

Pika 1.05 Release Info

A smattering of general comments &
technical details

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Biggest changes in Pika 1.05

* The new default option is to use the raw spectra where the baselines, as calculated by the squirrel-baseline parameters, have been removed.

Pika version 1.04 and previous found a constant baseline for each integer m/z, each run (more on this later).

* There is a more detailed interface for peak width/shapes. A method to identify a set of peak width/shape parameters for each run is now in place. The use of the more intuitive 'peak' shape is used throughout (instead of the "u" curve).

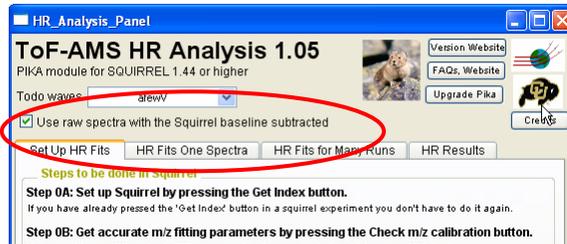
* Some uncertainty values are now automatically calculated to help diagnose issues.

* New features allow users to create average HR or unit mass spectra and time series and in NO₃-eq. ug/m³ units, with/without an airbeam correction.

* New family distinctions between C_wO_xH_yN_z HR fragments for when x = 1 and x >=2. Specifically, CHO1 and CHOgt1, CHO1N and CHOgt1N.

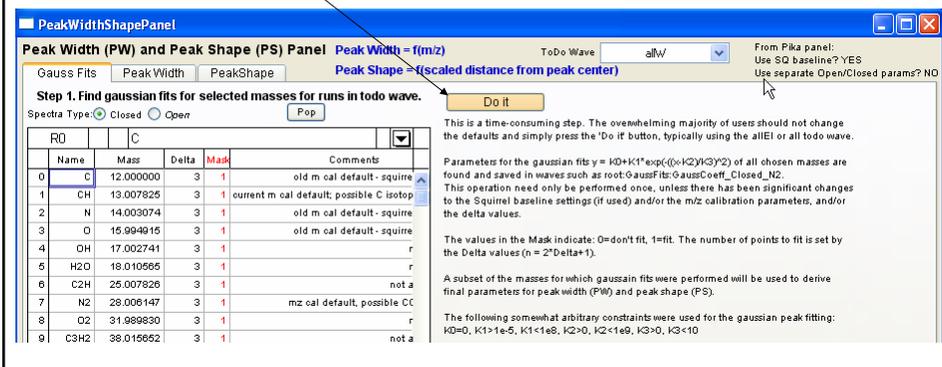
New Pika Panel - raw spectra

The decision to use raw spectra with squirrel baselines removed should be done first, so that the peak shape analysis and pika fits are performed on the same spectra.



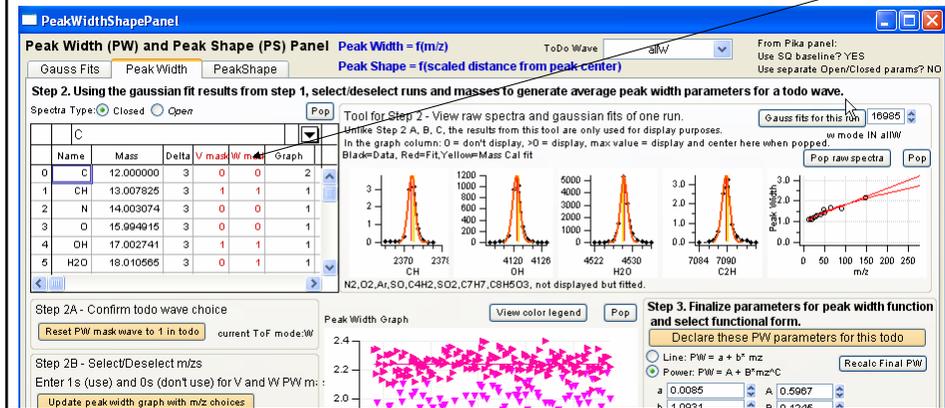
New Peak Width/Shape Panel - gauss fits

* The first step is the fitting to gaussian peaks of raw spectra. This time-consuming task is done first, and needn't be done again. The 4 parameters in $y = K0 + K1 * \exp(-(x-K2)/K3)^2$ for each run and 25 HR fragments are saved in a data folder called GaussFits.



