Uncovering the Volatile Profile of Potato Taste Defect in Roasted Arabica Coffee using GC-MS, GC×GC-MS, and Chemometrics

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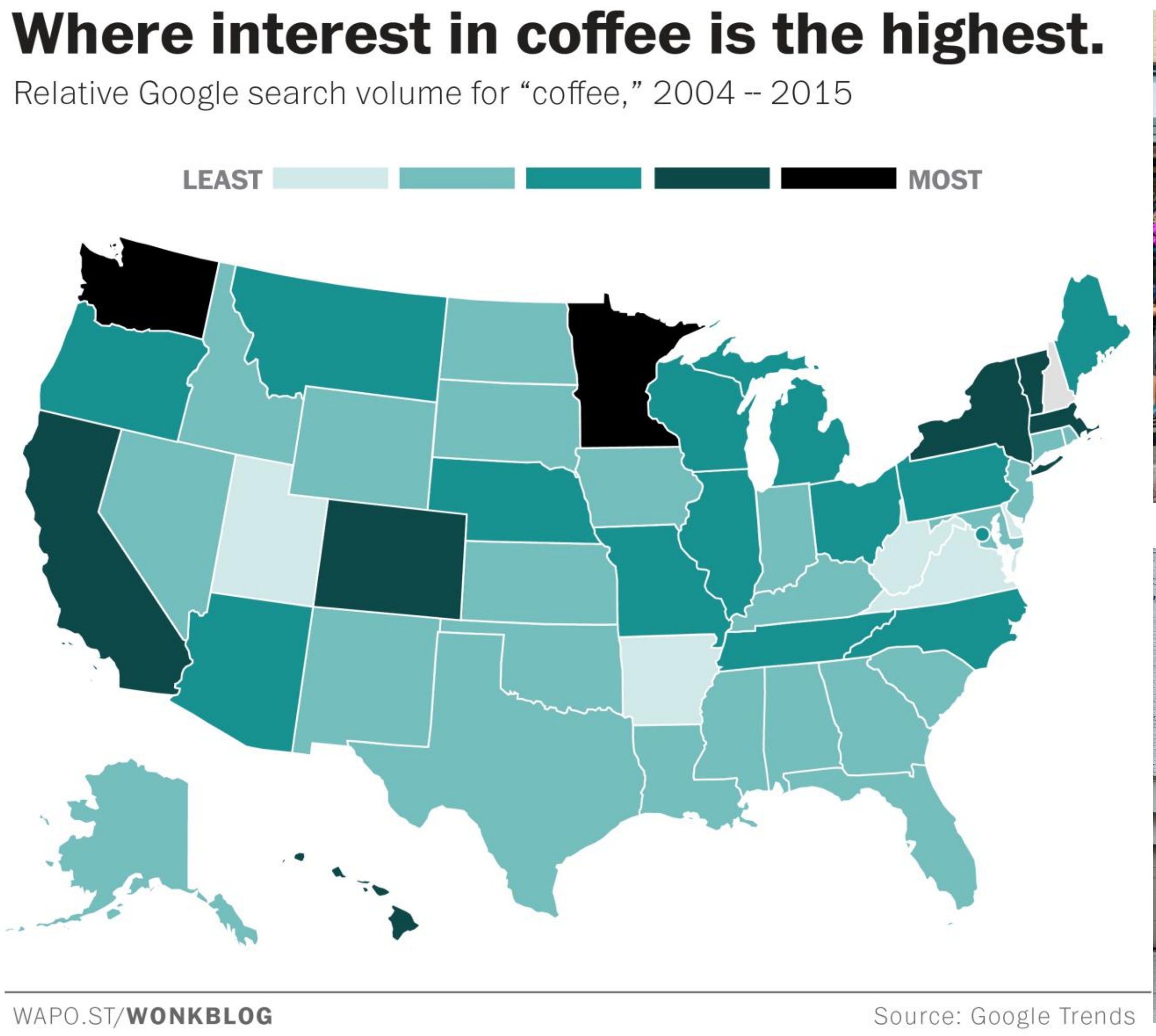
15th Multidimensional Chromatography Workshop

Project Motivation



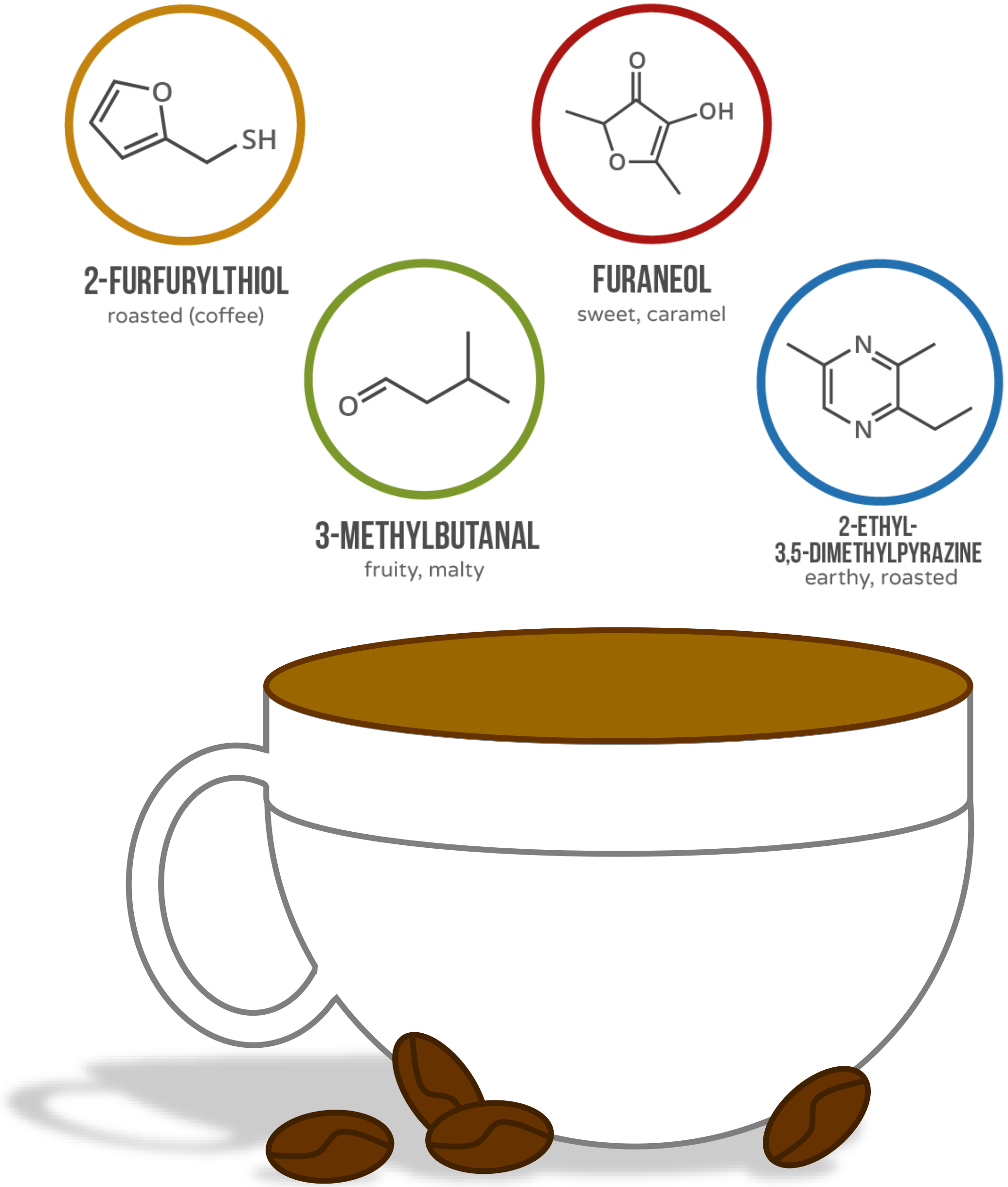
Desirable aromas

Examples: cocoa, nutty, fruity

Undesirable aromas

Examples: sour, musty, vegetable

Coffee Complexity



- Roasted coffee contains hundreds to thousands of compounds from a wide range of chemical classes
- The chemical composition of coffee is highly dependent on:
  - Pre-harvest agricultural variables
  - Post-harvest processing and roasting conditions

Sunarharum, W.; Williams, D.; Smyth, H. *Food Res. Int.* **2014**, *62*, 325-325.

