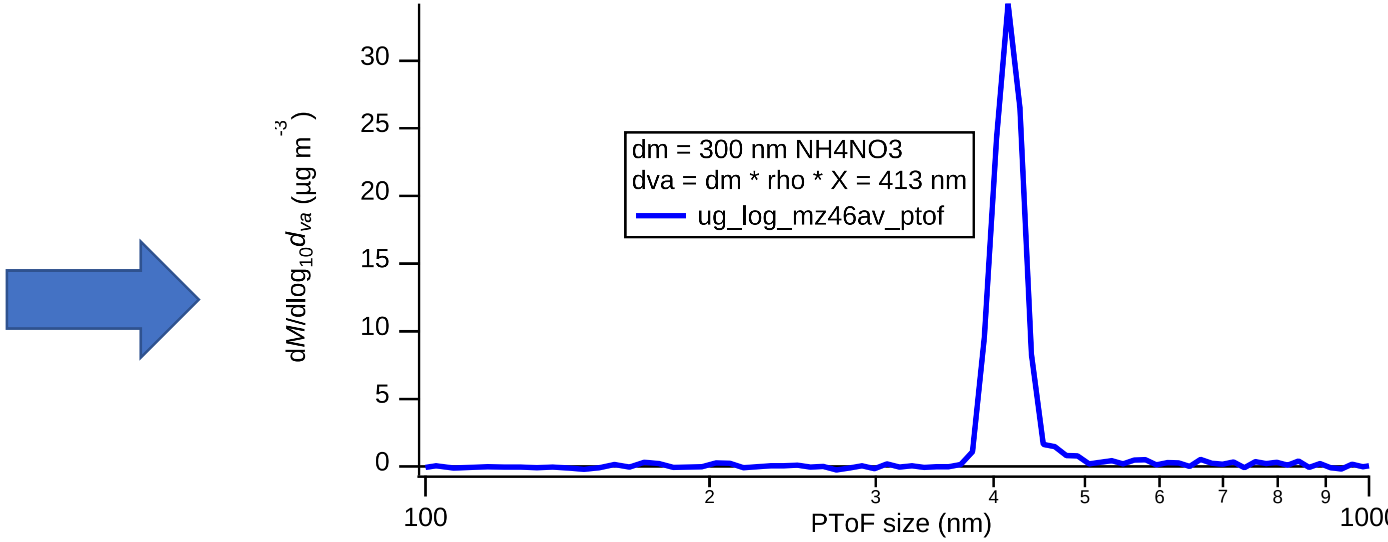


eptofvsptof_Sep2015_2.pxp

Convert pToF to Size with Velocity Calibration







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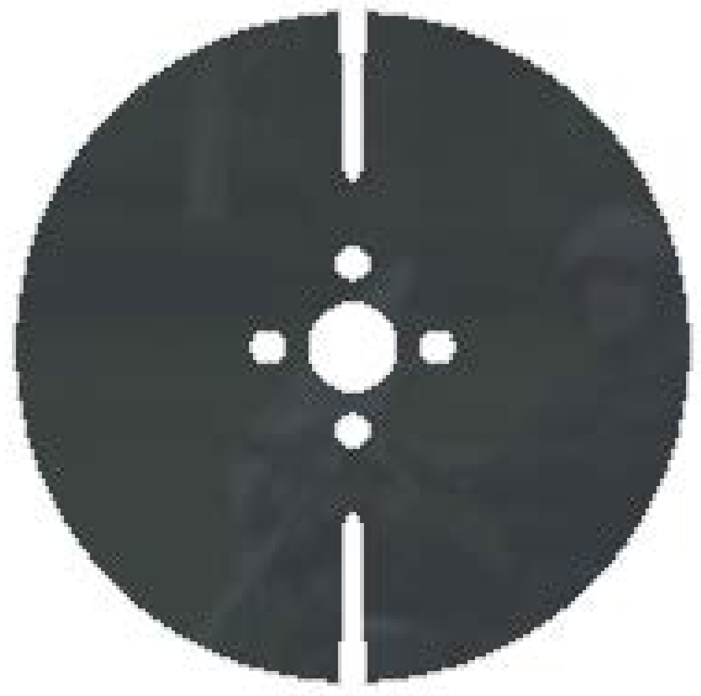
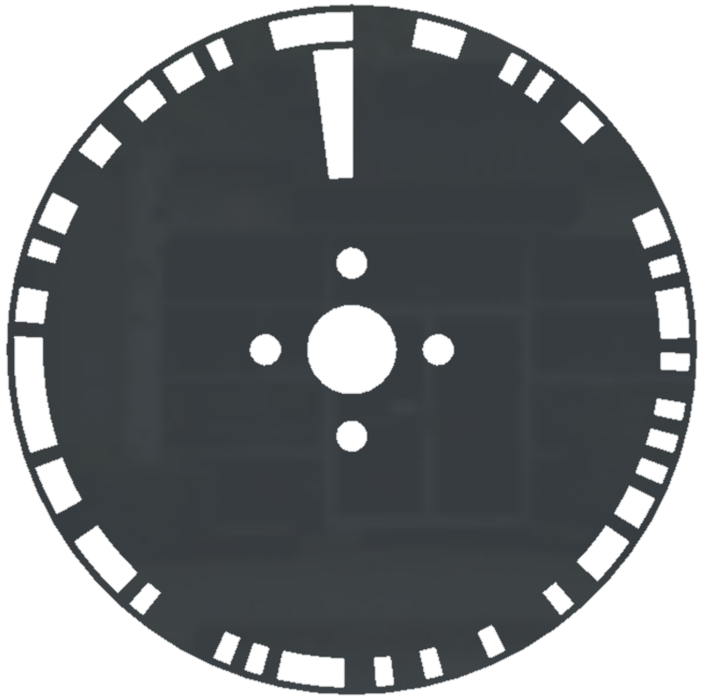
Increase Duty Cycle with Multi-Slit Chopper