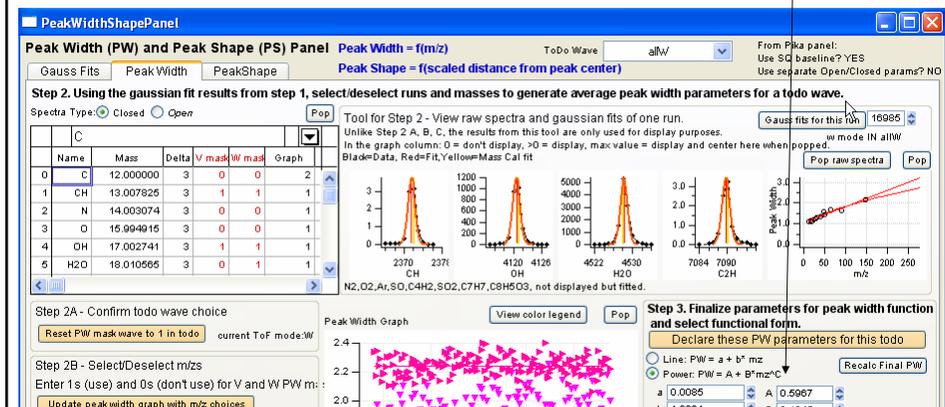
New Peak Width/Shape Panel – peak width

In the second step the user chooses which todo wave and which masses to use to generate peak width parameters. There are lots of tools to examine/add/remove masses, runs.



New Peak Width/Shape Panel – peak width

In the third step the user generates final parameters (slope, intercept) for V and W modes. The user now has the option to generate a fit using the power law function type.



New Peak Width/Shape Panel – peak width

PeakWidthShapePanel

Peak Width (PW) and Peak Shape (PS) Panel Peak Width = f(m/z) Peak Shape = f(scaled distance from peak center)

Gauss Fits Peak Width PeakShape

Step 2. Using the gaussian fit results from step 1, select/deselect runs and

Name	Mass	Delta	V mask	W mask	Graph
C	12.000000	3	0	0	2
1 CH	13.007825	3	1	1	1
2 N	14.003074	3	0	0	1
3 O	15.994915	3	0	0	1
4 OH	17.002741	3	1	1	1
5 H2O	18.010565	3	0	1	1

More tools are available and more intuitive plots are generated. The peak width parameters are now todo-wave dependent.

Step 2A - Confirm todo wave choice
 Step 2B - Select/Deselect m/zs
 Step 2C - Deselect problematic runs
 Step 2C ii. Remove one run
 Step 2C iii. Recalculate mass PW averages.

Step 3. Finalize parameters for peak width function and select functional form.

Line: $PW = a + b \cdot m/z$
 Power: $PW = A + B \cdot m/z^C$

Parameters:
 a: 0.0085, A: 0.5967, B: 1.0631, C: 0.5178

Peak Width Graph

Average Peak Width and Fit Graph

New Peak Width/Shape Panel – peak shape

PeakWidthShapePanel

Peak Width (PW) and Peak Shape (PS) Panel Peak Width = f(m/z) Peak Shape = f(scaled distance from peak center)

Gauss Fits Peak Width PeakShape

Step 4. Using masses, runs, and peak width parameters from Step 3, generate a peak shape candidate of current todo wave.

Number of points in PS candidates: 1281 Max and -Min sigma: 7

Step 4A. Generate a new peak shape by combining left and right mass peak shapes.

Left side masses: SO₂, SO₂, Ar Right side masses: CH, C₂H, OH

Smooth peak shape (with 3 pt boxcar)?
 Enforce y value monotonicity at x < -3, x > 3
 Minimum y values at x < -3, x > 3 be = gaussian

Normalized peak shape:
 y axis: data/gaussian peak height
 x axis: distance from peak center scaled by peak width

Final peak shape 1.0526

Users press the gold "Find PS.." button and retrieve peak shape data for selected masses. This takes some time to execute, but only needs to be done once.

Users can generate a candidate using different left and right-side masses and to deal with tail noise (this is quick). The more intuitive 'peak' wave is used.

New Peak Width/Shape Panel – peak shape

Peak Width (PW) and Peak Shape (PS) Panel Peak Width = f(m/z) To Do Wave: all/W From Pika panel: Use SQ baseline? YES Use separate Open/Closed params? NO

Gauss Fits PeakWidth PeakShape Peak Shape = f(scaled distance from peak center)

Step 4. U generate
 In the fifth step the user declares final peak shapes from the current candidate.
 Confirm t
 Calculate

Step 4A.
 The user now has the option to plot individual mass peak shape residuals.
 Left side t
 Sino
 Enfo
 Minir
 Update
 Left #
 View
 View
 Edit/View

Step 5. Declare candidate as final peak shape.
 PS Name (with prefix of FinalPS_V_(onW); blank = todo
 Declare candidate as final peak shape for runs in todo
 Calculate, append to graph m/z residuals: CH
 Left Axis Log
 Show residuals
 Show final peak shape Pop

ape: peak height
 peak center
 kwidth
 52:C7H7,C8H5O3
 Date with masses
 6

Final peak shape 1.0526 PS Table PW/PS table

Detailed, normalised peak shape
 (left) residuals
 (right) residuals
 1.0
 0.8
 0.6
 0.4
 0.2
 0.0
 -100·10⁻³
 -6 -4 -2 0 2 4 6
 (-10) peak width

New Pika Panel - results

Users can now convert HR sticks to NO_3 eq. $\mu\text{g}/\text{m}^3$ units, can generate HR average mass spectra.

