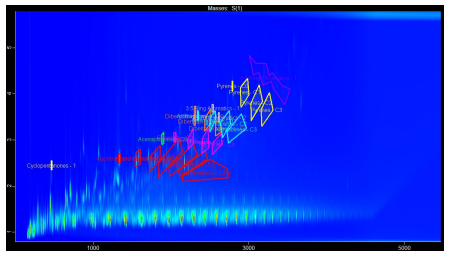
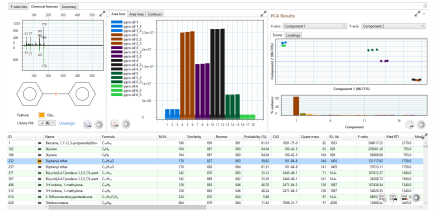
Characterization and Quantitative Hydrocarbon Group-Type Analysis of Plastic-Derived Pyrolysis Oils by GCxGC-TOFMS/FID

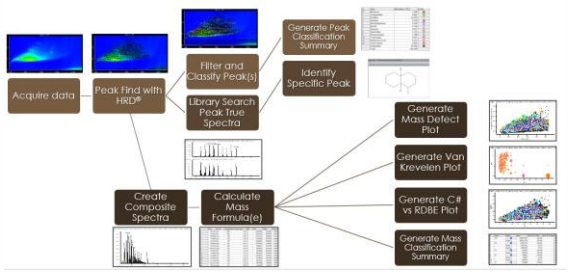
15th Multidimensional Chromatography Workshop

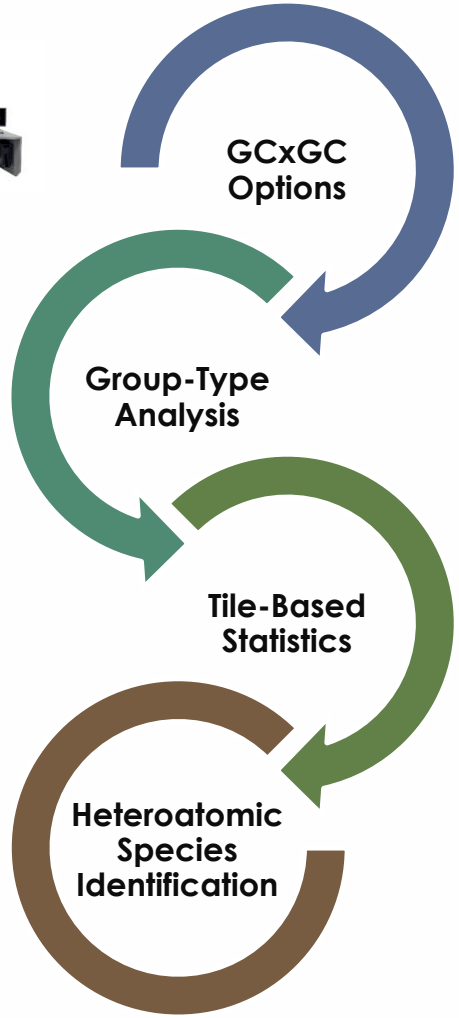
January 2024

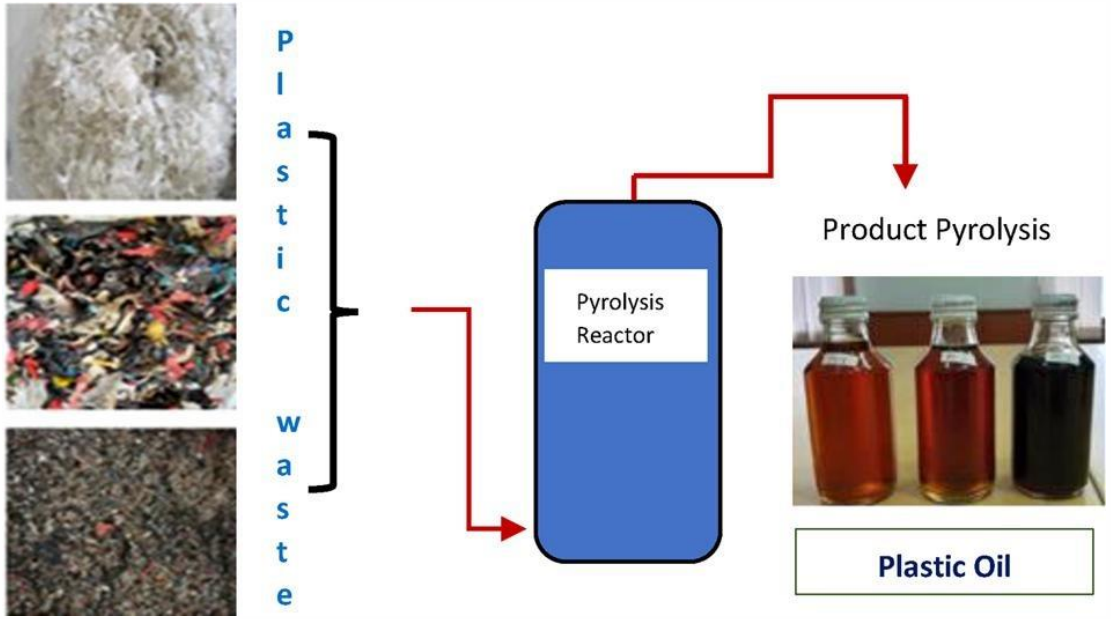
Pyrolysis Oils Characterization Workflow







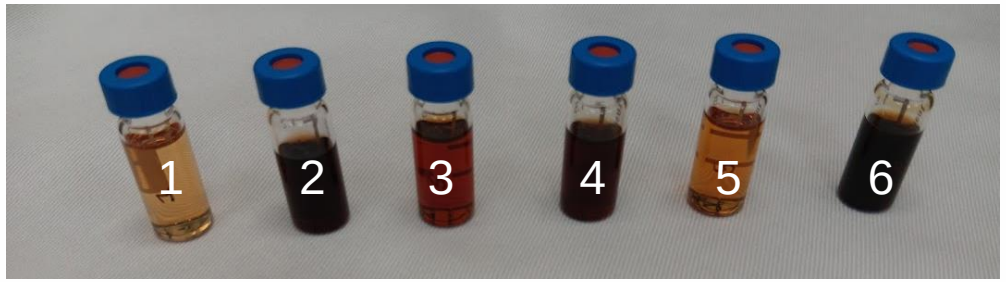




https://www.sciencedirect.com/science/article/pii/S2451904921000342

GCxGC Options

Plastic-Derived Pyrolysis Oil Samples



Polyethylene/polypropylene pyrolysis oil samples were taken on different dates from a variety of points along the process stream.

Condenser Line (CL)

- Process line from unit to production tank
- Cleanest sample

Product Tank (LT)

- Sample goes here from unit before collection tanks

Collection Tank (CT)

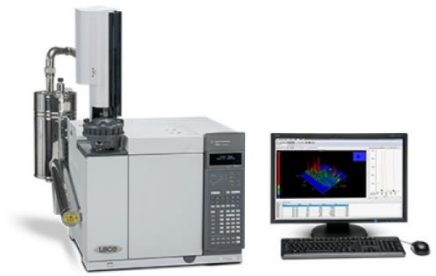
- Samples are put in various collection tanks after product tank
- Variable sample type

Knock Tank (KT)

- Bottom-of-the-barrel collection tank
- Heavy and full of particulates

GCxGC Options

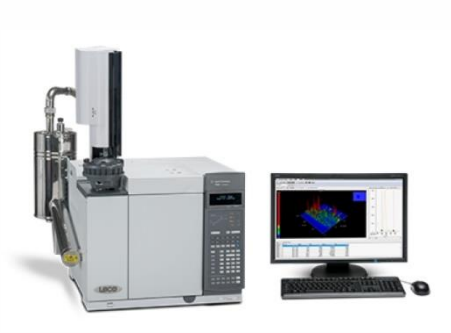
Choosing a GCxGC system



Features	QuadJet SD (FID)	Pegasus BT 4D	Pegasus HRT+ 4D
Modulator	Quad-Jet Thermal	Quad-Jet Thermal; FLUX	Quad-Jet Thermal
Secondary Oven?	Yes	Yes	Yes
Max Acquisition Rate	500 spectra/s	500 spectra/s	200 spectra/s
Mass Range	--	10-1500 m/z	10-1500 m/z
Mass Resolution	--	1000 (better-than-nominal)	25,000 HR/ 50,000 UHR
Chemical Ionization	--	No	Yes, PCI and ECNI (with MMS)
Software Platform	ChromaTOF SD	ChromaTOF 5 BT	ChromaTOF 5 HRT

GCxGC Options

Choosing a GCxGC system



Features	QuadJet SD (FID)	Paradigm Shift (FID+MS)	Pegasus BT 4D	Pegasus HRT+ 4D
Modulator	Quad-Jet Thermal	Reverse Fill-flush Flow	Quad-Jet Thermal; FLUX	Quad-Jet Thermal
Secondary Oven?	Yes	No	Yes	Yes
Max Acquisition Rate	500 spectra/s	500 spectra/s	500 spectra/s	200 spectra/s
Mass Range	--	10-1500 m/z	10-1500 m/z	10-1500 m/z
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Chemical Ionization	--	No	No	Yes, PCI and ECNI (with MMS)
Software Platform	ChromaTOF SD	ChromaTOF 5 BT	ChromaTOF 5 BT	ChromaTOF 5 HRT

GCxGC Options

Benefits of the Pegasus BT 4D MS

- **High-performance MS** matches well with commercial spectral libraries for compound identification
- **Quantitative** for calibrated components
- **Fast acquisition rate** pairs perfectly with GCxGC
  - Structured chromatogram adds ID
  - Group-type clusters
  - Better-than-nominal mass filtering
- **High sensitivity** allows for trace-level discovery AND pairing for quantitation with FID

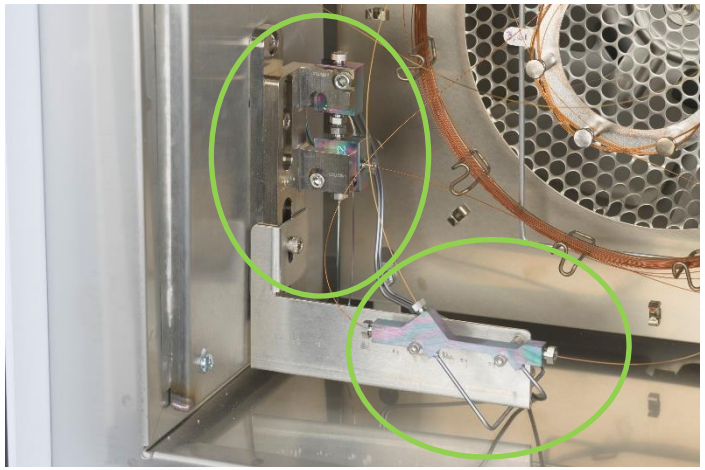
GCxGC Options

Benefits of the Paradigm Shift System

- **Paradigm** GCxGC acquisition parameters ensure full transfer of analytes and optimal separations

