Aroma Profiling of Coffee with GC, GC×GC, and TOF MS

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LECO Corporation

Coffee

- Coffee Industry is an important part of the economy[1]
  - Most consumed beverage in the US
  - In 2015, US Consumers spent
    - $74.2 billion on coffee and
    - $6 billion on related goods (brewers, sweeteners, etc.)
  - In 2015, total economic impact of coffee related activity in US
    - $225.2 billion or 1.6% of GDP
- Understanding product is important for,
  - Quality control
  - Process optimization
  - Consumer's informed purchasing

1. "The Economic Impact of the Coffee Industry" National Coffee Association and Technomic Inc. (USA), ncausa.org

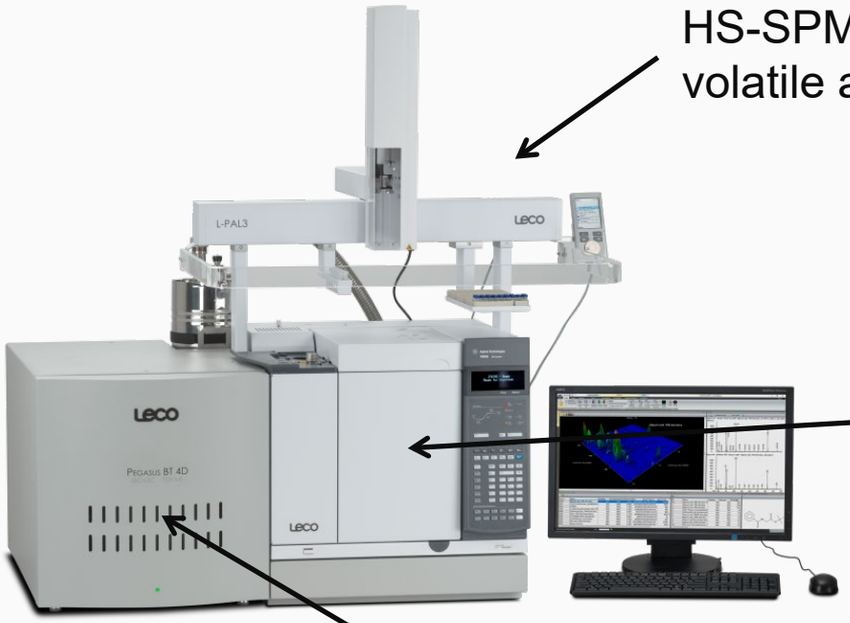
Sample Complexity and Variability

- Product variation can relate to
  - Bean variety
  - Geographical origin
  - Storage and processing conditions
  - Roasting level
  - Brewing style
  - etc.
- Aroma profile for coffee is quite complex and comprised of a large number of individual analytes
- Non-targeted analytical tools provide good insight

Sample Comparisons

	Type of Bean	Description Notes
MEDIUM	Peru	toffee and chocolate
	Costa Rica	sweet, lemony, toffee, sugar, raisin
	Kona	simple, rich, complex aroma, acidic
	Colombian	rich, big, chocolatey, fragrant, acidic
DARK	French Roast (Costa Rica)	tangy and smoky
	Dark Kona	dark roasted – heavy rich tones

Non-Target Analytical Tool: GC×GC-TOFMS

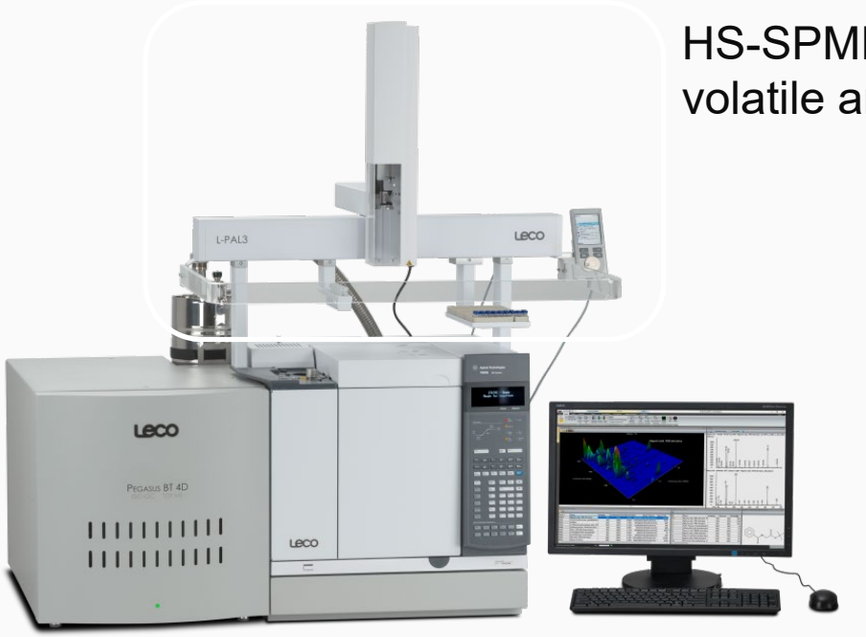


HS-SPME: sample collection for volatile and semi-volatile analytes

GC(×GC): separation of individual analytes from each other and complex matrix with one (or two) phase selectivity

TOFMS: Full mass range data for identification and quantification

Non-Target Analytical Tool: GC×GC-TOFMS



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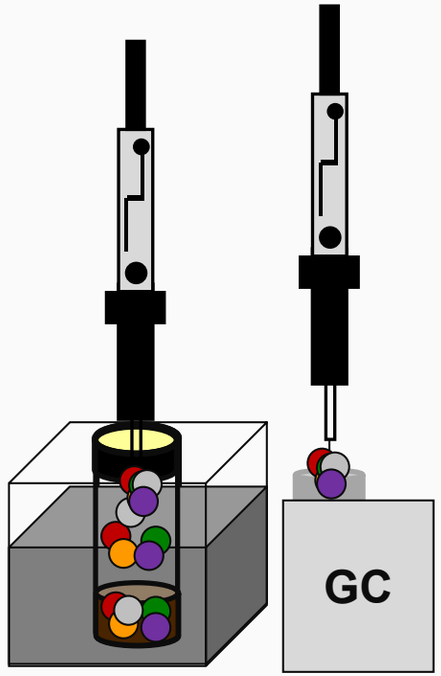

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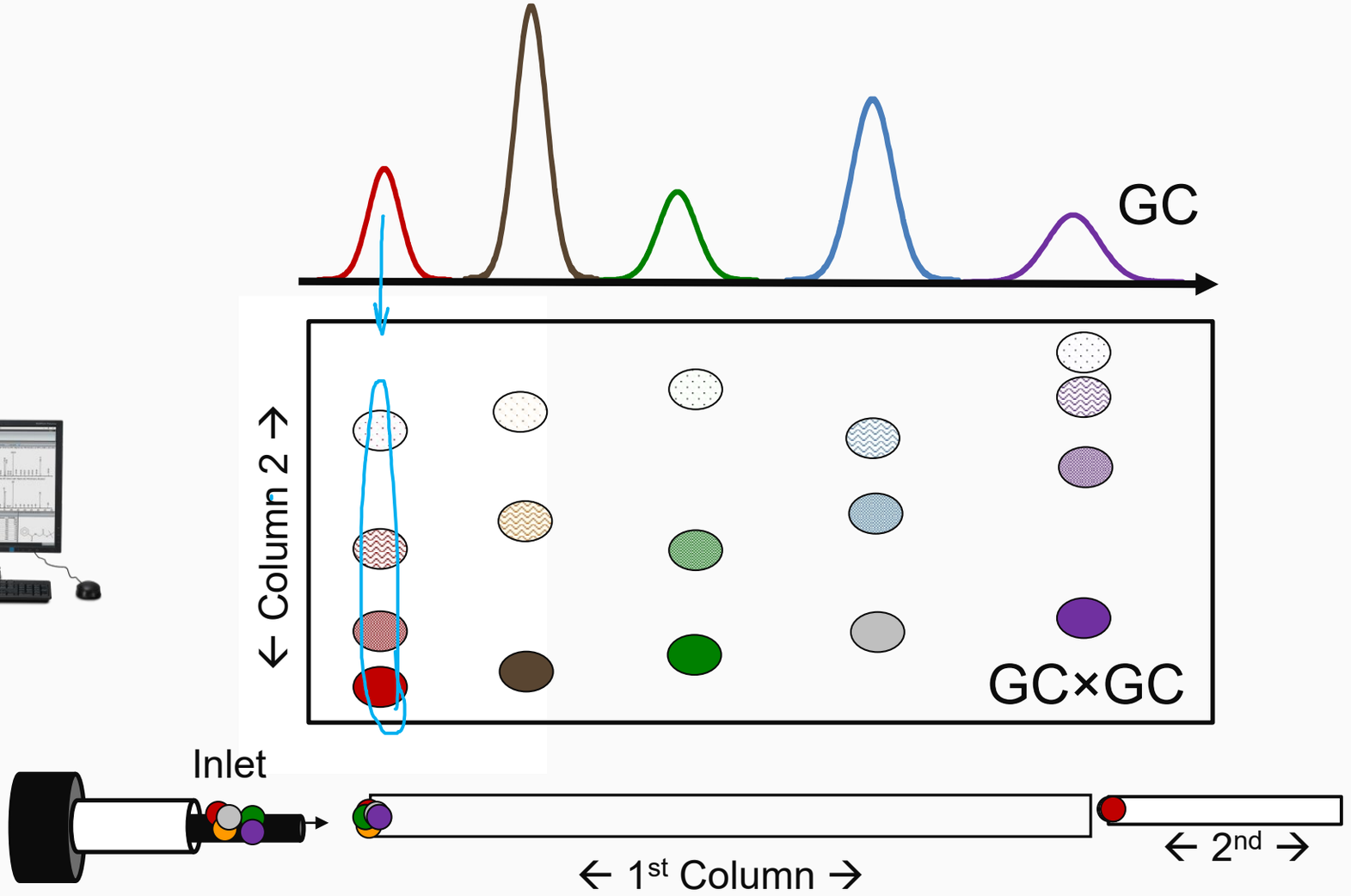
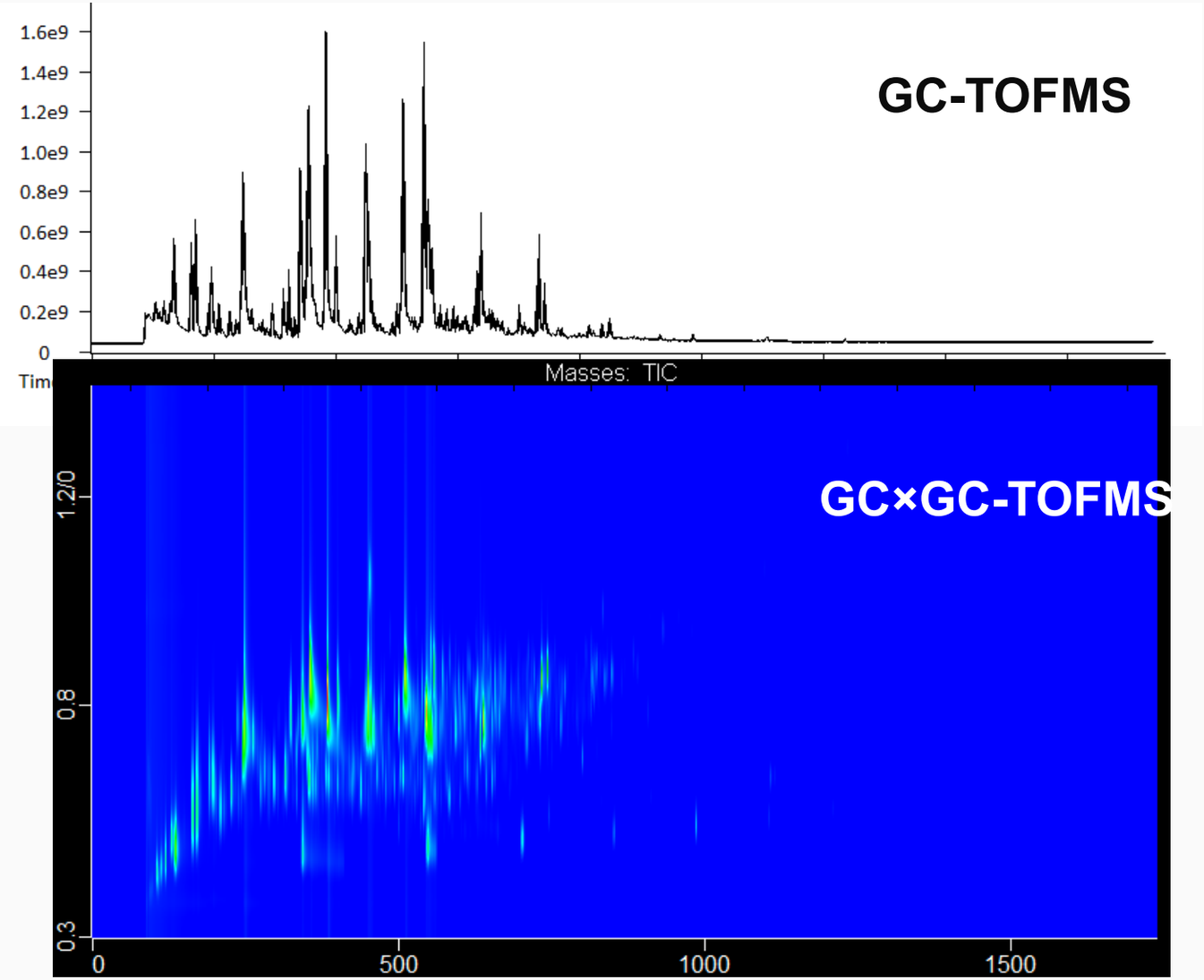


Non-Target Analytical Tool: GC×GC-TOFMS

SPME Conditions	**LECO L-PAL 3**
Sample Details	4 mL of French Press Coffee in 20 mL vial
Incubation/Extraction	5 min/5 min at 60°C with PDMS/DVB/CAR fiber (Supelco)
GC(×GC)	**Agilent 7890 with LECO secondary oven and thermal modulator**
Injection	3 minute desorb in 250°C inlet
Column	Rxi-5Sil MS, 30m x 0.25 mm i.d. x 0.25 µm coating (Restek) Rxi-17Sil MS, 0.3m x 0.25 mm i.d. x 0.25 µm coating (Restek)
Carrier Gas	He @ 1.4 ml/min
Oven Program	40°C (hold 3 min), ramp 10°C/min to 250°C hold 5 min Secondary oven, 10°C
Modulation	1.2 s
Transfer line	250°C with uncoated guard column
MS	**LECO Pegasus® BT**
Ion Source Temp	250°C
Mass Range	33-510
Acquisition Rate	10 spectra/s (GC) and 100 spectra/s (GC×GC)

