Fractional Occupancy Strategies for Handling Peak Overlaps in Atom Probe Data

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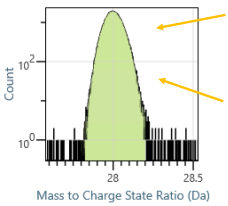
What is a "Range"?



Traditional Interpretation:
An ion in this peak corresponds to exactly 1 ion.
A .rrng file specifies exactly which ion in should be, i.e. one Si^+ ion, or one N_2^+, or one Fe^{++}, or whatever.
We refer to this as "integer occupancy"

Fractional Occupancy Interpretation:
An ion in this peak corresponds to some combination of fractional representation of one or more ions.
For example, it might correspond to 0.78 of a Si^+ ion, and 0.21 of a N_2^+ ion, and 0.01 percent background noise.
We refer to this as "fractional occupancy"

Our Motivation:
Implementing ranges with fractional occupancy should allow the effects of known peak overlaps and background noise to be meaningfully and more consistently incorporated into downstream analyses

Fractional Occupancy Definition in IVAS

A) via RRNG file

Traditionally, the ion assignment for a particular range can be defined by a .RRNG file.

Here's how we propose extending the standard .RRNG file to specify occupancy:

In the past, if a single range was used more than once in RRNG file, the exact behavior was undefined. IVAS has up until now worked on the "last one wins" principle.

```
[Ions]
Number=2
Ion1=Si
Ion2=N

[Ranges]
Number=5
Range1=27.8 28.2 Vol:0.02 Occupancy:0.78  Si:1 Color:CCCCCC
Range2=27.8 28.2 Vol:0.04 Occupancy:0.21  N:2  Color:33CCFF
Range3=28.8 29.2 Vol:0.02 Occupancy:0.99  Si:1 Color:CCCCCC
Range4=28.8 29.2 Vol:0.04 Occupancy:0.001 N:2  Color:33CCFF
Range5=29.8 30.2 Vol:0.02 Occupancy:0.99  Si:1 Color:CCCCCC
```

B) via Peak Decomposition

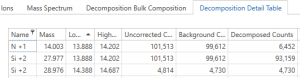
When a "Decomposition of Peaks" node is defined for a region of interest (ROI), the result of the decomposition is exactly the information required to define the fractional occupancies for ranges.

We explored implementing a strategy for defining occupancies by simply copying the Peak Decomposition fractions.

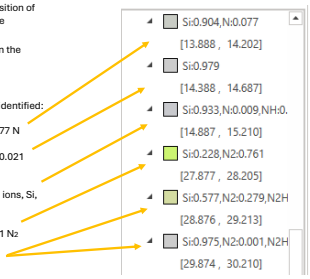
Any SubROI node or Detached ROI node can override its ranging by selecting an "Ion Build Strategy".

The "Peak Decomposition Verbatim" strategy applies the results of the Decomposition of Peaks to every range identified in the Decomposition.

The resulting ranges are displayed in the Mass Spectrum Analysis Pane.



Name	Mass	Lo...	High...	Uncorrected C...	Background C...	Decomposed Counts
N +1	14.003	13.888	14.202	101,513	99,612	6,452
Si +2	27.977	13.888	14.202	101,513	99,612	93,159
Si +2	28.976	14.388	14.687	4,814	4,730	4,730
N +1	15.000	14.887	15.210	3,393	3,313	23
Si +2	29.974	14.887	15.210	3,393	3,313	3,118
N2 +1	28.006	27.877	28.205	86,562	85,787	63,350
Si +1	27.977	27.877	28.205	86,562	85,787	22,437
N2 +1	29.003	28.876	29.213	1,722	1,692	465
Si +1	28.976	28.876	29.213	1,722	1,692	1,139
N2 +1	30.000	29.874	30.210	766	752	0
Si +1	29.974	29.874	30.210	766	752	751



Here, Decomposition of Peaks has identified:

The peak at 14 Da is .904 Si and 0.077 N

The peak at 14.5 Da is 0.979 Si and 0.021 noise.