- **Shift** splitter maintains constant ratio between MS & FID throughout run for accurate quantitation

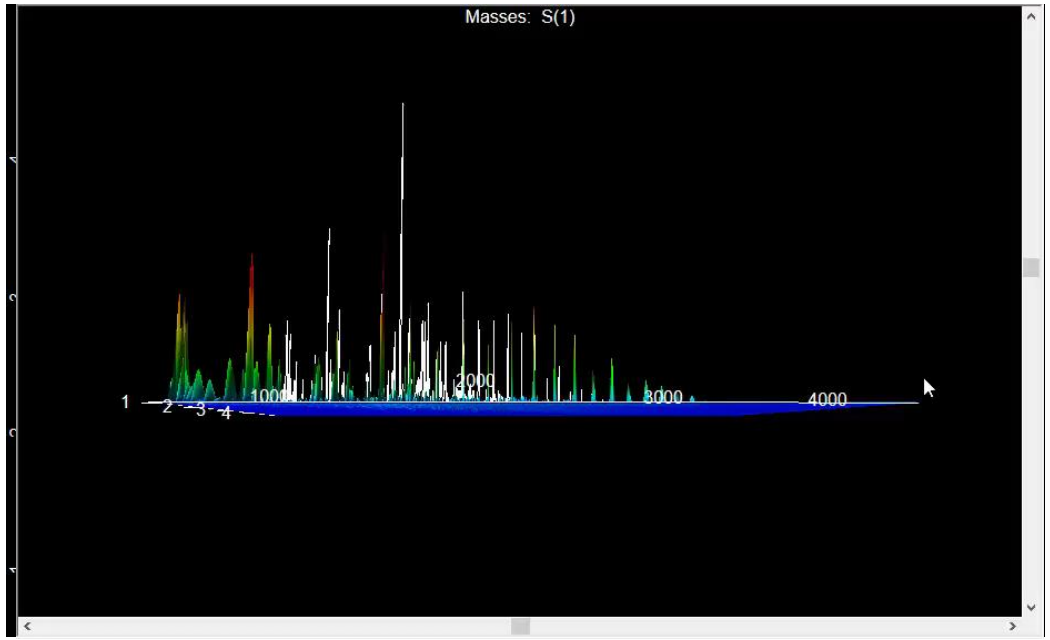
- Simultaneous qualitative and quantitative information!

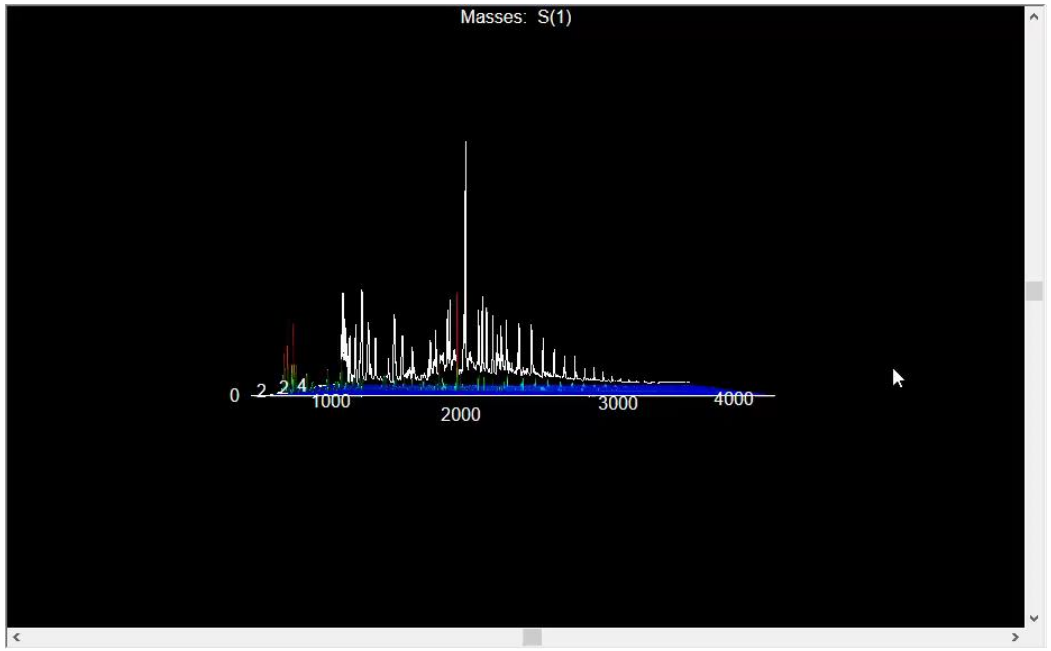


GCxGC Options

Choosing a GCxGC column set…

Column phase selectivity influences the pattern of the GCxGC structured chromatogram





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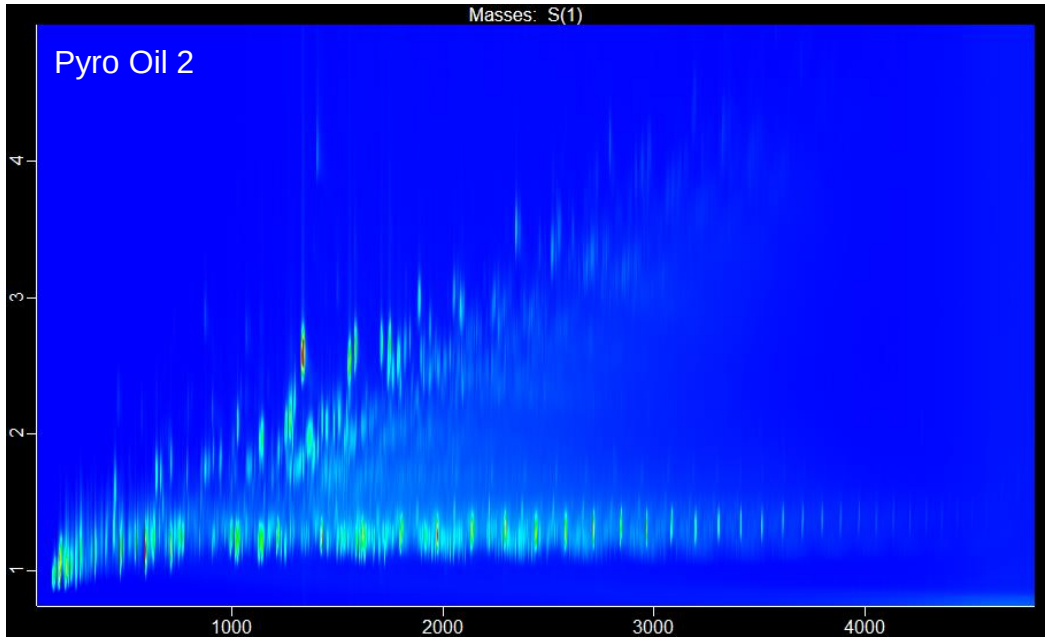
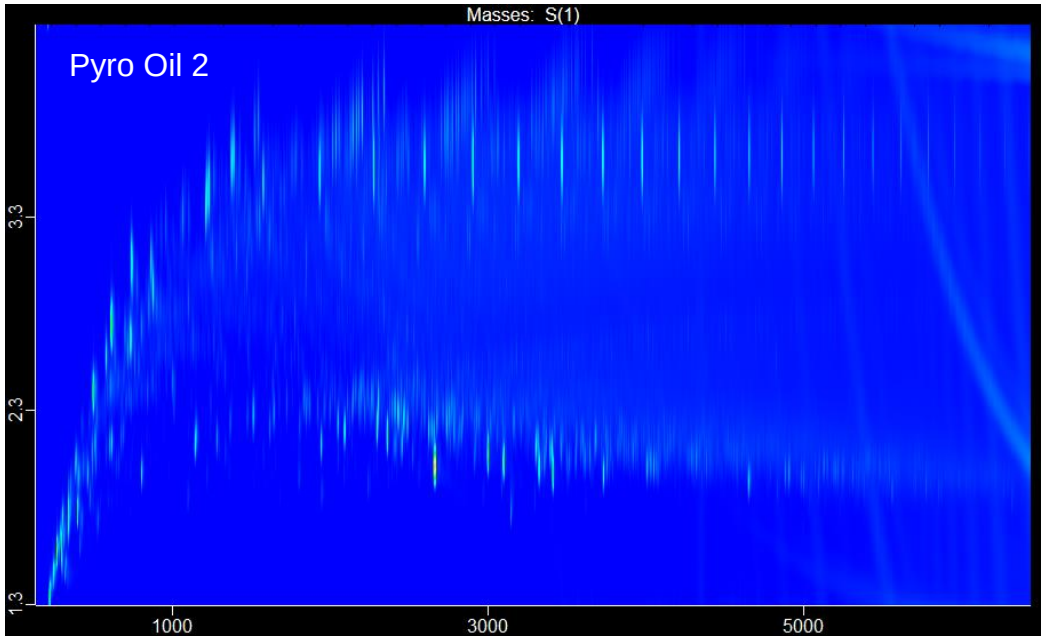


"Normal" phase: nonpolar-polar
Primary Column: Rxi-1MS 20 m x 0.18 mm x 0.18 um
Secondary Column: Rxi-17SilMS 3.35 m x 0.25 mm x 0.25 um

- Better separation of polycyclic aromatics region
- Clear bands based on ring # and clusters by C#

