Custom Mass Ranging Extension 2.1

Ty J. Prosa

May 13, 2025

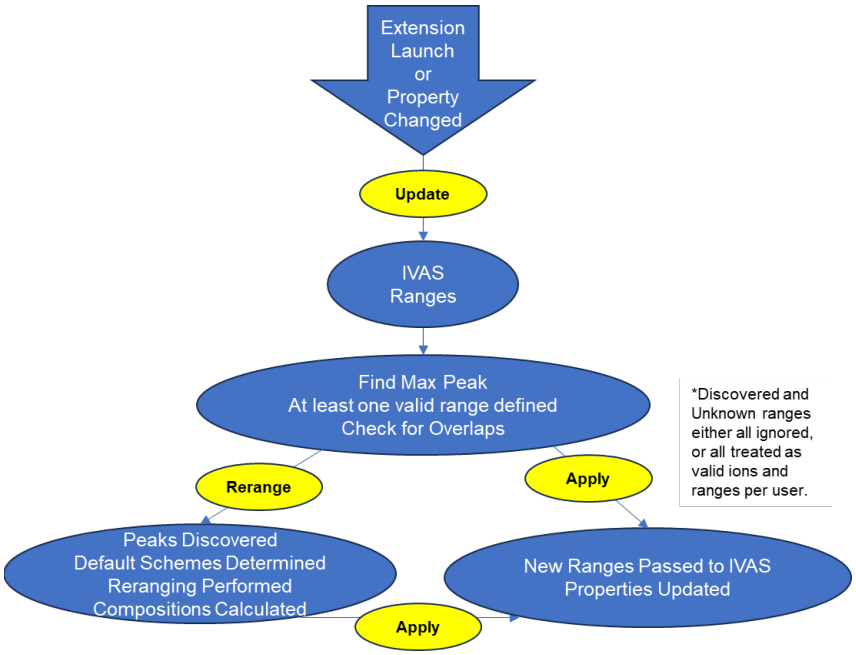
The “CustomMassRanging” extension provides an automated re-ranging scheme of existing IVAS ranges. An adjacent-to-peak background estimation and is used based on the initial list of ions and ranges provided by IVAS. Adding or deleting ion ranges must be done in IVAS, before passing them on to this extension. A peak discovery feature displays found peaks and allows the user to add all these ranges (which can be passed back to IVAS for identification and then returned to the extension for computation).

Input: A set of pre-defined ion ranges from a normal IVAS session.

Extension Function: Four ranging schemes are available: Left, Half, Quarter, and LeftTail. The extension auto-determines which of the first three schemes is appropriate on a peak-by-peak basis (any save or manual changes by the user are remembered for subsequent iterations). The user can override the scheme for any given peak, and choose the LeftTail option, which attempts to fit the tail of the peak with a decaying exponential fit or unranged regions in the tail. Ionic and decomposed ion bulk compositions are then determined with full statistical consideration for detection threshold and resulting compositional uncertainty. When using the LeftTail option, the user specifies their estimated uncertainty in the tail estimate and that error is also propagated to the bulk compositions.

Any missing peak are “Discovered”, and the user can optionally add these ranges or ignore them (default). Added ranges become part of the ionic composition but are excluded from the atomic composition calculations (unless the user identifies the ion types in IVAS and then returns the ranges to the extension).

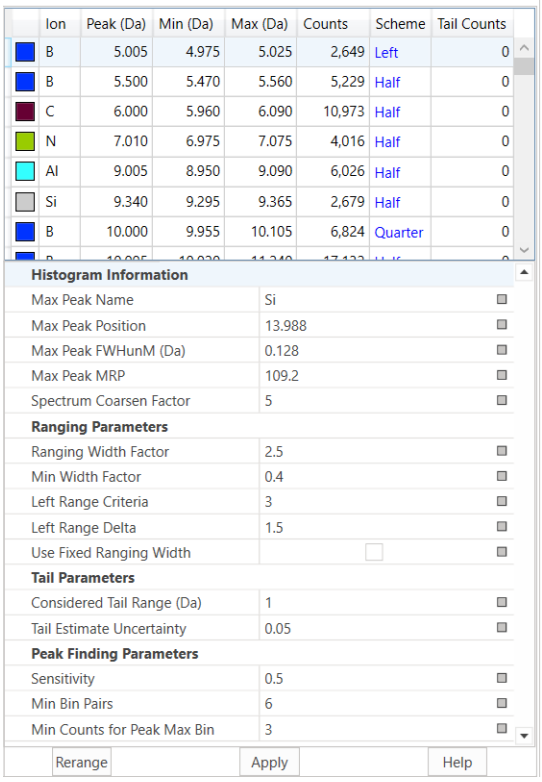
Output: Background estimates are displayed on the mass histogram as well as any tail estimate (and all discovered peaks). The user can then choose to pass/apply new ion ranges back to IVAS or change ranging parameters and re-range again. The utilized extension parameters, those from the last apply operation, are moved to the Properties section so that they can be saved as part of any subsequent “save analysis tree” operation. It also requires “Update” to the extension before continuing.