Old Chopper:
Two 1% slits = 2% duty cycle

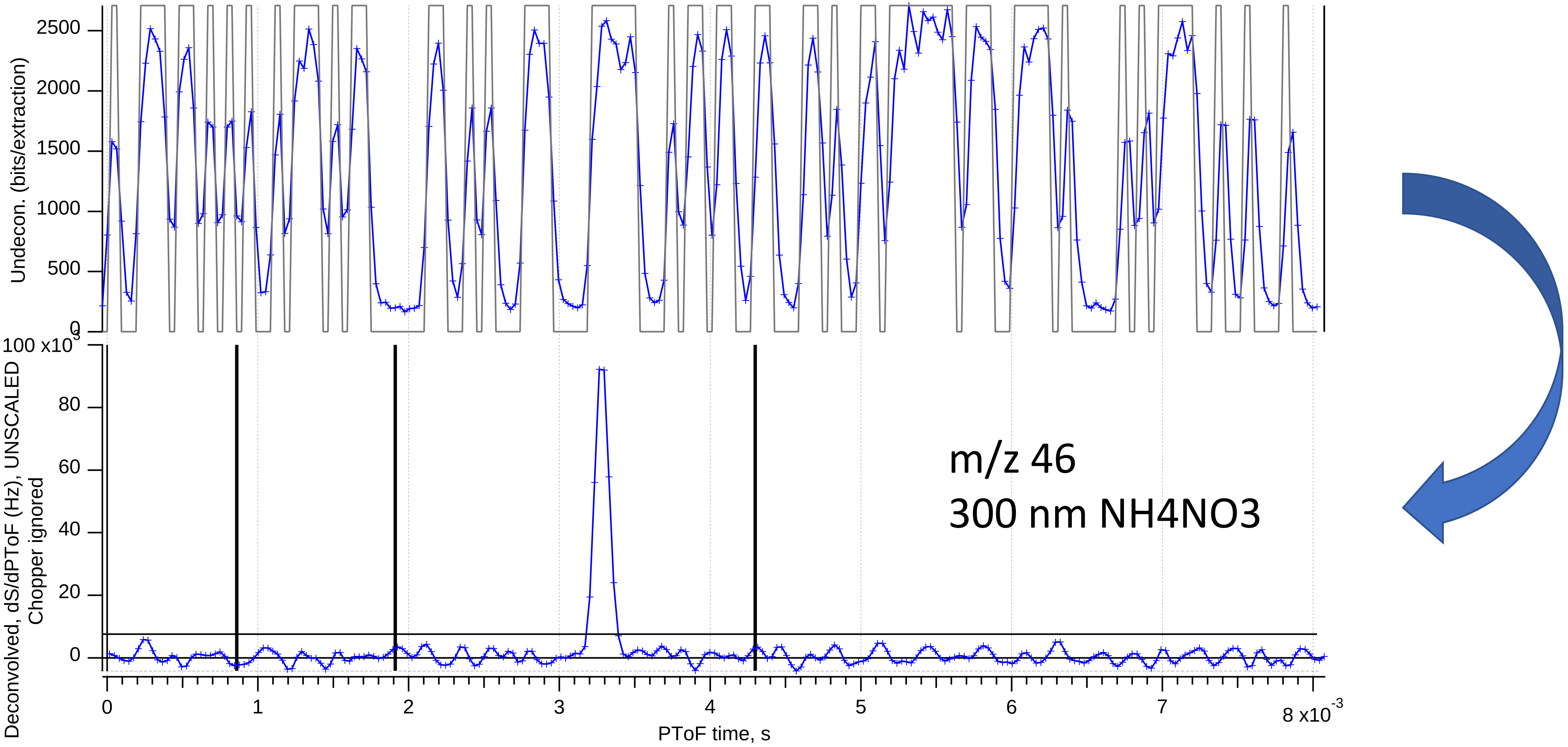


New chopper:
Multi-slit = 50% duty cycle
Also, single 2% slit



Hadamard Sequence

127 Segments/2 Extractions per Segment
128 open/126 closed = 50.4 % duty cycle



Deconvolution Approaches

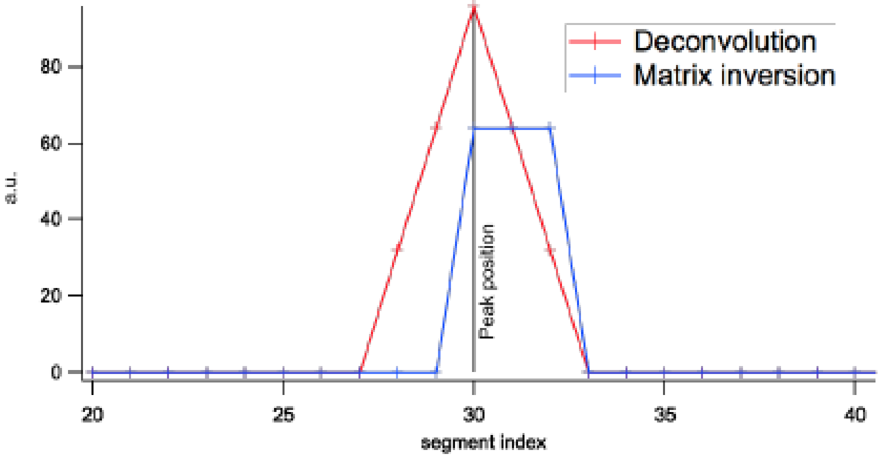
- Matrix deconvolution
  - Linear
- Tofwerk deconvolution v1
  - Developed by Rich Knochenmuss for IMS data
  - Used sharpening and denoising algorithms to pull small signals out of noisy baseline
  - Not appropriate for ptof because shape of ptof matters
- Tofwerk deconvolution v2
  - Developed by Mike Cubison
  - Looks for signals correlated with sequence
  - Smooths signals based on noise
  - Requires scaling factor

Timing Issues Resolved in SQ 1.61A

Matrix (m) vs Tofwerk (tw) deconvolution

epToF vs pToF

1.1 Explain difference between peak position observed in matrix inversion and deconvolution



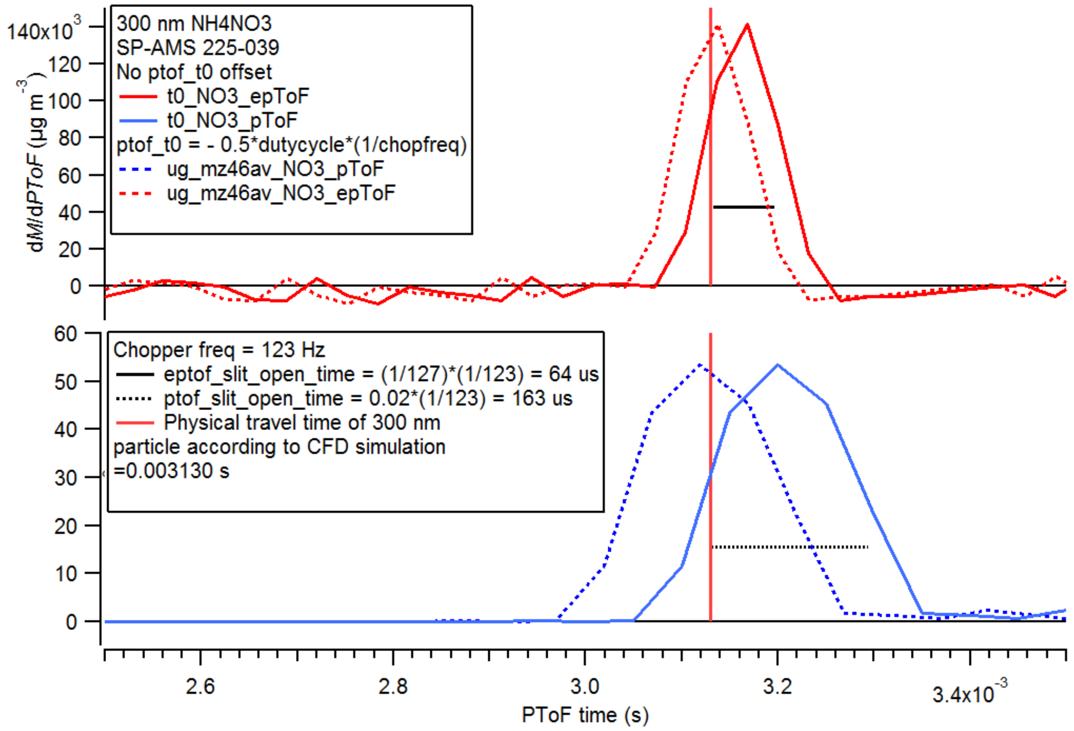
Test dataset also shows this shift.

