Implementing Tile-Based Fisher Ratio Analysis of GC×GC-TOFMS Data to Obtain a Master Peak Table of All Detected Analyte Compounds in Many Petroleum-Based Samples

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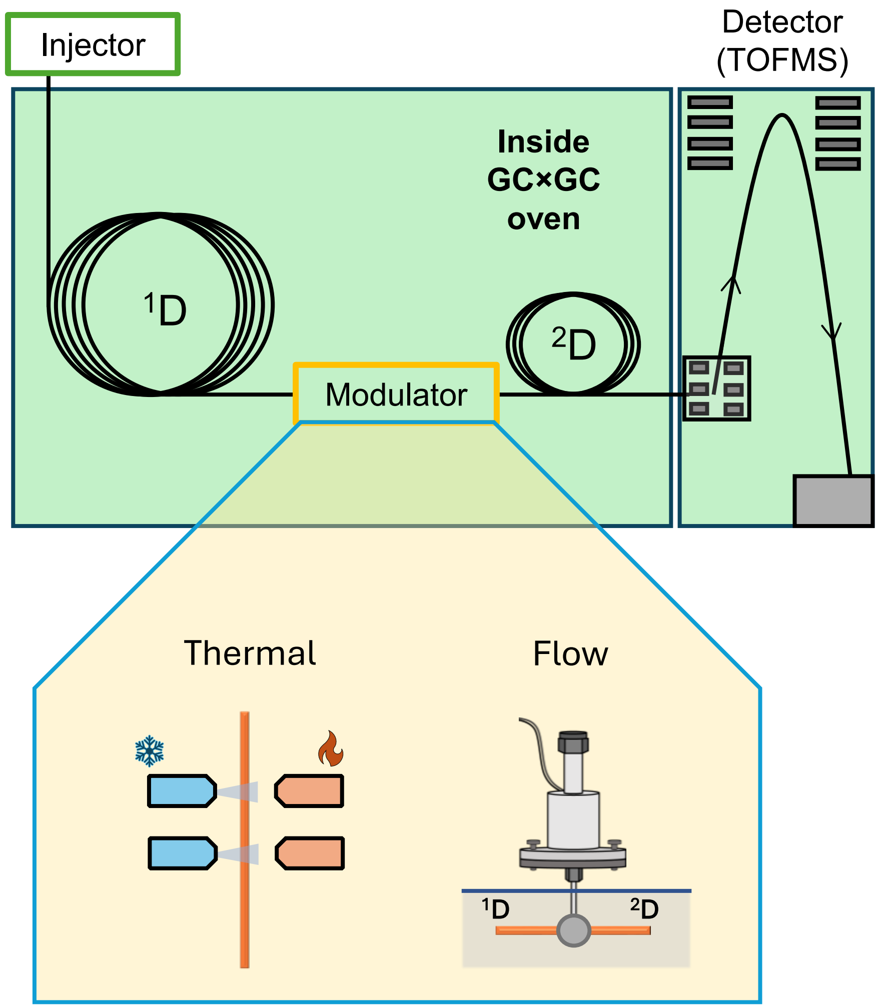
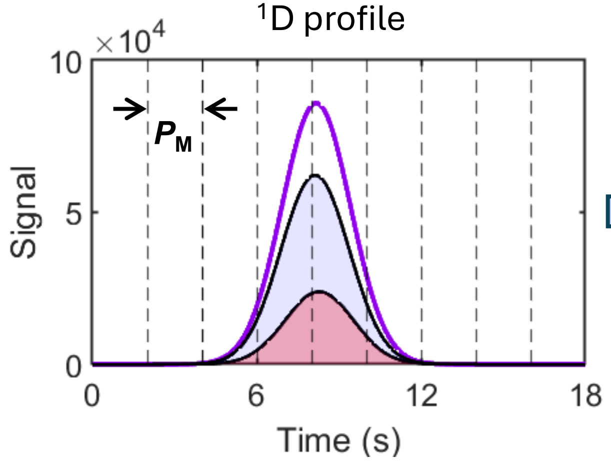
1/13/26

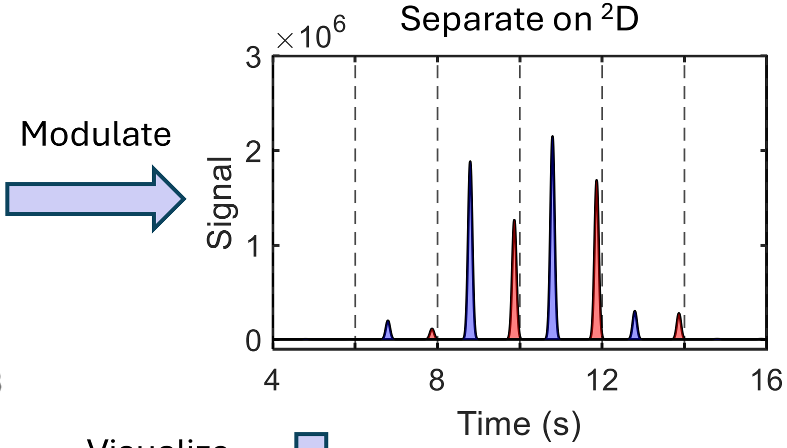
Study Background: Fuel Sample Analysis

- Chevron's Technical Center contracted group to develop more advanced fuel analysis techniques
- Direct improvement by simply moving from GC to GC×GC for separation
- Increased peak capacity and resolution necessitated improved chemometrics for peak tables
- Novel method adapted from tool used to find peak differences between samples forwarded