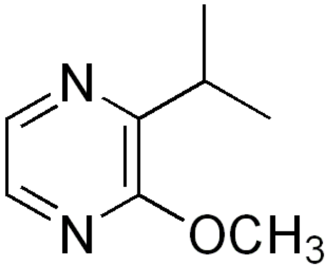
Coffee Complexity

- Roasted coffee contains hundreds to thousands of compounds from a wide range of chemical classes
- The chemical composition of coffee is highly dependent on:
  - Pre-harvest agricultural variables
  - Post-harvest processing and roasting conditions
- Defective beans can cause off-flavors and aromas in coffee

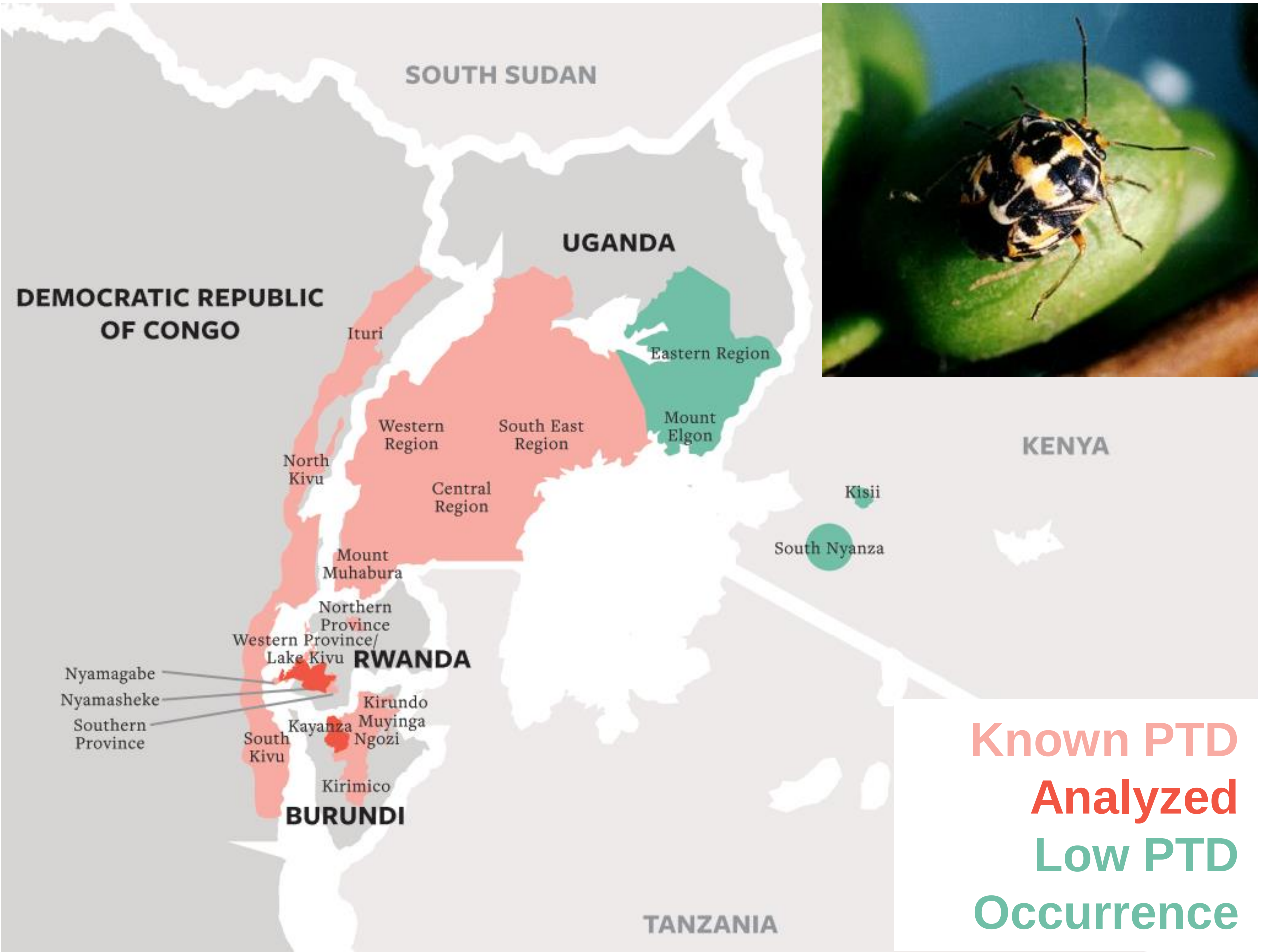
Toci, A.; Farah, A. *Food Chem.* **2014**, *153*, 298-314.

Potato Taste Defect (PTD)

- Sporadic flavor defect that affects coffee beans from the African Great Lakes region
- Linked to the presence of the antestia bug (*Antestiopsis orbitalis*)
- Contributes to a flavor of "dirty potato" in green and roasted coffee beans
  - Hypothesized to be due to 2-isopropyl-3-methoxypyrazine (IPMP)



IPMP



Jackels, S.C.; et al. *J. Agric. Food Chem.* **2014**, *62*, 10222–10229.

Targeted Analysis of IPMP

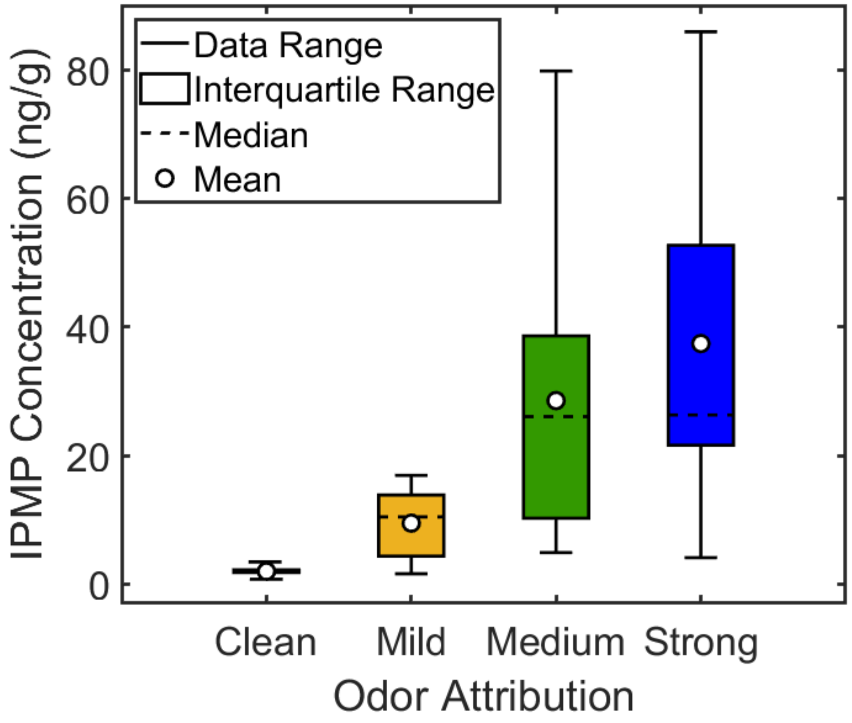
13 clean samples

9 mild PTD samples

12 medium PTD samples

15 strong PTD samples

GC-MS



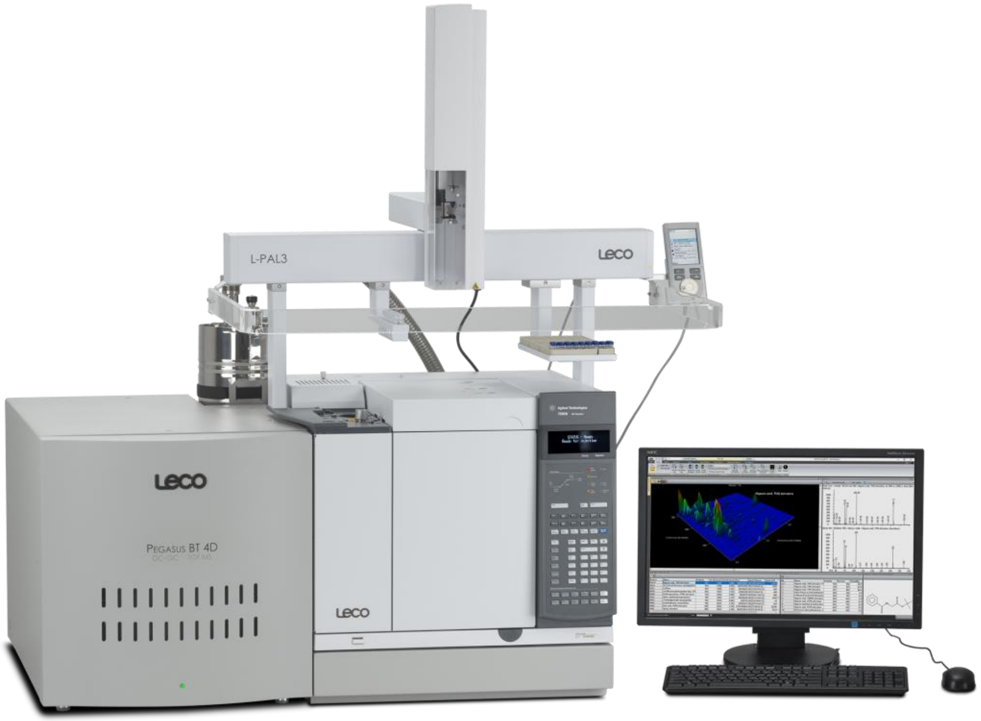
One-way ANOVA showed that the IPMP concentration was **statistically different** between the samples (p-value < 0.05)

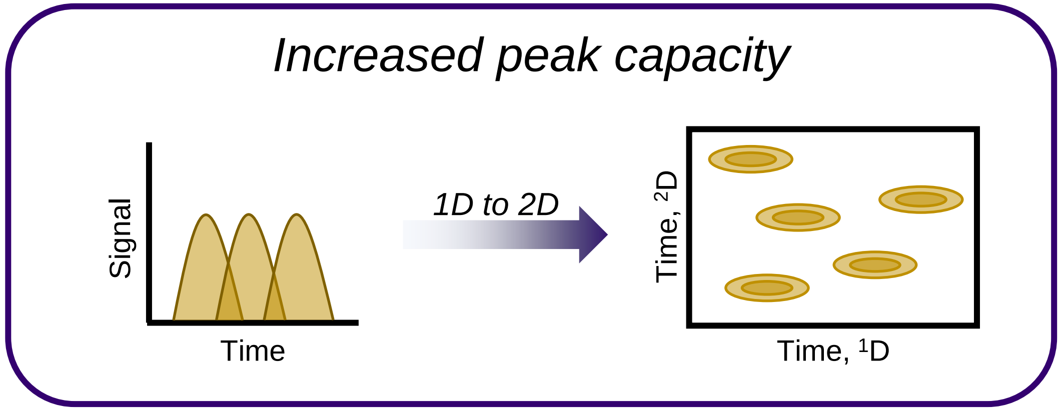
Are other volatiles in the headspace of roasted coffee also affected by PTD?