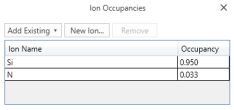
The peak at 15 Da is composed of 3 ions, Si, N and NH

The peak at 28 Da is .228 Si and .761 N_2

The peaks at 29 and 30 Da are both composed of 3 ions, Si, N_2 and NzH

C) via Manual Editing

There's also a simple editor UI for adding fractional occupancies to a range



Deriving an integer-occupancy dataset

When needed, a fractional occupancy dataset can be converted to an integer occupancy dataset if needed, but with some data loss. The algorithm we use is an accumulative model, which we use for rendering the ion maps:

The goal of the algorithm is to assign each datapoint an integer ion. Each candidate Ion with fractional occupancy is assigned a "remainder", initialized at 0.5.

The algorithm is iterative: For each ion coordinate in the range:

A) each remainder is incremented by the amount of its Ion's occupancy.

B) if the Candidate Ion with the highest remainder has a remainder of greater than or equal to 1.0, that Ion is chosen for that datapoint, and its remainder is reduced by 1.0. It is possible that no Ion has remainder of higher than 1.0, in which case that datapoint is considered 'background'.

Here's a table that shows how the process works for 15 ion coordinates in a range with IonA at 0.7 occupancy, IonB at 0.25 occupancy (background is 0.05),

The first ion is determined to be A. RemainderA is incremented to 1.2, and RemainderB is incremented to 0.75. 1.2 is largest and greater than 1, so the ion is A and RemainderA is decremented to 0.2. The process continues iteratively for each datapoint, with the previous remainders used as input for the next cycle.

In this example, the 9th and 25th data points are not drawn – they represent background ions. Over a larger sample, exactly 5% of the coordinates will be background, 75% of the datapoints will be IonA, and 20% of the datapoints will be IonB.

This strategy is deterministic, in that it produces the same output every time given the same input.

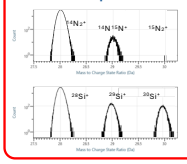
There is also room for manipulation of the initial remainder values to generate a different deterministic output from the same input. That is, if different values are used for the initial remainders, different ion assignments will be made. This could be useful for multiple runs of a cluster search algorithm using fractional occupancy input data.

Rem A	RemB	Ion
0.5	0.5	A
0.2	0.75	B
0.9	0	A
0.6	0.25	A
0.3	0.5	A
0	0.75	B
0.7	0	A
0.4	0.25	A
0.1	0.5	
0.8	0.75	A
0.5	1	B
1.2	0.25	A
0.9	0.5	A
0.6	0.75	A
0.3	1	B
1	0.25	A
0.7	0.5	A
0.4	0.75	A
0.1	1	B
0.8	0.25	A
0.5	0.5	A
0.2	0.75	B
0.9	0	A
0.6	0.25	A
0.3	0.5	
1	0.75	A

Prototype System: SiN / Si with varying layer thickness

To demonstrate the technique and test its limits, a series of datasets were made for Si / SiN layers, which has significant peak overlaps.

Peak Overlap at 28–30 Da



Simulated Samples

Simulated samples of SiN and Si layers were made with ion populations similar to a real sample. The ion fractions used were,

Si layers:		SiN layers:	
Si^+	25.8%	Si^+	10.1%
Si^{++}	73.6%	Si^{++}	53.2%
H^+	0.4%	N_2^+	30.8%
Hz^+	0.1%	SiN^+	1.1%
		Si_2N^{++}	1.4%
		N^+	2.8%
		NzH^+	0.14%
		NH^+	0.03%
		SiN^+	1.1%
		H^+	0.28%
		Hz^+	0.05%

Additionally, a 2% noise background was applied to the entire spectrum, decaying quadratically with increasing Da.

The resulting data should correspond exactly to 100% Si in the Si layers, and to 50% Si / 50%N in the SiN layers if only the Si and N atoms are considered.