Simulating a "perfect peak" by rotating the expanded sequence 30 points demonstrates the source of the discrepancy:

- Deconv returns a triangular peak of width "multiplier" (in example = 3) *centered* about index 30
- Matrix inversion returns square peak of width multiplier *with leading edge* at index 30

→ matrix inversion results need to be rotated by -(multiplier-1)/2

Note that with no multiplier there would be no difference in the results using the two methods.



Single velocity calibration works for eptof (m or tw) and ptof

Do We Need Open Data?

Standard Operating Mode

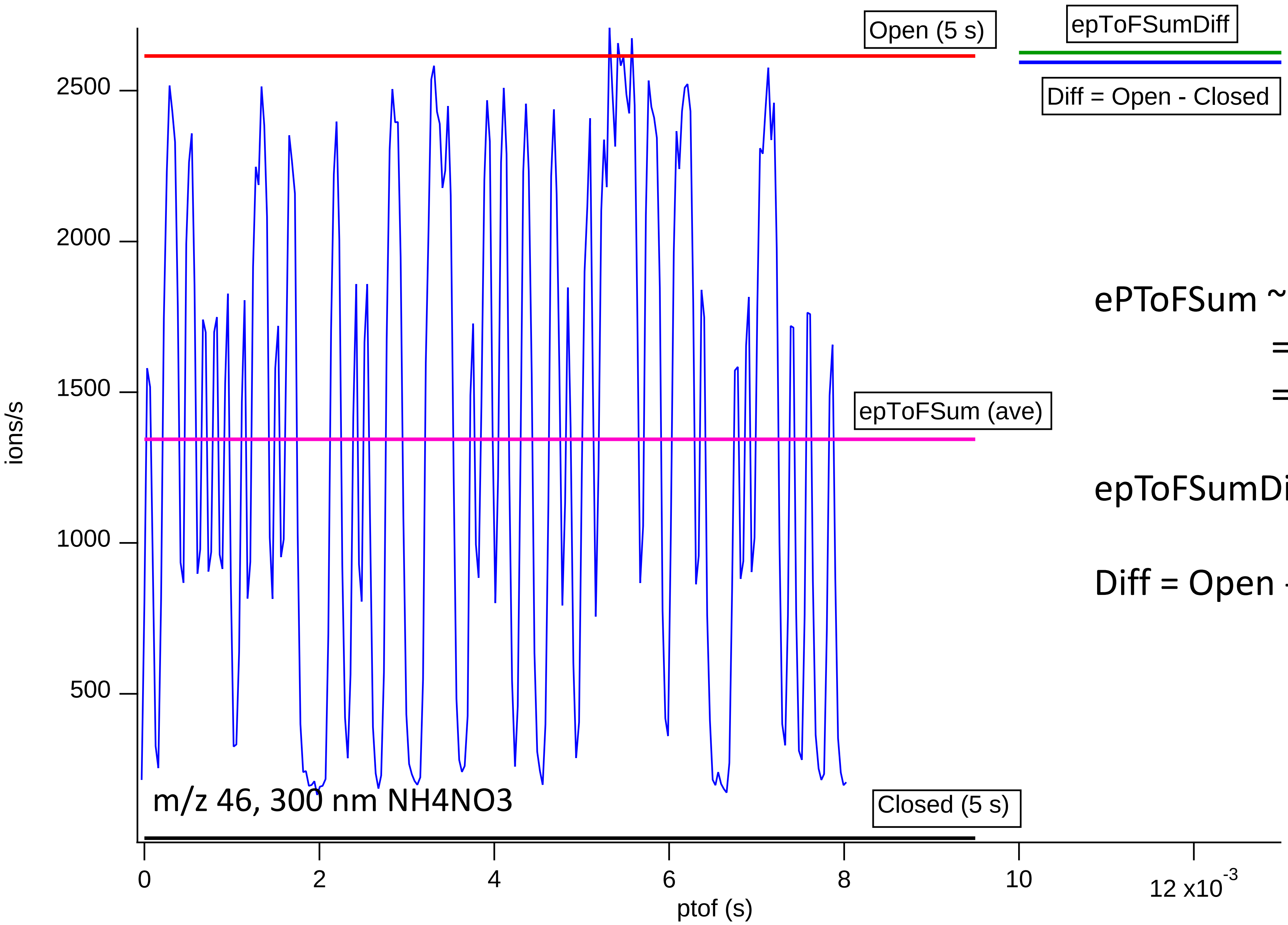
Mode	**MS Closed**	**MS Open**	**PToF (ePToF)**	**MS Closed**	**MS Open**	**PToF (ePToF)**	**MS Closed**	**MS Open**	**PToF (ePToF)**
Time [s]	5	5	10	5	5	10	5	5	10
Duty Cycle [%]	95	95	2 (49*)	95	95	2 (49*)	95	95	2 (49*)

Possible Operating Mode without Open

Mode	**MS Closed**	**ePToF**	**MS Closed**	**ePToF**	**MS Closed**	**ePToF**	**MS Closed**	**ePToF**	**MS Closed**	**ePToF**	**MS Closed**	**ePToF**
Time [s]	5	5	5	5	5	5	5	5	5	5	5	5
Duty Cycle [%]	95	48*	95	48*	95	48*	95	48*	95	48*	95	48*

*DAQ issue greatly reduces ePToF data collection duty cycle.

Do We Need Open Data (cont.)?