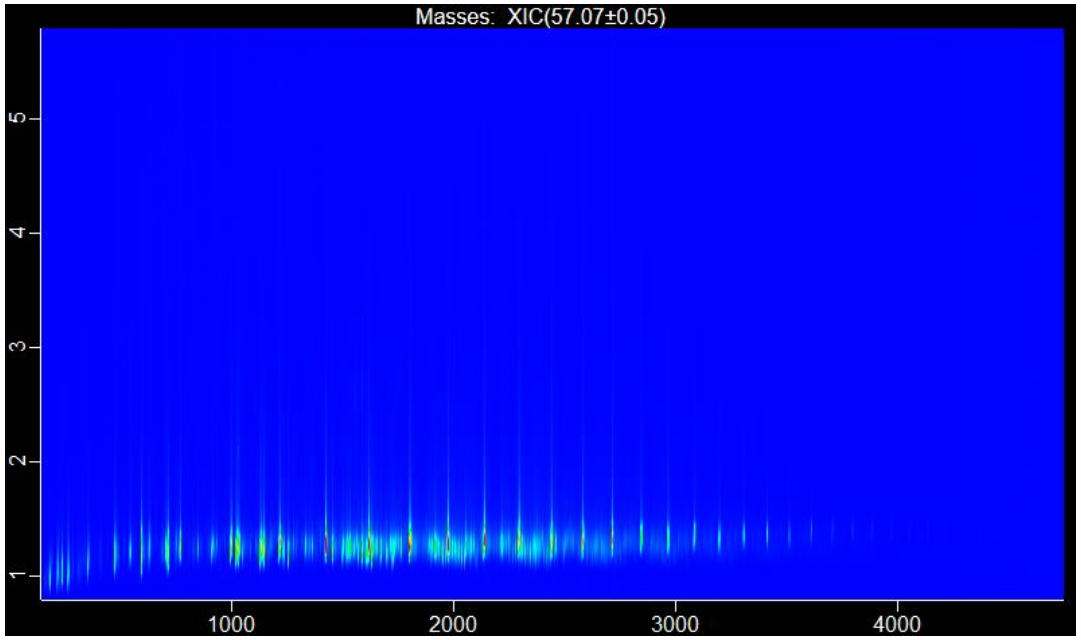


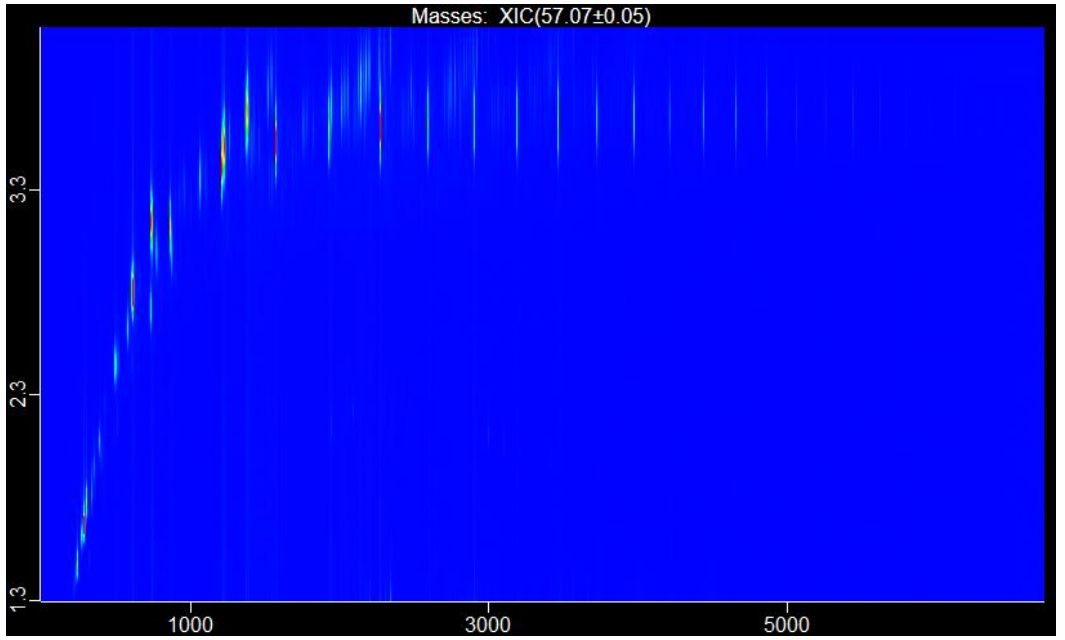
"Reverse" phase: polar-nonpolar
Primary Column: DB-17 20 m x 0.18 mm x 0.30 um
Secondary Column: DB-5 3.65 m x 0.25 mm x 0.25 um

- Better separation of paraffinic region
- Pulls aromatics away from naphthenes

GCxGC Options

Mapping out the GCxGC Space



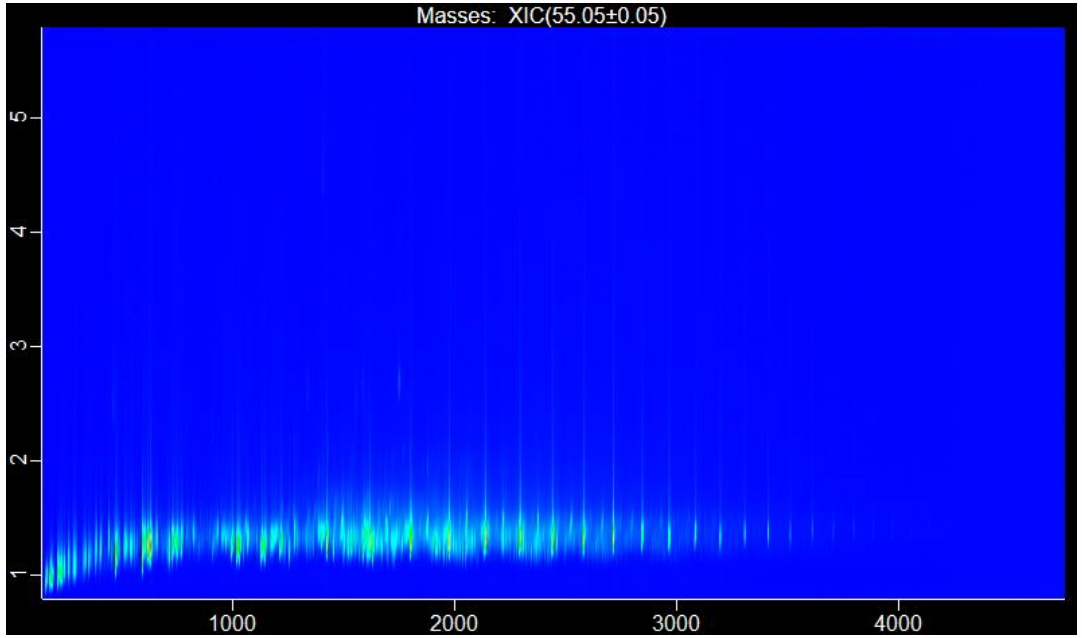


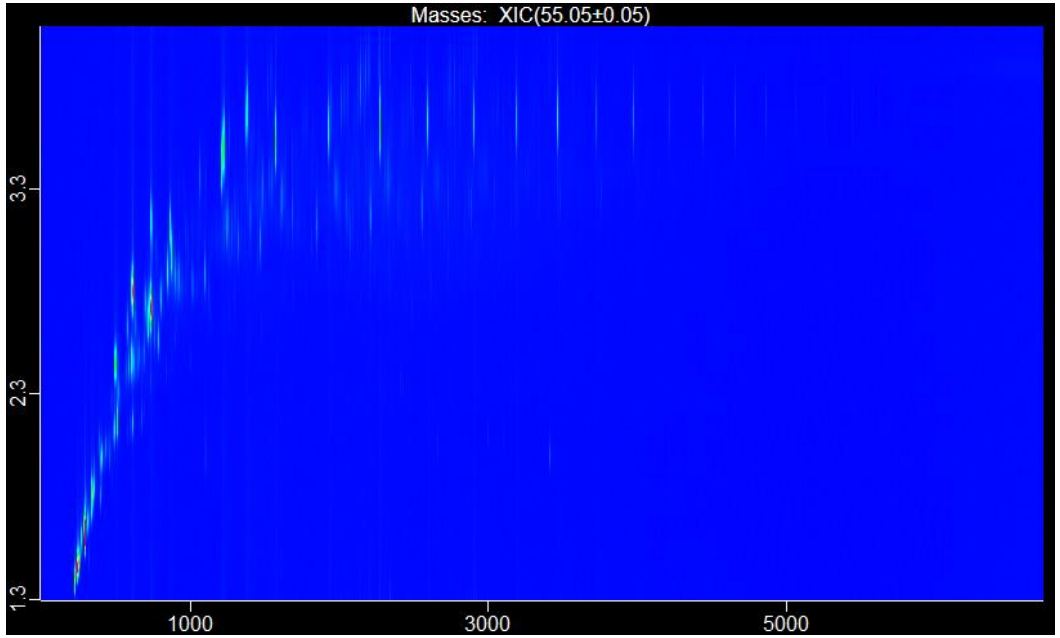
alkanes

Using characteristic masses from the mass spectrometer makes it easy to lay out the structured chromatogram

GCxGC Options

Mapping out the GCxGC Space





alkenes/cycloparaffins

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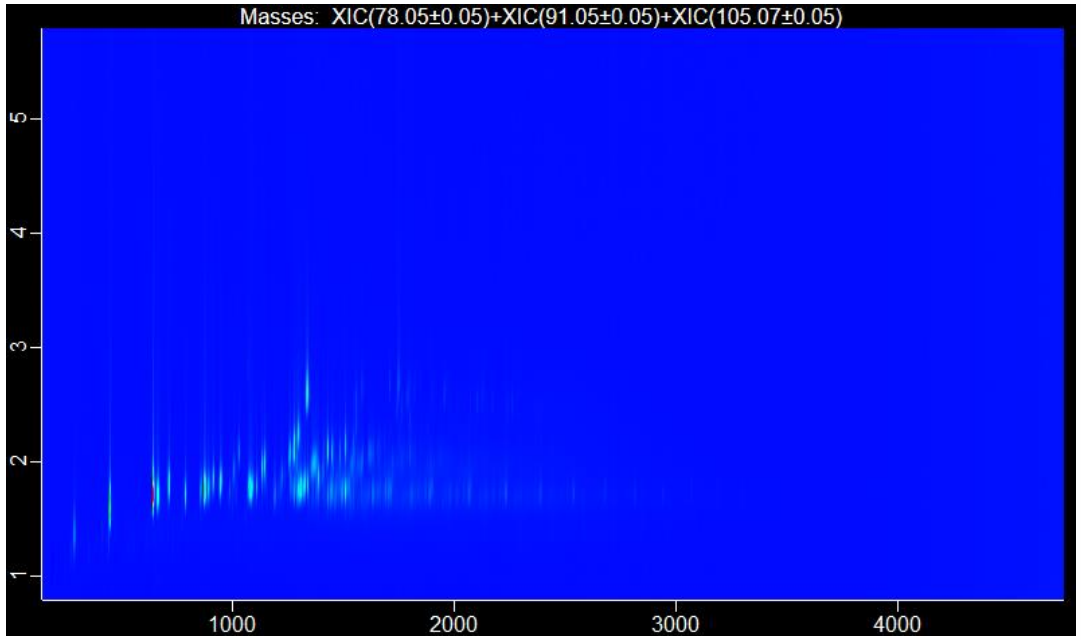
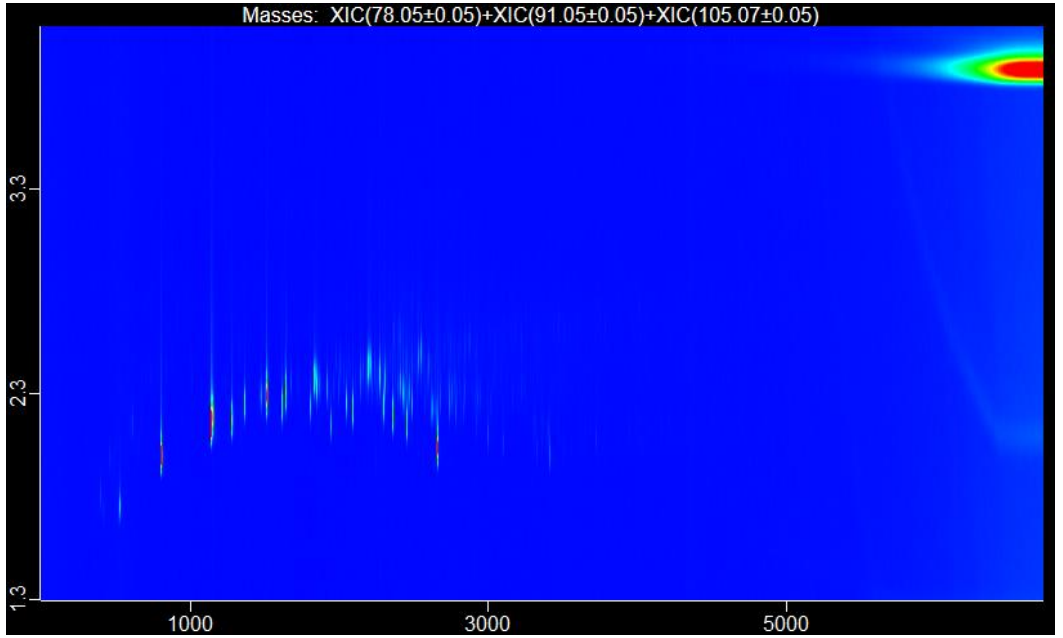
GCxGC Options