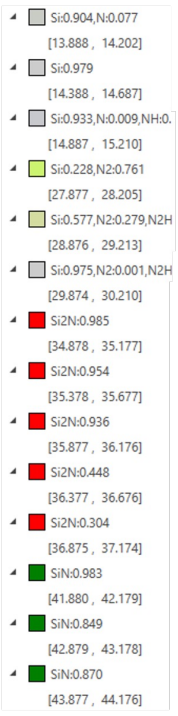
Isosurface Definition

After importing to IVAS, a .RRNG file was loaded corresponding to each component. Overlapping components were assigned to be equally divided between each component. (i.e., the 28 Da peak was assigned to be 50% N_2^+ and 50% Si^+)

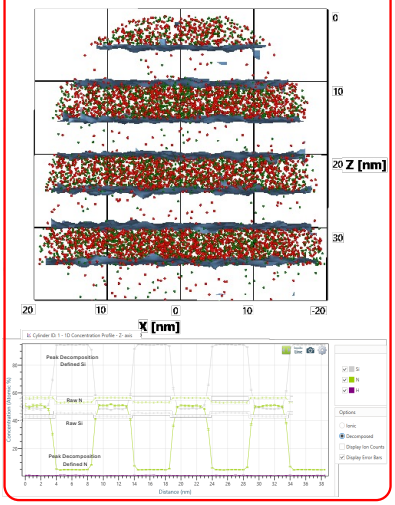
An isosurface was generated from the SiN^+, Si_2N^{++} and N^+ counts, which was used to partition the sample into two ROIs. Decomposition of Peaks was used to supply fractional occupancies for each ROI.

Occupancy Definition

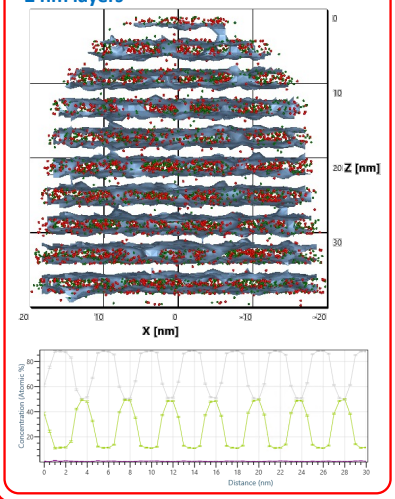
After ROI definition and Decomposition of Peaks, fractional occupancies are automatically assigned to ranges using the Peak Decomposition results, resulting ranges like these:



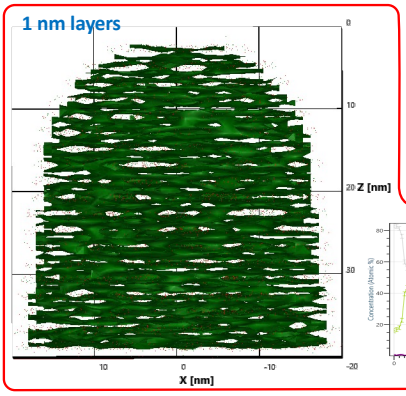
5 nm layers



2 nm layers



1 nm layers



1D Profile Calculations

The 1D Profile through the 5nm layers shows very good agreement with the expected compositions, with progressive deterioration as the layers get thinner.

Errors in calculating compositions are due to imprecision in defining isosurfaces, and error cascades through peak decomposition to the 1D profiles.

Previous Work

Much work has been done on spatially resolved peak decomposition, and indeed, various strategies for applying peak deconvolution to improve experimental results have been successful. The references listed here are only a small sampling.

What is new in this work is implementing a fractional occupancy ranging treatment as a **general purpose** feature of software (see the title of the poster!).

That is, there may be many ways to define regions of interest, or to apply different fractional occupancies, based on spatial techniques. Many, if not all, of these techniques, could use a fractional occupancy approach to leverage those techniques.

We hope that our proof-of-concept in integrating fractional occupancy into the IVAS platform will be enabling for everyone trying to overcome peak overlap challenges in APT data

References

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Conclusions

The fractional occupancy ranging strategy is both useful for handling peak overlaps in atom probe data and can be applied to any system that has peak overlaps. It may also be useful simply as a strategy for handling background subtraction.

When using the Decomposition of Peaks method for automatic setting of occupancy fractions, it is important to be able to define regions of interest appropriately and consistently. We show that quality of the data analysis suffers when the regions of interest cannot be delineated well.

Other strategies for determining peak range occupancies are open for investigation. The fractional occupancy approach is applicable no matter how occupancies are determined.

Our proof-of-concept implementation of fractional occupancy in the IVAS demonstrates feasibility as a general purpose technique, able to be integrated with other APT data analysis techniques.

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