Coffee Samples



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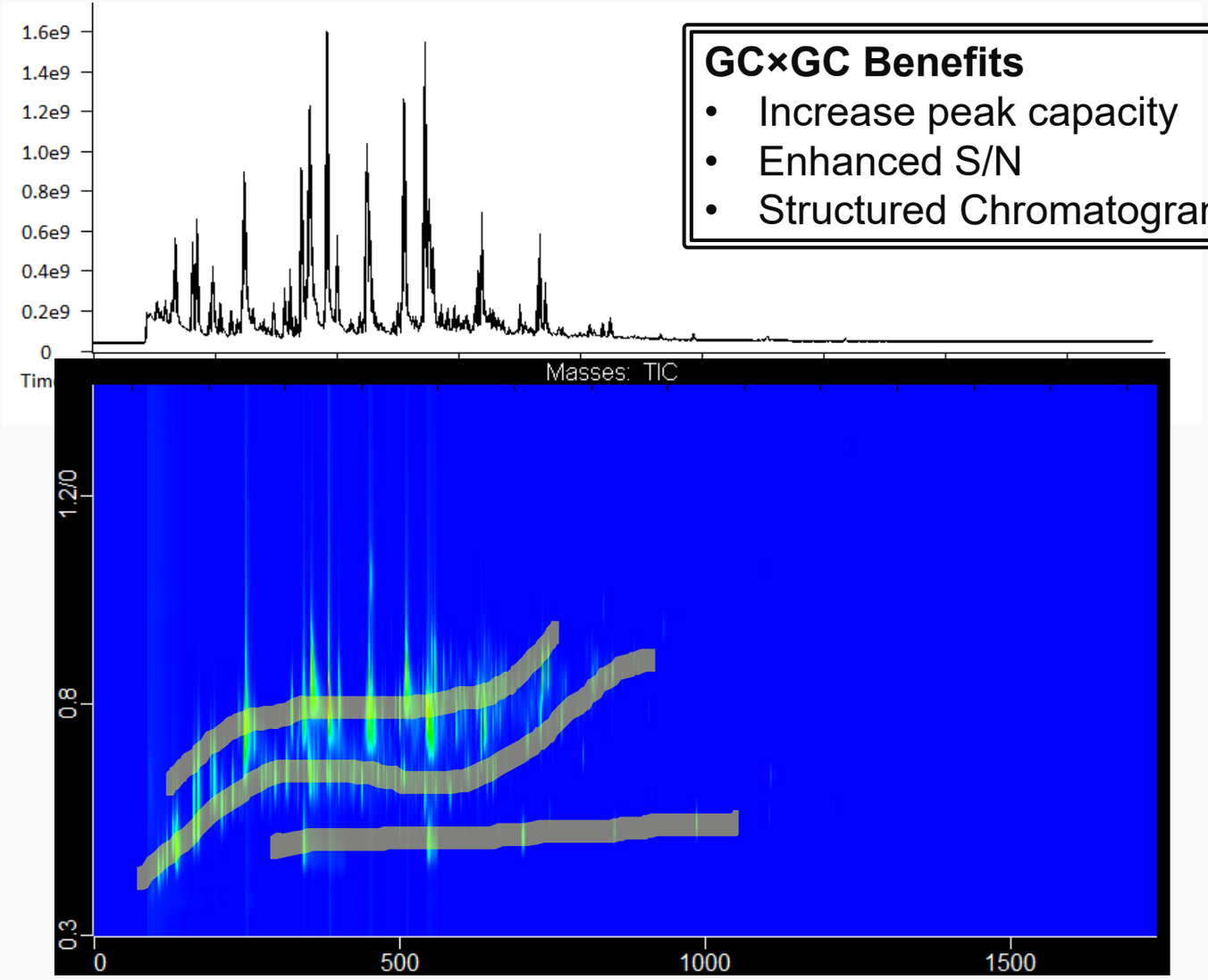
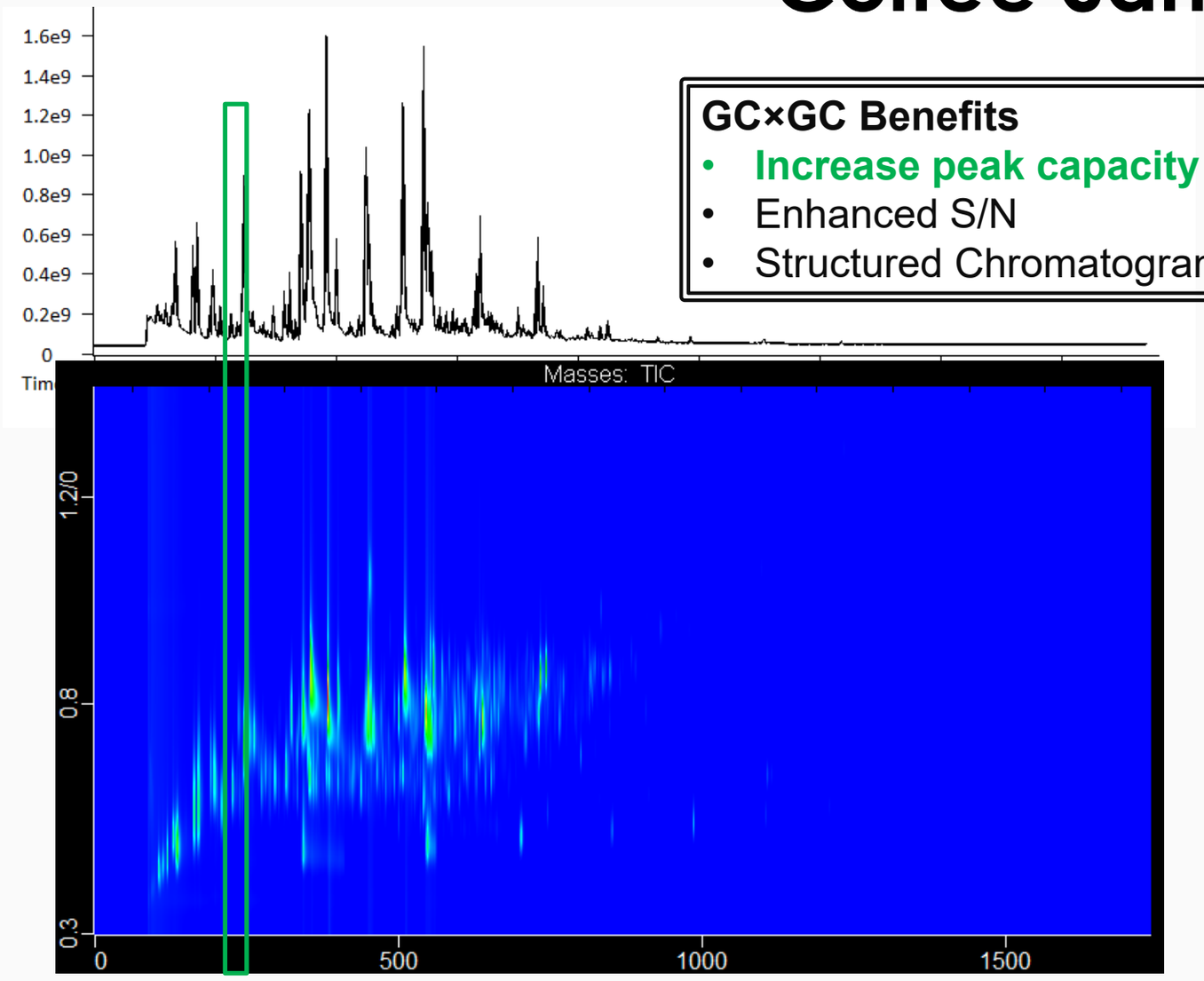


GC×GC Benefits

- Increase peak capacity
- Enhanced S/N
- Structured Chromatograms

Coffee Samples



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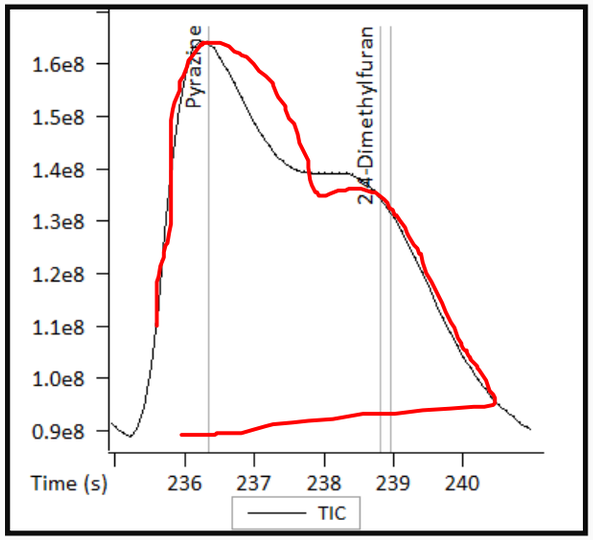
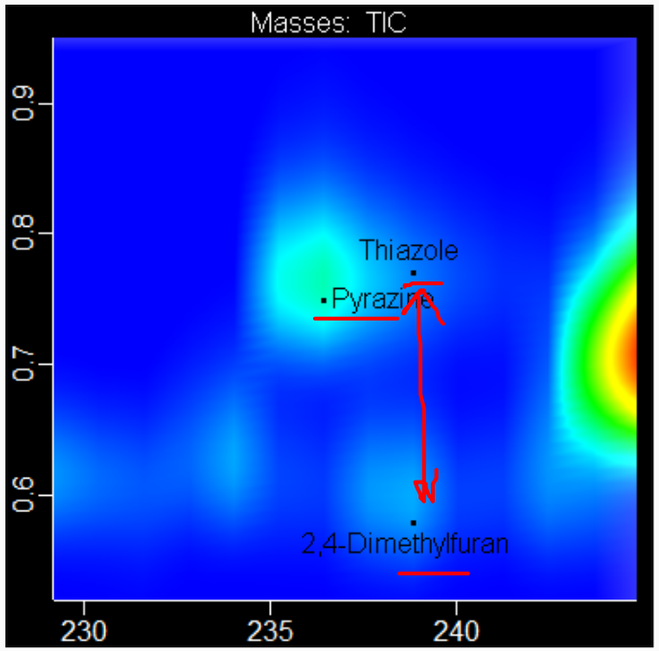
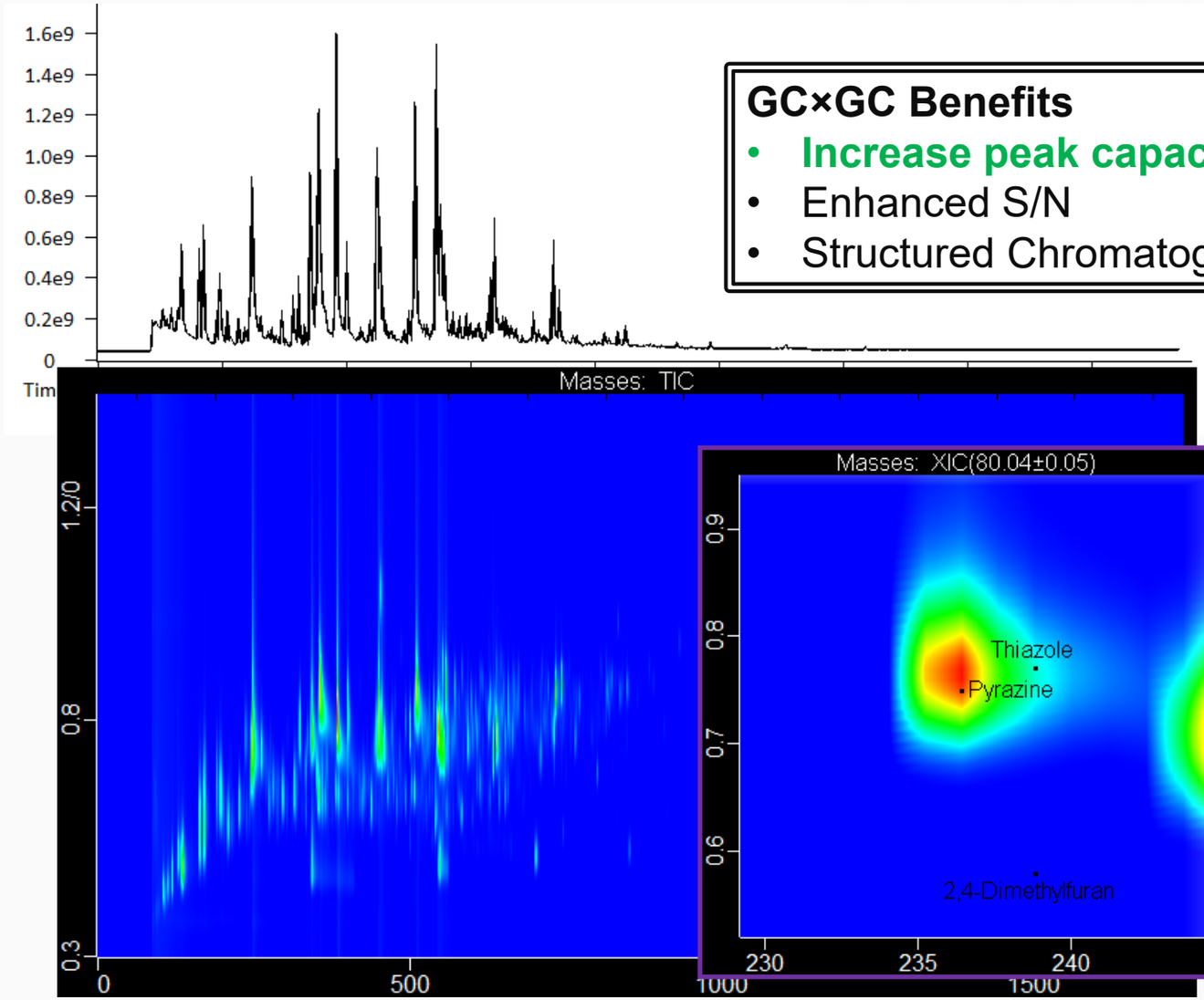




Chromatographic separation of 1D coelution requiring deconvolution

Coffee Samples



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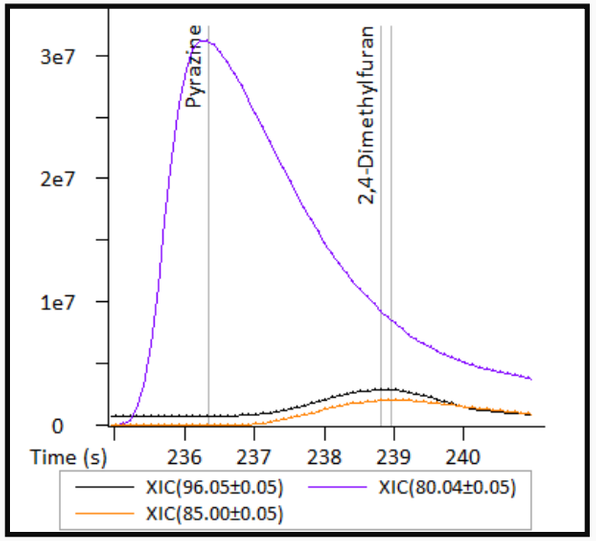
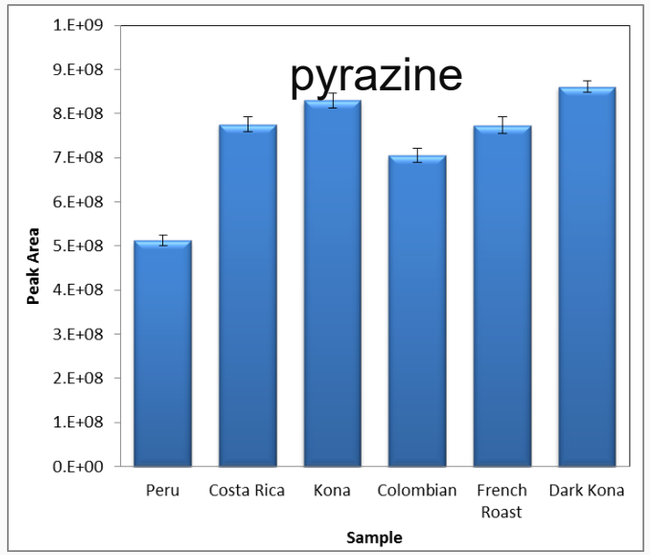
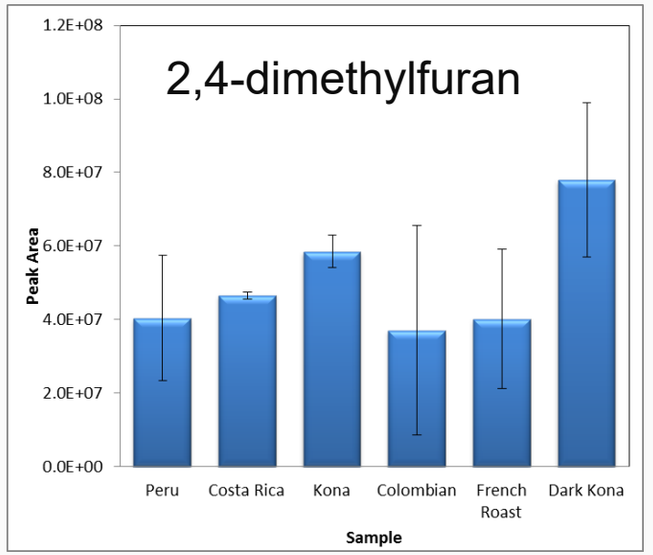


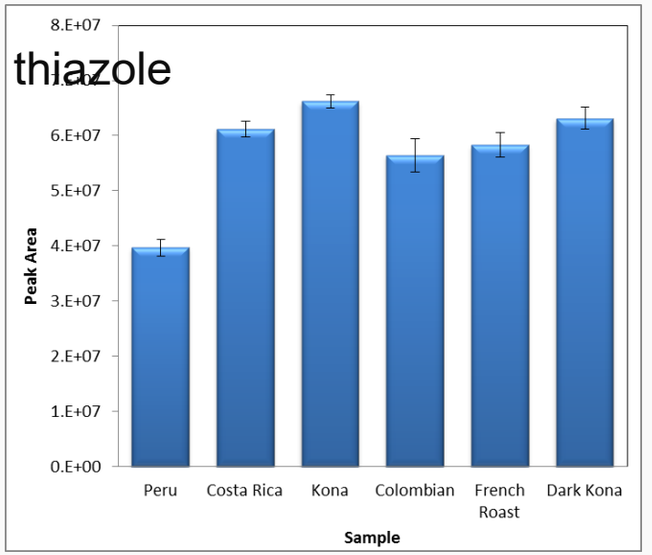
Chromatographic separation of 1D coelution requiring deconvolution

Coffee Samples

Name	Formula	CAS	GC Similarity	GC×GC Similarity	Odor Notes
pyrazine	$C_4H_4N_2$	290-37-9	957	969	roasted, hazelnut, barley, pungent, sweet, corn like
2,4-dimethylfuran	C_6H_8O	3710-43-8	734	850	
thiazole	C_3H_3NS	288-47-1	845	925	nutty, meaty, pyridine