Mapping out the GCxGC Space





monocyclic aromatics

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GCxGC Options

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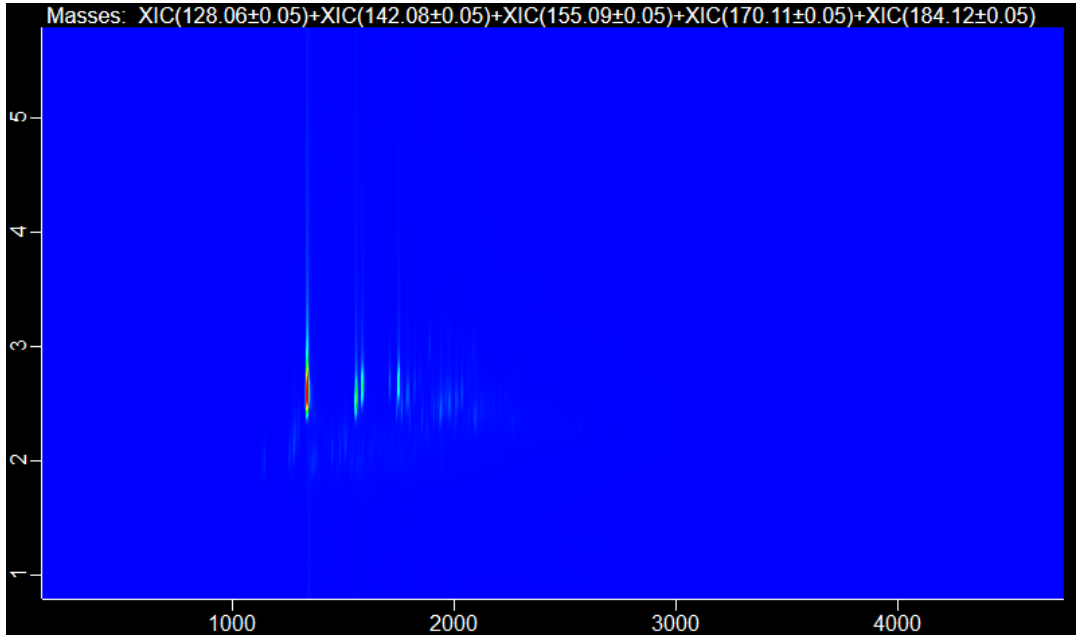

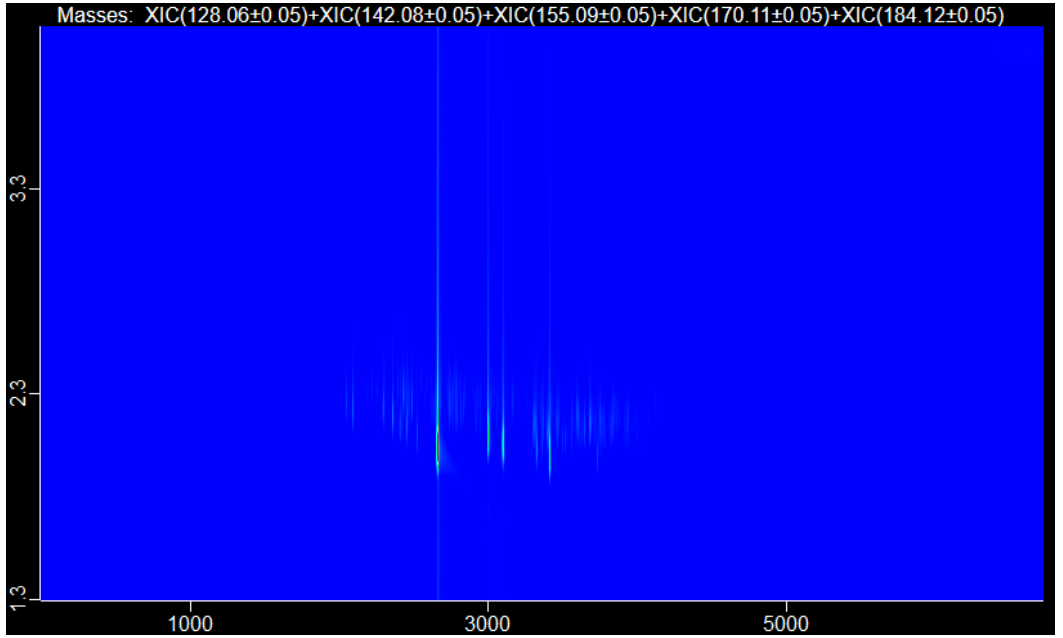

dicyclic aromatics

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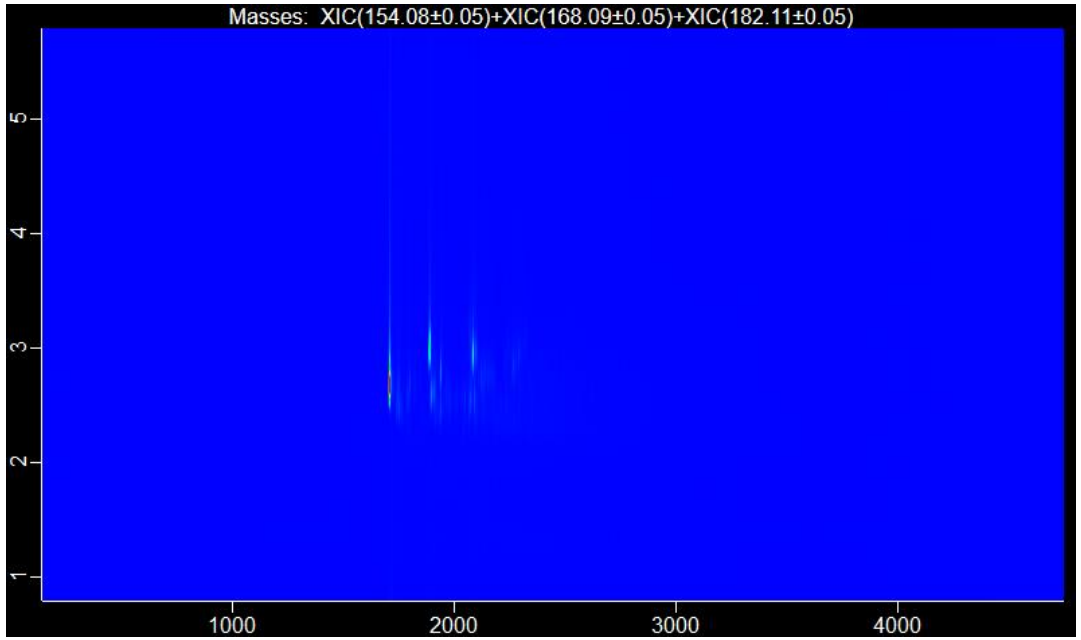
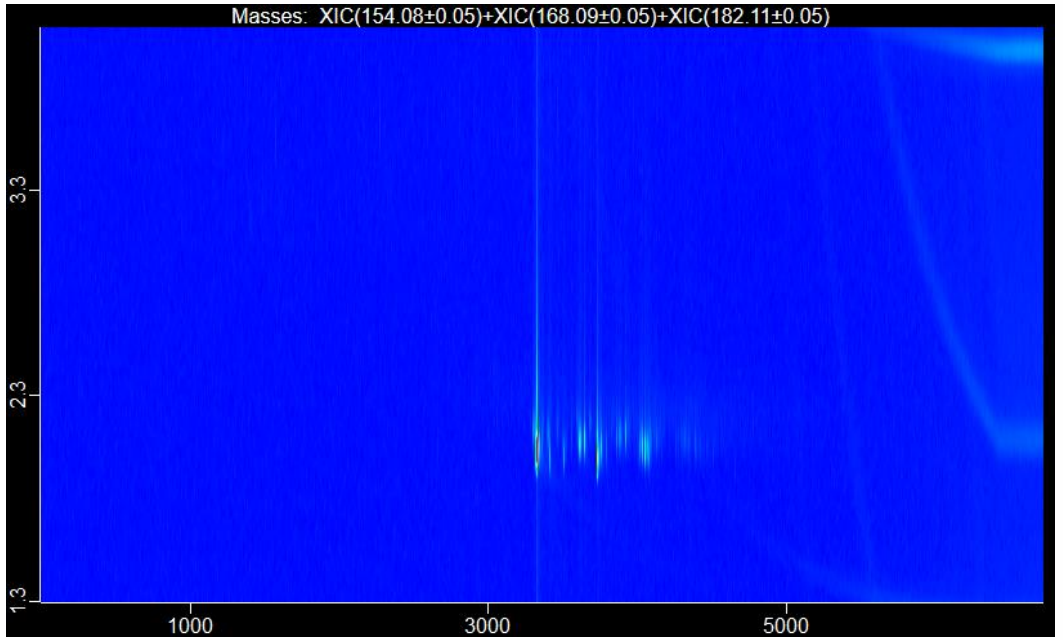
GCxGC Options