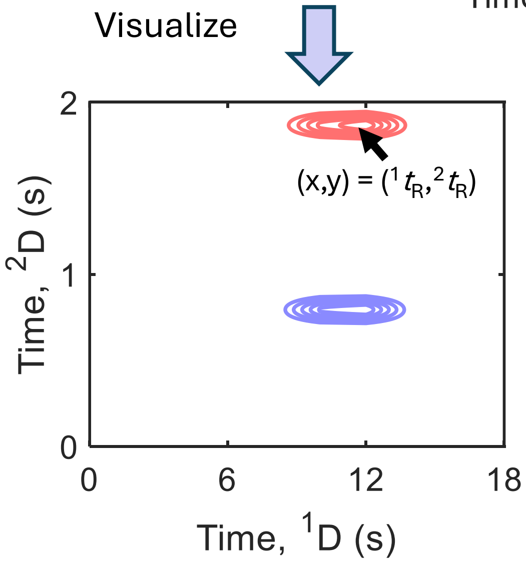
Quick Overview of GC×GC





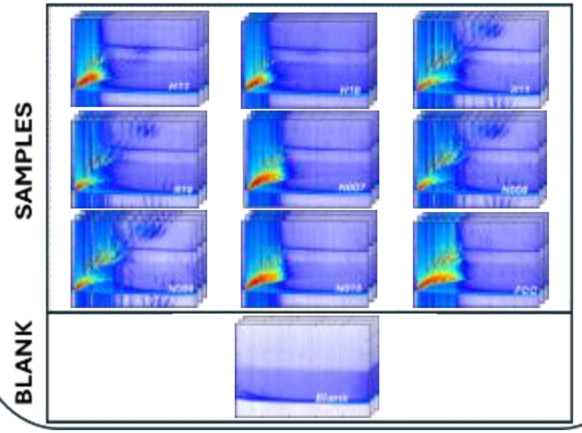


P_M: Length of ^{2}D separation.



Chemometric Method Overview

Sample Data
[3 Replicates × (Sample Classes + Blank)]



Tile-Based F-Ratio →

Single Comprehensive Hit List

Hit #	$^{1}D\ t_R$ (min)	$^{2}D\ t_R$ (sec)	F-Ratio	ID	MV
1	3.97	1.66	High	Pentane	877
...	...	...	...	...	...
...	...	...	...	...	...
N	31	5.16	Low	Dodecane	923

p-Test →

Master Peak Table Contents

Hit #	S_1	S_2	S_3	...	S_N
1	Pass	Pass	Pass	...	Fail
...	...	...	...	...	...
...	...	...	...	...	...
N	Fail	Pass	Fail	...	Pass

H11 SSPT
H18 SSPT
R11 SSPT
R18 SSPT
N007 SSPT
N008 SSPT
N009 SSPT
N010 SSPT
FCC SSPT

SSPT: Sample Specific Peak Table

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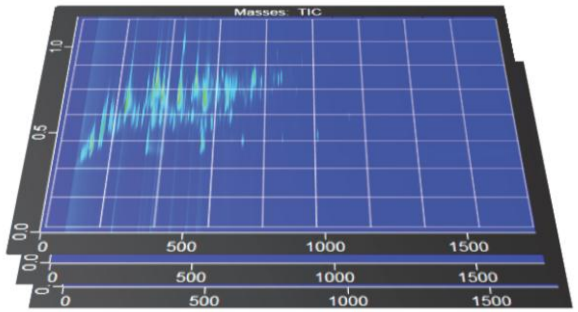
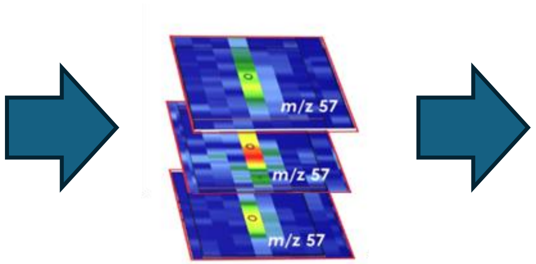
Tile-Based F-Ratio (Through ChromaTOF Tile)

Utilize a tile-based fisher ratio method that discovers analytes that are statistically different in concentration between sample classes.

$$\textit{Fisher Ratio} = \frac{\textit{Between Class Variance}}{\sum(\textit{Within Class Variance})}$$