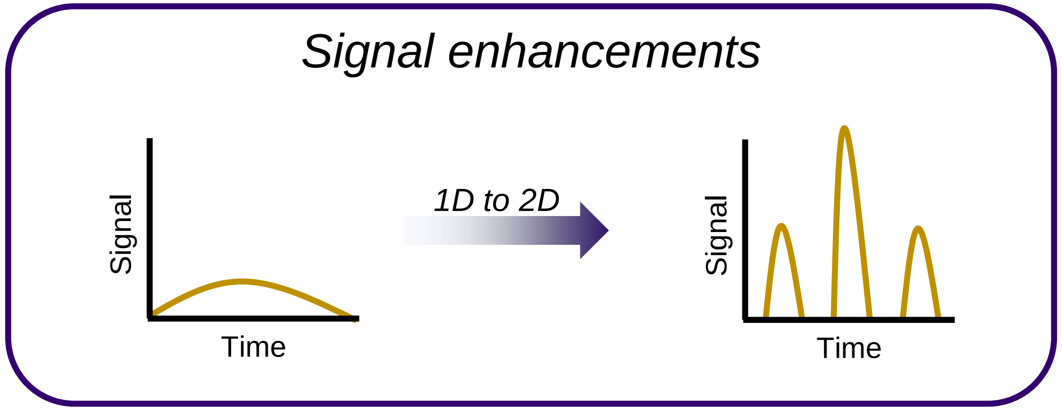
Cain, C. N., et al. *J. Agric. Food Chem.*, **2021**, *69*, 2253-2261.

Aim and Methodology

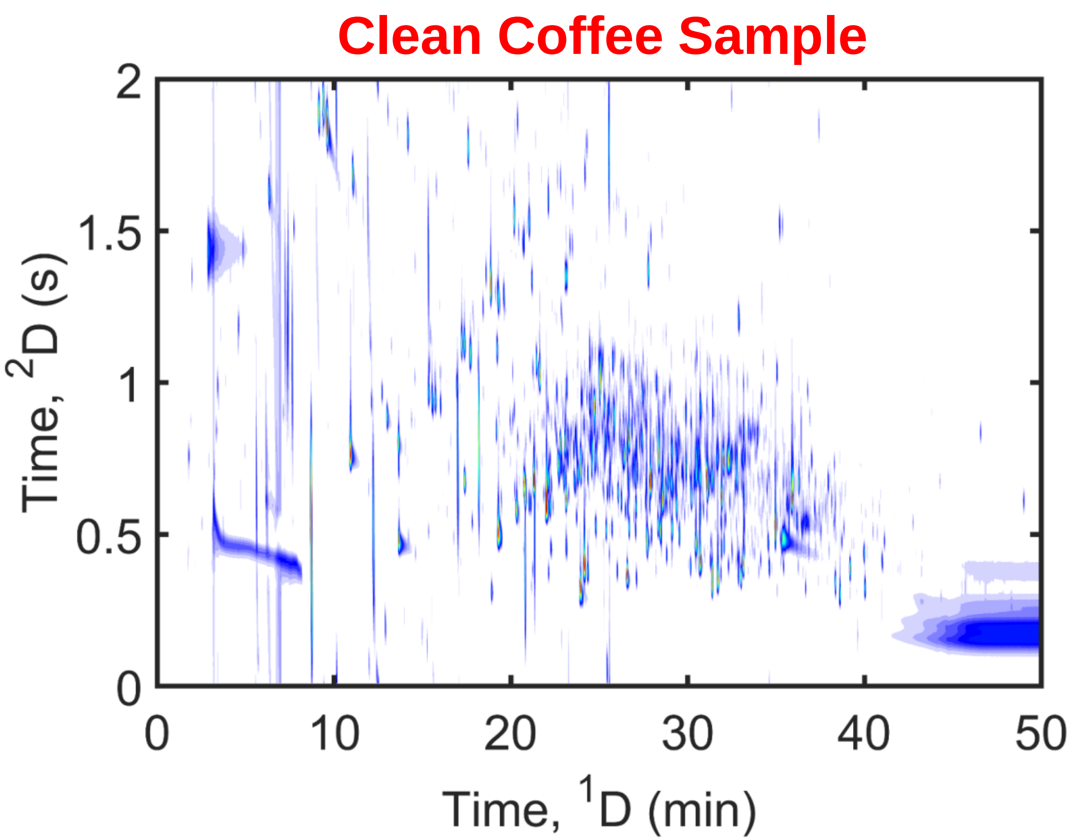
- To **fully characterize the volatile profile of PTD** using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS) and chemometrics

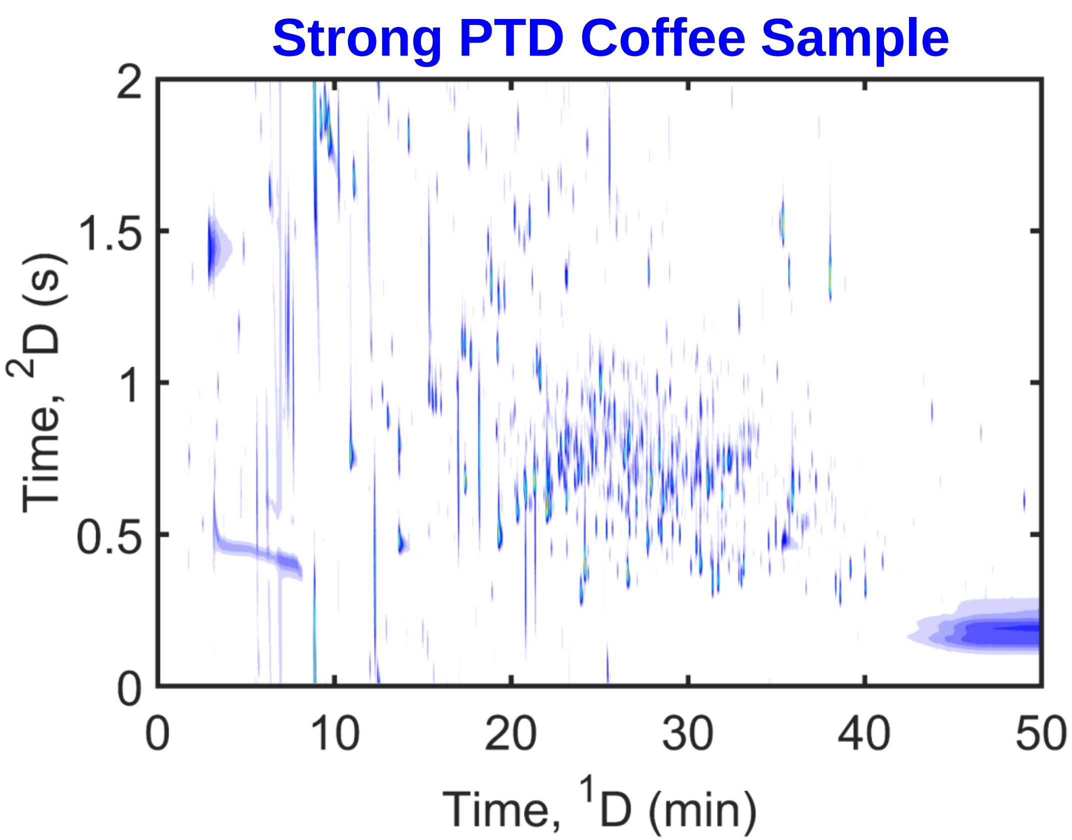






Comparative Analysis of GC×GC-TOFMS Data





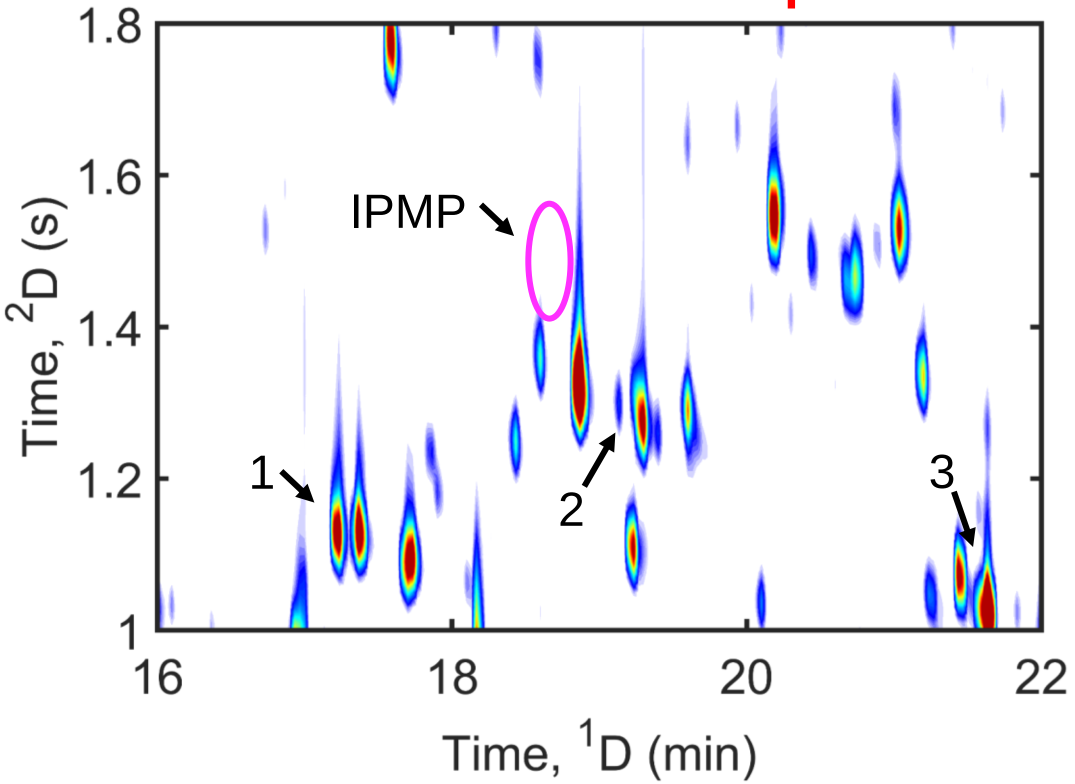
~ 500 peaks detected in the TIC chromatogram