Mapping out the GCxGC Space





2.5-ring aromatics

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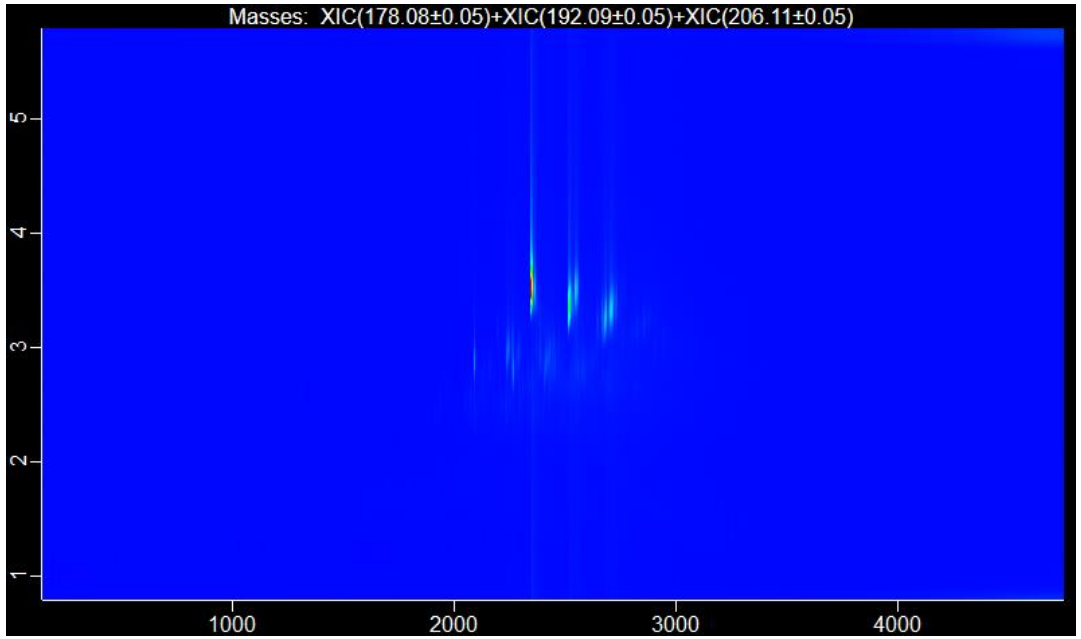

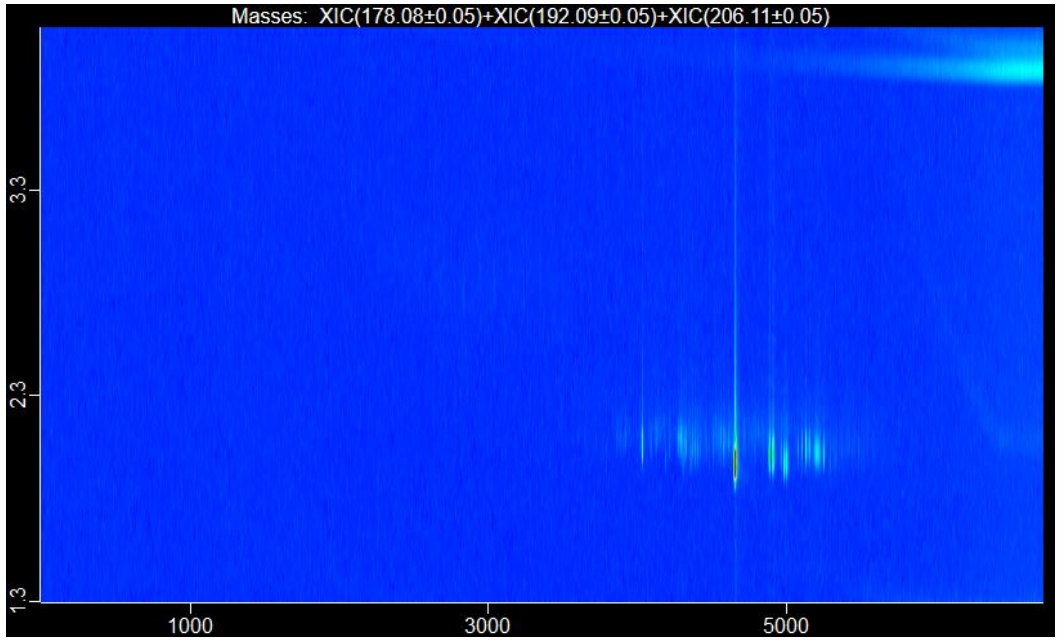

tricyclic aromatics

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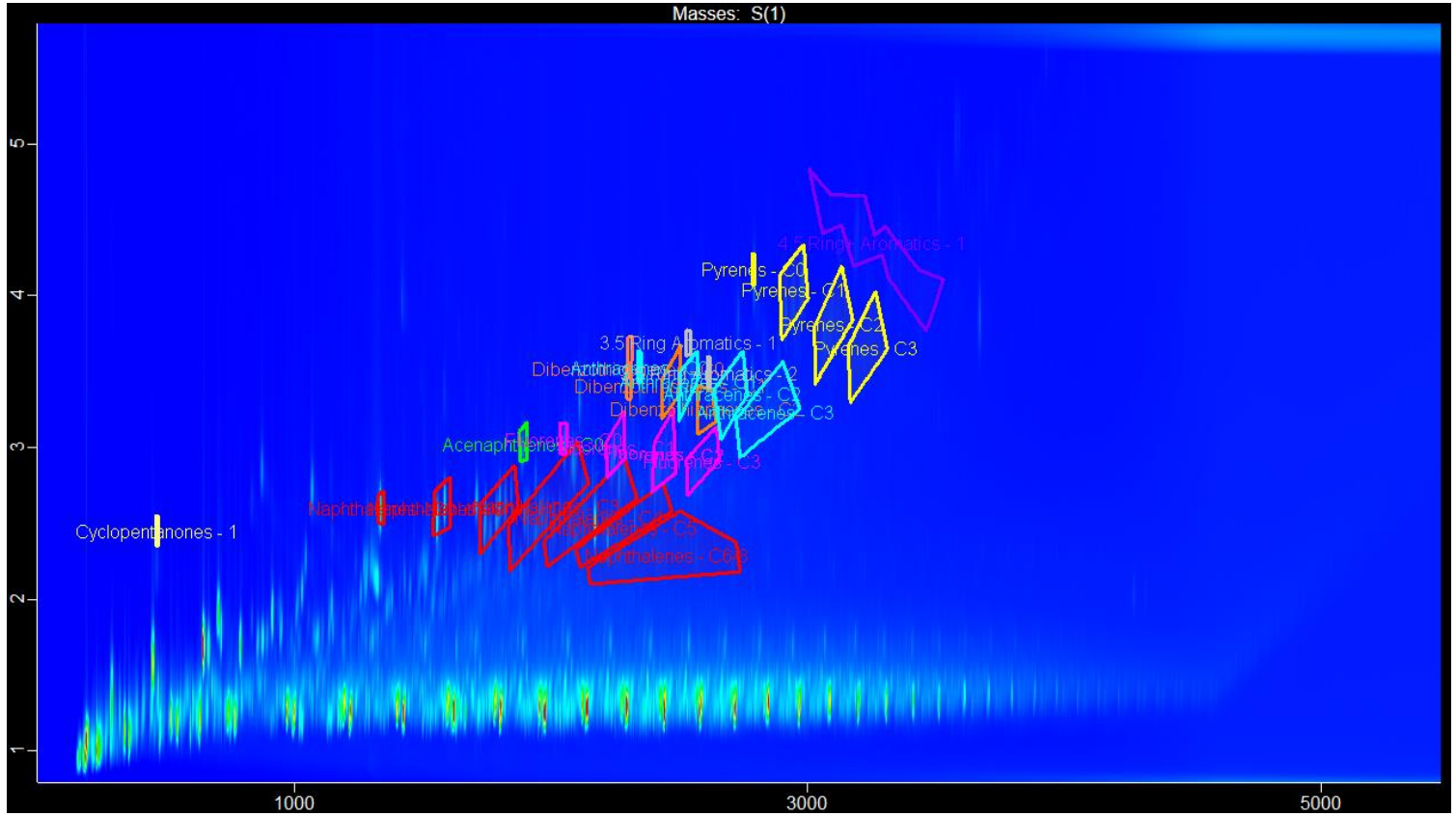
Group-Type Analysis

Group-Type Analysis of Pyrolysis Oils

Classification Regions are drawn around compounds of interest

Area% values from FID are used for the classified regions



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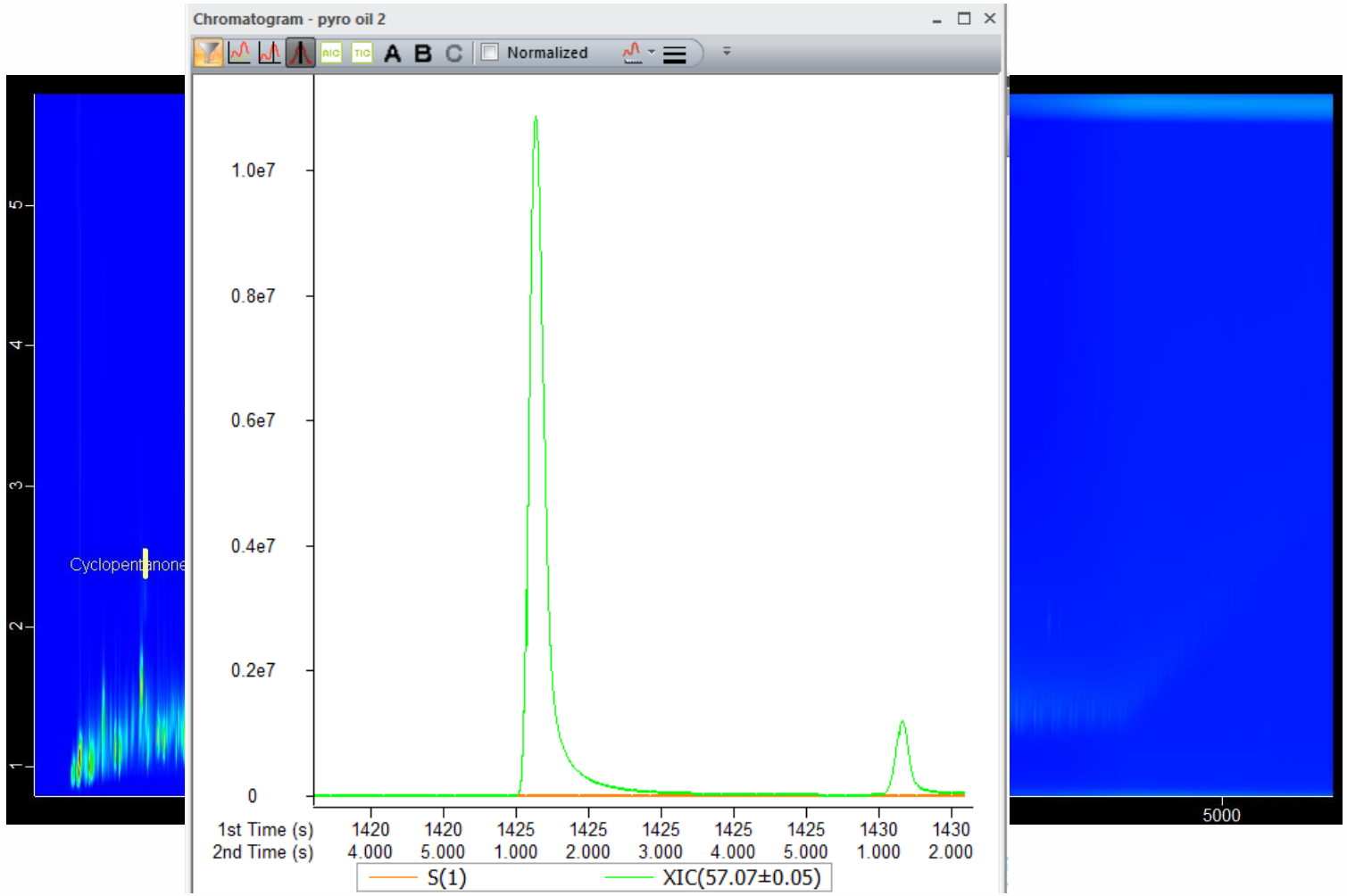
This is possible because of novel alignment algorithm!