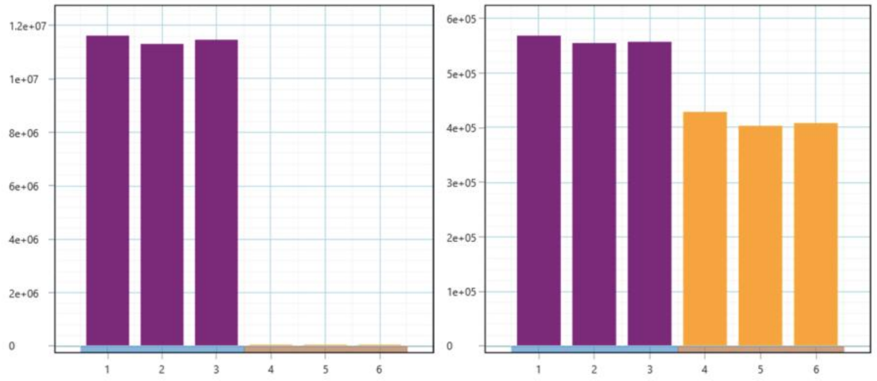


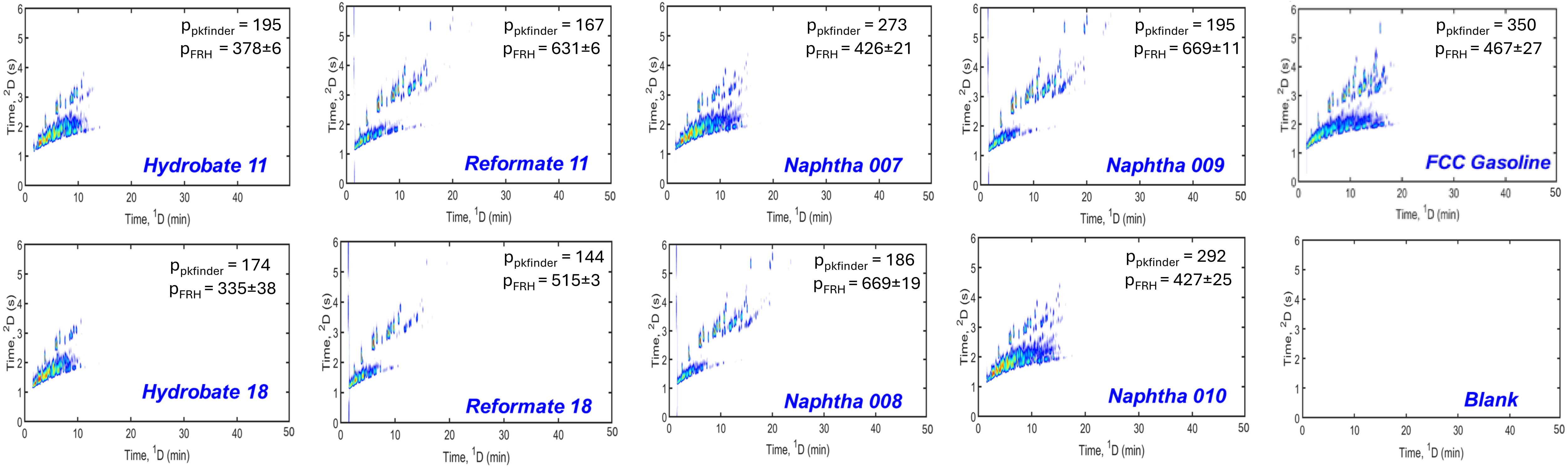
Figure 1. GCxGC chromatographic plane divided into rectangular tiles.

Figure 2. Feature intensity vs. sample number for two significant (high F-ratio or low p=-value) features. Samples 1, 2, and 3 (purple) belong to one sample class and features 4, 5, and 6 (orange) belong to the other sample class.

https://gcms.cz/labrulez-bucket-strapi-h3hsga3/LECO_Skola_hmotnostni_spektrometrie_2021_Chroma_TOF_Tile_001aee1bfc/LECO-Skola-hmotnostni-spektrometrie-2021-ChromaTOF-Tile.pdf