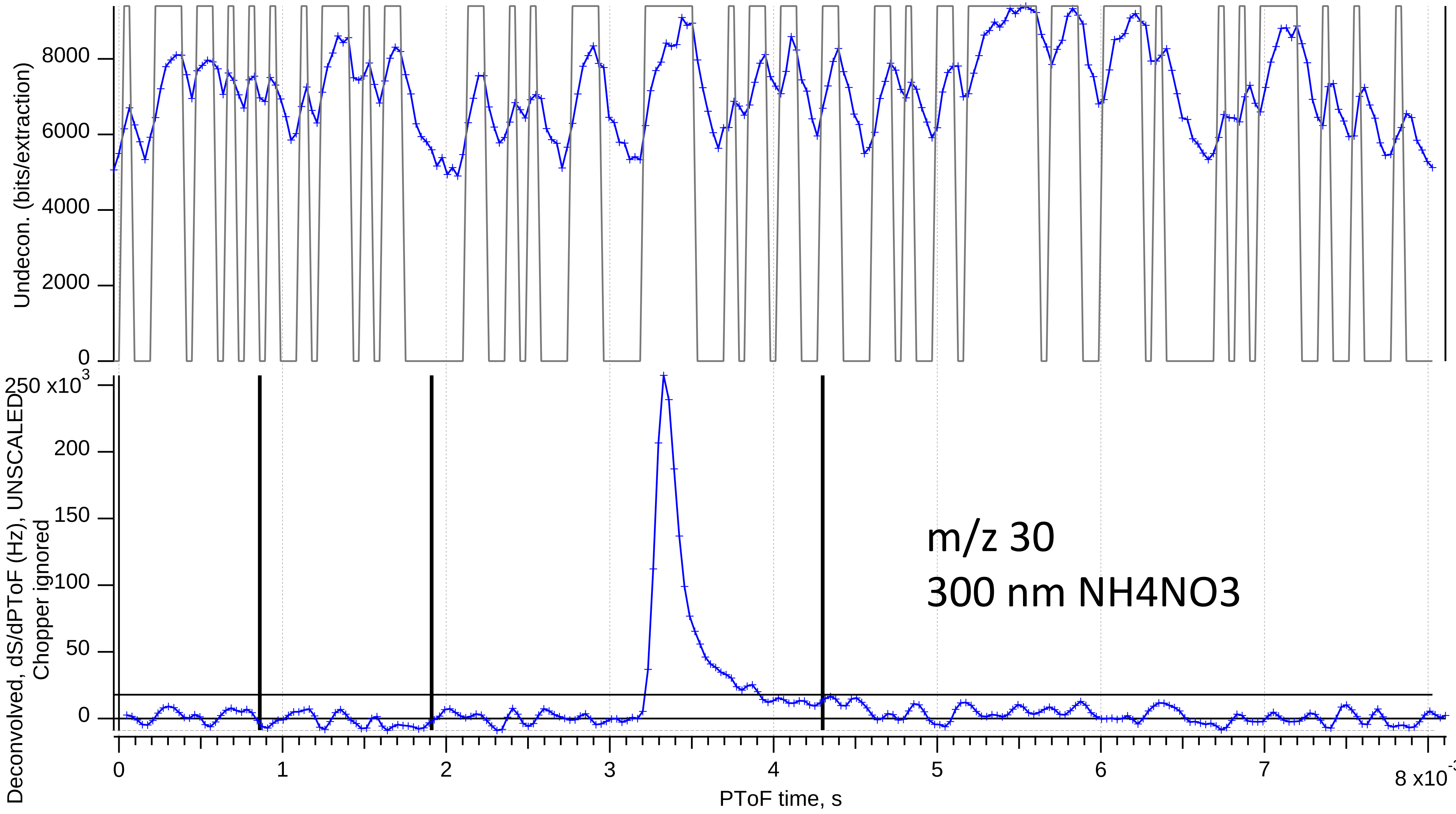
ePToFSum ~ ½ *open + ½* closed
= ½ *(diff+closed) + ½ *closed
= ½ *diff + closed

epToFSumDiff = 2* (1/2*diff + closed – closed)

Diff = Open - Closed

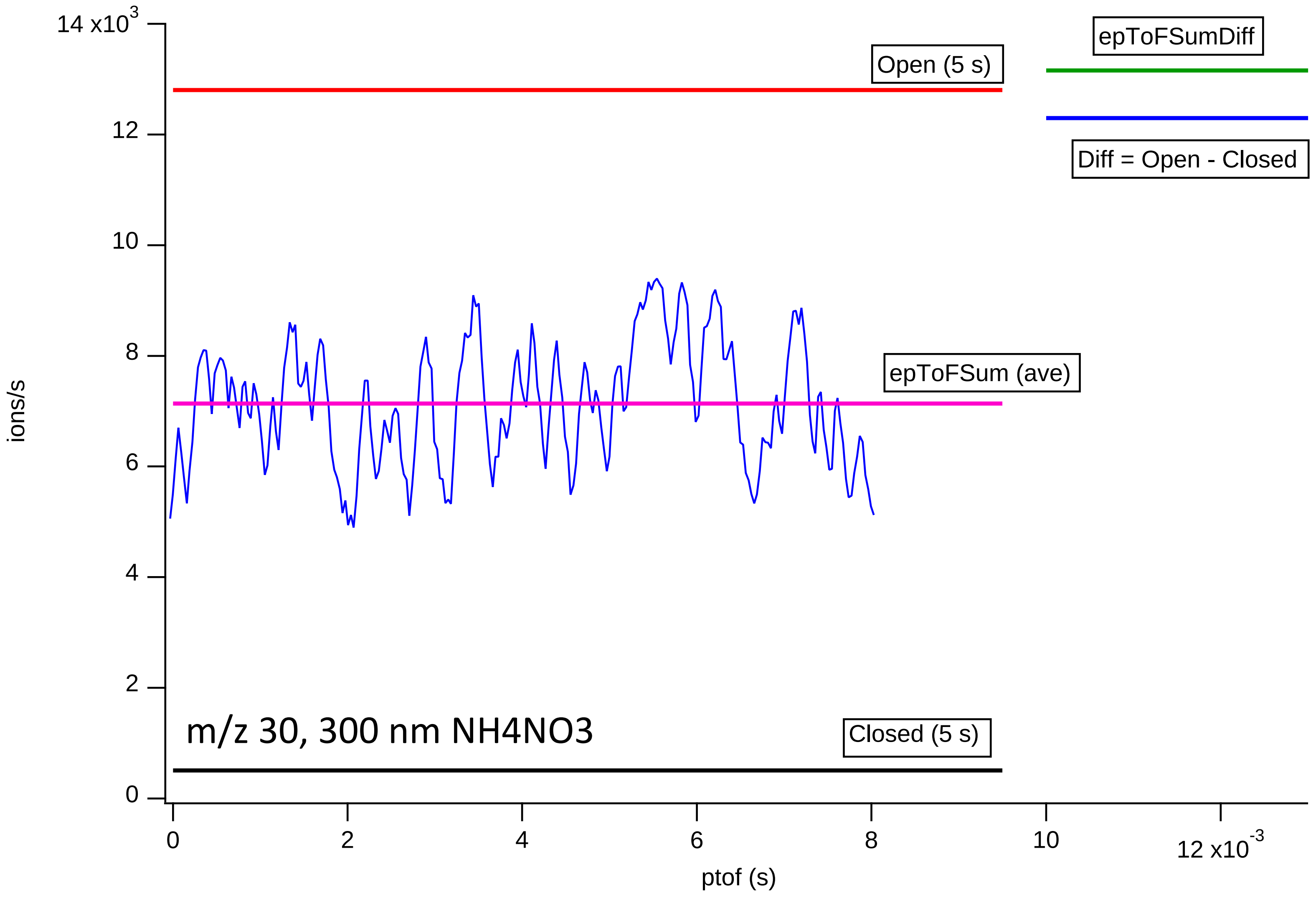
eptofvsptof_Sep2015_2.pxp

More Slowly Vaporizing Fragment (m/z 30)