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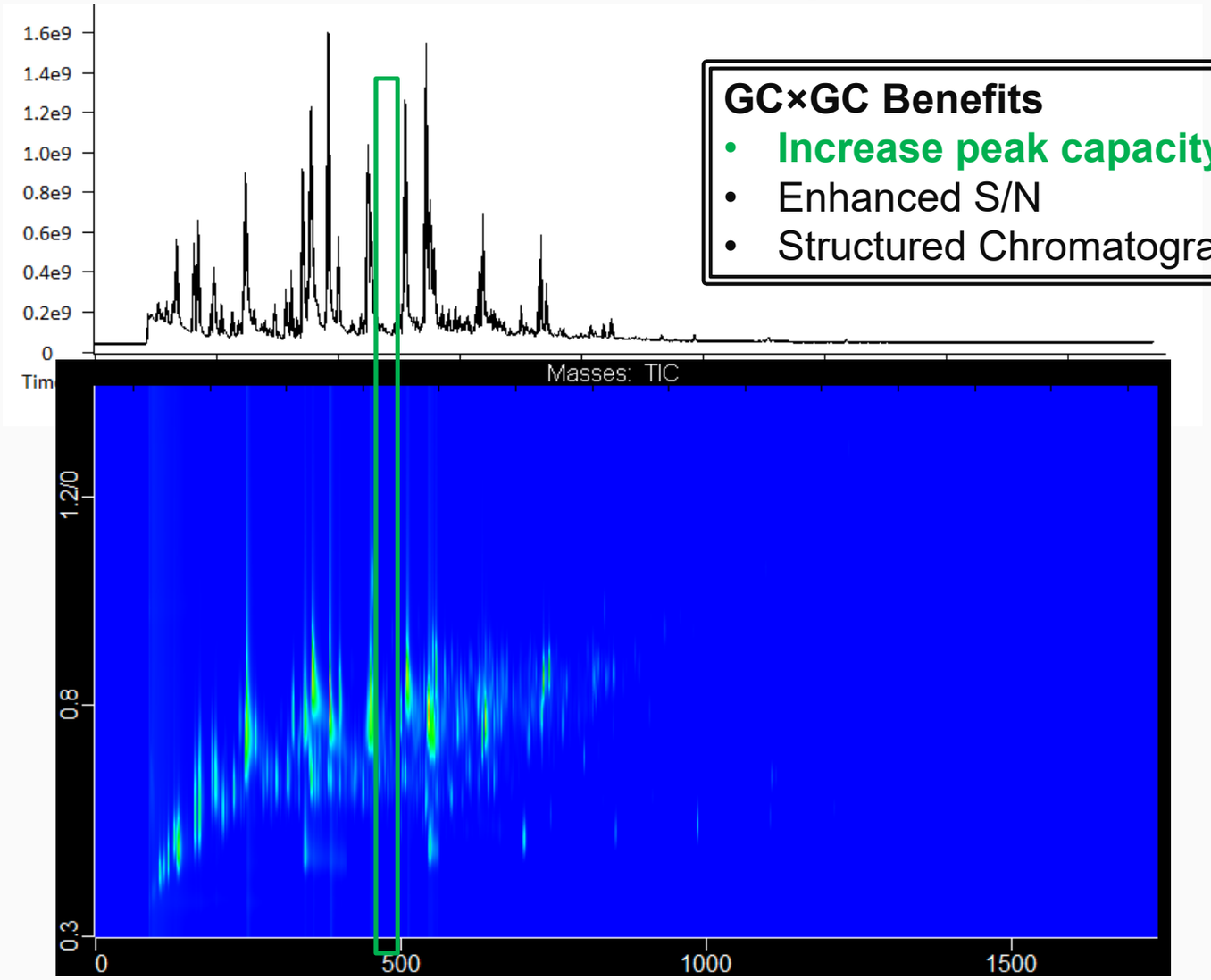

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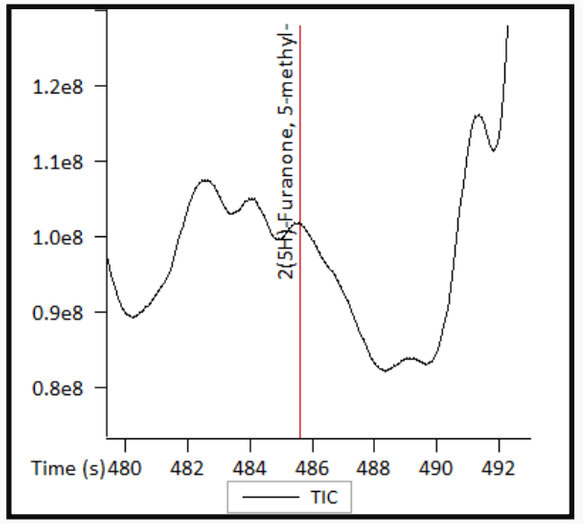

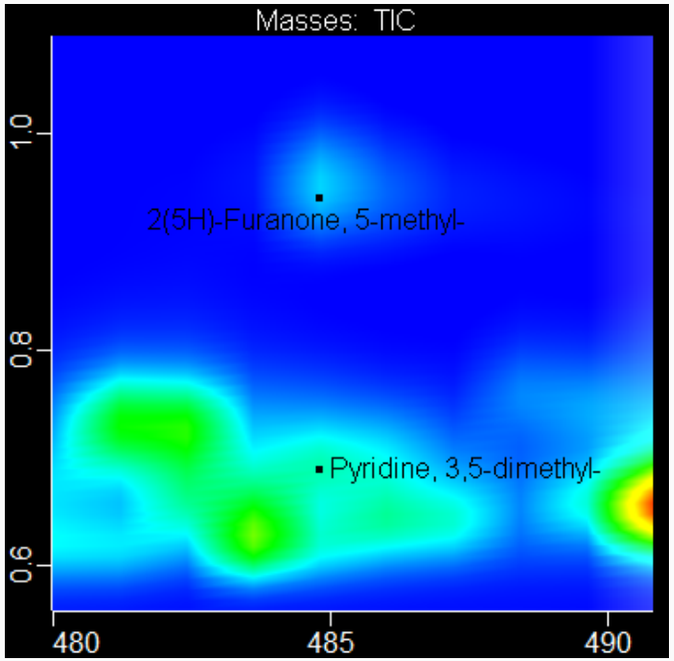

Chromatographic separation of 1D coelution exceeding deconvolution

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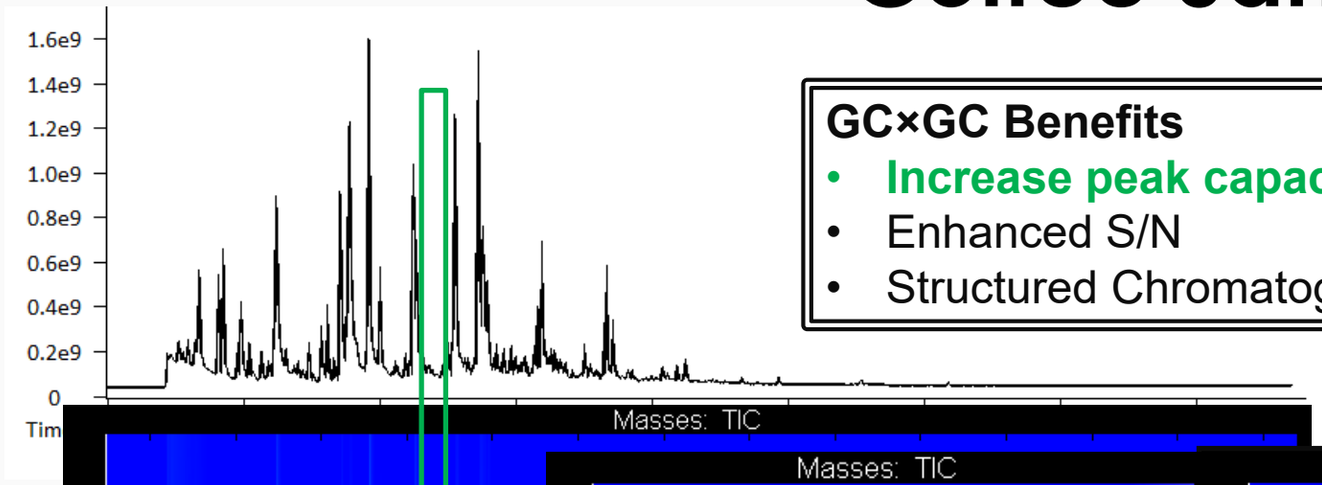