Strong PTD sample appears to have less overall signal

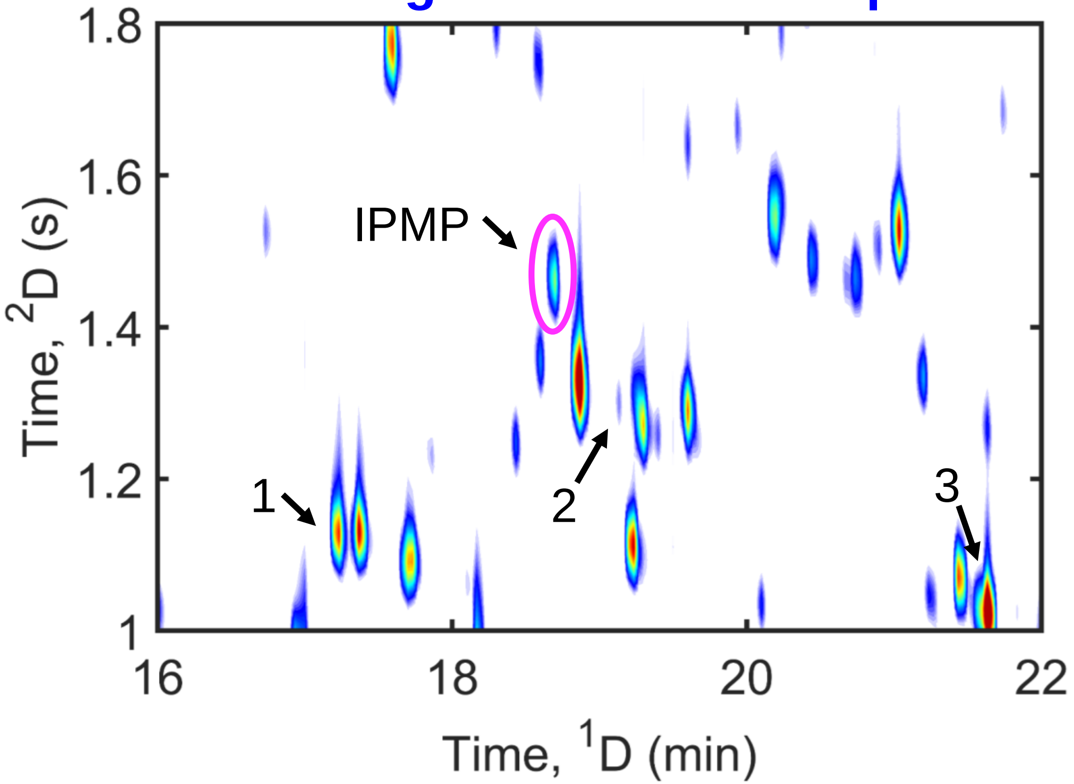
Cain, C. N., et al. *Microchem. J.*, **2024**, *196*, 109578.

Comparative Analysis of GC×GC-TOFMS Data

Clean Coffee Sample



Strong PTD Coffee Sample



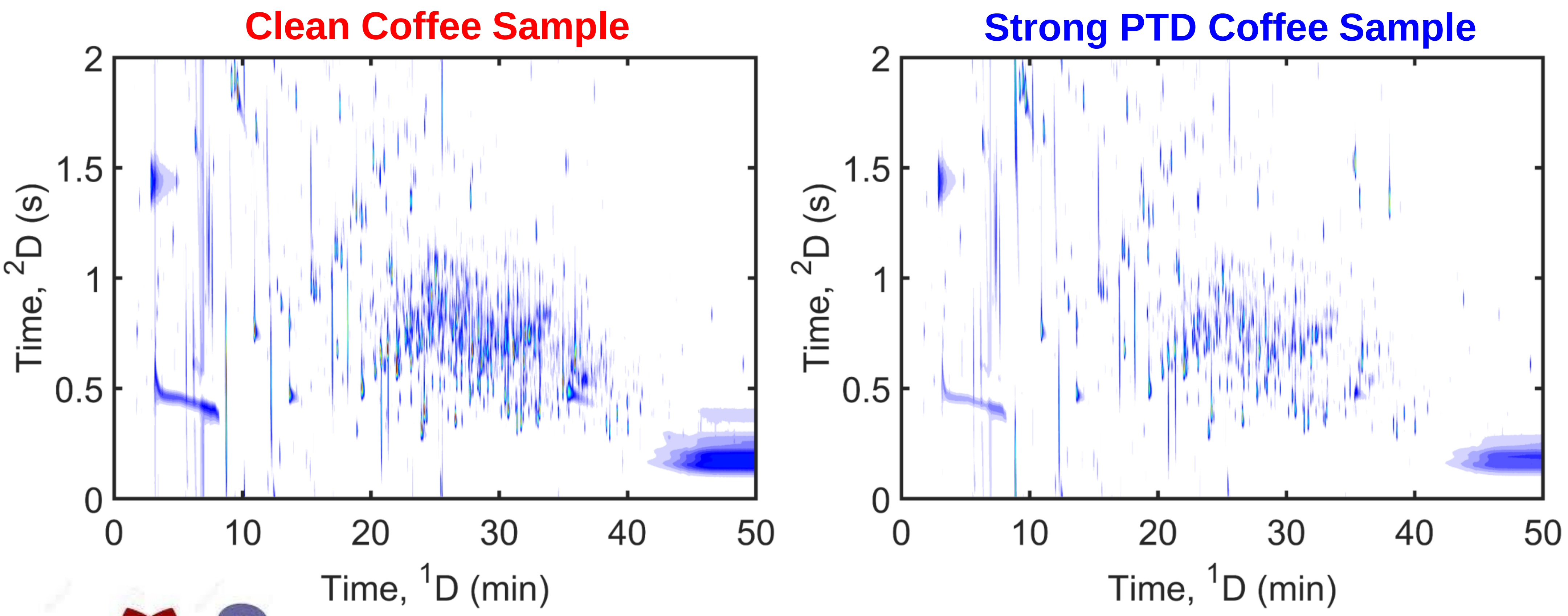
Other identified analytes:

1. 2-ethyl-6-methylpyrazine (nutty, roasted)
2. 2,3-diethylpyrazine (nutty, roasted)
3. Linalool (floral, fruity)

*There are a lot of fine differences between the coffee samples – **too many** to manually identify and quantify!*

Cain, C. N., et al. *Microchem. J.*, **2024**, *196*, 109578.

Comparative Analysis of GC×GC-TOFMS Data



"How do we confidently discover the chemically relevant differences between two (or more) sample classes?"