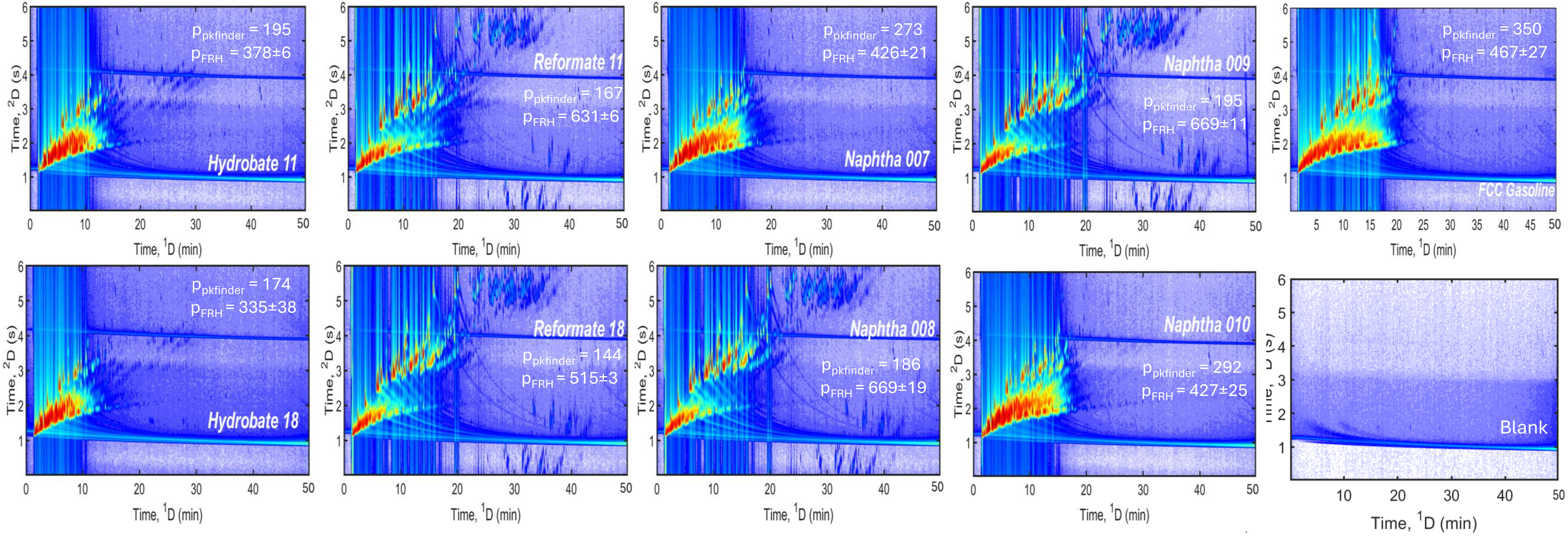
Sample Class Linear-Scale Chromatograms

FRH: Fisher Ratio Hitlist



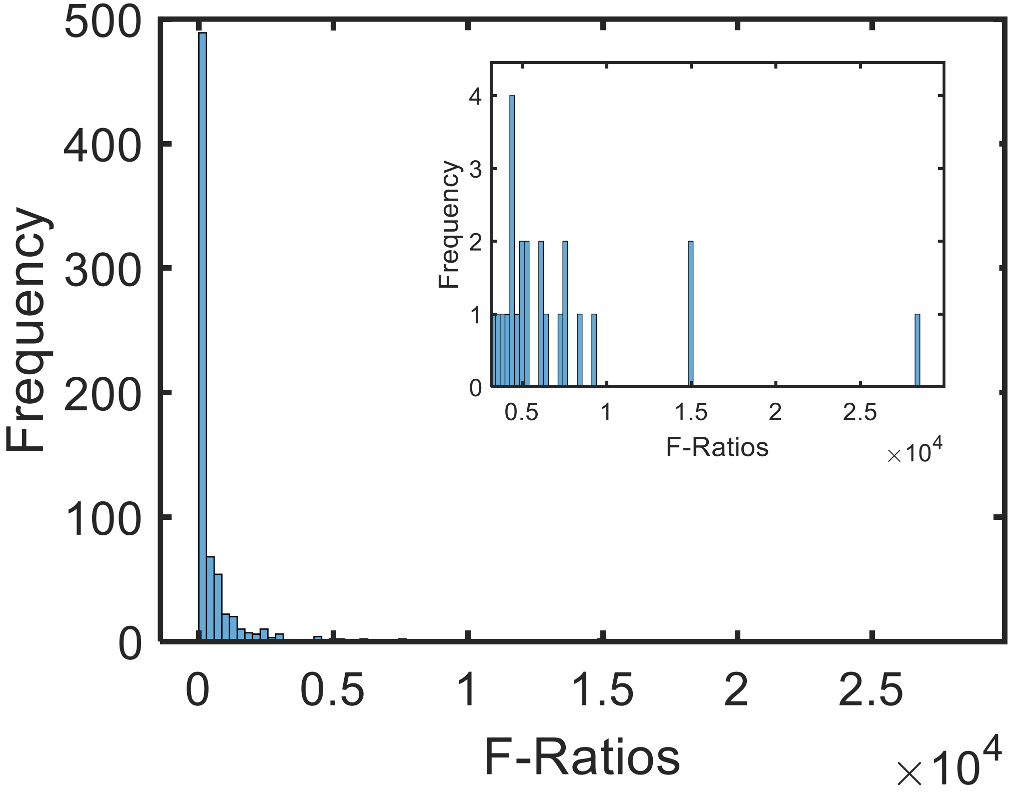
- Samples run on Rxi-1 column (30 m × 0.25 mm × 0.25 μm) first dimension and Rxi-17MS column (2.0 m × 0.18 mm × 0.20 μm) on second dimension.
- Sample classes are all fuels, mixture of different manufacturing methods and samples taken from different batches
- Major components all elute earlier than 15-27 minutes depending on sample

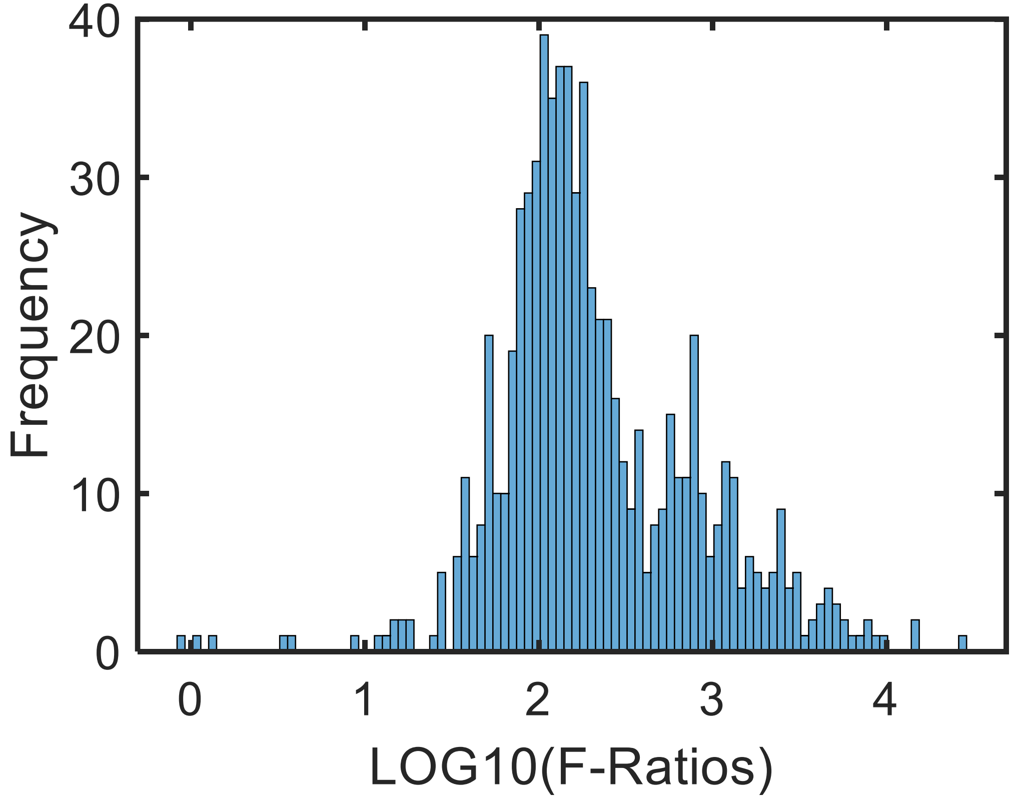
Sample Classes: Log-Scale Chromatograms



- ➢ Several samples have many more late-eluting minor components!
- ➢ Variations in these minor components also more pronounced between sample batches