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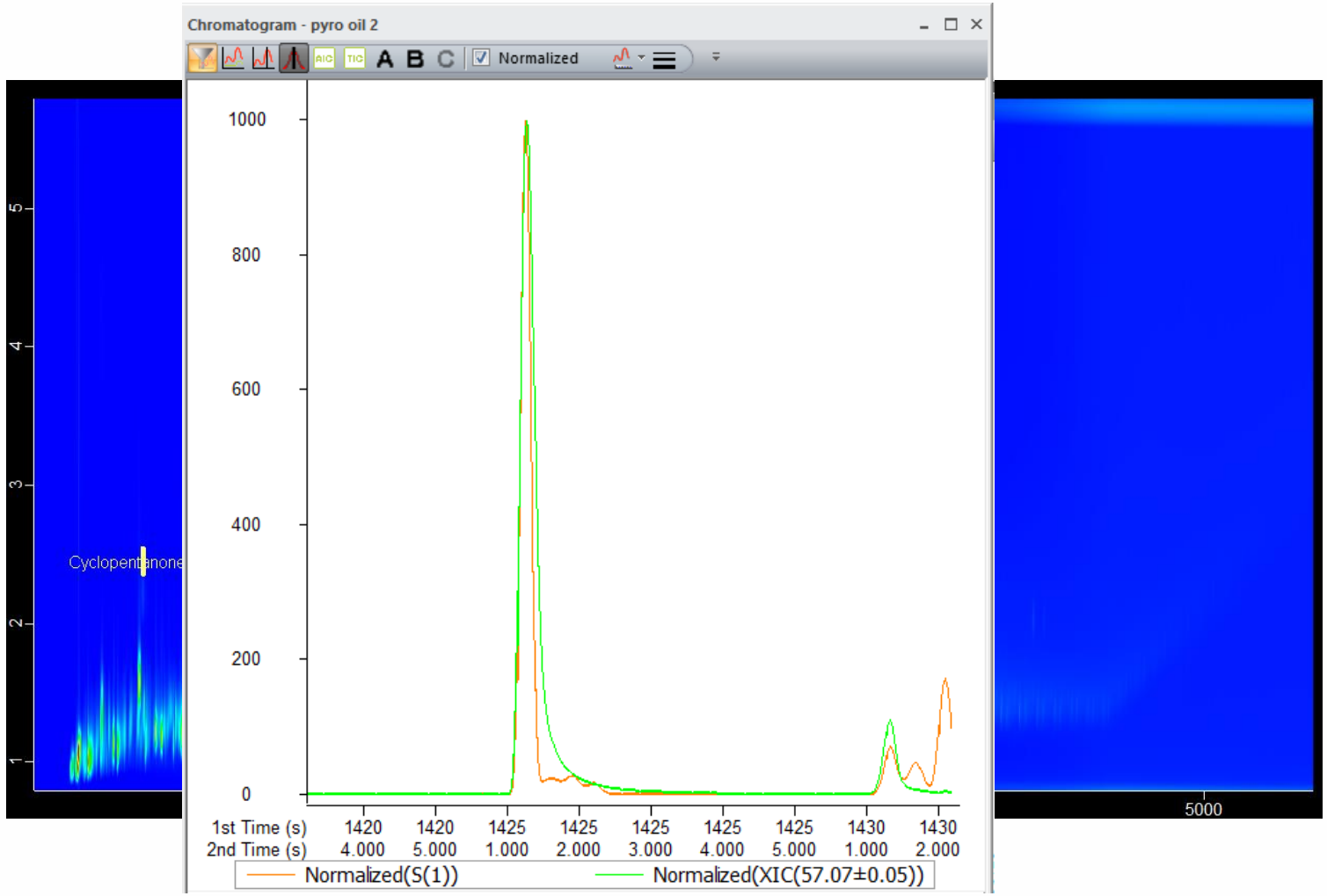

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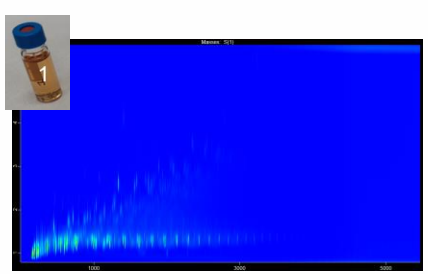
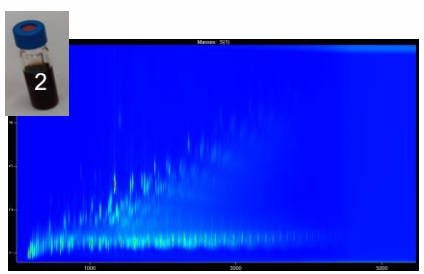
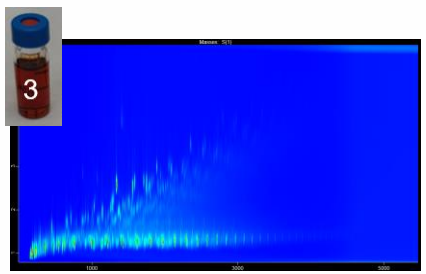
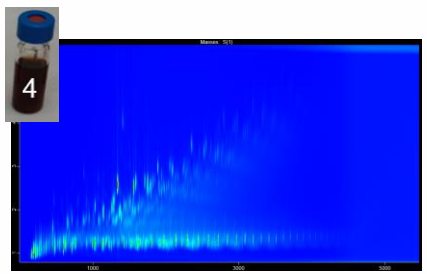
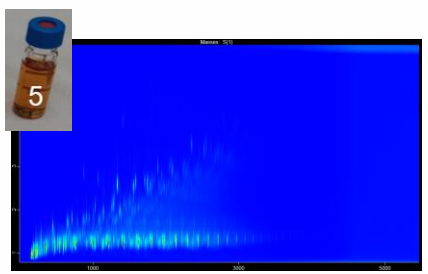
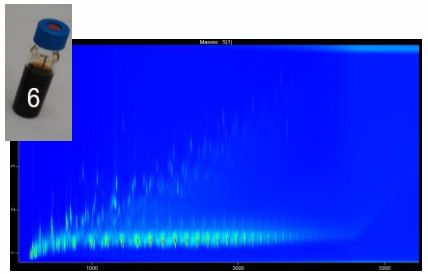