eptofvsptof_Sep2015_2.pxp

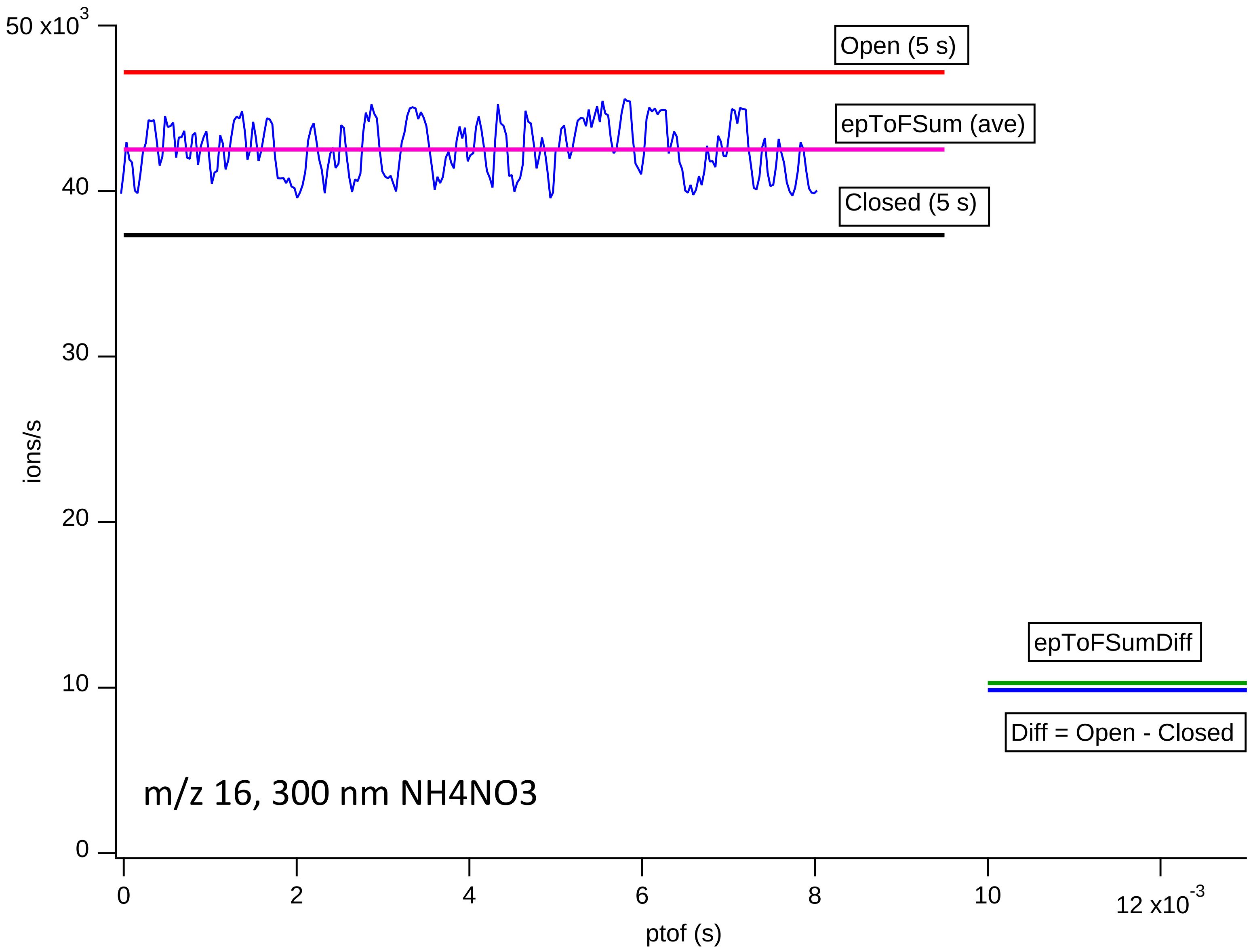
More Slowly Vaporizing Fragment (m/z 30)



epToFSumDiff > Diff by 8%. Will impact, e.g., f44 vs f43.

eptofvsptof_Sep2015_2.pxp

High Background (m/z 16)



eptofvsptof_Sep2015_2.pxp

Do We Need Open Data? Yes!

Standard Operating Mode

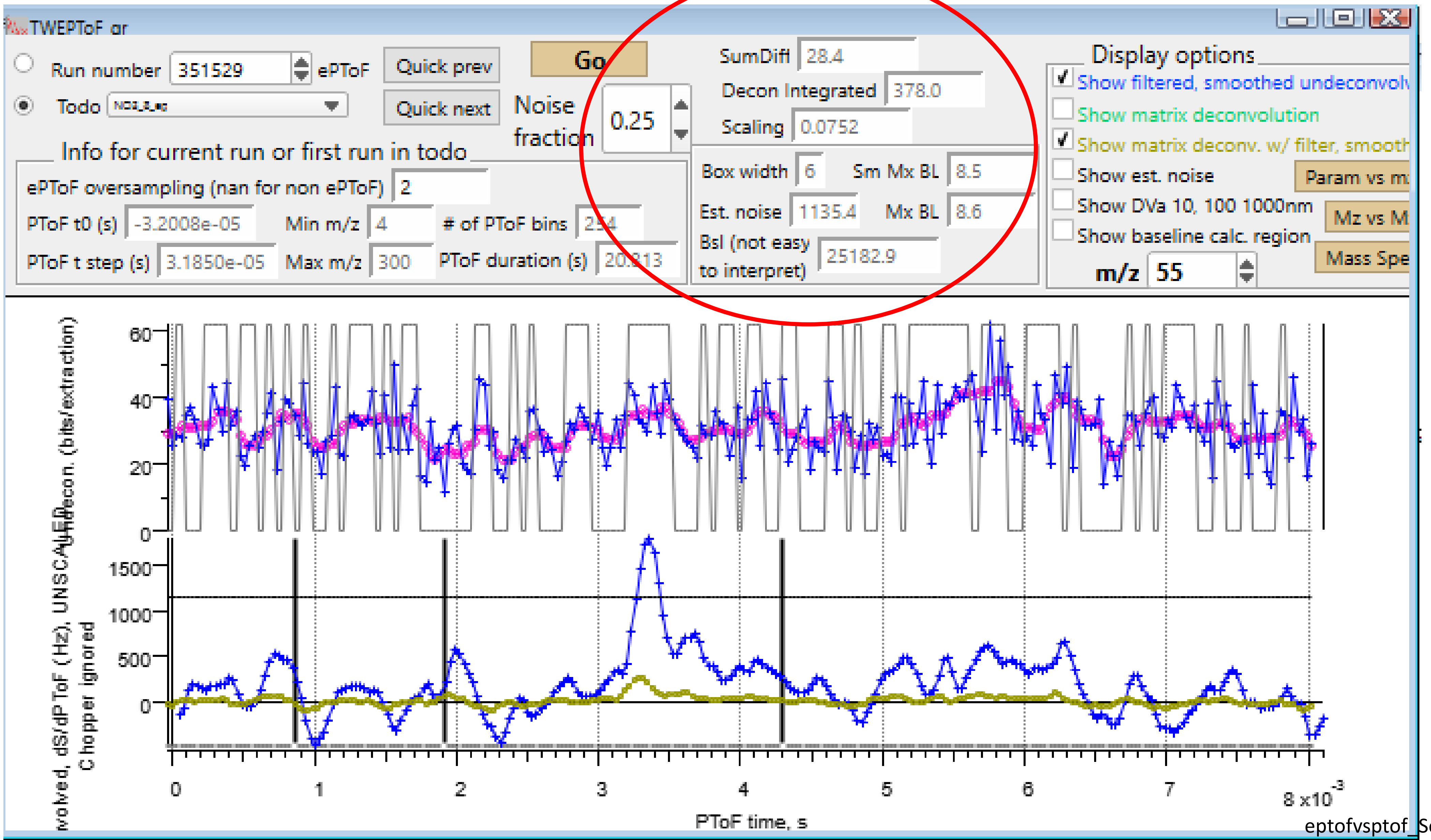
Mode	MS Closed	MS Open	PToF (ePToF)	MS Closed	MS Open	PToF (ePToF)	MS Closed	MS Open	PToF (ePToF)
Time [s]	5	5	10	5	5	10	5	5	10
Duty Cycle [%]	95	95	2 (49*)	95	95	2 (49*)	95	95	2 (49*)