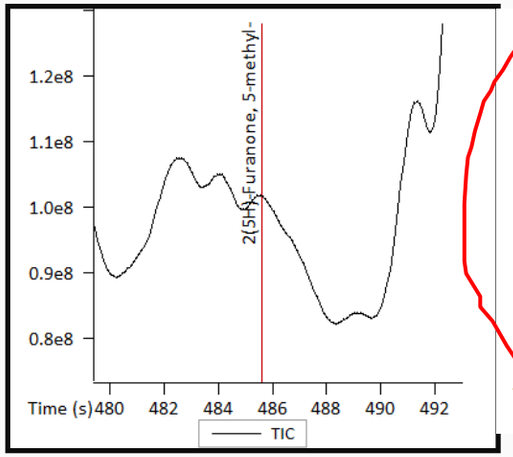

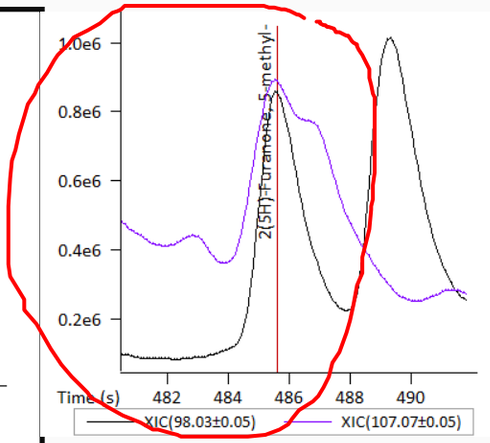

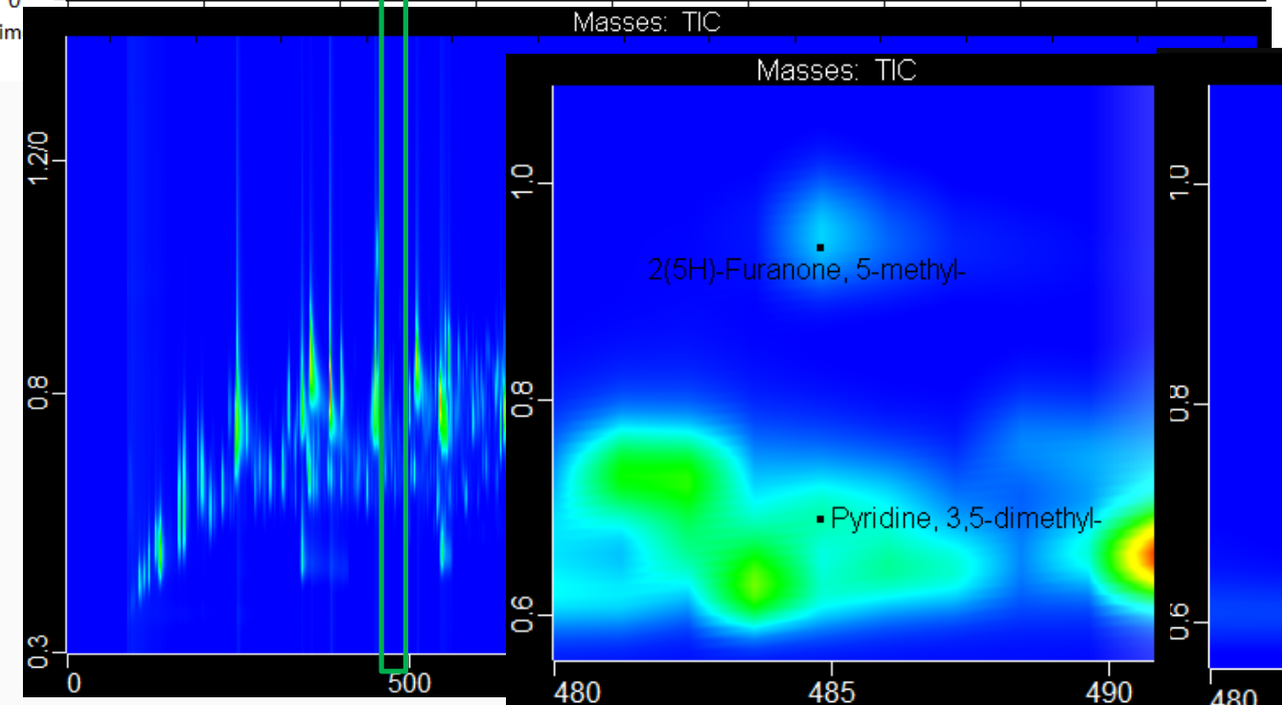

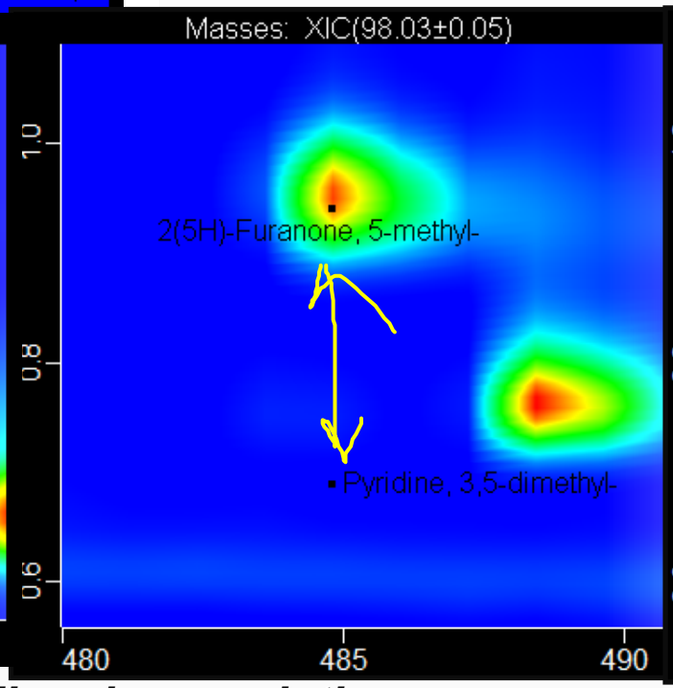

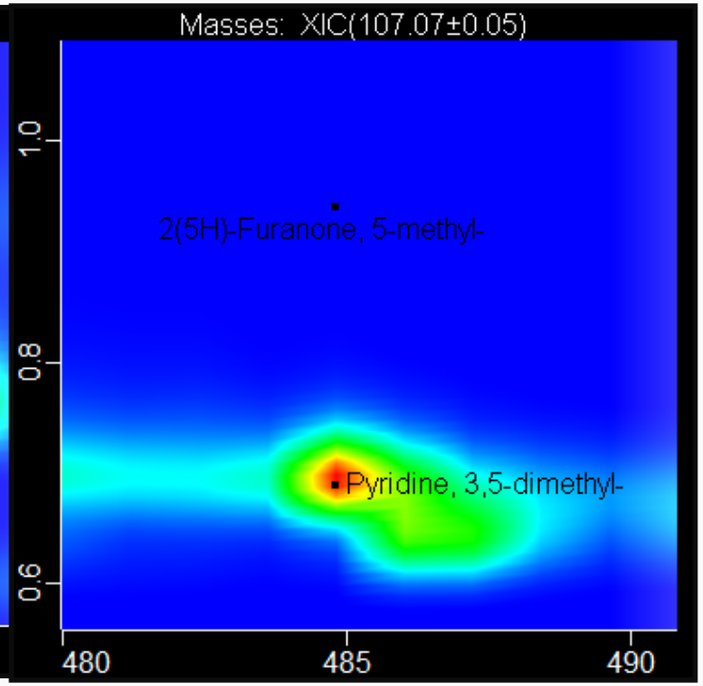

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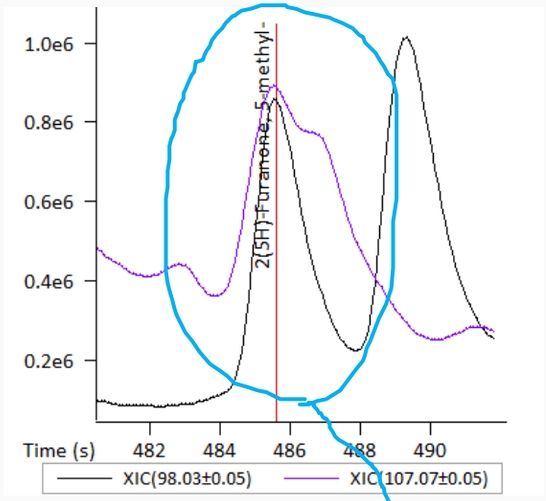
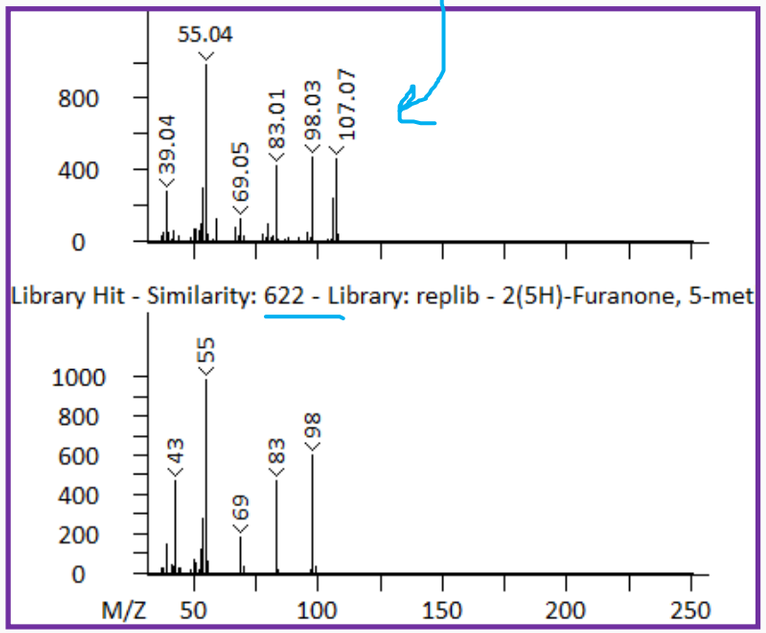
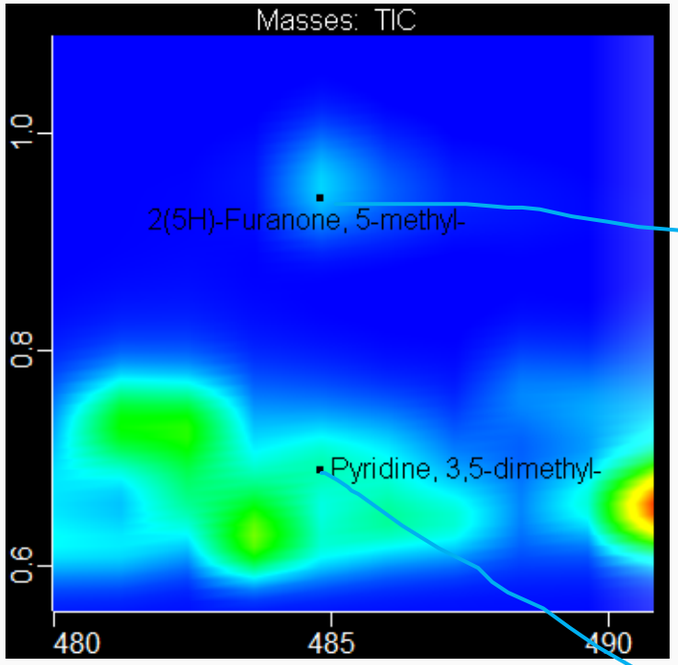
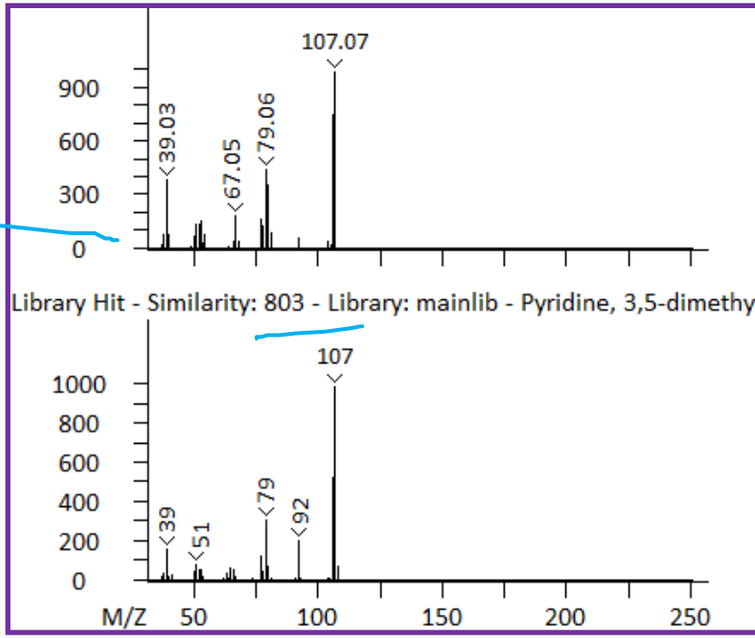
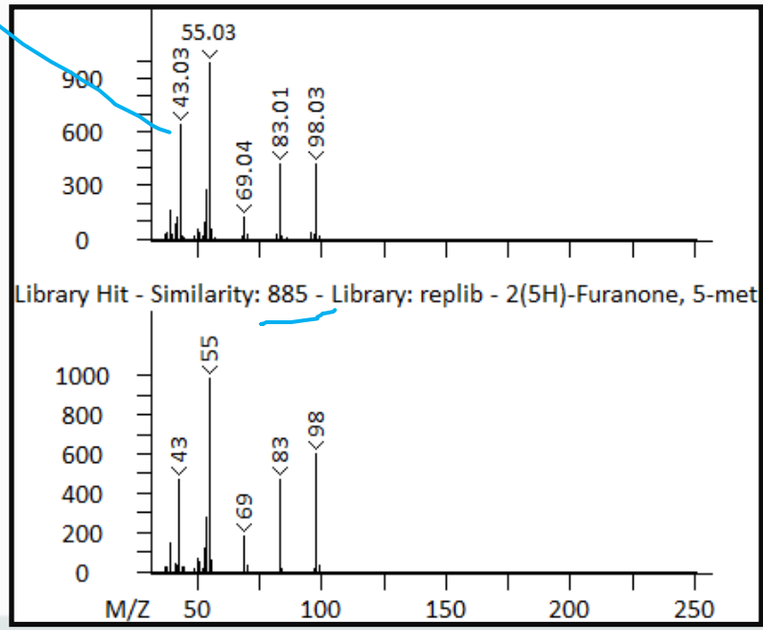

1.0e6
0.8e6
0.6e6
0.4e6
0.2e6
2(5H)-Furanone, 5-methyl-
Time (s)
482
484
486
488
490
XIC(98.03±0.05)
XIC(107.07±0.05)

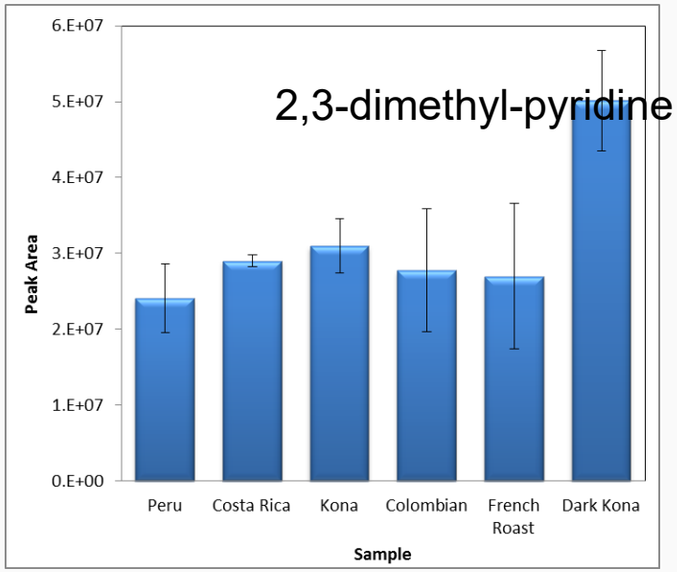

55.04
800
400
0
39.04
69.05
83.01
98.03
107.07
Library Hit - Similarity: 622 - Library: replib - 2(5H)-Furanone, 5-met
1000
800
600
400
200
0
55
43
69
83
98
M/Z
50
100
150
200
250

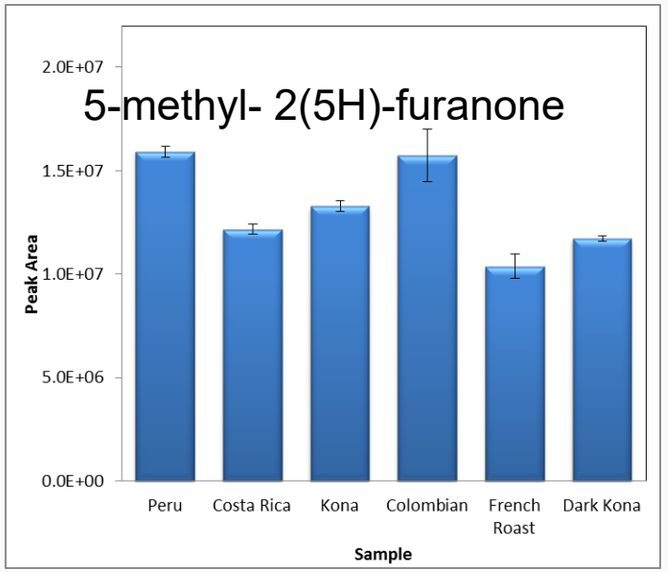

Masses: TIC
1.0
0.8
0.6
2(5H)-Furanone, 5-methyl-
Pyridine, 3,5-dimethyl-
480
485
490


107.07
900
600
300
0
39.03
67.05
79.06
Library Hit - Similarity: 803 - Library: mainlib - Pyridine, 3,5-dimethy
107
1000
800
600
400
200
0
39
51
79
92
M/Z
50
100
150
200
250


55.03
900
600
300
0
43.03
69.04
83.01
98.03
Library Hit - Similarity: 885 - Library: replib - 2(5H)-Furanone, 5-met
1000
800
600
400
200
0
55
43
69
83
98
M/Z
50
100
150
200
250

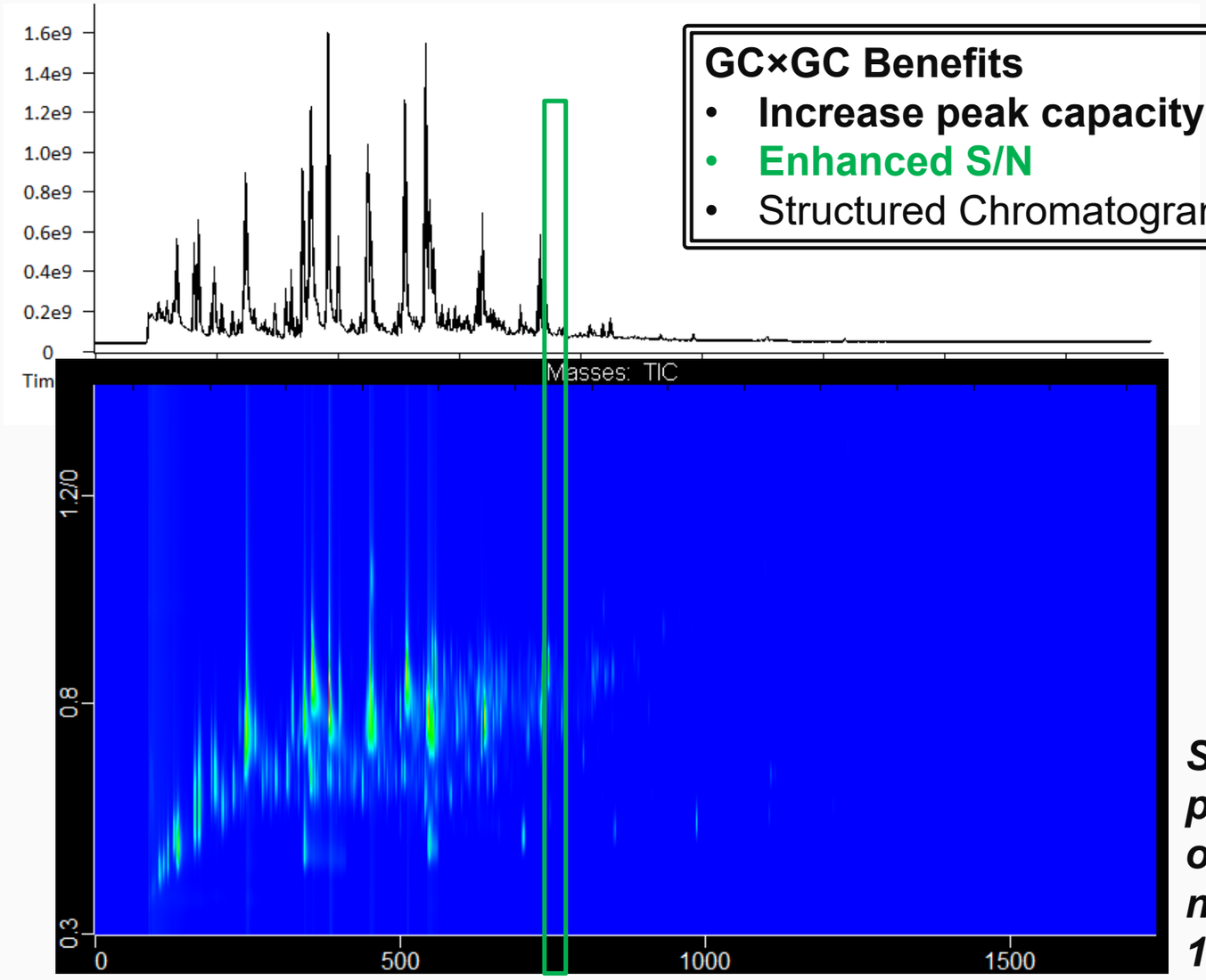
Name	Formula	CAS	GC Similarity	GC×GC Similarity	Odor Notes
2,3-dimethyl-pyridine	C_7H_9N	583-61-9	X	803	coffee, caramel
5-methyl- 2(5H)-furanone	$C_5H_6O_2$	591-11-7	622	885	





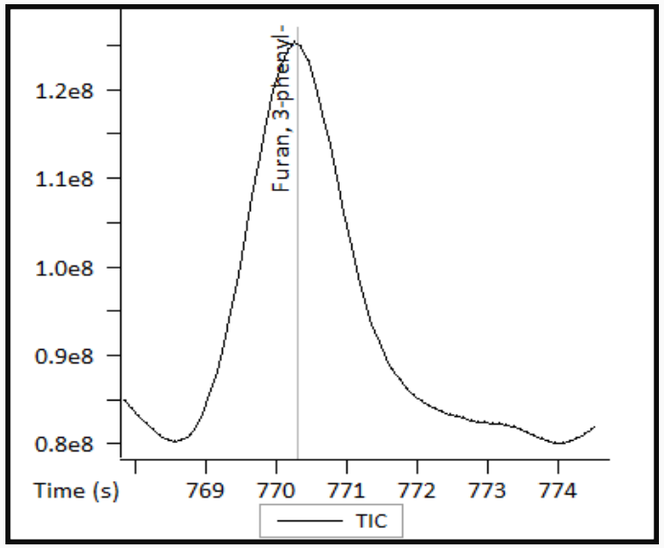
Chromatographic separation of 1D coelution exceeding deconvolution

Coffee Samples

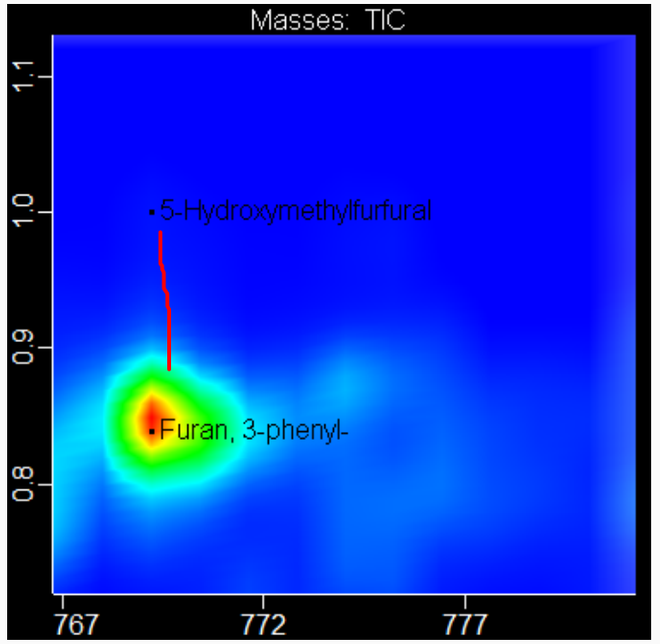


GC×GC Benefits

- **Increase peak capacity**
- **Enhanced S/N**
- Structured Chromatograms



S/N enhancement provides detection of low level analyte not observed in 1D separation



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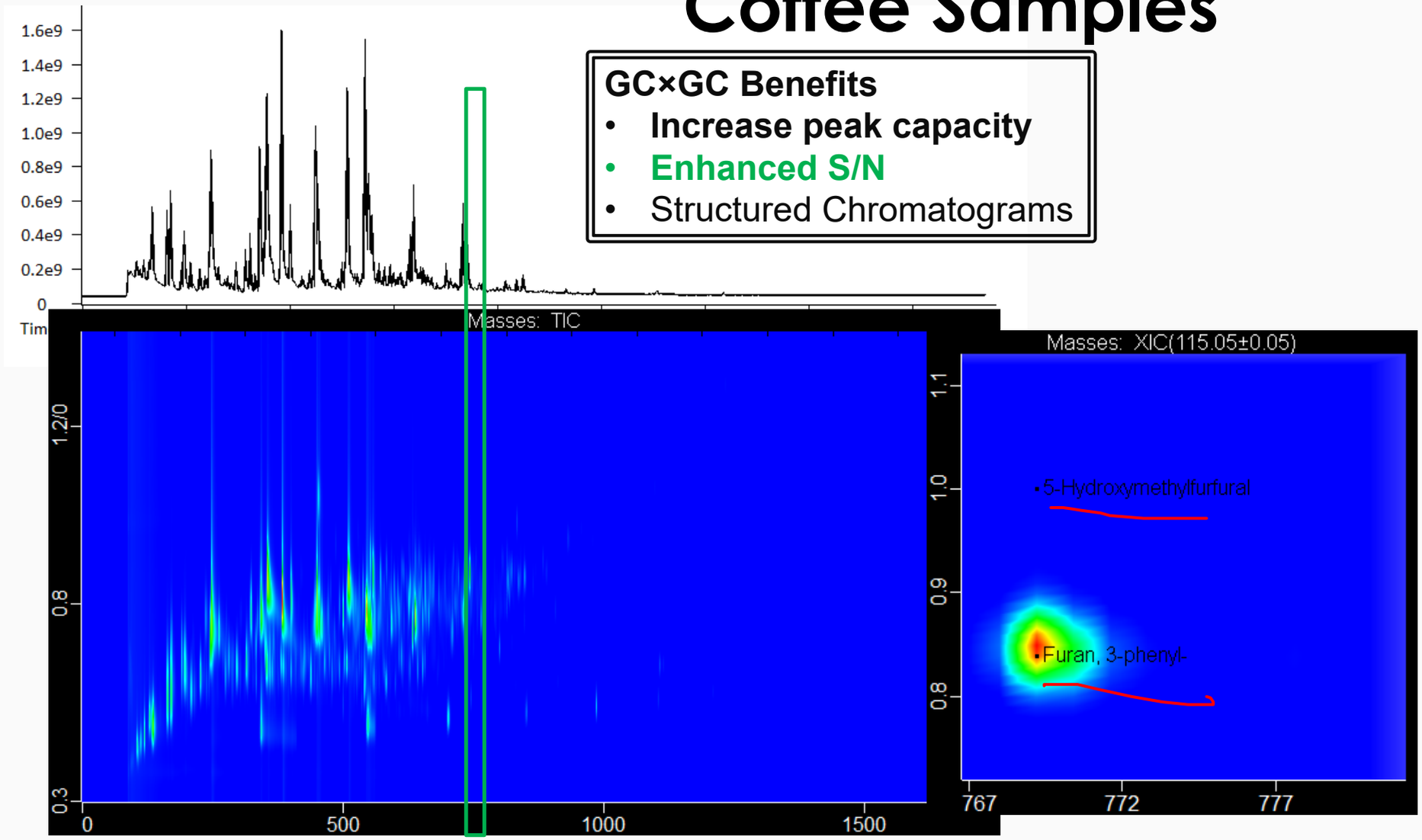