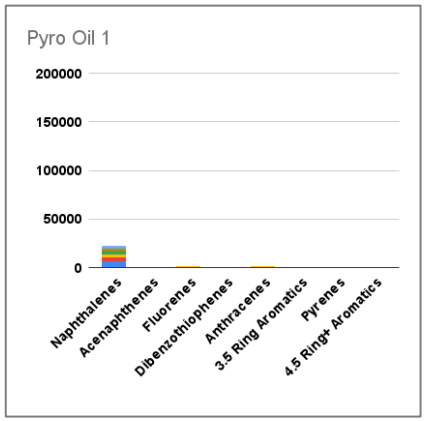


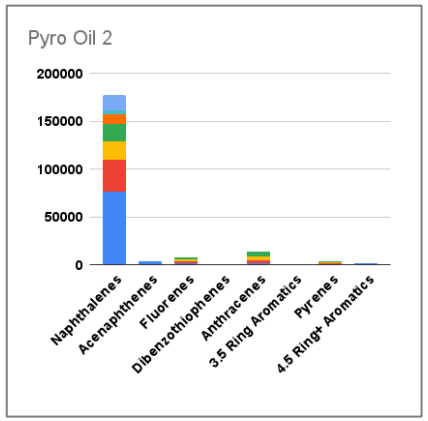


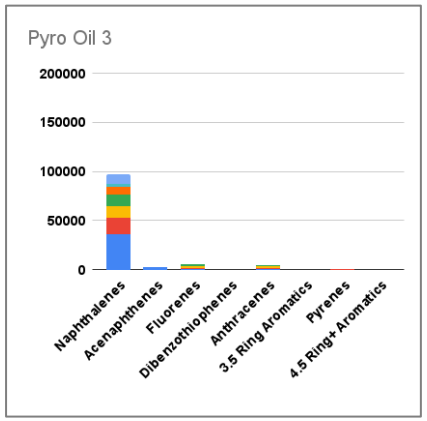


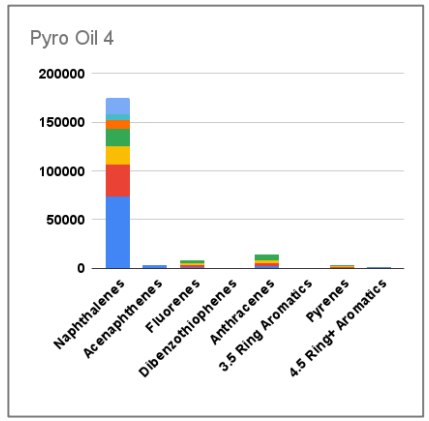


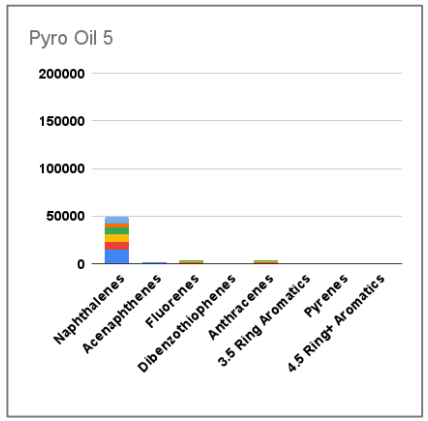


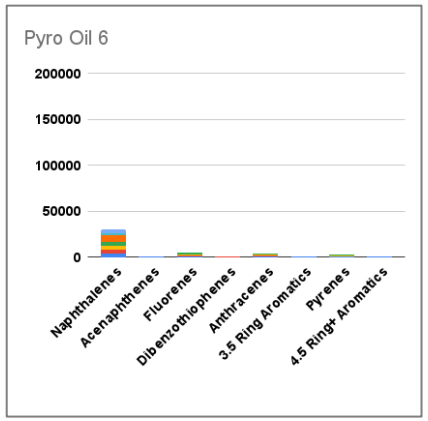








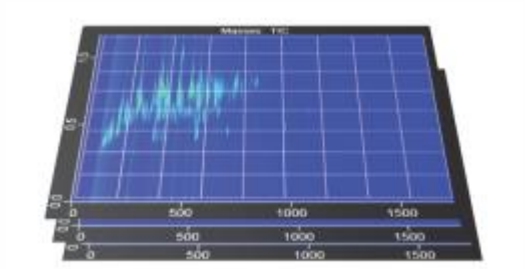




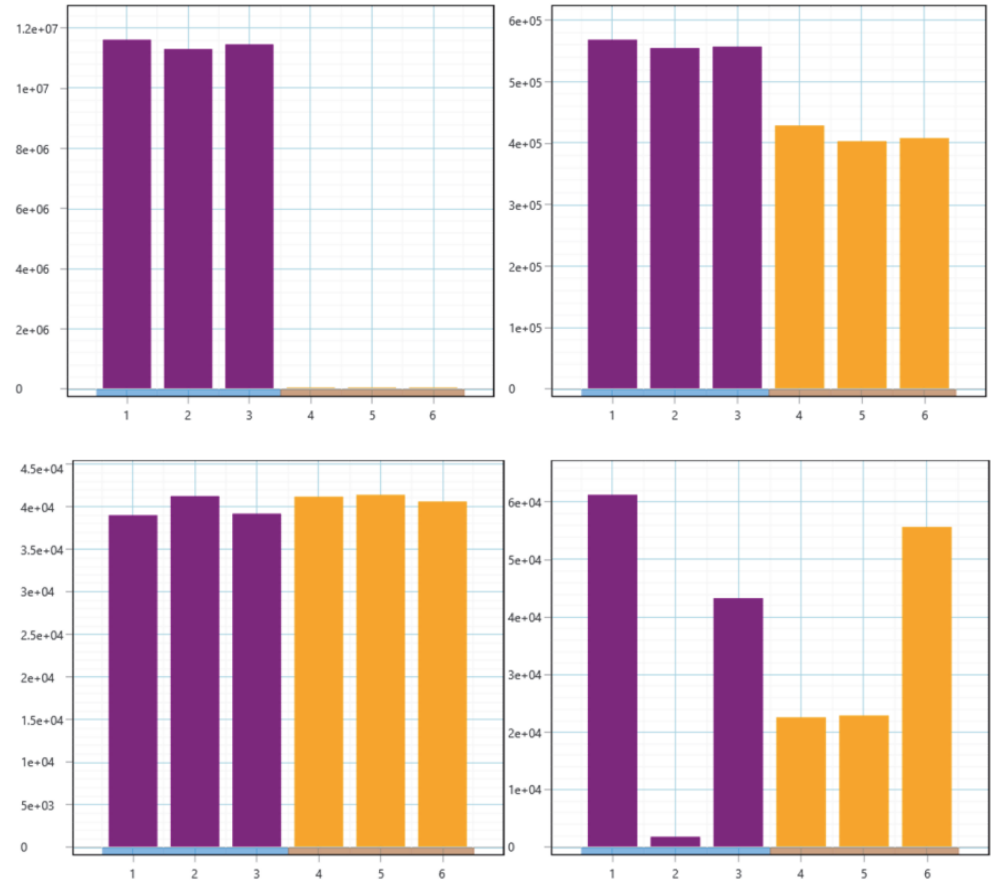
Tile-Based Statistics

ChromaTOF TILE

ChromaTOF TILE uses statistical differences in GCxGC samples to highlight differences

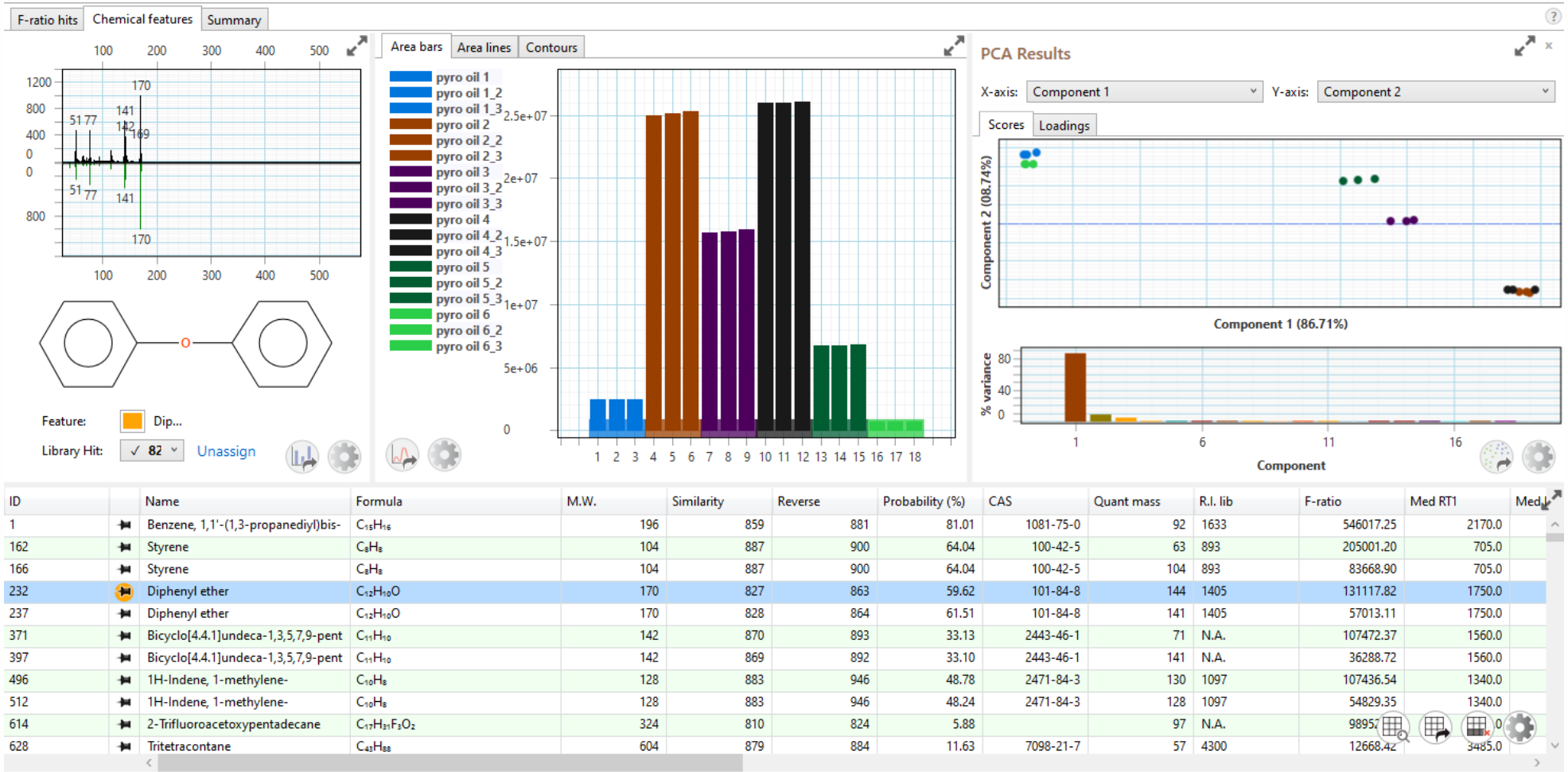


$$Fisher\ Ratio = \frac{\sigma 2_{cl}}{\sigma 2_{err}} = \frac{class\ to\ class\ variation}{within\ class\ variation}$$



Tile-Based Statistics

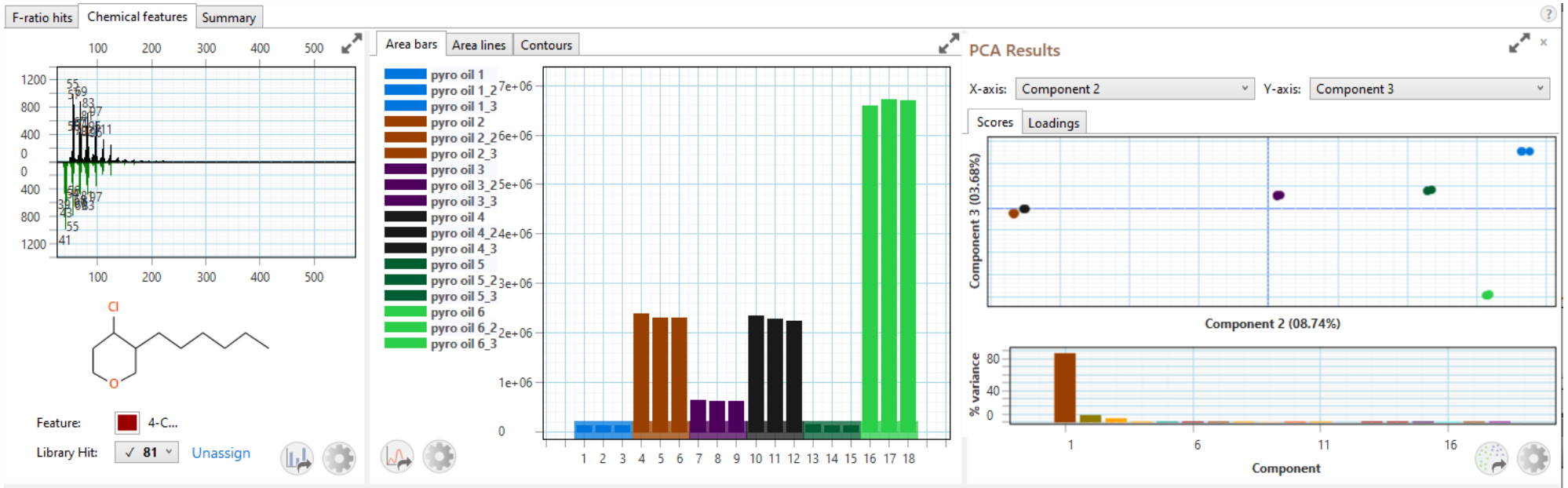
Areas of Interest + PCA



ID		Name	Formula	M.W.	Similarity	Reverse	Probability (%)	CAS	Quant mass	R.I. lib	F-ratio	Med RT1	Med
1		Benzene, 1,1'-(1,3-propanediyl)bis-	$C_{15}H_{16}$	196	859	881	81.01	1081-75-0	92	1633	546017.25	2170.0	
162		Styrene	C_8H_8	104	887	900	64.04	100-42-5	63	893	205001.20	705.0	
166		Styrene	C_8H_8	104	887	900	64.04	100-42-5	104	893	83668.90	705.0	
232		Diphenyl ether	$C_{12}H_{10}O$	170	827	863	59.62	101-84-8	144	1405	131117.82	1750.0	
237		Diphenyl ether	$C_{12}H_{10}O$	170	828	864	61.51	101-84-8	141	1405	57013.11	1750.0	
371		Bicyclo[4.4.1]undeca-1,3,5,7,9-pent	$C_{11}H_{10}$	142	870	893	33.13	2443-46-1	71	N.A.	107472.37	1560.0	
397		Bicyclo[4.4.1]undeca-1,3,5,7,9-pent	$C_{11}H_{10}$	142	869	892	33.10	2443-46-1	141	N.A.	36288.72	1560.0	
496		1H-Indene, 1-methylene-	$C_{10}H_8$	128	883	946	48.78	2471-84-3	130	1097	107436.54	1340.0	
512		1H-Indene, 1-methylene-	$C_{10}H_8$	128	883	946	48.24	2471-84-3	128	1097	54829.35	1340.0	
614		2-Trifluoroacetoxypentadecane	$C_{17}H_{31}F_3O_2$	324	810	824	5.88		97	N.A.	98957	0	
628		Tritetracontane	$C_{43}H_{88}$	604	879	884	11.63	7098-21-7	57	4300	12668.42	3485.0	