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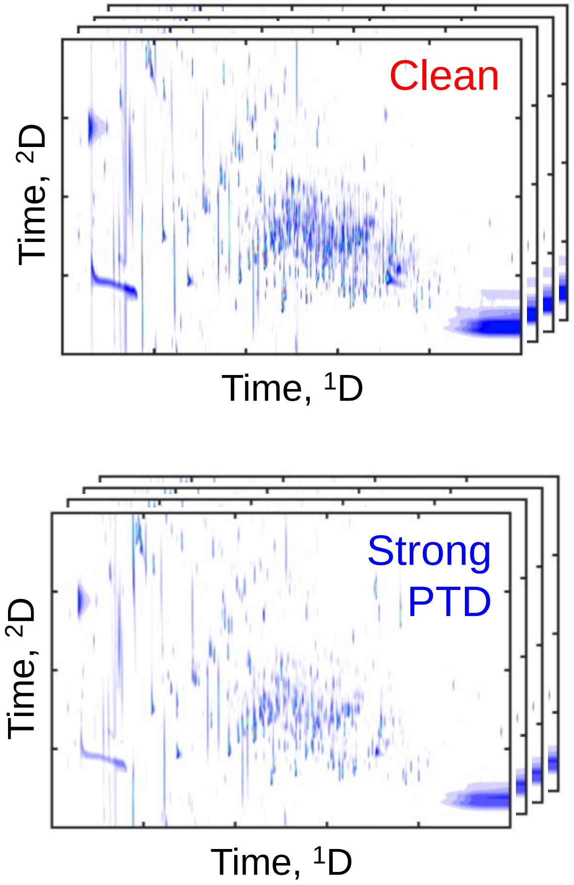
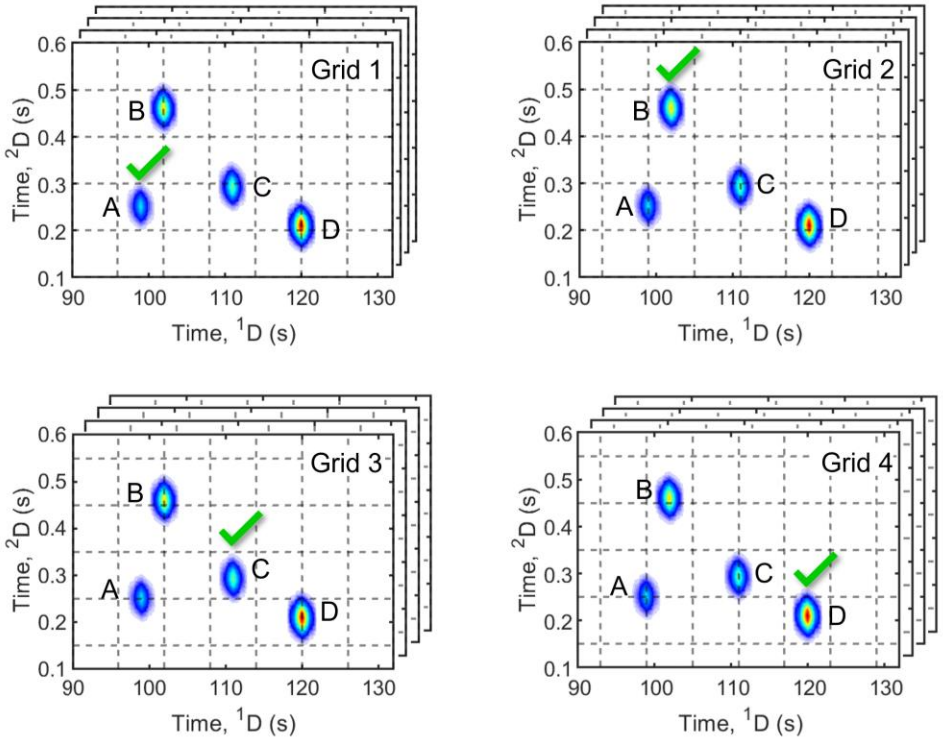
Tile-Based Fisher Ratio (F-ratio) Analysis

A supervised, non-targeted method that discovers analytes that are statistically different in concentration between sample classes

$$F - ratio = \frac{\boldsymbol{Between\ Class\ Variance}}{\sum(\boldsymbol{Within\ Class\ Variance})}$$





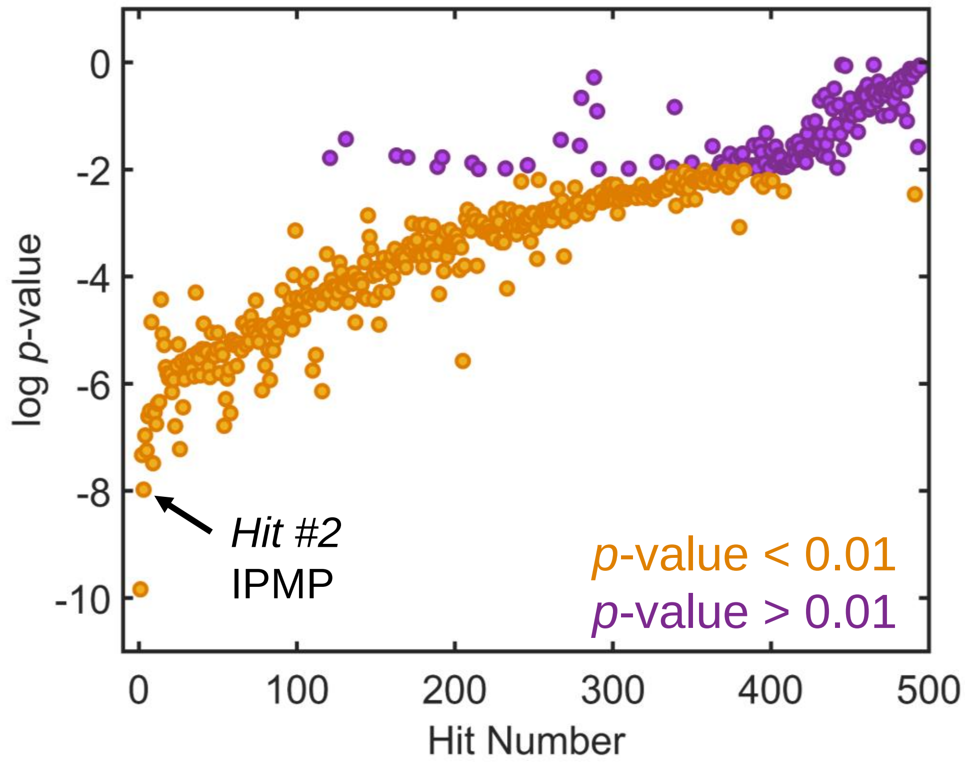
Hit List

Hit #	**F-ratio**	**(^1t_R, ^2t_R)**
1	High	(x,y)
N	Low	(x_N,y_N)

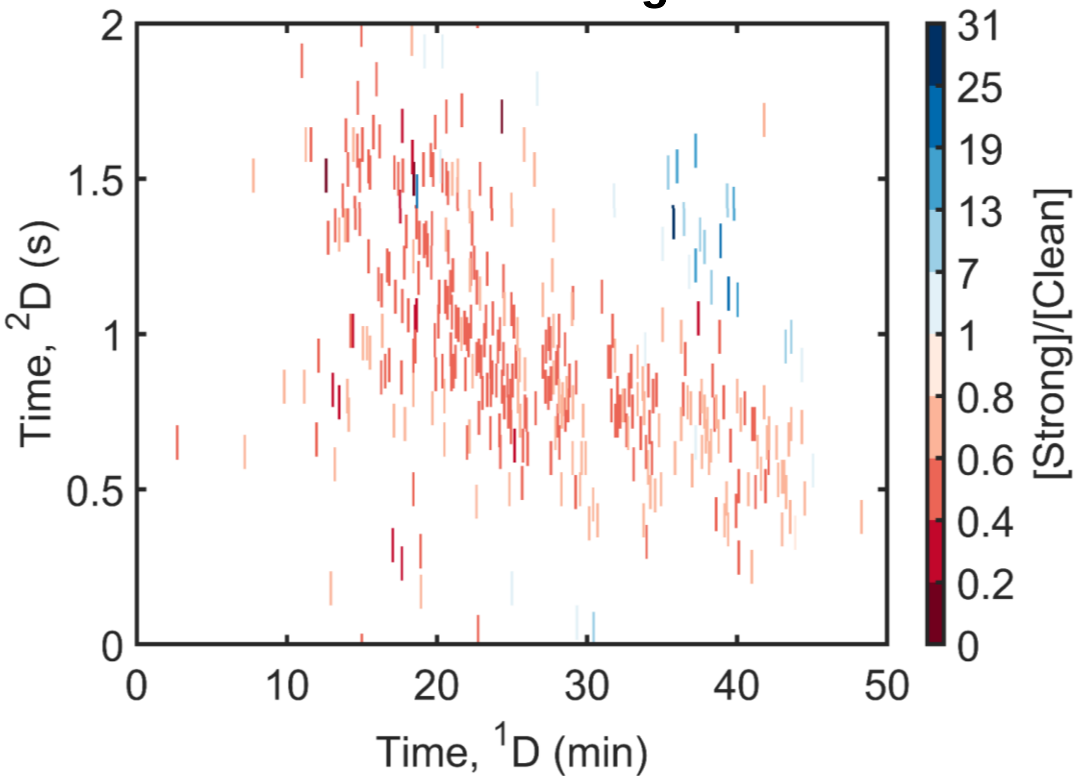
Marney, L. C.; et. al. *Talanta*, **2013**, *115*, 887-895.
Parsons, B. A.; et. al. *Anal. Chem.*, **2015**, 87, 3812-3819.