Histogram of 719 hits' F-Ratios

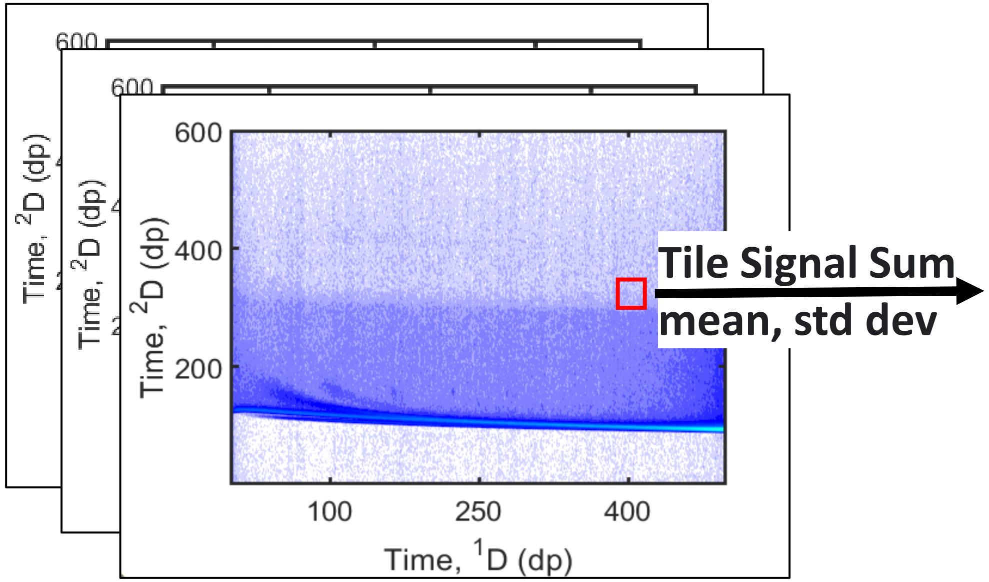




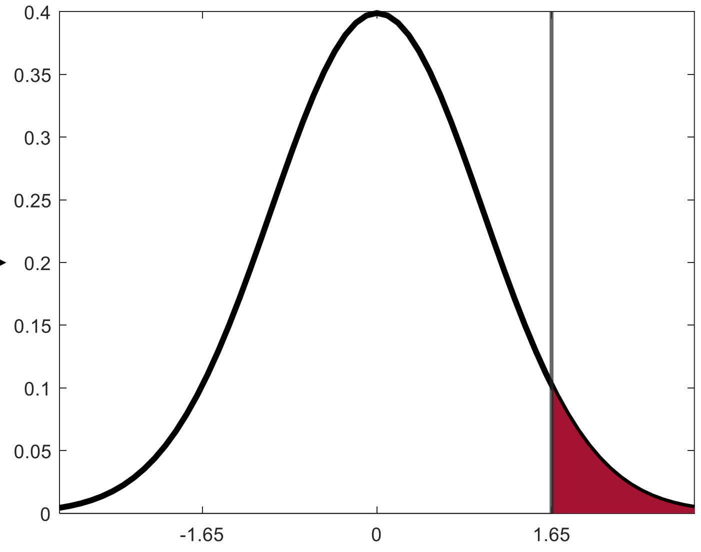
- ➢ As expected from chromatograms showing a variety of large and small peaks across differing samples, we get a wide range of F-Ratios for our hits. While traditionally we'd discard hits below a certain F-Ratio, we take a different approach here
- ➢ Too many variables for F-Ratio alone to tell us much about each hit

Use of Blank Tiles for p-testing

- Using ChromaTOF Tile tells us which samples have relatively higher peaks for given compounds but does not tell us directly which compounds are detectable.
- To resolve this, three blank chromatograms are used to generate per-tile p-tests to be applied to all hits across nine sample classes.
- To p-test, we need a Confidence Interval – how to choose?



3 Blank Replicates



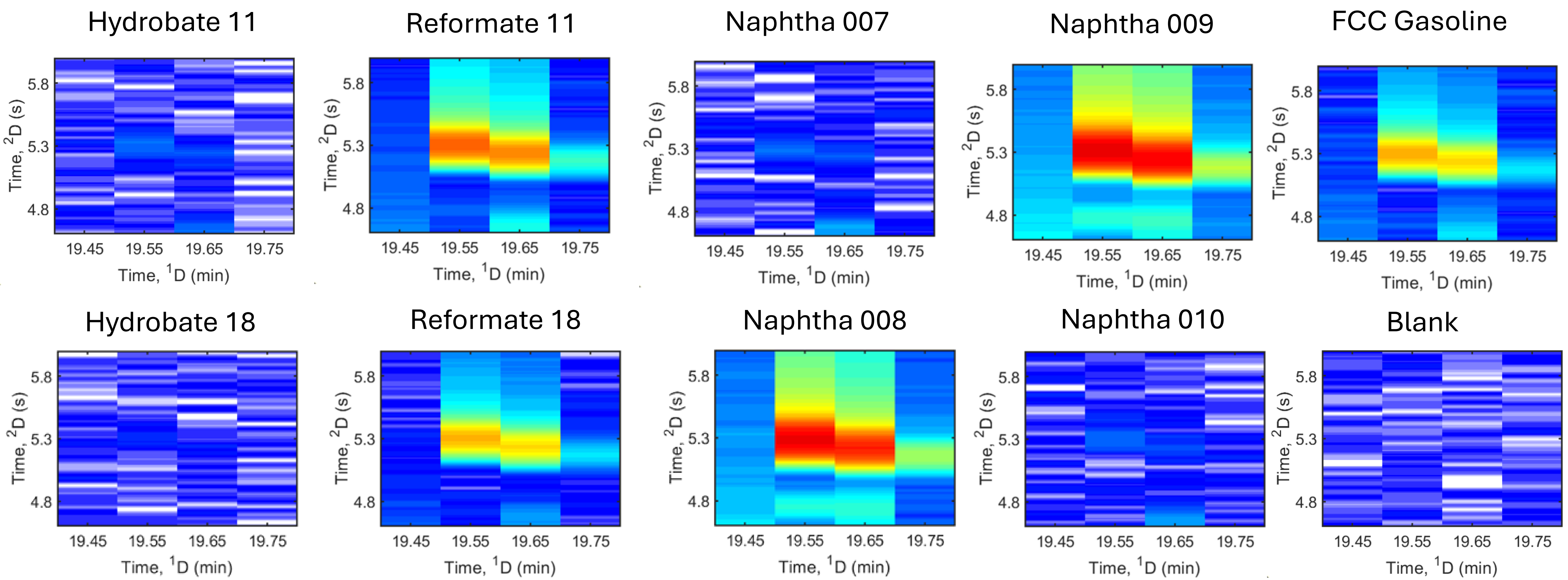
Inferred Gaussian Distribution of Summed Tile Blank Signal