Details

The initial ion list and range definitions are the RRNG-type data passed from IVAS, and the range list items cannot be added to or deleted within the extension (the user needs to do that in IVAS and then pass that list to the extension). The ranging procedure is consistent with the analysis described in Prosa and Oltman, 2022 (attached at end):

Overlapping initial range definitions are not allowed (although IVAS does allow). An exception will be generated and the user notified when input ranges have overlaps.



Ion	Peak (Da)	Min (Da)	Max (Da)	Counts	Scheme	Tail Counts
B	5.005	4.975	5.025	2,649	Left	0
B	5.500	5.470	5.560	5,229	Half	0
C	6.000	5.960	6.090	10,973	Half	0
N	7.010	6.975	7.075	4,016	Half	0
Al	9.005	8.950	9.090	6,026	Half	0
Si	9.340	9.295	9.365	2,679	Half	0
B	10.000	9.955	10.105	6,824	Quarter	0

Histogram Information	
Max Peak Name	Si
Max Peak Position	13.988
Max Peak FWHunM (Da)	0.128
Max Peak MRP	109.2
Spectrum Coarsen Factor	5
Ranging Parameters	
Ranging Width Factor	2.5
Min Width Factor	0.4
Left Range Criteria	3
Left Range Delta	1.5
Use Fixed Ranging Width	
Tail Parameters	
Considered Tail Range (Da)	1
Tail Estimate Uncertainty	0.05
Peak Finding Parameters	
Sensitivity	0.5
Min Bin Pairs	6
Min Counts for Peak Max Bin	3

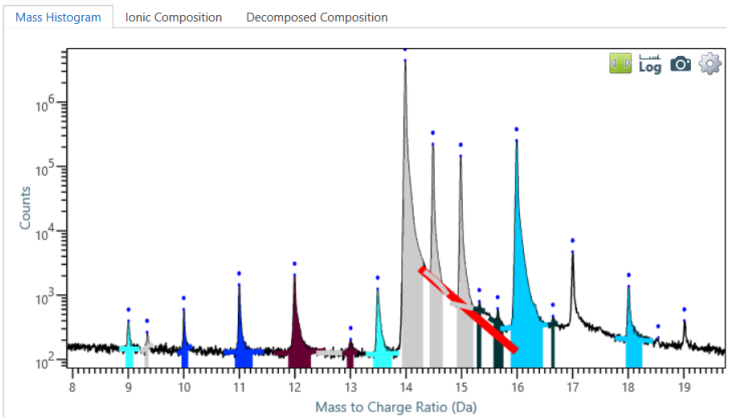
Rerange Apply Help

1) The most intense histogram bin in the mass spectrum is discovered and processed for peak m/z position and full-width-hundredth max (FWHunM, note in the publication, the FW0.001M was used, but that metric may is not sufficiently robust for general mass spectra).
2) FWHunM is used to determine the histogram m/z resolution. Typically, the input mass histogram has a resolution of 0.001 Da. The algorithm coarsens the resolution so that 15-30 bins encompass

the FWHunM of the main peak (typically, somewhere between 0.002 Da to 0.01 Da).