HR_Analysis_Panel

ToF-AMS HR Analysis 1.05
 PIKA module for SQUIRREL 1.44 or higher
 Todo waves: Get List
 Use raw spectra with the Squirrel baseline subtracted
 Version Website
 FAQs Website
 Upgrade Pika
 Credits

Set Up HR Fits HR Fits One Spectra HR Fits for Many Runs HR Results

Step 6 View results of Step 5 as time series or average mass spectra.
 Data: Open Graph output: Plot single Use MS airbeam correction? ug/m³ *
 ***** WARNING *****
 * The conversion of HR sticks from Hz to $\mu\text{g}/\text{m}^3$ in version 1.05 uses an RIE and CE of 1 which is "NOT" correct for all HR fragments. In version 1.05 users must modify the generated ' $\mu\text{g}/\text{m}^3$ ' values for appropriate RIE, CE values.

Time Series
 Masses (Example: C3H5,34S,familyCH) | Ar
 Append to list above all chosen masses at this amu Integer m/z: 40
 Calculate

Average Mass Spectrum
 Masses (Example: C3H5,34S,familyCH) familyCH,familyCHO1,familyCHOgt1,familyCHN,familyCHO1N,family
 Sum to UMR space All HR families (see button after Step 3)
 Stack sticks in display
 Truncate sticks to 0
 Calculate Be aware that displays for HR average mass spectra are such that the colors may be wrong and sticks may not be stacked.
 Calculate and display 5 graph UMR summary

Time Series Spectra
 Export Matrices (Leave mass list blank for every HR stick)

Pika 1.05

Thing **not** yet incorporated, in order of importance:

- * The HR frag table, batch table functionality.
- * Fitting uncertainty values be plotted throughout. (Note: Fitting uncertainty is one component of several errors to sum for use in PMF)
- * Better organization scheme for HR sticks. Likely scheme: organize HR sticks not by column number, but by column labels. This is to prevent the necessity of redoing pika fits of all runs when a single HR fragment is added/removed from HR fragment chosen list).
- * Regularly have available two sets of difference sticks – one found by pika fitting raw difference spectra (HRDiffStick), one found by the simple open – closed HR sticks (HROminusCStick).
- * Mike C's tools,  tools

Pika 1.05

To use:

<http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html#Analysis3>

For new Pika experiments: download 1_05.pxt from the web site above.

For upgrading Pika experiments 3 issues:

(1) Igor Procedure Files (.ipfs)

- Download and import all PK_***1_05.ipfs
- Kill all old pika PK_**.ipfs
- Kill and recreate the main Pika Panel.
- One does not have to update their squirrel ipfs from version 1.44 to the current 1.46, but it doesn't hurt.
- Uncheck 'Use squirrel baseline' (unless you want to redo Pika step 1)

(2) Chosen HR Mass fragments

- One does not have to update their all masses list, but it is encouraged. If no new HR fragments were identified in the old experiment, all HR mass choices (what masses to fit) and all HR fits can be retained.
- If not redoing the fits you still need to reselect them. Pika 1.05 creates new HR families and the HR family mask waves need initializing.

For upgrading Pika experiments 3 issues, cont.:

(3) Converting Peak Width and Peak Shape information

Open the new peak shape/width panel

From the command line run:

`Pk_upgradePWPSfrom104(todowave, PWIntercept, PWSlope, PSwave)`

where

- Todowave is the name of a todo wave (for example AllW)
- PW intercept is the numerical value (or global variable) for the PW intercept value for all runs in the chosen todo wave
- PW slope is the numerical value (or global variable) for the PW slope value for all runs in the chosen todo wave
- PS wave is the name of the todo wave that contains the Pika version 1.04 peak shape coefficients ('U'-shaped curve)

As an example:

`Pk_upgradePWPSfrom104(allW, root:HR_PeakShape:PWIntercept,
root:HR_PeakShape:PWSlope, root:HR_PeakShape:PeakShapeW)`

A template command is at the bottom of the PK_PeakShape ipf.

*** This must be done for all peak shapes groups (each V group, each W group)