99% CI
p-test threshold

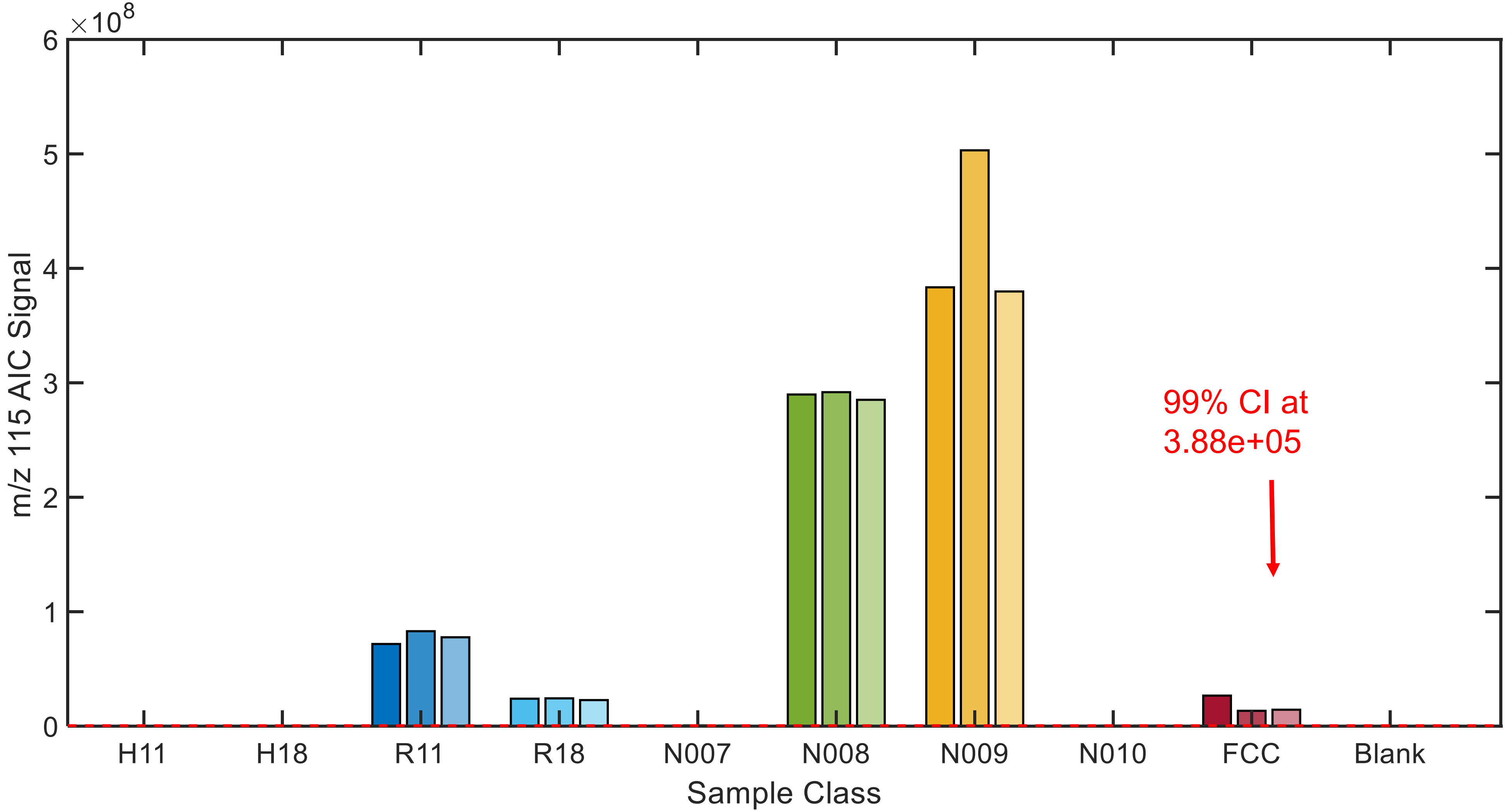
Hit #	H11	H18	...
1	Pass	Pass	...
2	Pass	Pass	...
3	Pass	Fail	...
4	Fail	Pass	...

Master Peak Table (MPT)

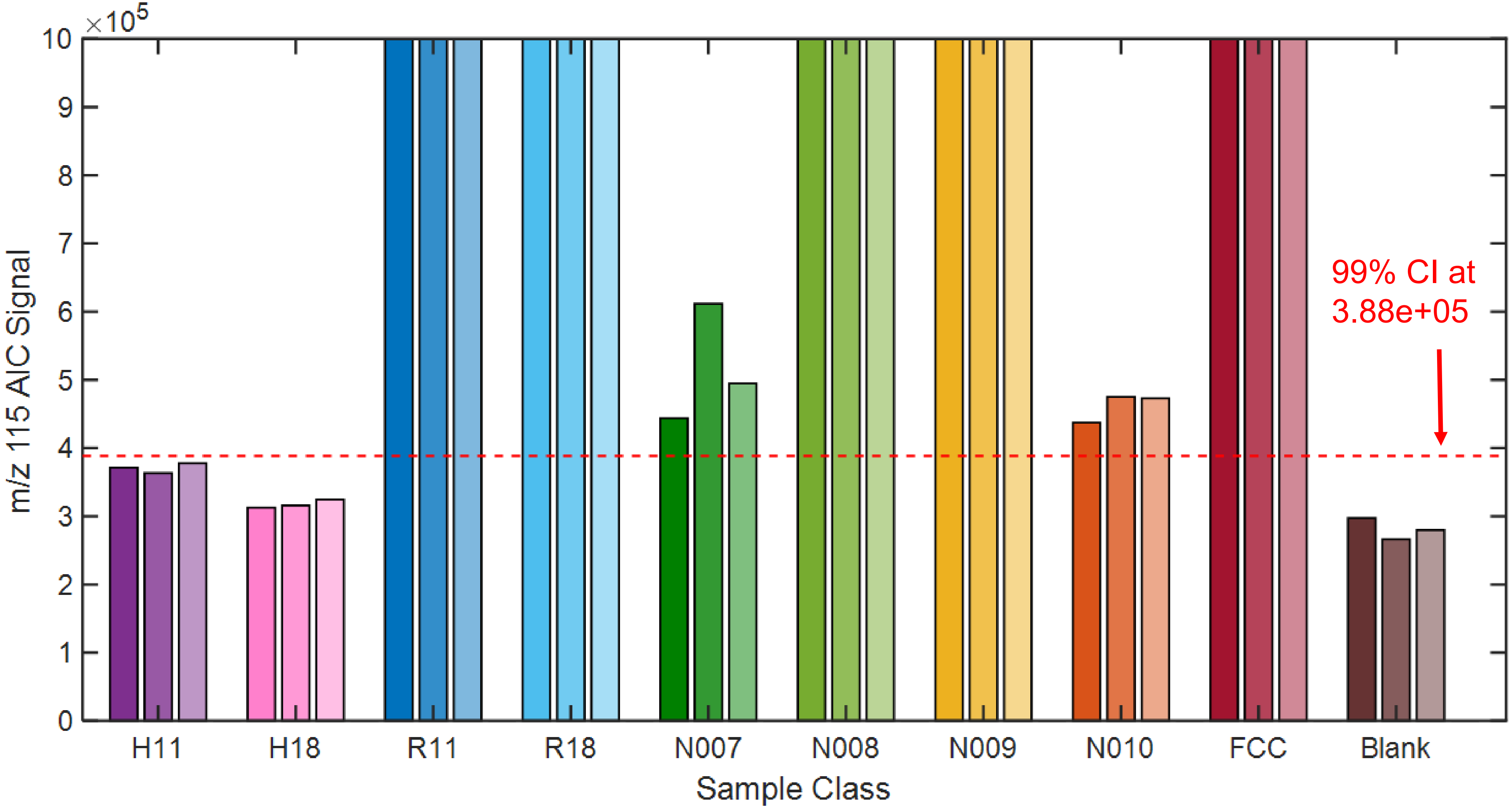
Example of Detectable Peak: 1-Methylnapthalene @ m/z 115