Possible Operating Mode without Open

Mode	MS Closed	ePToF	MS Closed	ePToF	MS Closed	ePToF	MS Closed	ePToF	MS Closed	ePToF	MS Closed	ePToF
Time [s]	5	5	5	5	5	5	5	5	5	5	5	5
Duty Cycle [%]	95	48*	95	48*	95	48*	95	48*	95	48*	95	48*

* DAQ issue greatly reduces ePToF data collection duty cycle.

Do We Need TW Deconvolution? Scaling Issues



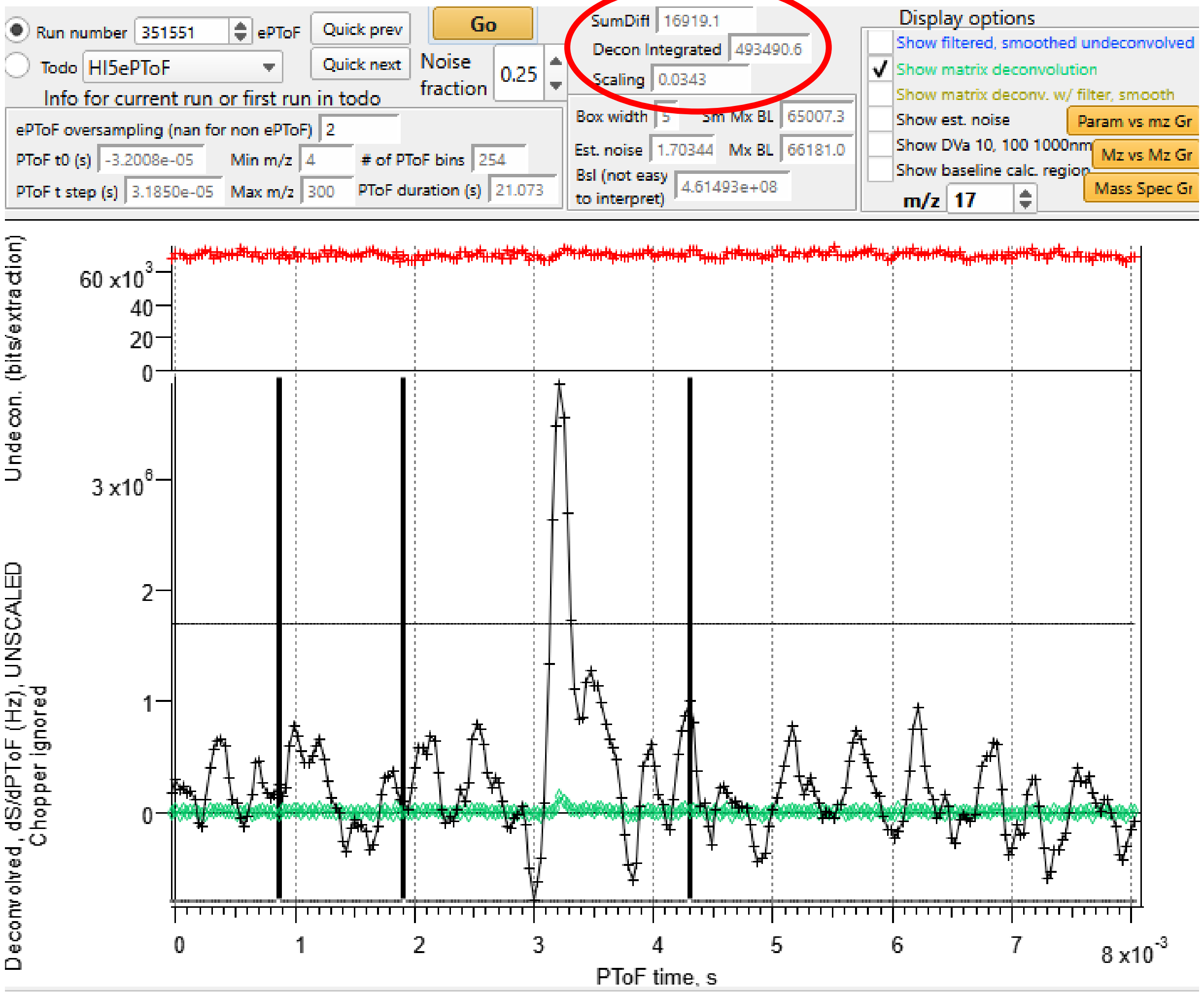
eptofvsptof_Sep2015_2.pxp

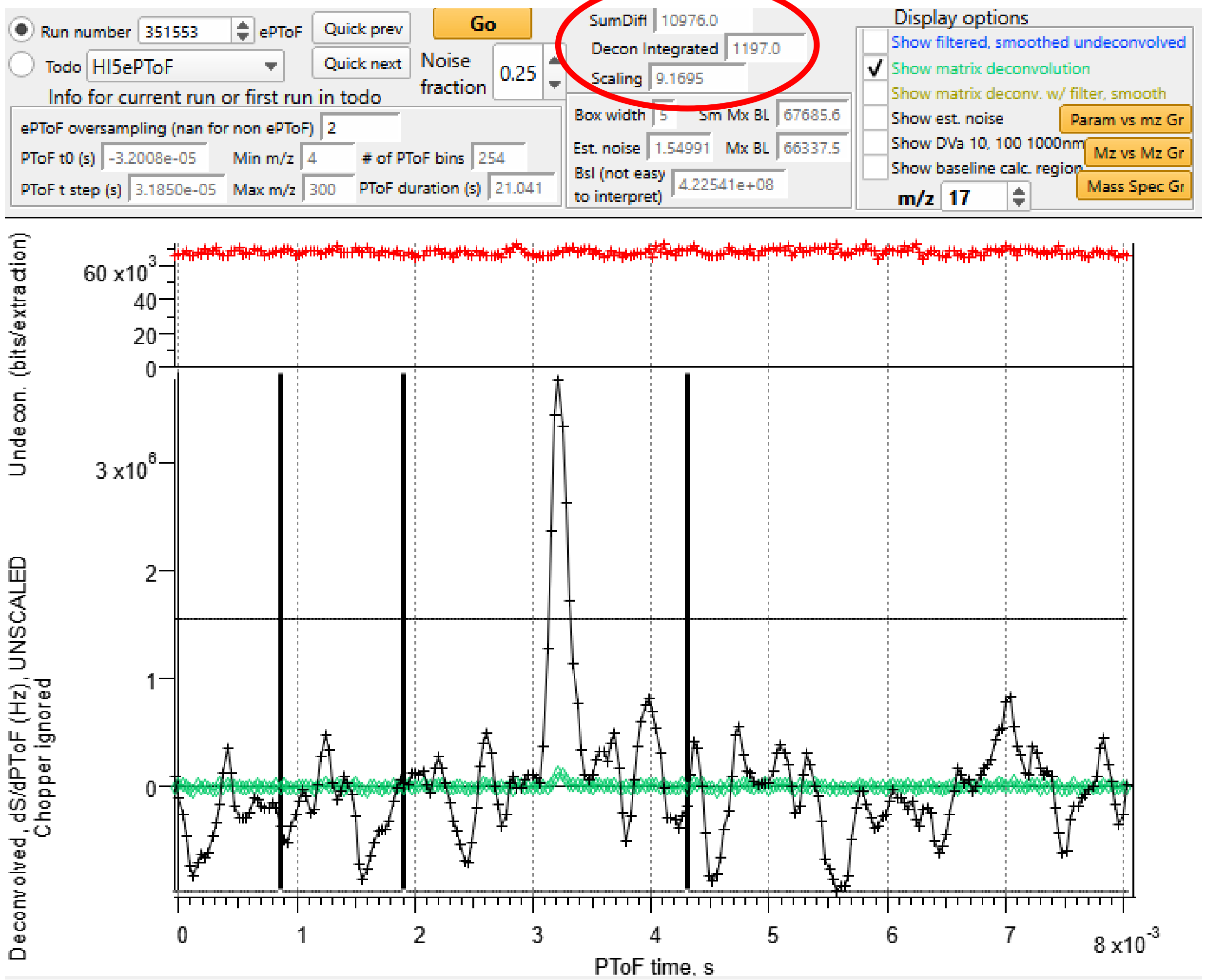
TW scalar calculations: Highly varying scalar values