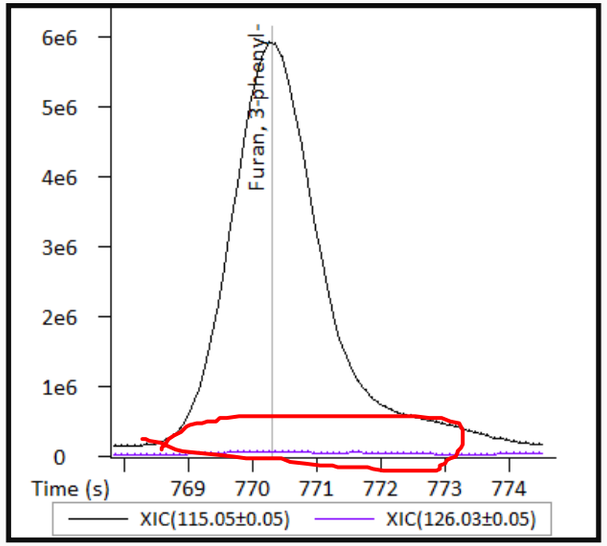

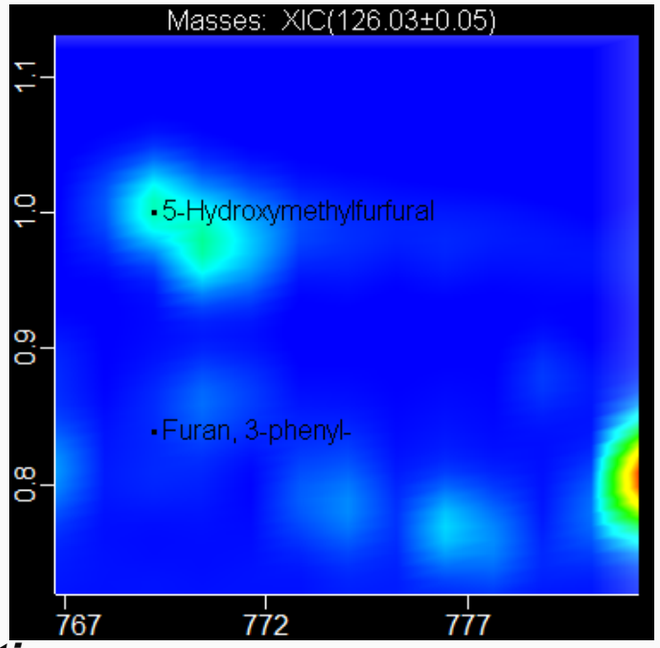

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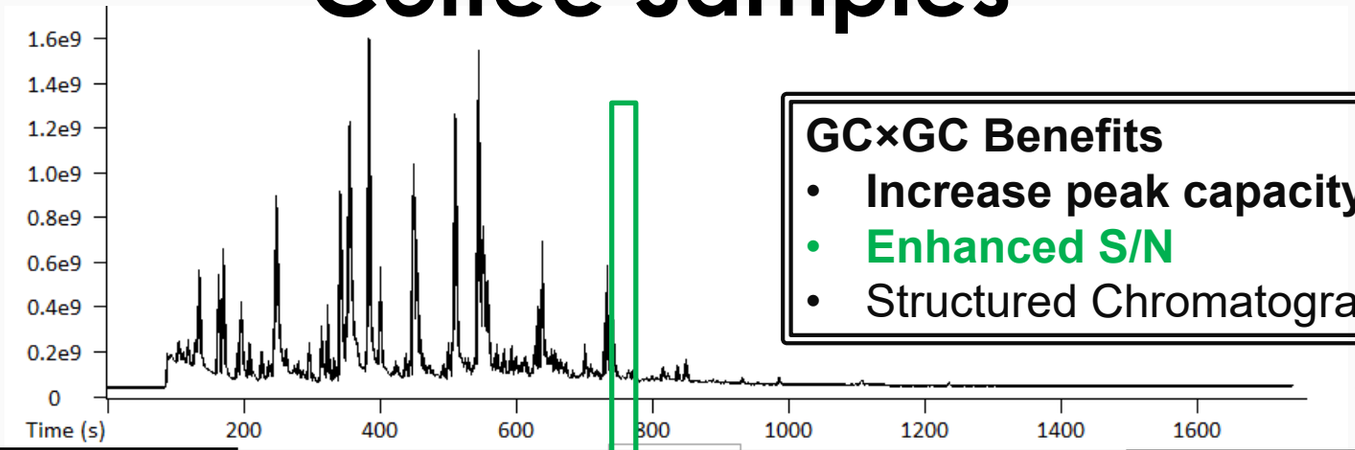

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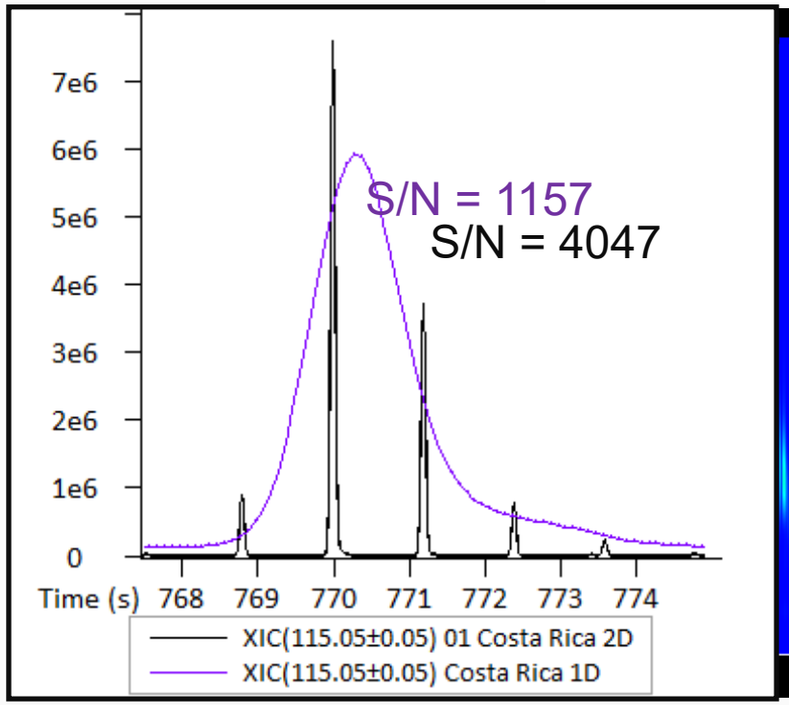
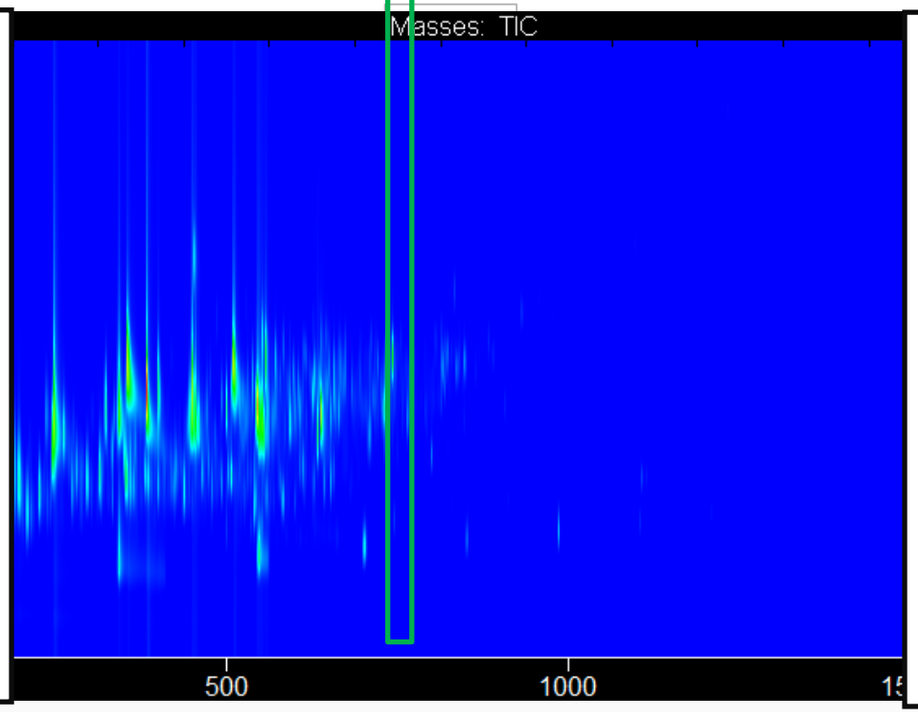
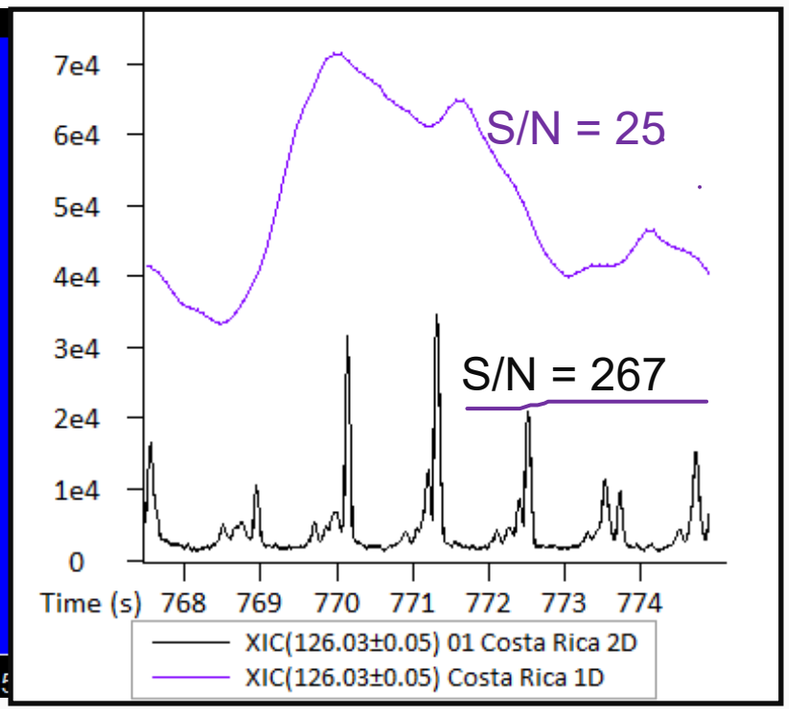
Furan, 3-methyl



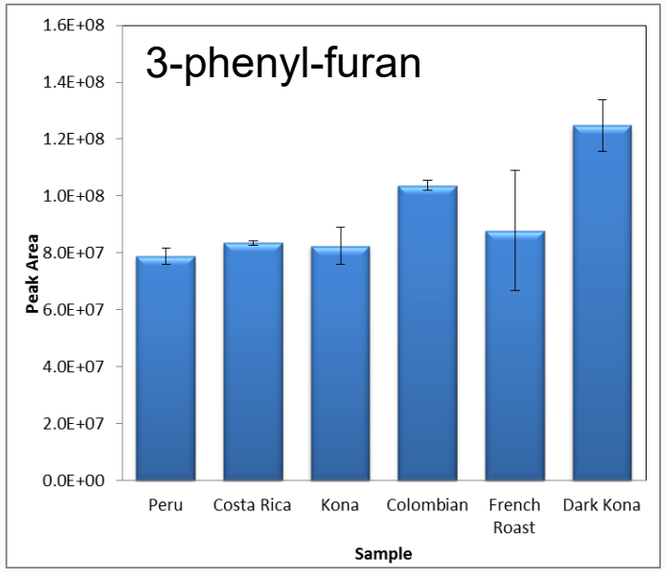


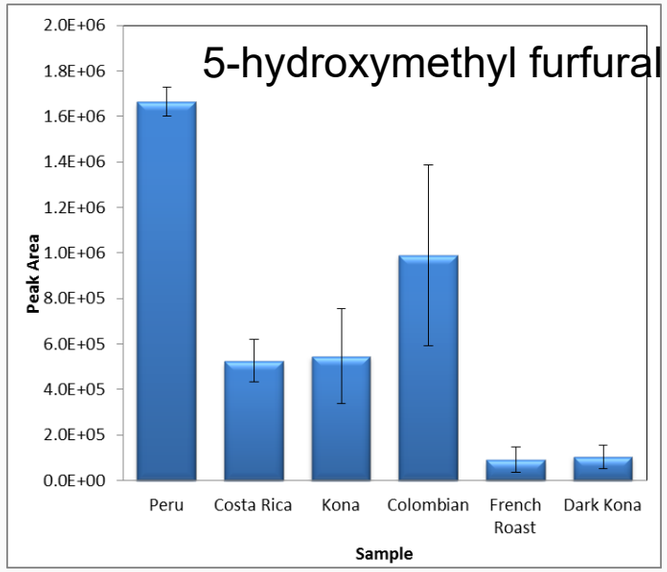
5-hydroxymethylfurfural



Coffee Samples

Name	Formula	CAS	GC Similarity	GC×GC Similarity	Odor Notes
3-phenyl-furan	$C_{10}H_8O$	13679-41-9	907	928	known to occur in coffee
5-hydroxymethyl furfural	$C_6H_6O_3$	67-47-0	x	760	caramel, buttery, fatty, musty, waxy





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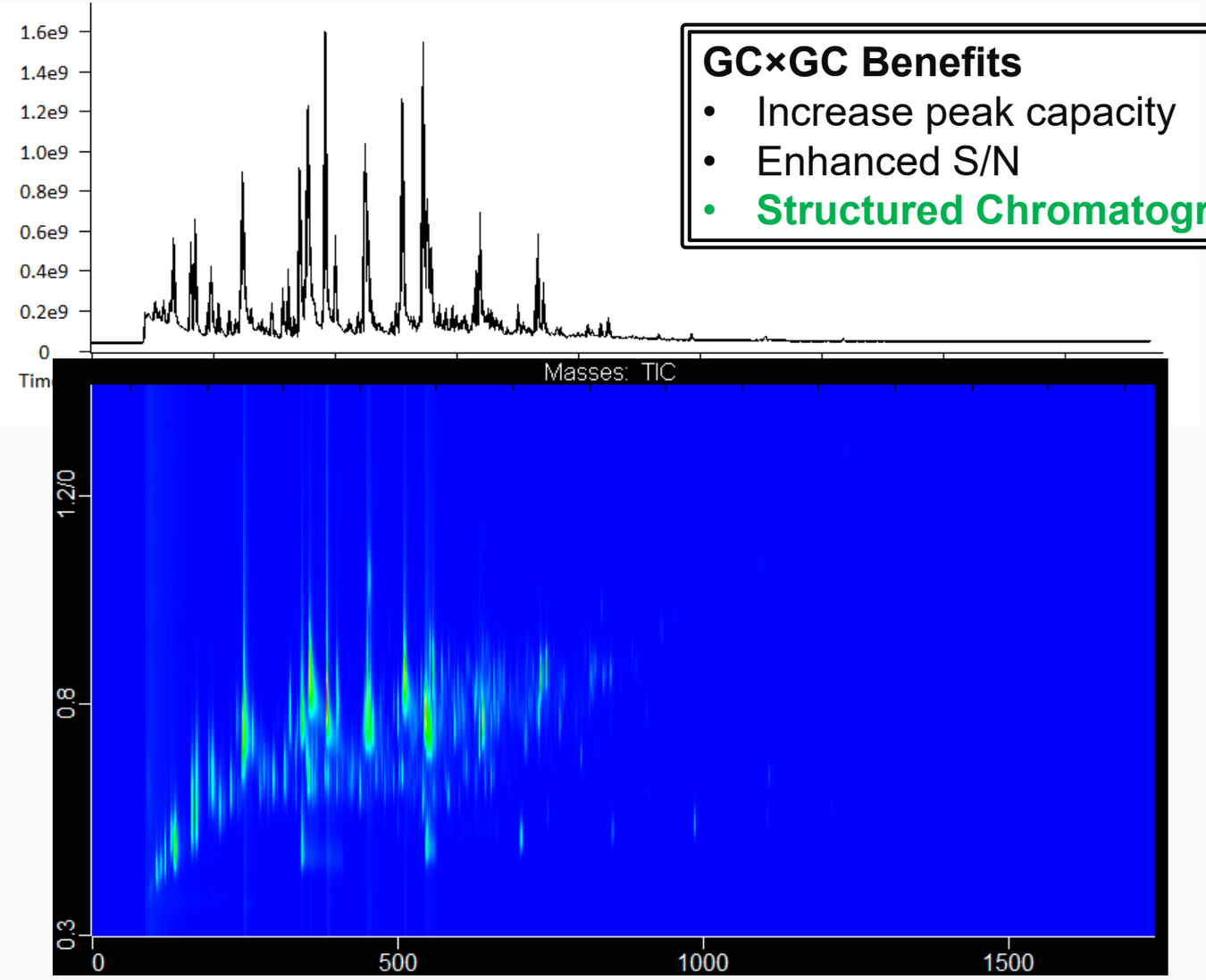