3) The peaks are processed from left to right along the mass spectrum to determine the appropriate ranging scheme. Ideally, a background range of the same width as the ranged peak is used to estimate the background for a given peak. The scheme is determined as follows: If there are no peaks defined within a certain distance to the left of a given peak (as defined by "Left Range Criteria"), then the Left ranging scheme will be used. That is, a range defined at some specified distance to the left (as defined by "Left Range Delta") of the given peak and the same width. If the left-ranging criteria fail, then an evaluation is made for nearest peaks on either side of the given peak. Nearest peak >0.9 Da away is the criteria for a Half-width ranging scheme. Immediately adjacent to the left and right of a prospective peak range, background ranges of half the prospective peak range width are defined and used to estimate the background. The Half scheme is equivalent to estimating a linear background correction for that peak. Otherwise, the Quarter-width ranging scheme is used. Same as the Half scheme, except background counts need to be doubled to account for the range width and provide a linear background correction (and consequently the background uncertainty will be doubled as well).
4) Optimum ranges are determined given the initial ion range definitions and auto-determined schemes as follows:
    a. A minimum range-width is defined based on the FWHunM.
    b. The local maximum is determined for each initial ion range.
    c. Left-scheme peaks use a fixed range width as specified in Parameters. The position of the fixed-width range is adjusted to yield the maximum number of total/net counts, and a same-width range is defined to the left of this peak (as specified in Parameters) as a background estimate.
    d. For half-width and quarter-width schemes, the minimum range-width is positioned so that the net counts (total counts in ion range, minus the immediately adjacent background estimate) is maximum. Then the prospective range width is expanded 2 bins (or 4 bins for quarter-width ranging) at a time and re-evaluated. The process stops when the net counts begin to decrease.
    e. Background ranging lines are added to the mass spectrum histogram. Note they are lines in linear-scale but curved in log-scale.

f. LeftTail performs an exponential fit to the ToF tail ($\sqrt{m/z}$). Starting at the range maximum point and continuing for "Considered Tail Range", ignoring any values defined by other ranges, these points are fit to an exponential function and those estimated counts are added to the various tables. Should the exponent be non-negative or span more than 5 Da before intersecting with the background, then the tail is rejected. The user specifies "Tail Estimate Uncertainty" as a fraction of the total number of counts. A value between 0.01 and 0.1 might be reasonable (1% and 10%). This uncertainty estimate and is propagated to the final composition results.



Mass Histogram | Ionic Composition | Decomposed Composition

Ion	Composition	Sigma/DT (95% CL)	Counts	Background	Net	Tail
Si	83.187%	0.028%	23,587,420	178,753	23,629,359	217,382
O	5.9438%	0.0044%	1,738,326	50,207	1,688,338	0
SiO2	2.4268%	0.0030%	766,703	77,941	689,343	0
Co	2.2346%	0.0028%	662,016	27,376	634,744	0
SiO	1.9812%	0.0052%	574,335	37,787	562,757	26,206
Ge	1.5898%	0.0025%	510,312	59,169	451,579	0
TiO	1.0701%	0.0022%	379,190	76,041	303,963	0
Ti	0.7554%	0.0021%	294,531	80,496	214,559	0
TiN	0.3105%	0.0011%	100,595	12,418	88,199	0
C	0.08732%	0.00074%	43,452	18,888	24,803	0
SiC	0.07234%	0.00065%	35,881	15,357	20,548	0
Al	0.07061%	0.00075%	38,919	18,969	20,058	0

Mass Histogram | Ionic Composition | Decomposed Composition

Element	Composition	Sigma/DT (9	Counts	Background	Net	Tail
Si	80.881%	0.027%	25,020,914	331,709	24,936,735	243,588
O	12.8237%	0.0070%	4,272,981	347,773	3,953,734	26,206
Co	2.0865%	0.0026%	687,877	44,677	643,304	0
Ti	1.9679%	0.0029%	774,316	168,955	606,721	0
Ge	1.4647%	0.0023%	510,312	59,169	451,579	0
N	0.3978%	0.0013%	159,398	36,851	122,635	0
C	0.1971%	0.0010%	108,640	48,149	60,777	0
Al	0.09551%	0.00081%	58,894	29,608	29,448	0
F	0.05301%	0.00055%	31,095	14,766	16,344	0
B	0.01964%	0.00070%	45,831	39,828	6,054	0
Hf	0.01302%	0.00038%	9,342	5,396	4,014	0
Au	-ND-	0.00069%	2,102	2,063	39	0

5) Once the ranging definitions are finalized, ionic and decomposed ion compositions are calculated. For each range (or ion type) the net counts are evaluated for statistical significance (has a peak been detected with a 95% confidence level). Note that any Not Detected (-ND-) ranges are removed from composition considerations and the 95% confidence level detection threshold is reported instead of sigma (the amount of that range/element that would be detected 95% of the time).
6) User must use the "Apply" button to transfer the new range definitions back to IVAS. The Parameters Table will then be transferred to the Properties area of AP Suite which is captured and can be restored via "Saved Analysis State."