Summed m/z 115 Tile Signal with 99% CI Limit



Summed m/z 115 Tile Signal with 99% CI Limit: Zoomed



More Example Hits at 99% CI

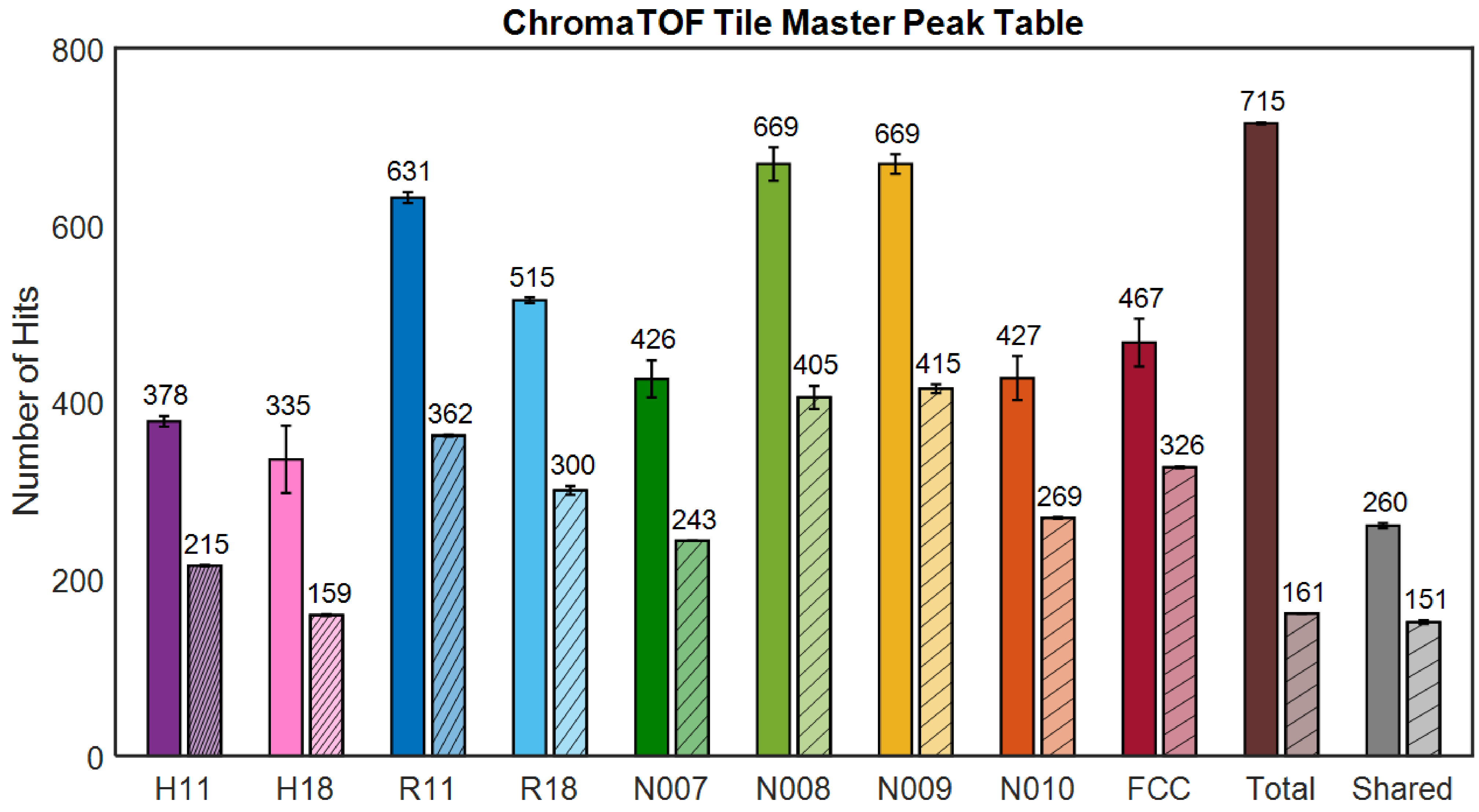
Hit #	F-ratio	F-ratio *m/z*	Nominal Identification	MV	RT1(min)	RT2 (sec)	In H11	In H18	In R11	In R18	In N007	In N008	In N009	In N010	In FCC
1	2.85E+04	110	1,2,3-trimethylcyclopentene	877	3.97	1.66	3	3	3	3	3	3	3	3	3
17	4.51E+03	98	2-octene	882	4.57	1.91	3	3	3	3	3	3	3	3	3
73	1.29E+03	202	β-vatirenene	818	29.26	4.06	3	3	0	0	3	0	0	3	0
80	1.22E+03	172	2,6,10,14-tetramethylheptadecane	872	14.87	1.94	0	0	0	0	0	0	0	3	3
83	1.17E+03	151	1-methylene-1H-indene	948	15.87	5.44	0	0	3	3	2	3	3	3	3
95	1.07E+03	119	1,2,4-timethylbenzene	867	9.07	2.89	3	3	3	3	3	3	3	3	3
169	5.47E+02	169	2,4-diethyl-1-methylbenzene	901	15.57	3.38	0	0	0	0	0	3	3	1	3
247	2.56E+02	64	1,2-dimethyl-4-(phenylmethyl)-benzene	872	31.46	5.18	0	0	3	3	0	3	3	0	0
292	2.06E+02	79	2,6-dimethylundecane	874	19.33	2.02	0	0	3	0	0	3	3	0	3
349	1.68E+02	115	1-methylnaphthalene	923	19.7	5.26	0	0	3	3	3	3	3	3	3