From Donna

details

Two adjacent runs of m/z 17 at 5 ug/m3 of AN appear similar when deconvolved. Yet their scalars are so different!



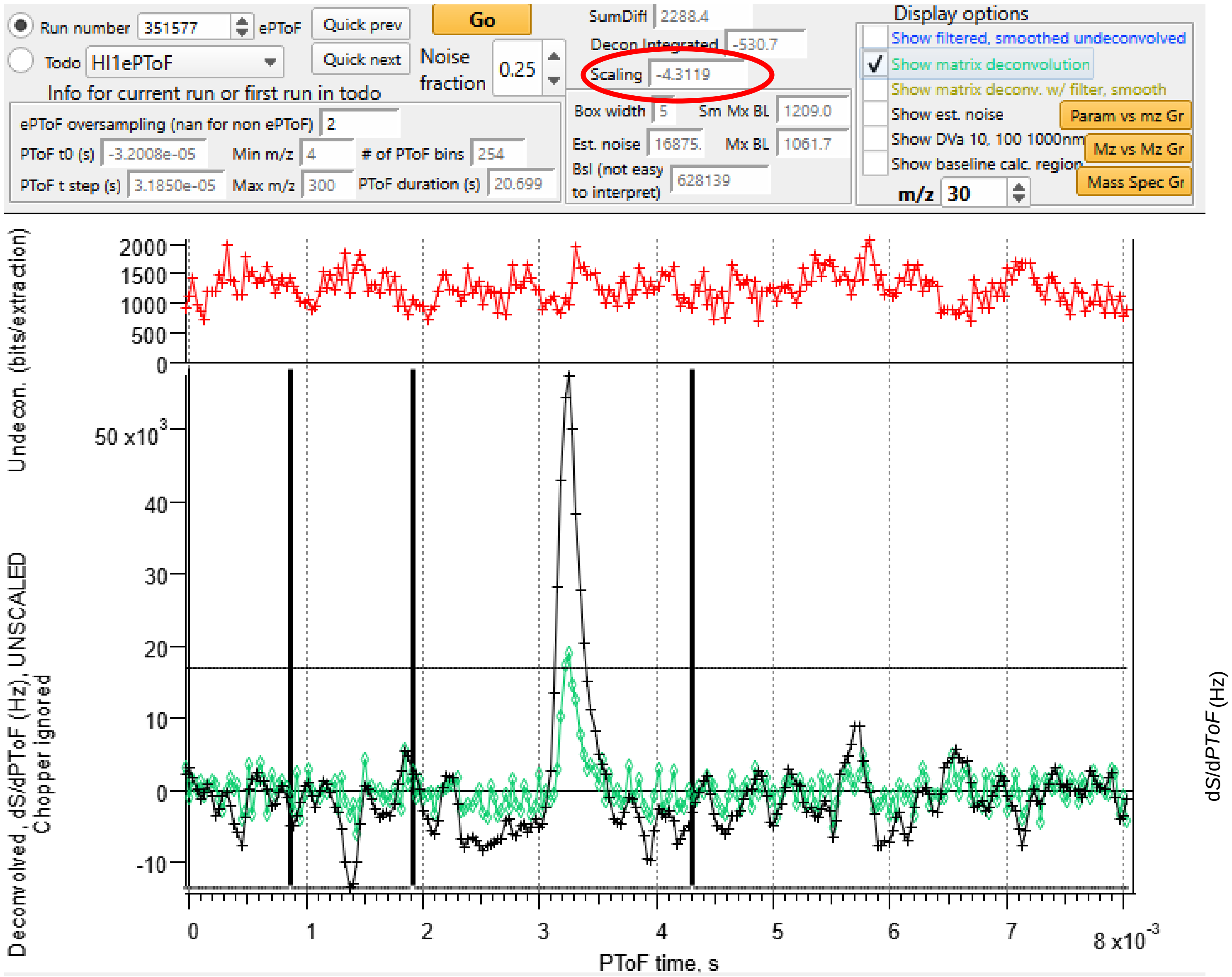


Difference in scalars due to baseline variations.

TW scalar calculations: Negative scalar???

From Donna

details

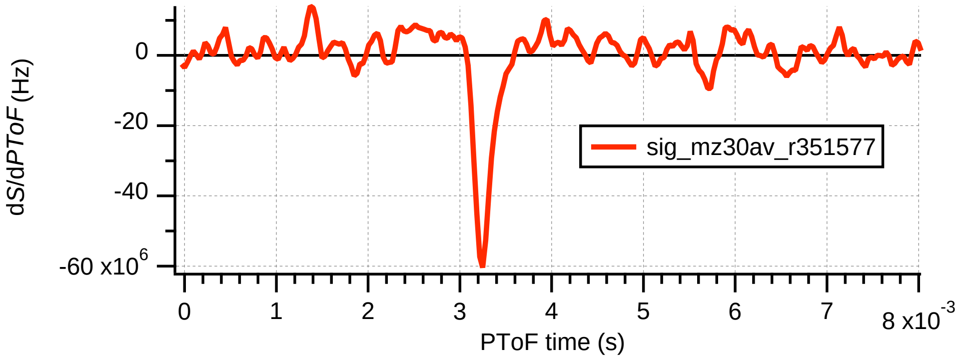


1 ug/m3 NH4NO3
This looks like a clear peak at m/z 30.
Yet the ePTOFSumDiff scalar would turn this into a NEGATIVE peak.