Results from Tile-Based F-ratio Analysis

Visualization of the Final Hit List



Visualization of the Signal Ratios



359 class-distinguishing compounds ($p < 0.01$) were discovered

327 analytes had a higher abundance in the clean samples

32 analytes had a higher abundance in the strong PTD samples

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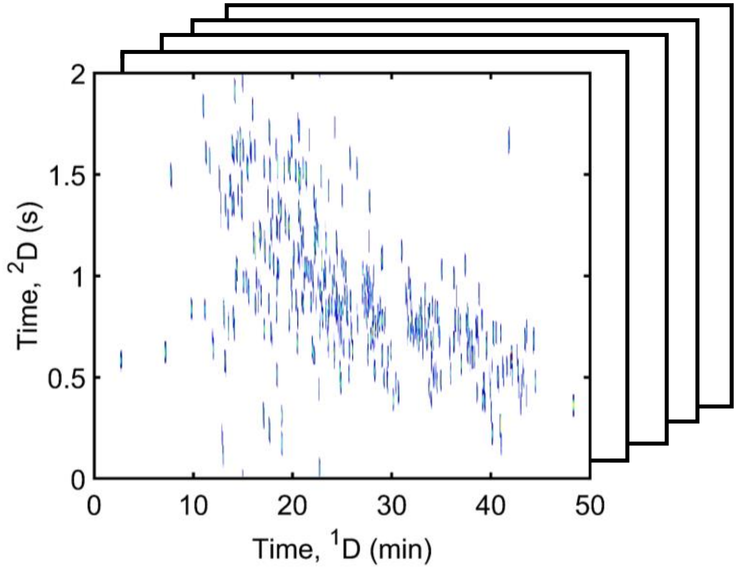
Correlating Discovered Analytes to [IPMP]

- Let's use **Partial Least Squares (PLS) Regression** to model [IPMP] with the F-ratio hits

X-Block
Chromatographic signal



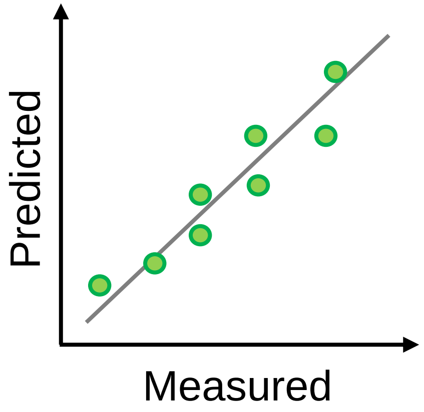
Signal from analytes discovered by F-ratio measured in every sample

Y-Block
Property measurements

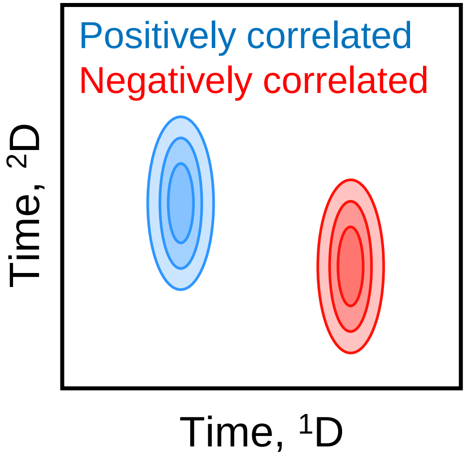
0.6
15.9
30.7
33.7
52.7
22.5
1.8

[IPMP]

Regression Plot



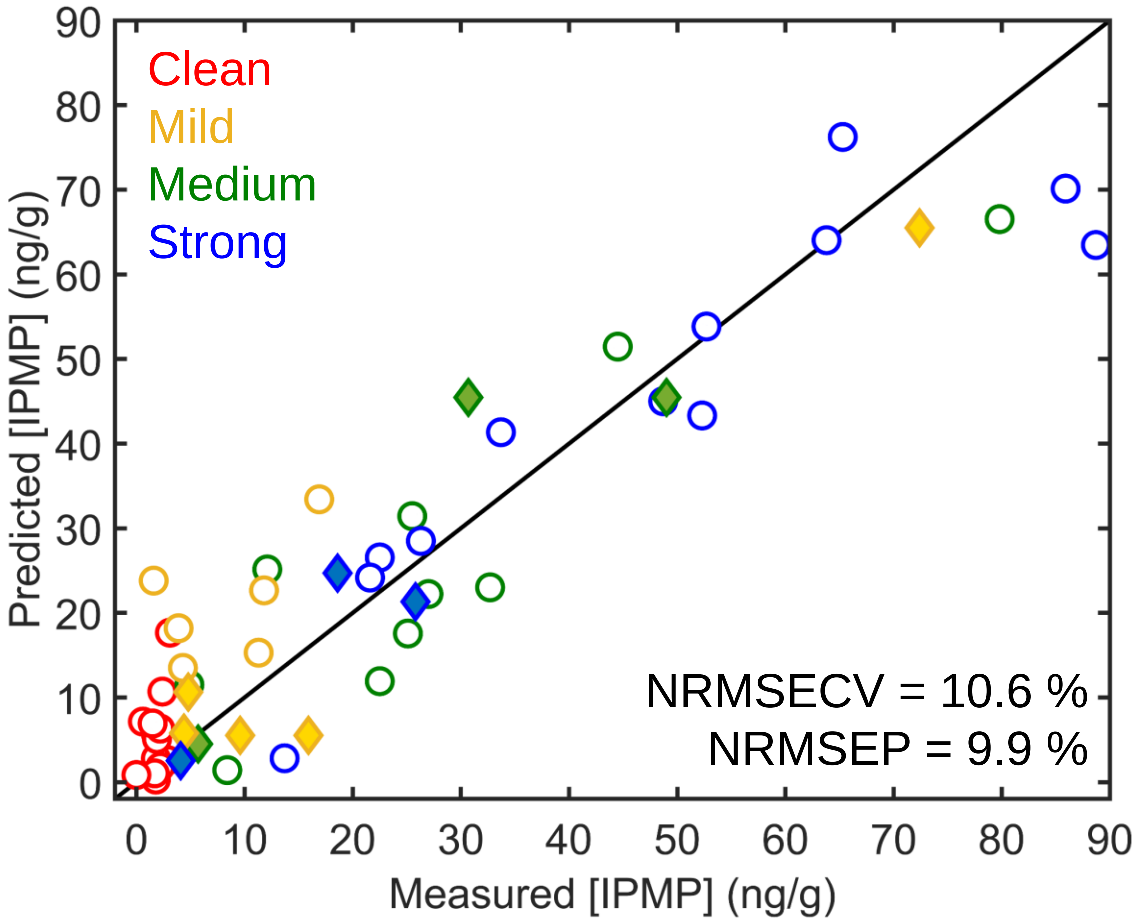
Linear Regression Vector



Partial Least Squares (PLS) Regression

- **Regression plot** highlights the linear relationship between the measured property values and those predicted by the PLS model

- Low measurements for the normalized root-mean-square errors indicates **accurate prediction of [IPMP]**



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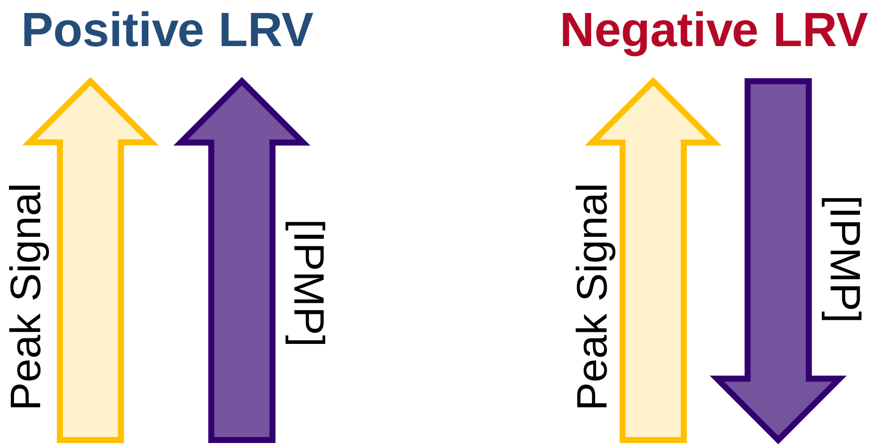
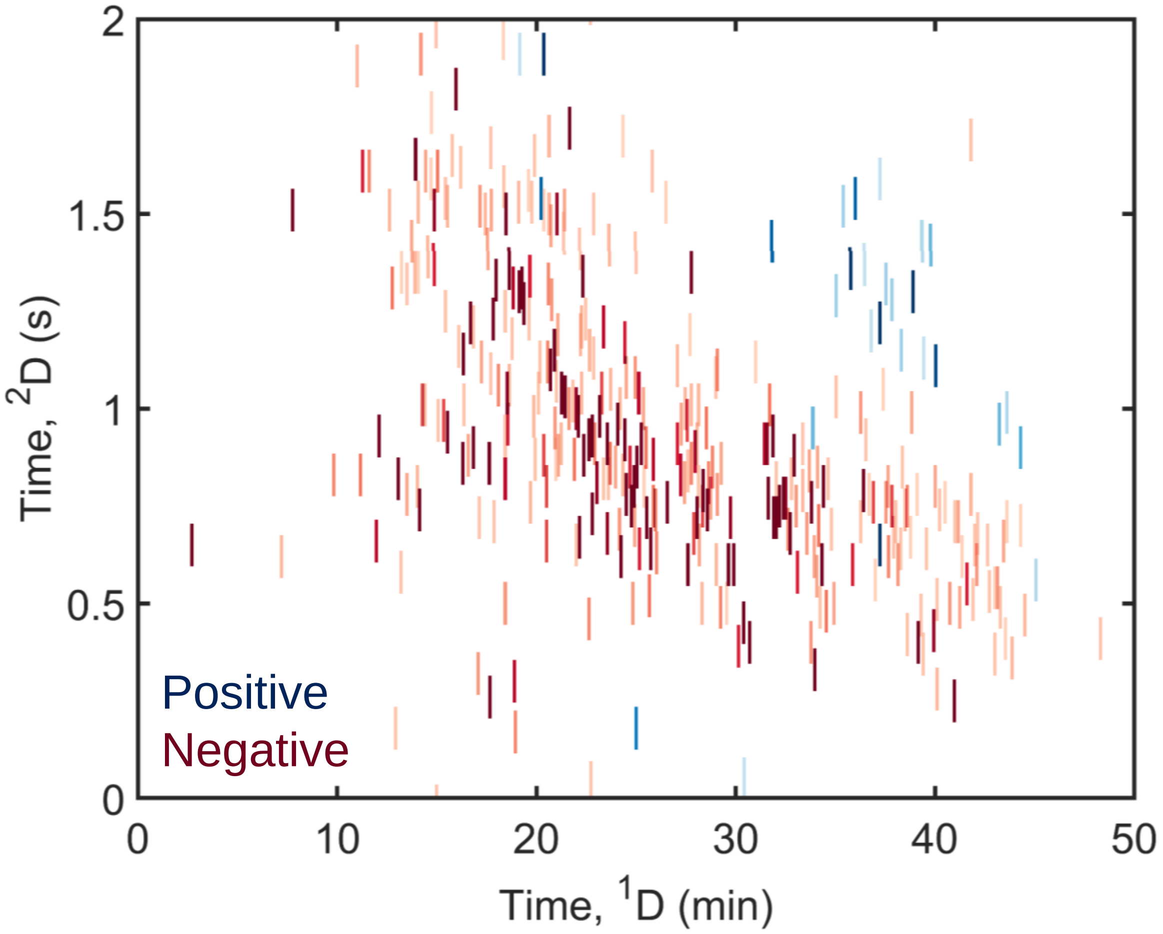
Partial Least Squares (PLS) Regression