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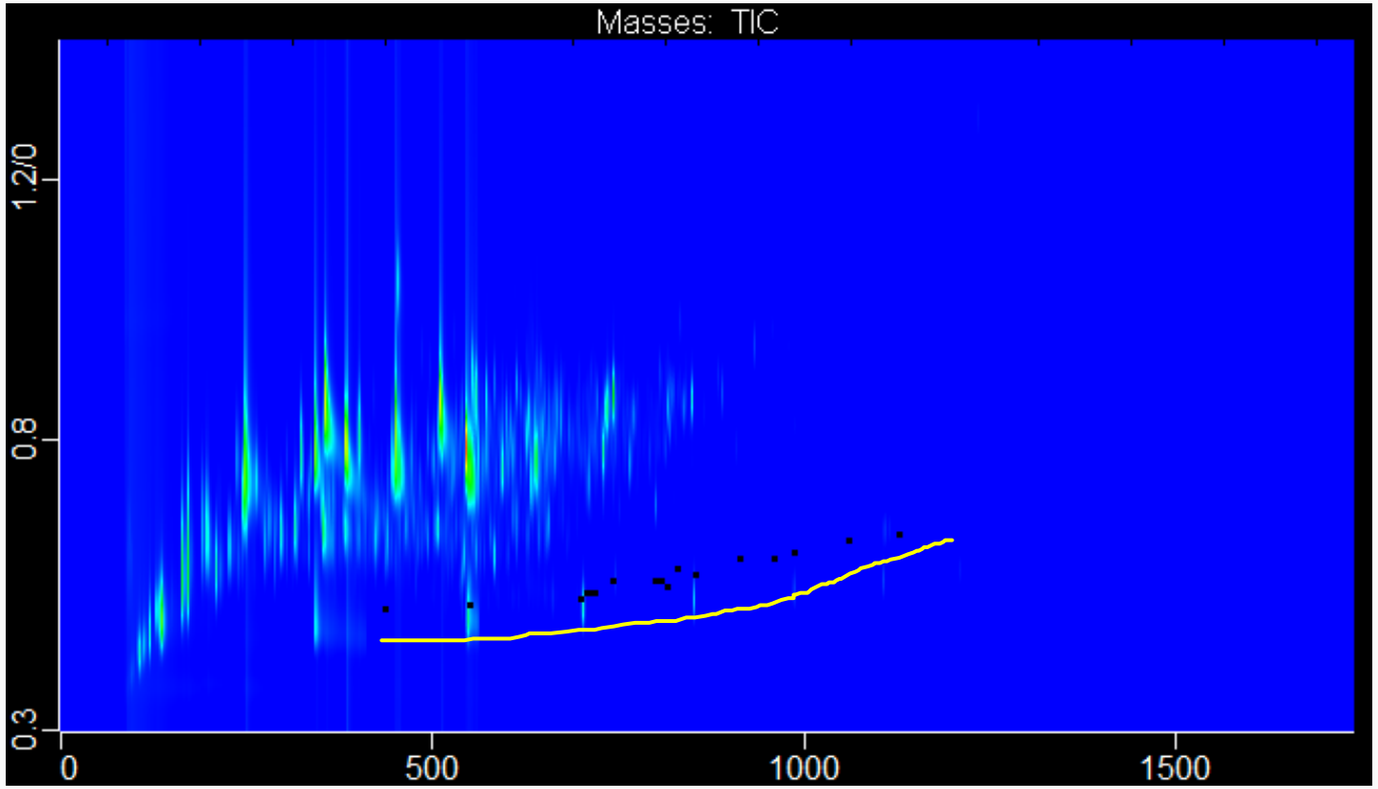
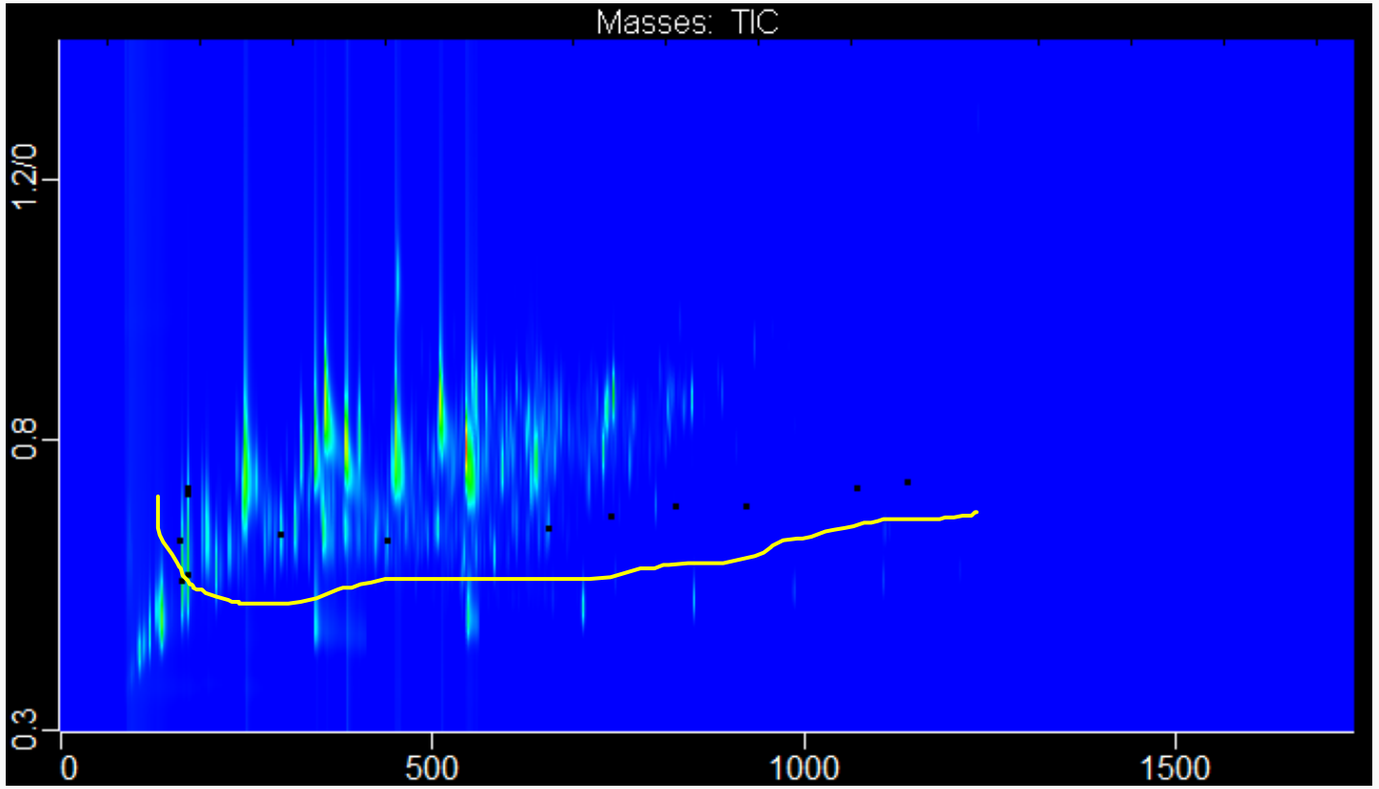
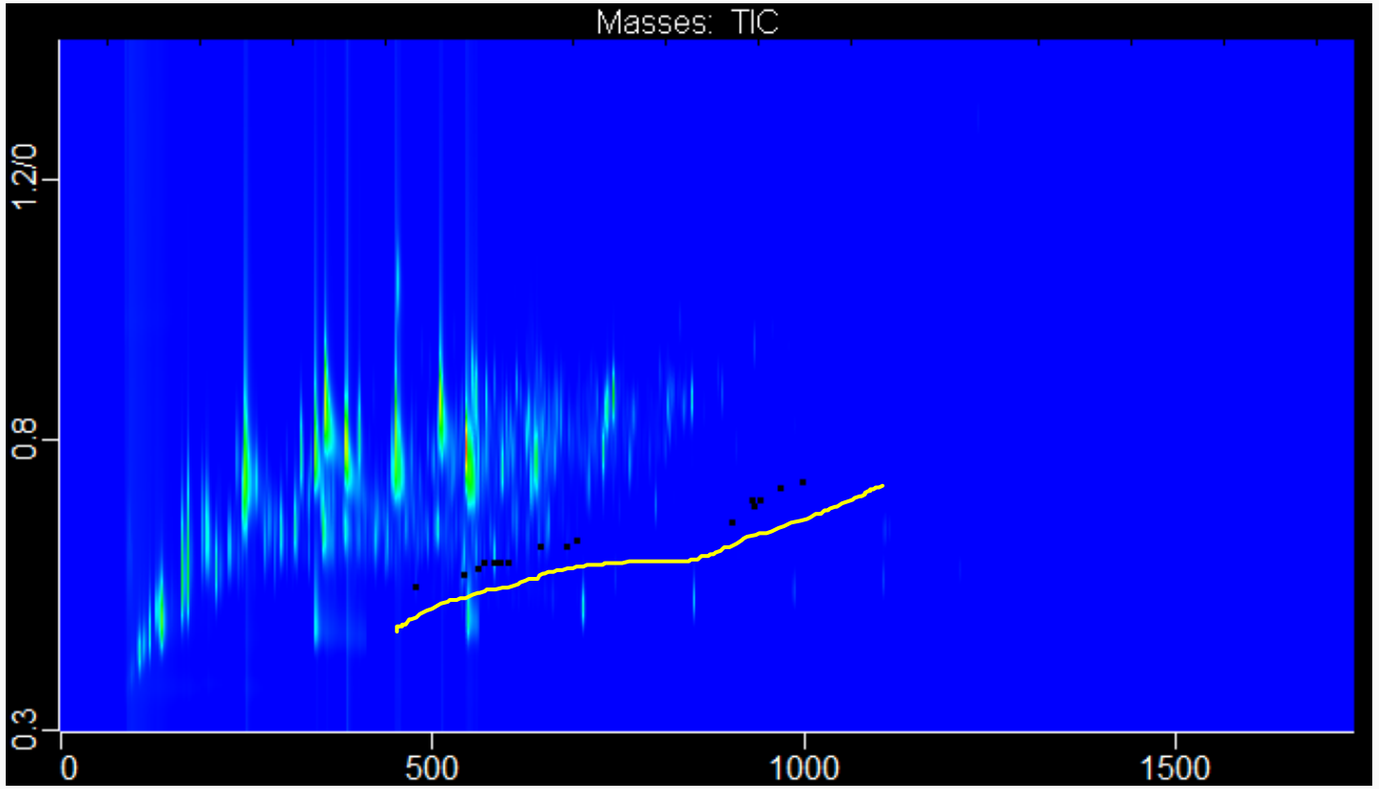
Structured Chromatograms: Alkanes



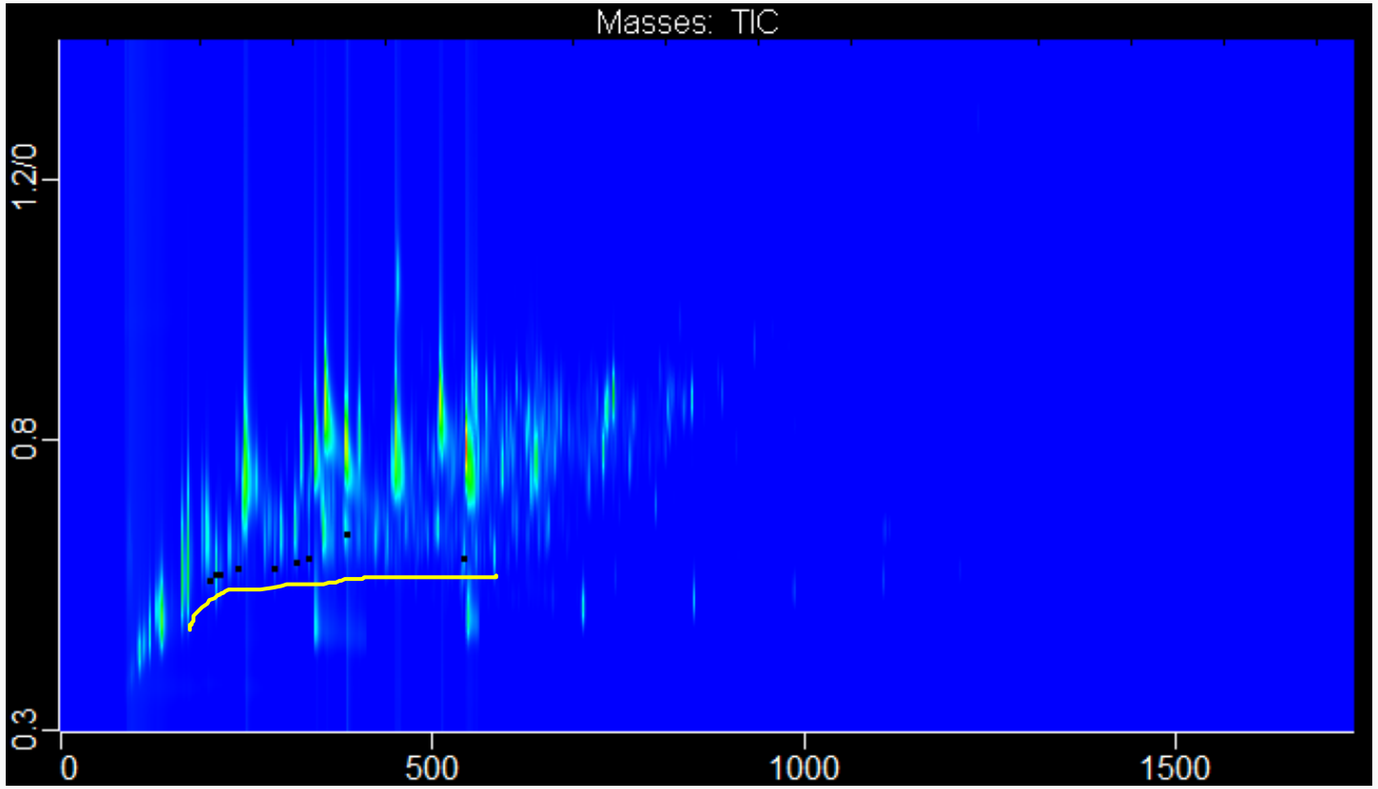
Structured Chromatograms: Aldehydes and Ketones