The math checks out in that if you sum the black trace you get the negative number in the panel.

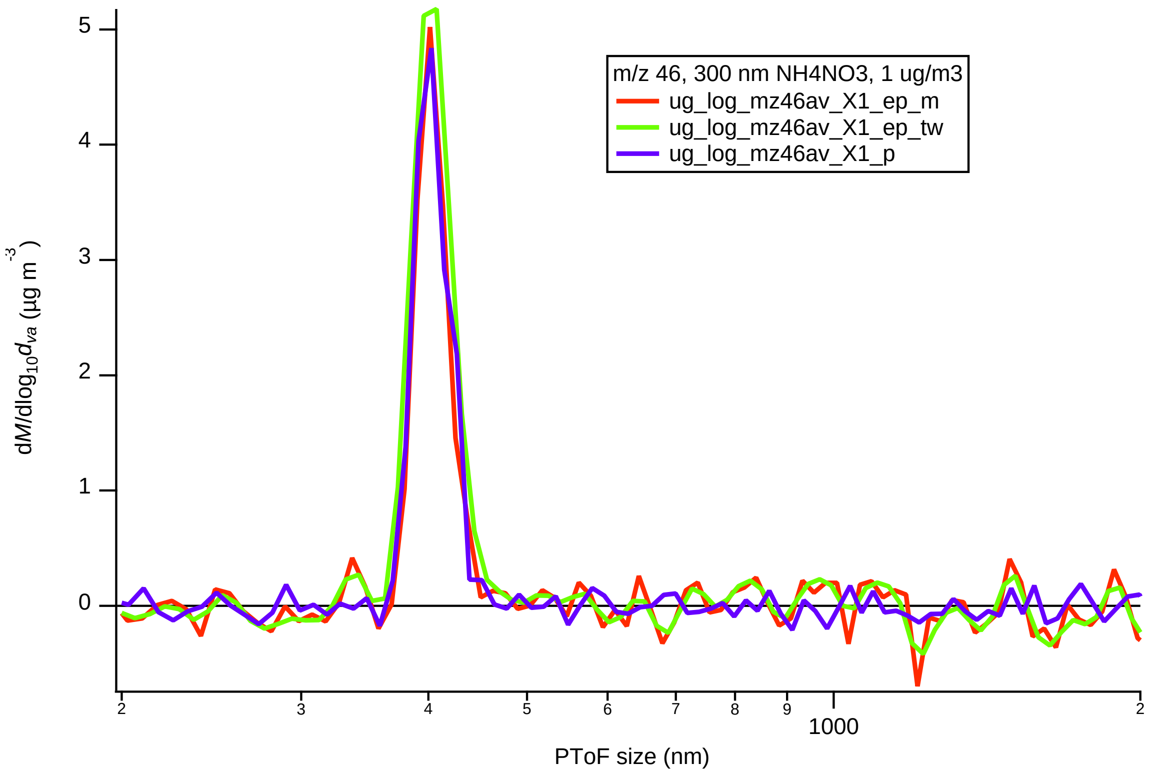
This seems bad!

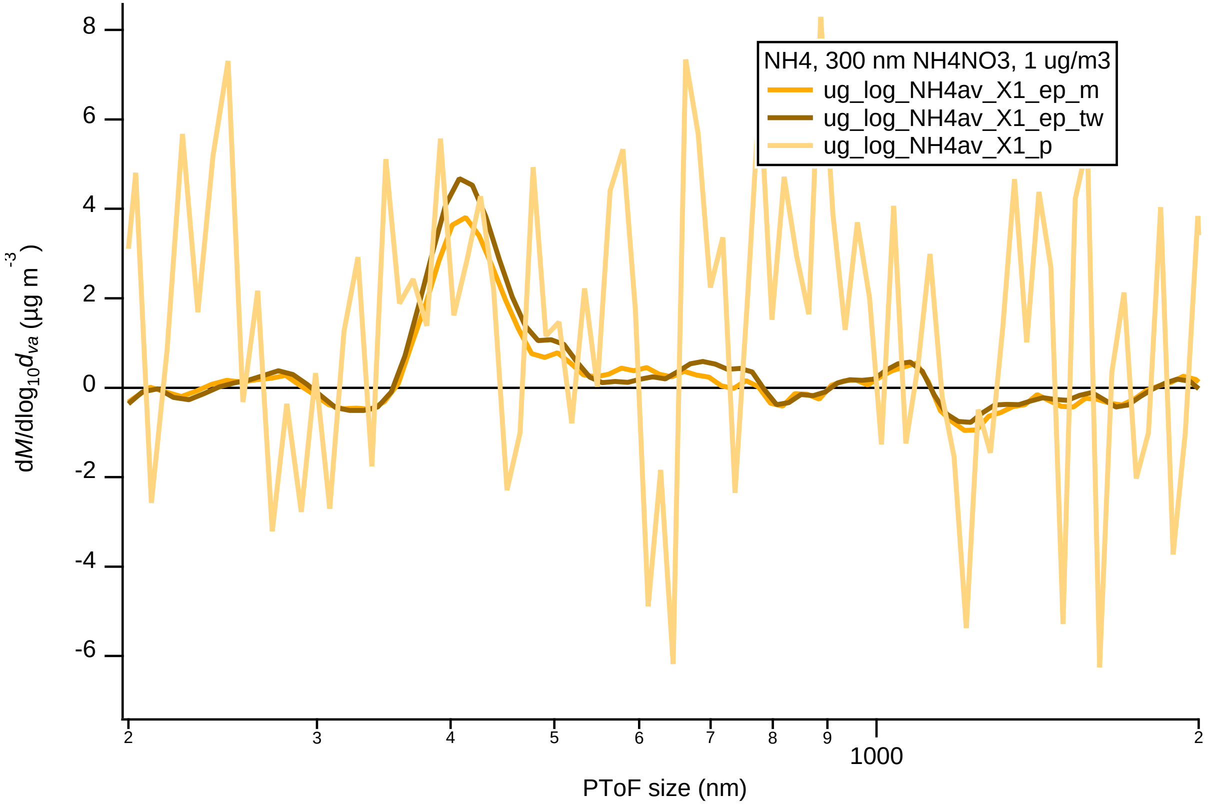
Squirrel result: for one run 351577



Comparing M, TW, and ptof

300 nm NH4NO3, 1 ug/m3





M and TW deconvolutions look similar. For NH4, eptof is big improvement over ptof.

Do We Need TW Deconvolution?

- M and TW deconvolution give very similar size distributions
- Disadvantages of TW deconvolution
  - Scaling required, scaling factor fluctuates wildly and is sometimes negative
    - M deconvolution is linear and does not require scaling factor
  - Baseline sometimes negative or positive
    - M deconvolution gives baseline at 0
  - Applies smoothing based on SNR, different for different m/z's, could be different run to run for the same m/z
  - Averaging runs together, then deconvolving gets better SNR than deconvolving individual runs, then averaging
    - But, confusing user interface
    - If applying time-varying corrections (AB, CE, frag), have to deconvolve individual runs
    - Order of deconvolution/averaging does not matter for M method

Should we make M deconvolution the only method in SQ?