- **Linear regression vector (LRV)** describes how features in the chromatograms are related to [IPMP]





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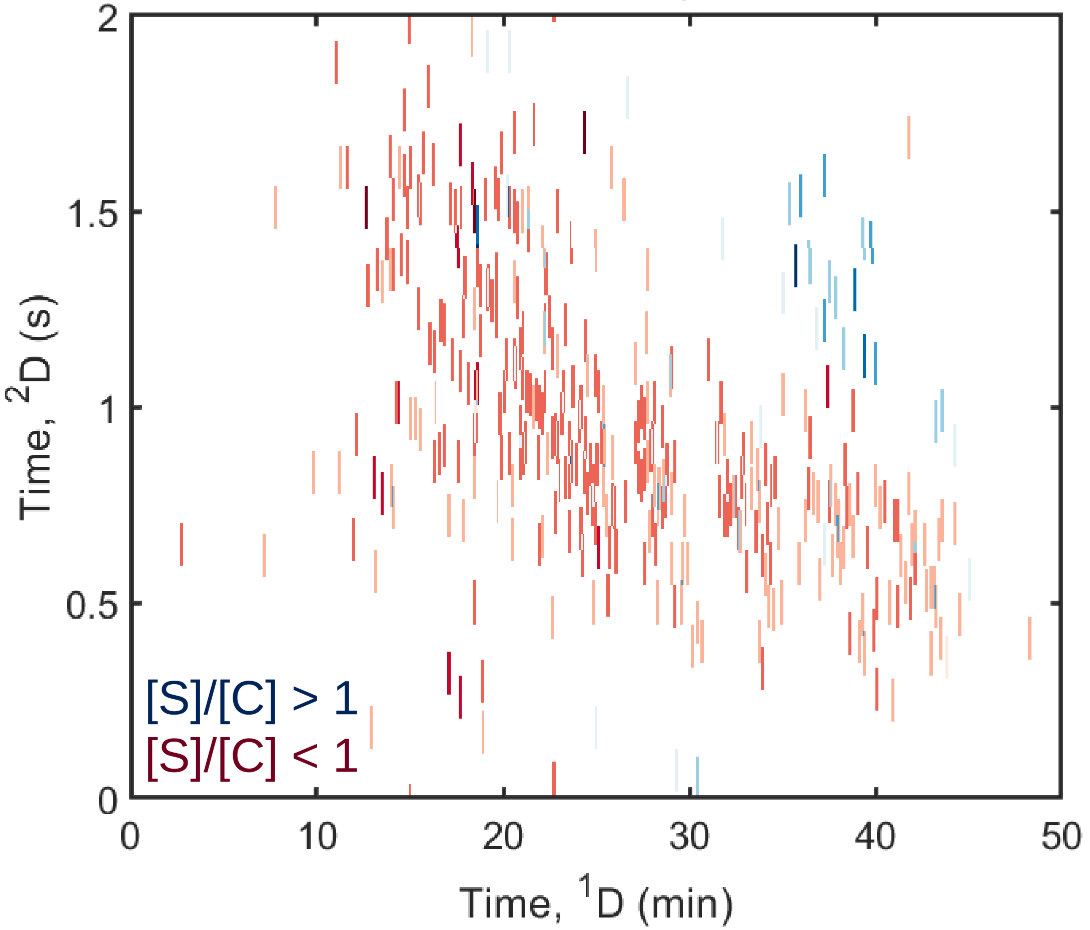
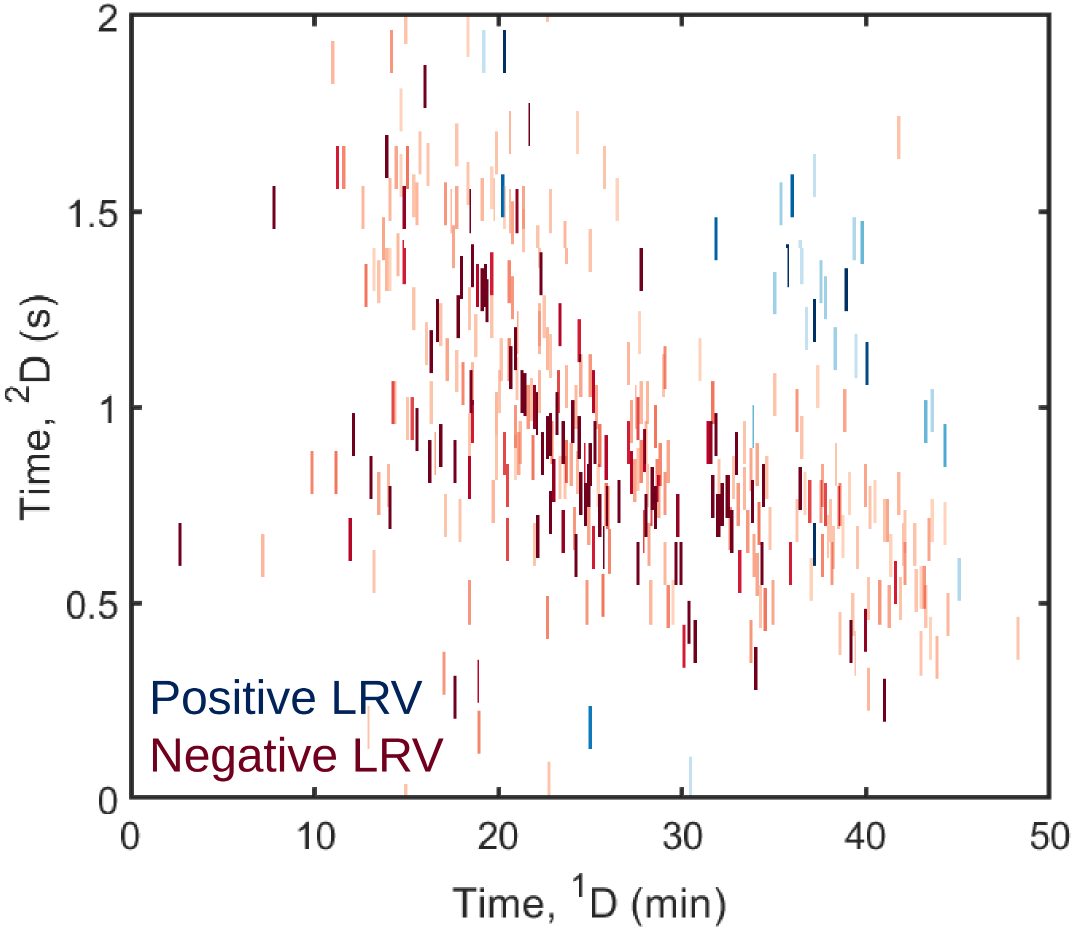
Partial Least Squares (PLS) Regression

Projection of the [Strong]/[Clean]



LRV from PLS Model



Every analyte with a [Strong]/[Clean] > 1 is positively correlated with [IPMP]
Every analyte with a [Strong]/[Clean] < 1 negatively correlated with [IPMP]

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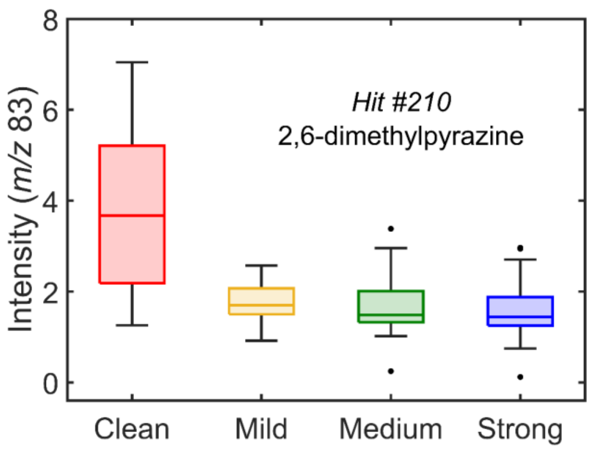
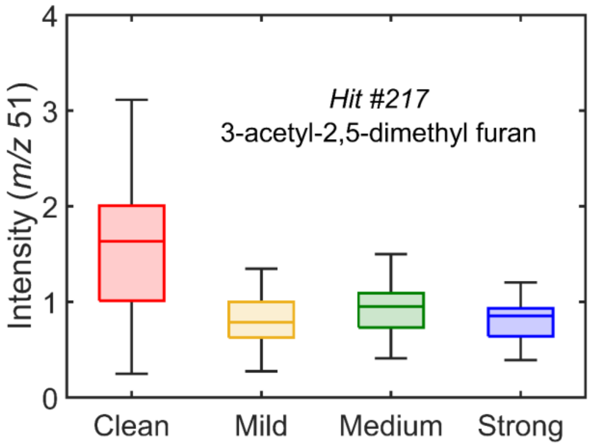
Volatiles Downregulated by PTD