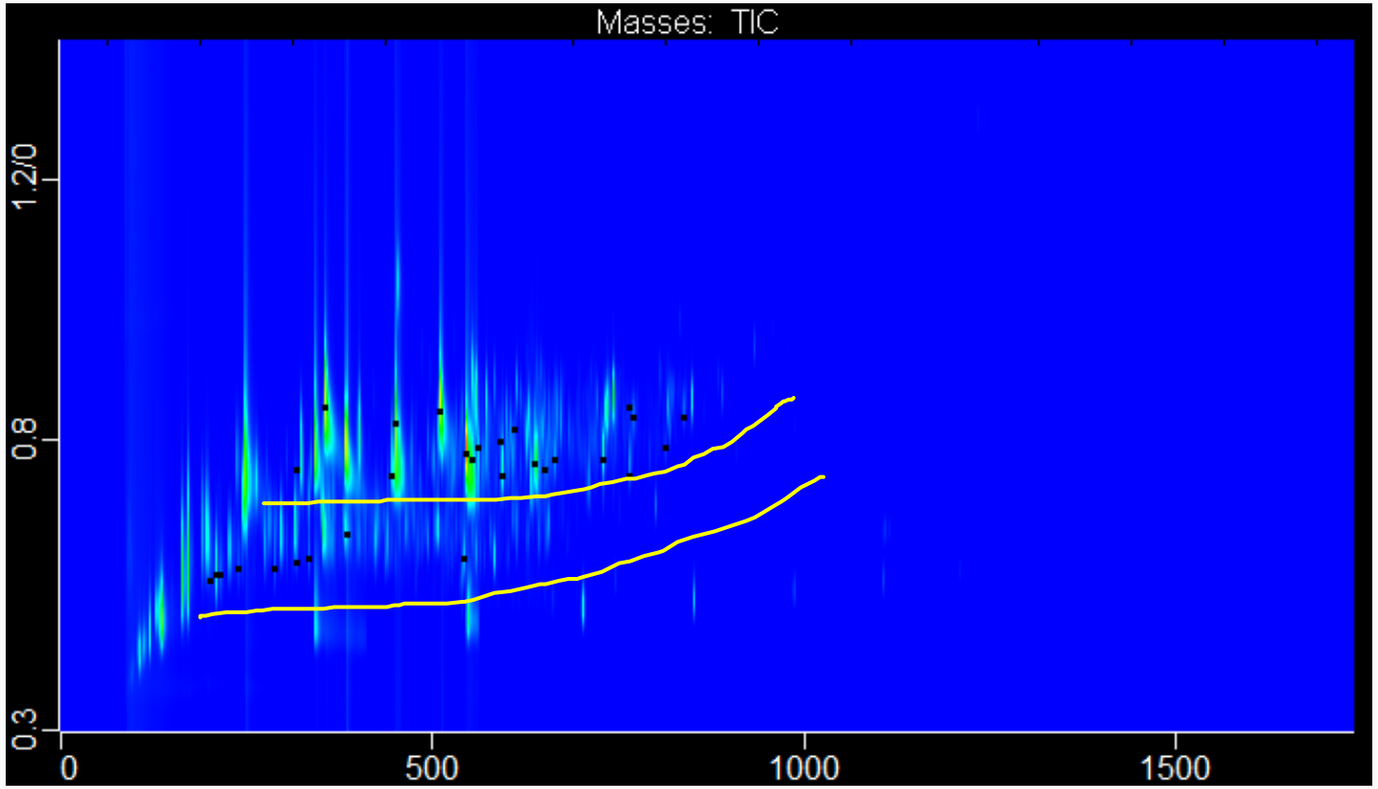
Structured Chromatograms: Terpenes



Structured Chromatograms: Furan

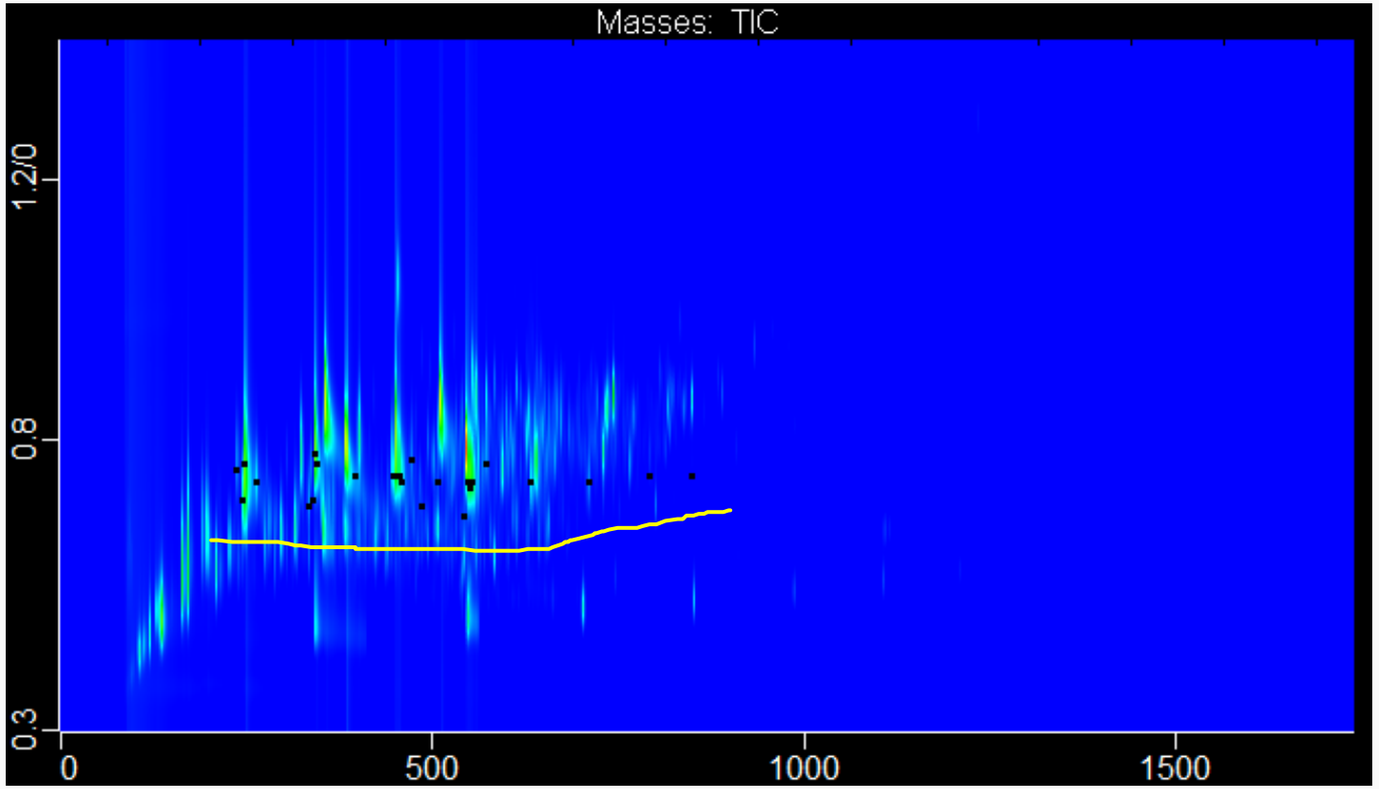


Structured Chromatograms: Substituted Furans



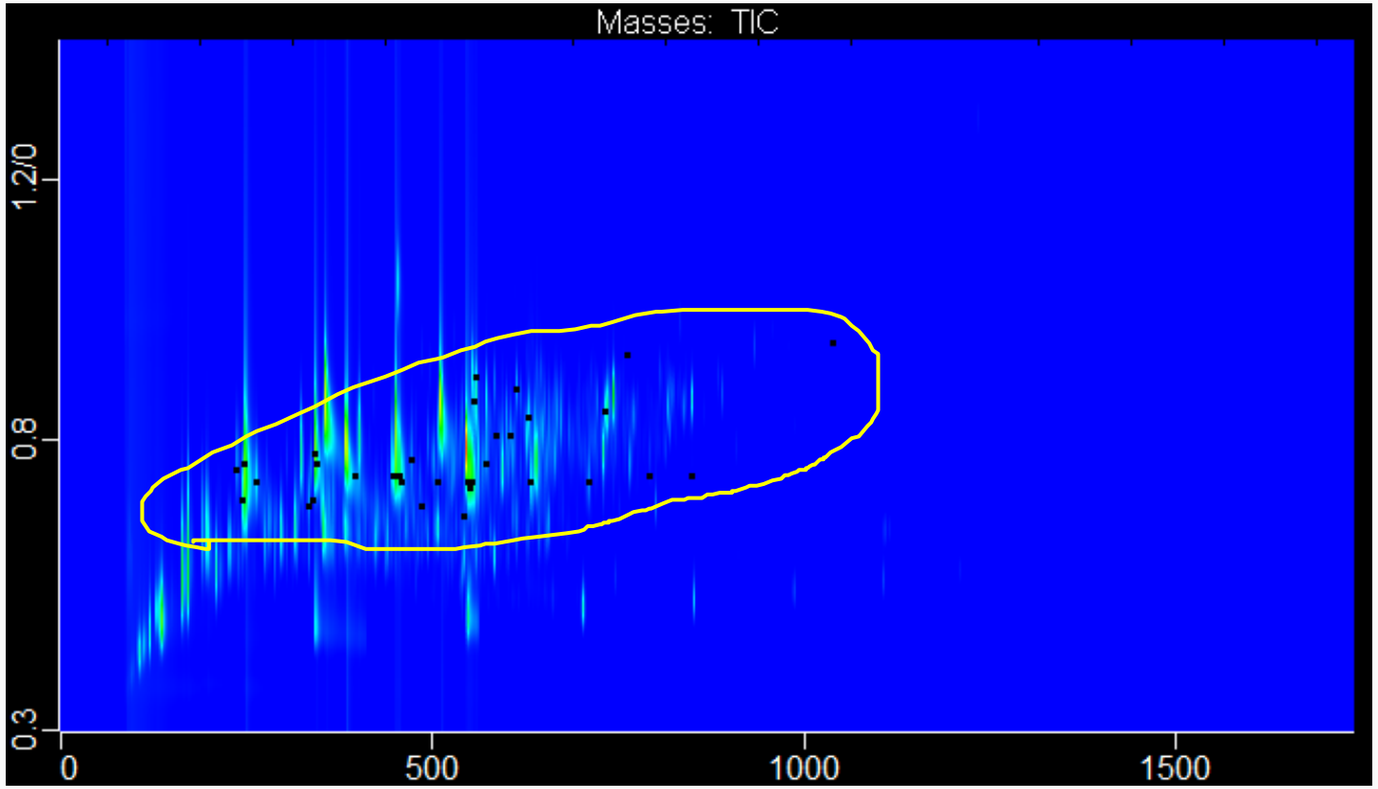
Structured Chromatograms: N-containing Rings

Pyrazine, Pyridine, Pyrrole

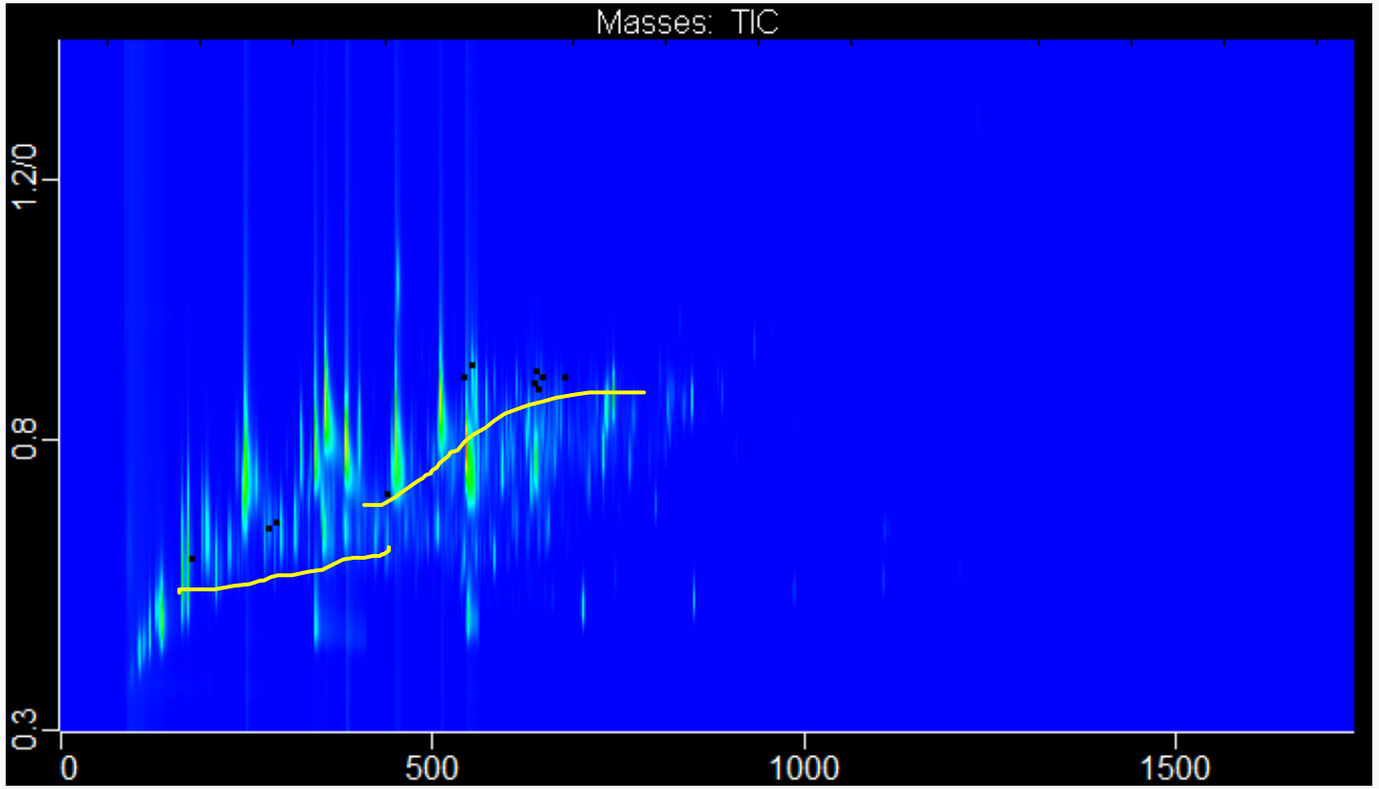


Structured Chromatograms: N-containing Rings

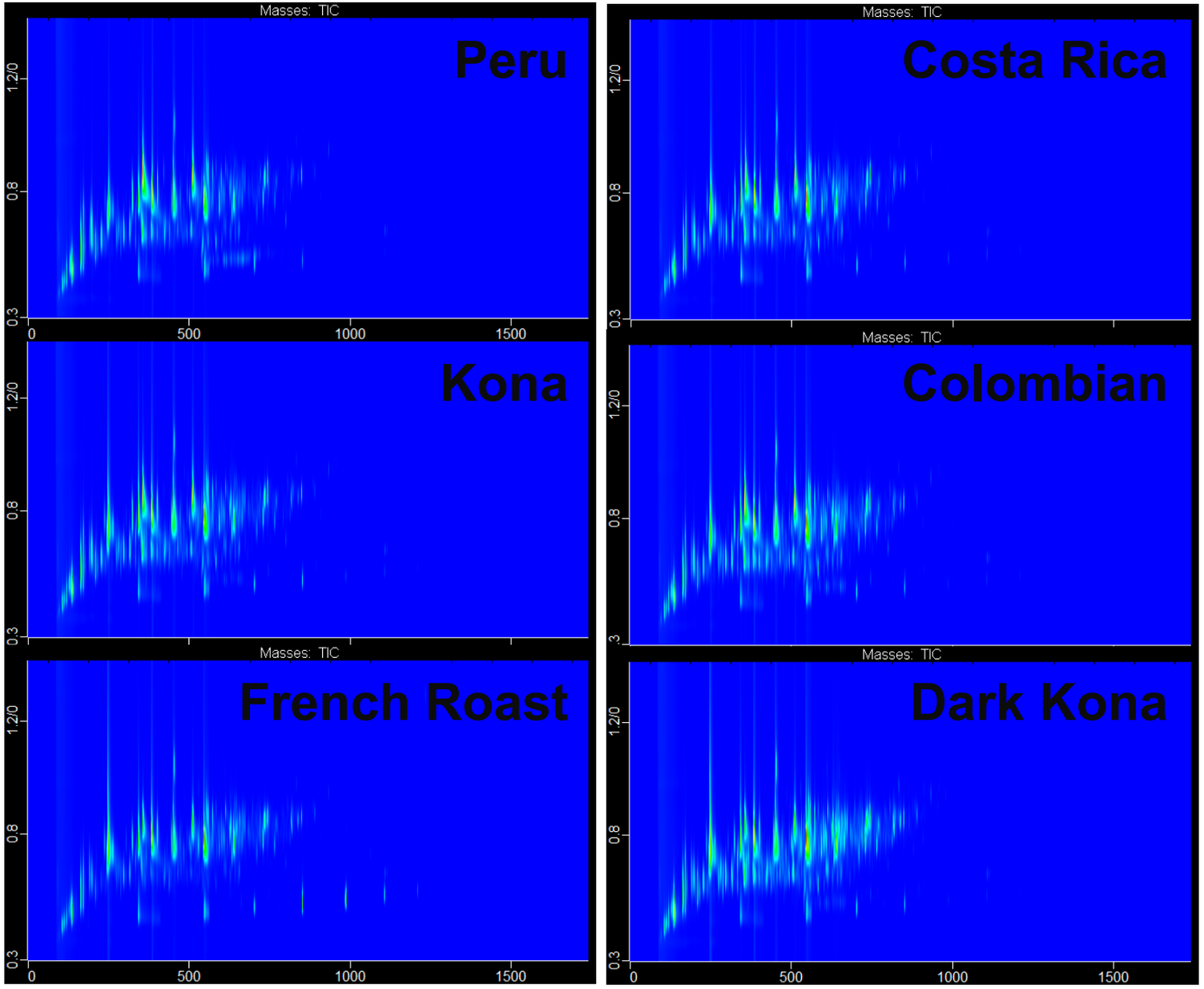
Substituted - pyrazine, Pyridine, Pyrrole