- Example hits align with our qualitative analysis (heavier analytes are found in heavier samples, more aromatic analytes are found in samples with higher aromatic content, etc.)

- Out of all classifications across all 719 hits, only 6.3% are heterogeneous across replicates (2.53% 1/3 passed and 3.77% 2/3 passed), this indicates good reproducibility.

Sample-Specific Peak Tables, Total #s of Peaks

(Unshaded for Entire Chromatogram, Shaded for 99% Summed TIC)



Conclusions

- Developed method gains benefits of tiling, particularly minimization of retention time shifting, and allows recovery of trace analytes with reduced need for user input/intervention
- Method should be widely applicable to other samples
- Similar approaches could likely be applied with different chemometric metrics other than F-Ratio to better fit experimental needs, e.g. variance ranking for cases where replicates are impractical

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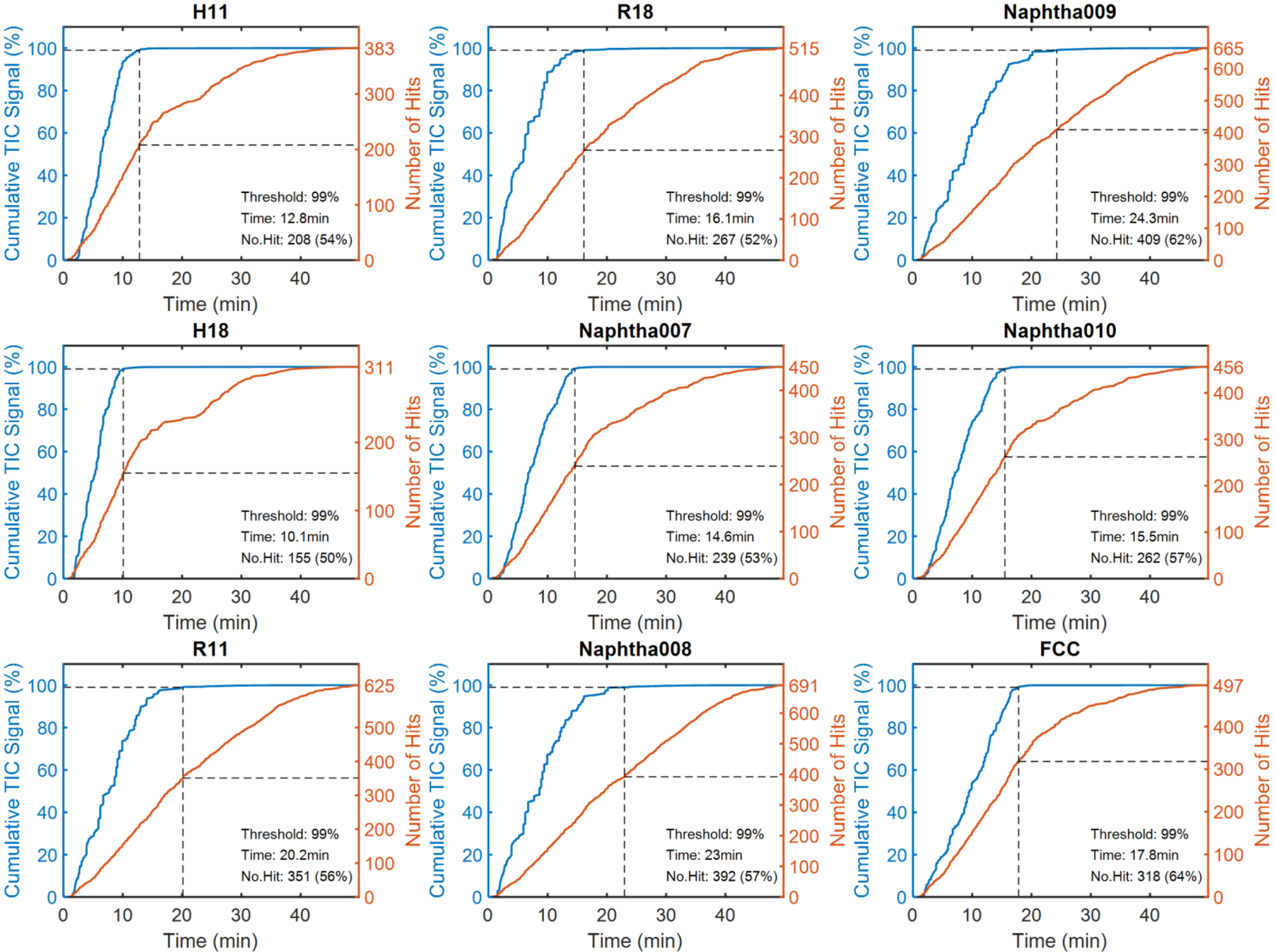
Synovec Lab

Gas Chromatography, Liquid Chromatography, and Mass Spectrometry, with Multi-Dimensional Data Analysis

http://depts.washington.edu/synlab/

TIC Signal-Based Rough Simulated Distillation Curves



Simulated Distillation Sample Class Comparisons