Compound	[Strong]/[Clean]	Sensory Description
Pyrazine, 2,6-dimethyl-	0.56	Cocoa, nutty, roasted
2-Naphthalenol	0.60	
3-Acetylpyrrole	0.60	Sweet, fruity
Furyl ethyl ketone	0.59	Fruity
2,7-Naphthalenediol	0.55	
Pyrazine, 2-methyl-5-(1-propenyl)-, (*Z*)-	0.50	
Pyrazine, 2-methyl-6-propyl-	0.31	Burnt, hazelnut, nutty
3(2H)-Benzofuranone, 7-methyl-	0.47	
2,2'-Bifuran	0.45	
3-Acetyl-2,5-dimethyl furan	0.52	Sweet, nutty, cocoa
3-Methyl-2-thiophenecarboxaldehyde	0.52	Sweet, saffron, honey
4-Hydroxybenzo[b]thiophene	0.54	
2-Acetyl-3-methylpyrazine	0.10	Nutty, roasted, hazelnut
7-Benzofuranamine, 2-methyl-	0.55	
2-Thiophenecarboxylic acid, 4-nitrophenyl ester	0.54	
Thiophene, 2-phenyl-	0.29	Hazelnut, bready
Benzofuran, 2-methyl-	0.42	Burnt





PTD directly impacts the aroma associated with roasted coffee beans

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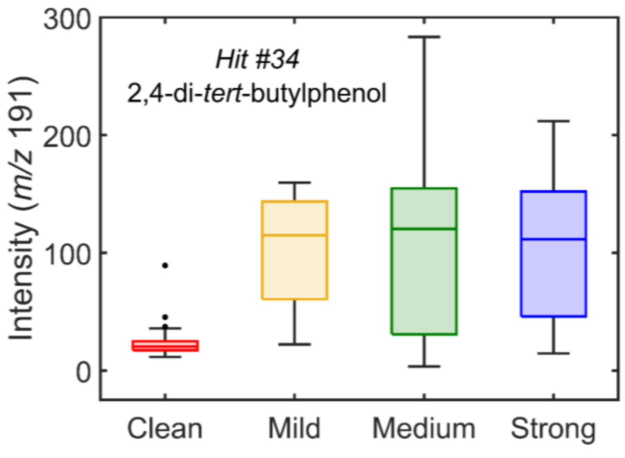
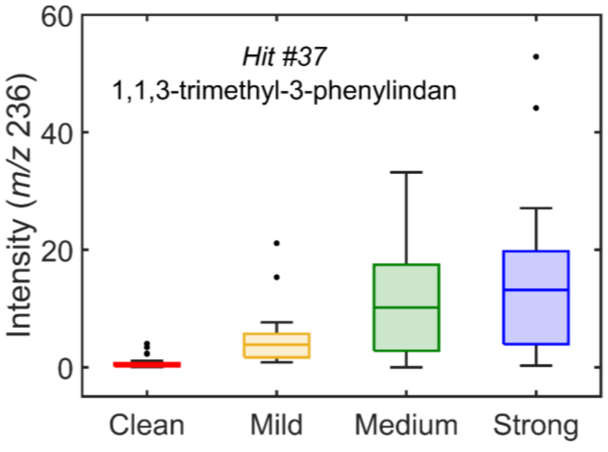
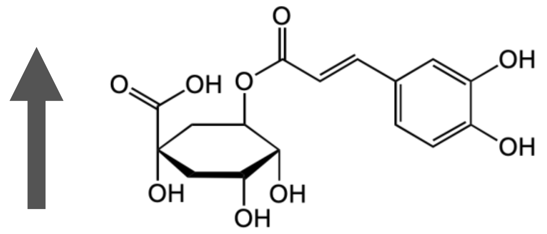
Volatiles Upregulated by PTD

Compound	[Strong]/[Clean]
2,4-Di-*tert*-butylphenol	4.50
2,4-Diphenyl-4-methyl-2(*E*)-pentene	19.8
Decanal	1.63
1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	29.8
Benzene, (1,3-dimethyl-3-butenyl)-	Strong only
Propane, 2-cyclohexyl-2-phenyl-	Strong only
2-Undecanone, 6,10-dimethyl-	1.36
Benzene, 1,1'-(1,1,2,2-tetramethyl-1,2-ethanediyl)bis-	20.7
Acenaphthene	2.04
1,1'-Biphenyl, 3,4-diethyl-	1.43
1,1,3-Trimethyl-3-phenylindan	19.6
1,5,6,7-Tetramethyl-3-phenylbicyclo[3.2.0]hepta-2,6-diene	15.1
1,3-Pentadiene, 1,1-diphenyl-, (*Z*)-	10.9
1,4-Benzenediol, 2,6-bis(1,1-dimethylethyl)-	1.38



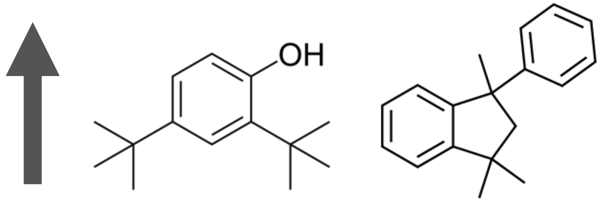


Microorganism growth



Increased chlorogenic acid

Roasting



Increased phenols and phenylindanes

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Conclusions

- IPMP concentrations were significantly different based on the severity of odor attributed to PTD

- Tile-based F-ratio analysis discovered 359 analytes affected by PTD
  - 327 analytes were elevated in the clean samples → many were linked to desirable aromas in coffee
  - 32 analytes were elevated in the PTD impacted samples

- Use of F-ratio results resulted in accurate prediction of [IPMP] concentration with PLS regression

- Changes in the volatile profile of coffee beans can heighten the odor severity and reveal potential pathways for PTD

Cain, C. N., et al. *J. Agric. Food Chem.*, **2021**, *69*, 2253-2261.
Cain, C. N., et al. *Microchem. J.*, **2024**, *196*, 109578.

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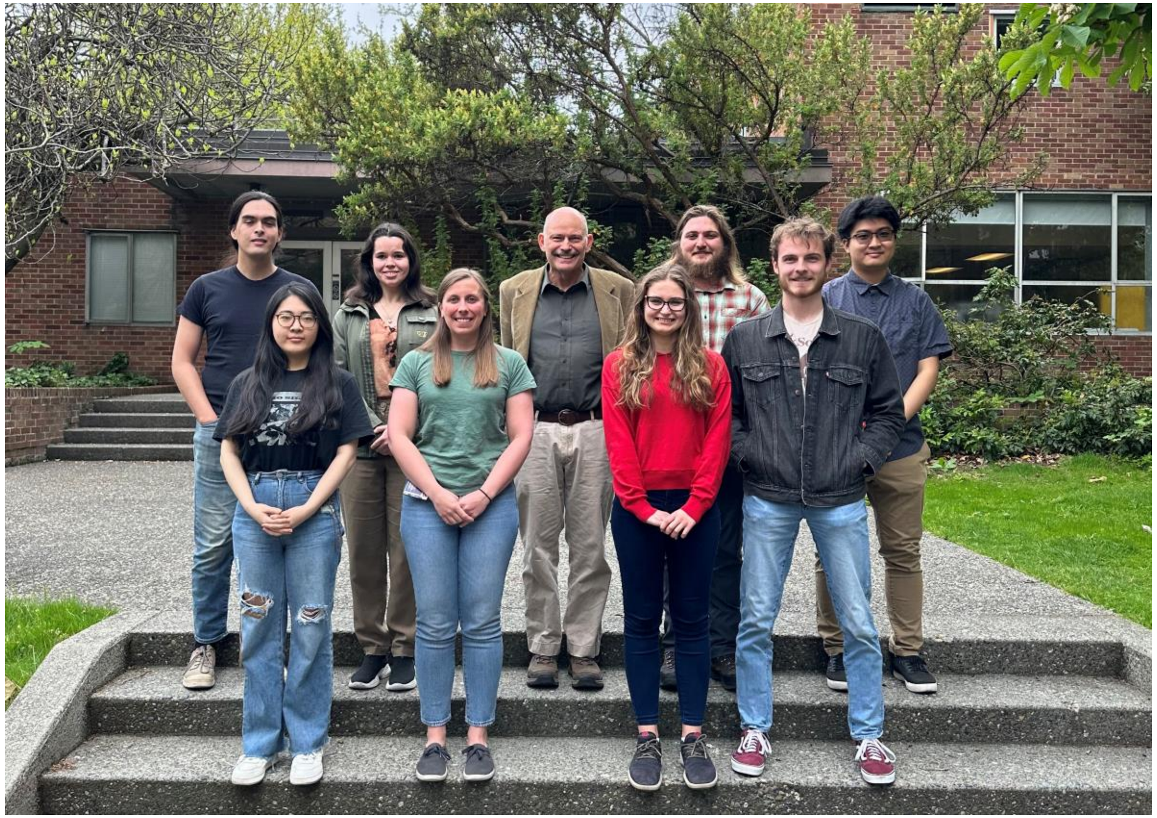

Univ. of Liège Collaborators

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