7) A version of the peak ranging algorithm is used to look for any net counts that statistically might be a peak. The minimum range size is used bin by bin, starting at 0.8 Da. When the net counts are greater than (99%CL-DT/ Sensitivity), this constitutes a discovered peak. The range position is adjusted to yield the maximum net counts for that peak, and then the search process continues starting at the far-right edge of the discovered peak's range extent. Blue dots (limited by plotting options) are displayed on the mass histogram.

Parameters Table:

Histogram Information

- Max Peak Name: Ion range of found max histogram position
- Max Peak Position: Position of found max histogram position
- Max Peak FWHunM (Da): Full width 0.01 maximum of found max histogram position region
- Max Peak MRP: Mass Resolving Power = 1/FWHunM
- Spectrum Coarsen Factor: Binning of extension mass spectrum used (number times the IVAS Binning (default 0.001 Da), so 15-30 bins covering the FWHunM)

Ranging Parameters

- Ranging Width Factor: Number times FWHunM for left-ranging or fixed ranging
- Min Width Factor: Number times FWHunM for minimum range width
- Left Range Criteria: Required region empty of defined ranges for left-ranging
- Left Range Delta: Position left of peak to center left background range
- Use Fixed Ranging Width: Do not use auto-width ranging (use fixed ranged determined by Ranging Width Factor above)
- Ignore Discovered Peaks: Ignore (or use) any discovered peaks and determine ranges.

Tail Parameters

- Considered Tail Range (Da): Range beyond right-range-edge to fit exponential tail
- Tail Estimate Uncertainty: User estimated fractional uncertainty of total tail counts

Peak Discovery Parameters

- Sensitivity: Number times FWHunM for left-ranging or fixed ranging
- Min Bin Pairs: Minimum bin width for peak evaluation in coarsened bin pairs
- Min Counts for Peak Max Bin: Discovered peaks must have a bin with at least this many counts

*Note: Minimum and Fixed Width Scaling: Generally, minimum and fixed peak widths scale in ToF (or $\sqrt{(m/z)}$) relative to the Max Peak, so only the Max Peak will have the specific values as set forth in the parameter table. Ranges to the left will be slightly more narrow, and those to the right more broad. Depending on parameter definitions, very low m/z peaks might require near zero-width minimums, so the "Min Bin Pairs" parameter prevents this.

Additional Notes:

1. “Rerange" can be done multiple times (needed when users change Parameters or modify any Schemes).
2. Select/Select-All and Copy/Paste functions should work on all tables (column headers are not captured in this operation). Export features have not been provided as Copy/Paste provides for this capability.
3. Double clicking in plot region will unzoom x-axis. A second time is needed to unzoom y-axis. Auto-y-axis scaling is not a current feature.
4. Table columns are also sortable by clicking the column header, but note to control precision display, some numerical columns are of type string, and these will not always sort in numerical order!
5. Quarter-width ranging will have slightly larger uncertainly because the background is scaled by a factor of two (greater background uncertainty).
6. Decomposed compositions error propagation means that any molecular ion with an element that has greater than one atom in the molecular formula (e.g., O in SiO_2) will result in a larger uncertainty because of the scaling of those counts in the decomposition calculation (not historically accounted for in this way in IVAS). This is almost always insignificant, but for materials with a significant fraction of multi-same-atomic molecular species, this could become significant.
7. Tool tips are available for many table column headers, Parameters, and Properties.
8. Any changes in the IVAS ranges associated with an active extension session will force an update of the extension (start from the beginning).
9. Save Analysis Tree saves the current parameters and schemes (those shown in the properties region, which are modified only after apply has been done). Using a Saved Analysis tree will also override auto-scheme (not shown in Properties) with the previously used scheme for any matching ranges (since a Saved Analysis Tree can be applied to a different dataset than the one from which the save was performed, the IVAS ranges/ions list may be different).
10. “Discovered” range names ignored upon load (user needs to assign new range type/name for them so survive initial load).
11. Ignore function: Reranges always starts with the orignal StartTable (internal for load)—the original Sheme Properties when they exist, or null. When null, then the scheme will be auto-determined.
12. Not Ignore: The peaks list of all found peaks is overridden by any StartTable entries. StartTable scheme is applied if found and null otherwise. When null, then the scheme will be auto-determined.

13. The discovery process can provide closely spaced peaks and the auto-ranging can result in overlapping peaks. The code attempts to resolve these overlaps using the following rules: Same named overlapping ranges, the lower net counts range is removed. Overlapping ranges where one is “Discovered”, the discovered is removed. Any other potential outcomes will cause the extension to fail.