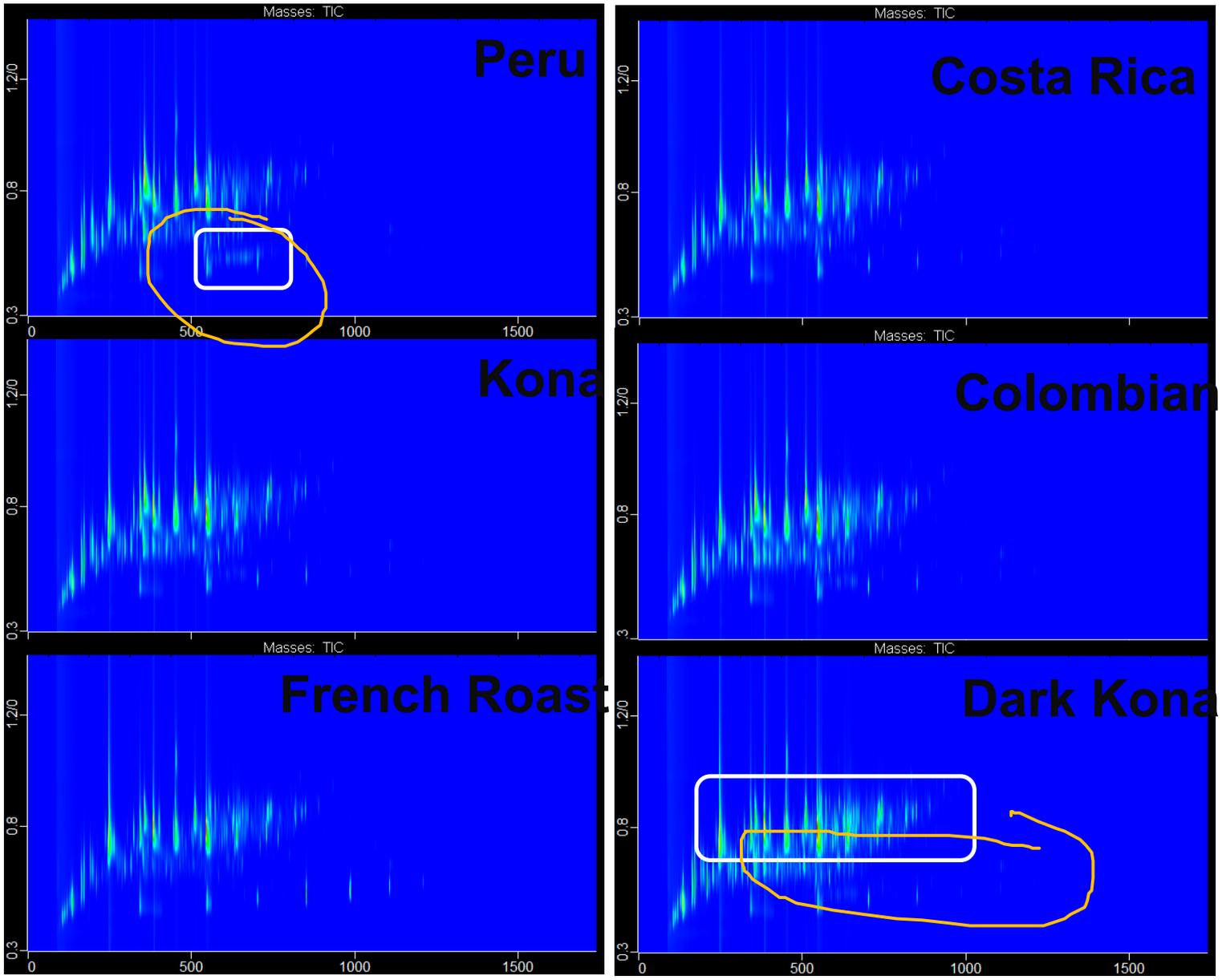
Structured Chromatograms: Thiophene Substituted



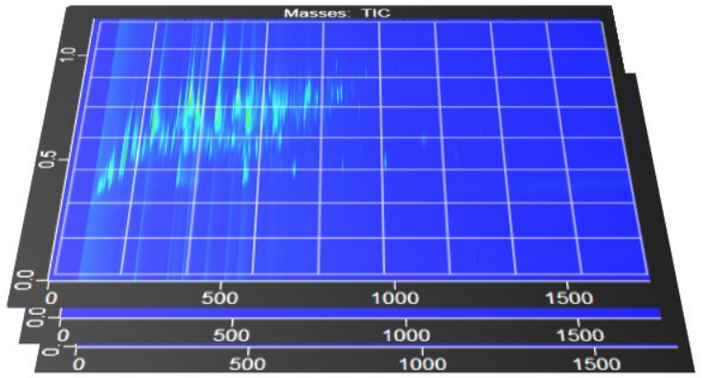
Sample Comparisons



Sample Comparisons



Specific Analyte Comparisons

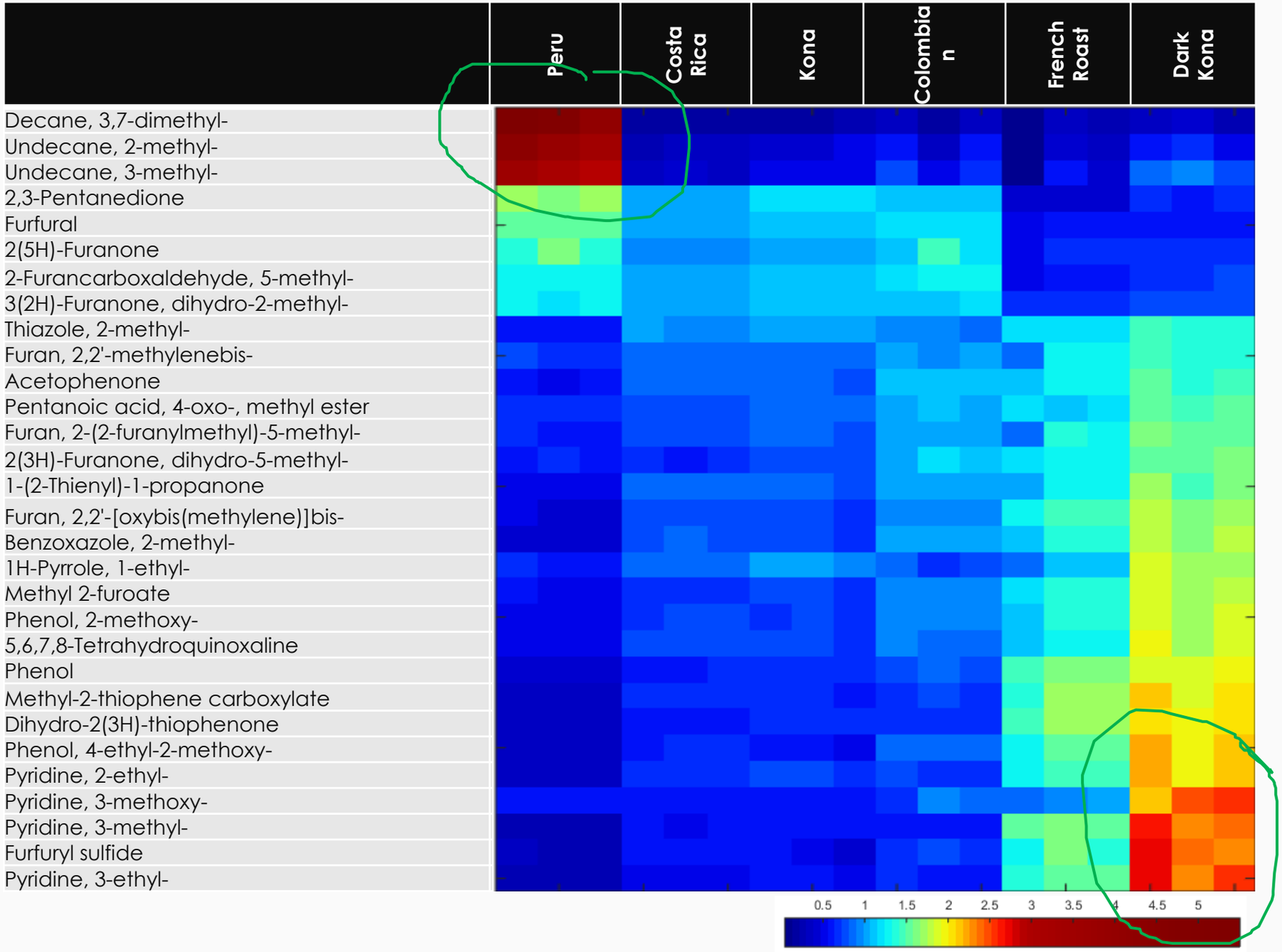


Data Alignment

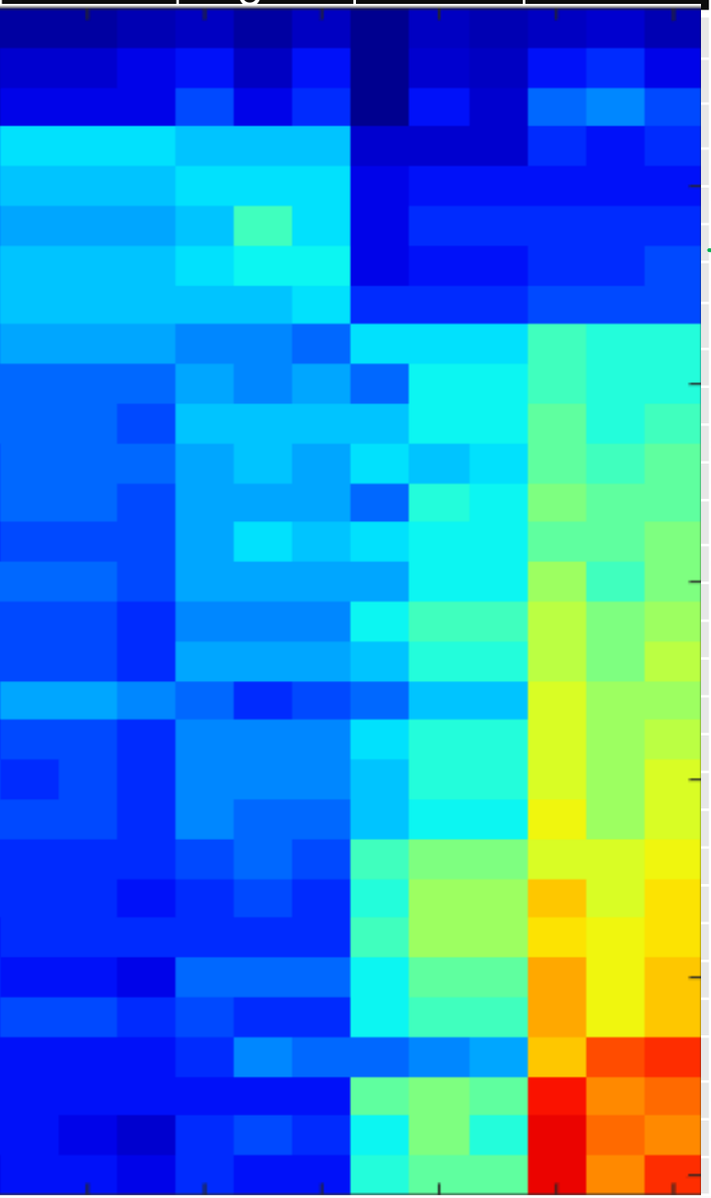
ChromaTOF Tile

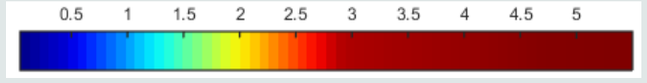
Beta-version

	tR	Similarity	Formula	CAS	RI (Obs)	RI (Lib)
Decane, 3,7-dimethyl-	673.2	867	$C_{12}H_{26}$	17312-54-8	1124	1125
Undecane, 2-methyl-	710.4	908	$C_{12}H_{26}$	7045-71-8	1163.8	1164
Undecane, 3-methyl-	716.4	949	$C_{12}H_{26}$	1002-43-3	1170	1170
2,3-Pentanedione	195.0	929	$C_5H_8O_2$	600-14-6	707.3	698
Furfural	356.0	966	$C_5H_4O_2$	98-01-1	835.9	833
2(5H)-Furanone	454.6	896	$C_4H_4O_2$	497-23-4	916.6	918
2-Furancarboxaldehyde, 5-methyl-	510.8	950	$C_6H_6O_2$	620-02-0	966.2	965
3(2H)-Furanone, dihydro-2-methyl-	323.5	938	$C_5H_8O_2$	3188-00-9	809.8	809
Thiazole, 2-methyl-	323.5	839	C_4H_5NS	3581-87-1	809.8	815
Furan, 2,2'-methylenebis-	637.9	935	$C_9H_8O_2$	1197-40-6	1086.7	1088
Acetophenone	621.2	894	C_8H_8O	98-86-2	1070.3	1065
Pentanoic acid, 4-oxo-, methyl ester	537.2	912	$C_6H_{10}O_3$	624-45-3	989.4	982
Furan, 2-(2-furanylmethyl)-5-methyl-	728.4	926	$C_{10}H_{10}O_2$	13678-51-8	1183	1190
2(3H)-Furanone, dihydro-5-methyl-	500.1	899	$C_5H_8O_2$	108-29-2	956.7	958
1-(2-Thienyl)-1-propanone	736.4	854	C_7H_8OS	13679-75-9	1190.7	1185
Furan, 2,2'-[oxybis(methylene)]bis-	836.0	915	$C_{10}H_{10}O_3$	4437-22-3	1305.5	1299
Benzoxazole, 2-methyl-	670.4	839	C_8H_7NO	95-21-6	1120.1	
1H-Pyrrole, 1-ethyl-	331.2	923	C_6H_9N	617-92-5	816.6	821
Methyl 2-furoate	524.0	888	$C_6H_6O_3$	611-13-2	977.8	980
Phenol, 2-methoxy-	644.0	941	$C_7H_8O_2$	90-05-1	1092.6	1090
5,6,7,8-Tetrahydroquinoxaline	759.2	845	$C_8H_{10}N_2$	34413-35-9	1216.4	1223
Phenol	529.9	949	C_6H_6O	108-95-2	983.1	980
Methyl-2-thiophene carboxylate	665.6	852	$C_6H_6O_2S$	5380-42-7	1115	
Dihydro-2(3H)-thiophenone	554.1	922	C_4H_6OS	1003-10-7	1004.7	
Phenol, 4-ethyl-2-methoxy-	818.0	900	$C_9H_{12}O_2$	2785-89-9	1284.3	1282
Pyridine, 2-ethyl-	444.6	853	C_7H_9N	100-71-0	908.2	906
Pyridine, 3-methoxy-	551.6	831	C_6H_7NO	7295-76-3	1002.3	1005
Pyridine, 3-methyl-	391.9	843	C_6H_7N	108-99-6	864.9	863
Furfuryl sulfide	969.3	888	$C_{10}H_{10}O_2S$	13678-67-6	1474.6	1463
Pyridine, 3-ethyl-	503.5	912	C_7H_9N	536-78-7	959.9	959


Peru
Costa Rica
Kona
Colombian
French Roast
Dark Kona
Decane, 3,7-dimethyl-
Undecane, 2-methyl-
Undecane, 3-methyl-
2,3-Pentanedione
Furfural
2(5H)-Furanone
2-Furancarboxaldehyde, 5-methyl-
3(2H)-Furanone, dihydro-2-methyl-
Thiazole, 2-methyl-
Furan, 2,2'-methylenebis-
Acetophenone
Pentanoic acid, 4-oxo-, methyl ester
Furan, 2-(2-furanylmethyl)-5-methyl-
2(3H)-Furanone, dihydro-5-methyl-
1-(2-Thienyl)-1-propanone
Furan, 2,2'-[oxybis(methylene)]bis-
Benzoxazole, 2-methyl-
1H-Pyrrole, 1-ethyl-
Methyl 2-furoate
Phenol, 2-methoxy-
5,6,7,8-Tetrahydroquinoxaline
Phenol
Methyl-2-thiophene carboxylate
Dihydro-2(3H)-thiophenone
Phenol, 4-ethyl-2-methoxy-
Pyridine, 2-ethyl-
Pyridine, 3-methoxy-
Pyridine, 3-methyl-
Furfuryl sulfide
Pyridine, 3-ethyl-
0.5 1 1.5 2 2.5 3 3.5 4 4.5 5

	Peru	Costa Rica	Kona	Colombian	French Roast	Dark Kona	Odor and flavor notes
Decane, 3,7-dimethyl-							
Undecane, 2-methyl-							
Undecane, 3-methyl-							
2,3-Pentanedione							caramel, nutty, sweet, butter, creamy, cheese, pungent
Furfural							woody, almond, fragrant, baked bread, sweet
2(5H)-Furanone							buttery
2-Furancarboxaldehyde, 5-methyl-							spice, caramel, maple
3(2H)-Furanone, dihydro-2-methyl-							bread, buttery, nutty, sweet, solvent
Thiazole, 2-methyl-							green, vegetable
Furan, 2,2'-methylenebis-							rich, roasted
Acetophenone							sweet, almond, pungent, hawthorn, mimosa, acacia, chemical
Pentanoic acid, 4-oxo-, methyl ester							caramellic
Furan, 2-(2-furanylmethyl)-5-methyl-							
2(3H)-Furanone, dihydro-5-methyl-							cocoa, woody, sweet, herbal, warm, tobacco
1-(2-Thienyl)-1-propanone							caramel, creamy
Furan, 2,2'-[oxybis(methylene)]bis-							coffee, nutty, earthy
Benzoxazole, 2-methyl-							burnt, tobacco, phenolic, meaty, powdery, capers
1H-Pyrrole, 1-ethyl-							burnt flavors
Methyl 2-furoate							tobacco, fruity, mushroom, fungus, sweet
Phenol, 2-methoxy-							smoke, spice, vanilla, woody, phenolic
5,6,7,8-Tetrahydroquinoxaline							roasted, nut, musty, bean, cereal, corn, chip, cheese
Phenol							phenolic plastic rubber
Methyl-2-thiophene carboxylate							burnt flavors
Dihydro-2(3H)-thiophenone							burnt, garlic
Phenol, 4-ethyl-2-methoxy-							spicy, smoky, bacon, phenolic, clove
Pyridine, 2-ethyl-							green, grassy
Pyridine, 3-methoxy-							
Pyridine, 3-methyl-							earthy, hazelnut, green flavors
Furfuryl sulfide							coffee, mushroom, earthy, powerful, meaty, sulfury
Pyridine, 3-ethyl-							roasted flavors; tobacco, oakmoss, leather odors





Conclusions

- LECO's Pegasus BT 4D efficiently combines HS-SPME, GC×GC, and TOFMS
- This set of analytical tools provides non-target aroma profiling for coffee
- Compared to GC, GC×GC provides key benefits and more information
- Sample-distinguishing analytes were determined that appear to relate to roast level

THANK YOU FOR ATTENTION

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