Tile-Based Statistics

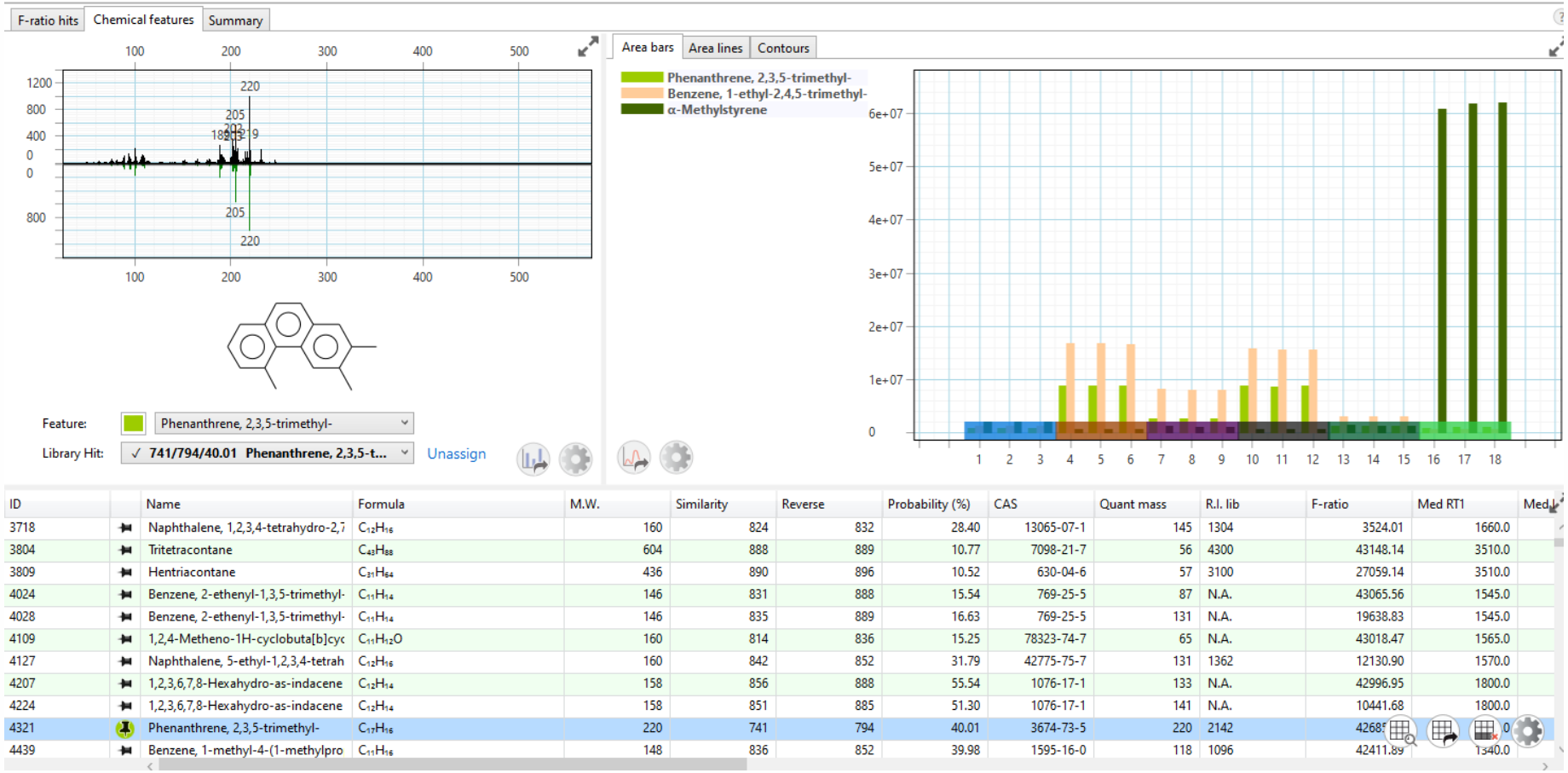
Areas of Interest + PCA



ID		Name	Formula	M.W.	Similarity	Reverse	Probability (%)	CAS	Quant mass	R.I. lib	F-ratio	Med RT1	Med
25359		Megastigma-4,6(Z),8(Z)-triene	$C_{13}H_{20}$	176	786	843	7.99	71186-25-9	119	1288	6213.55	1665.0	
25440		Feature 25440							155	N.A.	10467.27	2065.0	
25556		Naphthalene, 5-ethyl-1,2,3,4-tetrah	$C_{12}H_{16}$	160	783	818	21.05	42775-75-7	133	1362	18860.43	1625.0	
25583		4-Chloro-3-n-hexyltetrahydropyrar	$C_{11}H_{21}ClO$	204	814	851	5.58	66555-66-6	95	N.A.	5638.38	3520.0	
25670		1-Phenyl-2-propanol	$C_9H_{12}O$	136	853	919	35.28		92	N.A.	9241.57	1630.0	
25752		4a,10a-Methanophenanthren-9β-o	$C_{15}H_{17}BrO$	292	790	792	62.68		169	N.A.	3938.90	2345.0	
25853		5,8,11-Eicosatriynoic acid, methyl e	$C_{21}H_{30}O_2$	314	755	756	22.64		143	2465	18776.22	1930.0	
25876		1-Pentacontanol	$C_{50}H_{102}O$	718	856	881	10.00	40710-43-8	55	N.A.	13681.65	3765.0	
25981		1-Oxaspiro[2.5]octane, 5,5-dimethy	$C_{14}H_{22}O$	206	789	794	6.23		105	N.A.	9528.06	1800.0	
26047		1-Pentacontanol	$C_{50}H_{102}O$	718	879	902	14.15	40710-43-8	55	N.A.	535	0	
26119		Naphthalene, 1,2,3,4-tetrahydro-1,5	$C_{14}H_{18}$	174	789	805	17.91	21693-55-0	159	1250	14036.65	1890.0	

Tile-Based Statistics

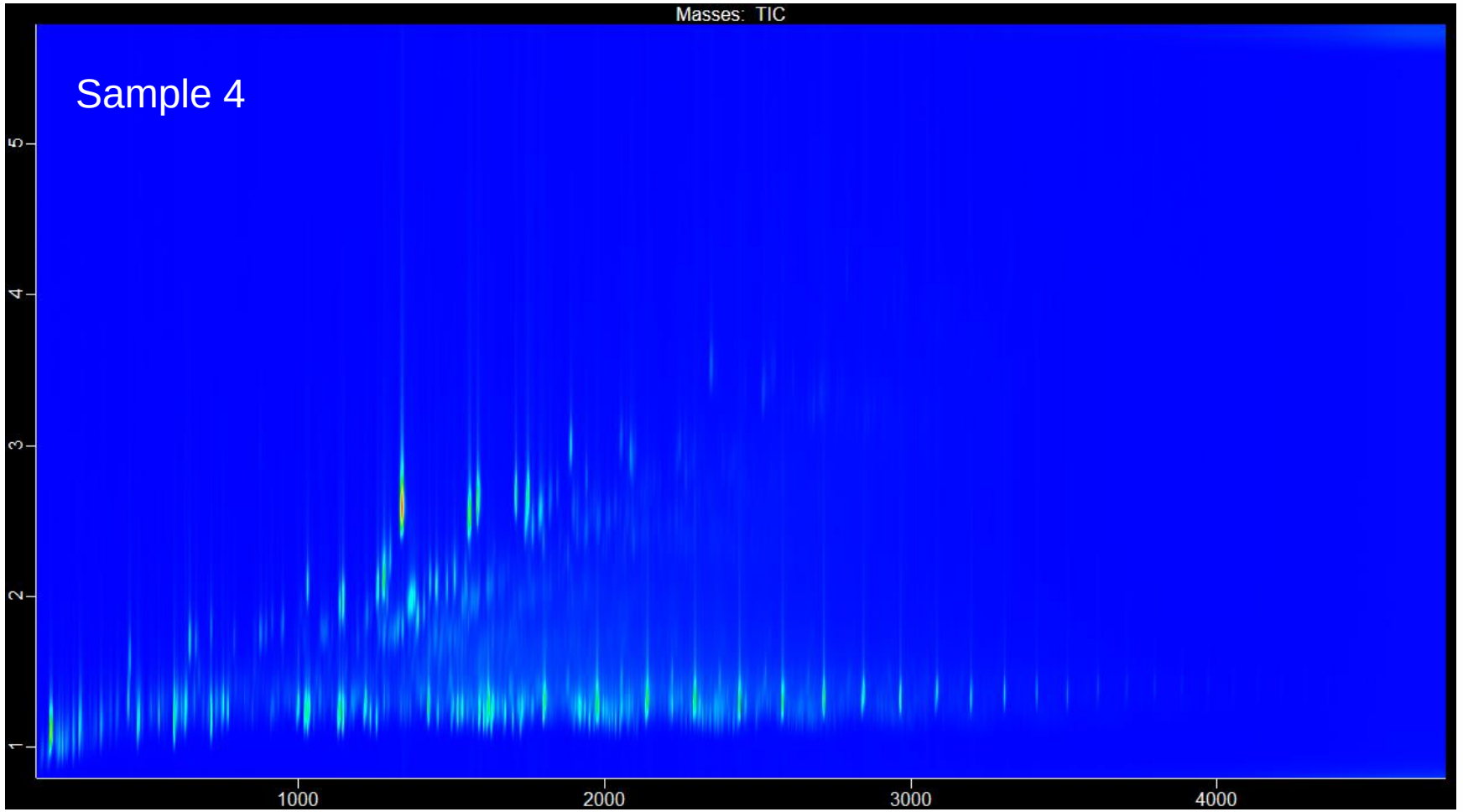
Comparing Trends of Multiple Features



ID	Name	Formula	M.W.	Similarity	Reverse	Probability (%)	CAS	Quant mass	R.I. lib	F-ratio	Med RT1	Med
3718	Naphthalene, 1,2,3,4-tetrahydro-2,7	$C_{12}H_{16}$	160	824	832	28.40	13065-07-1	145	1304	3524.01	1660.0	
3804	Tritetracontane	$C_{43}H_{88}$	604	888	889	10.77	7098-21-7	56	4300	43148.14	3510.0	
3809	Hentriacontane	$C_{31}H_{64}$	436	890	896	10.52	630-04-6	57	3100	27059.14	3510.0	
4024	Benzene, 2-ethenyl-1,3,5-trimethyl-	$C_{11}H_{14}$	146	831	888	15.54	769-25-5	87	N.A.	43065.56	1545.0	
4028	Benzene, 2-ethenyl-1,3,5-trimethyl-	$C_{11}H_{14}$	146	835	889	16.63	769-25-5	131	N.A.	19638.83	1545.0	
4109	1,2,4-Metheno-1H-cyclobuta[b]cyc	$C_{11}H_{12}O$	160	814	836	15.25	78323-74-7	65	N.A.	43018.47	1565.0	
4127	Naphthalene, 5-ethyl-1,2,3,4-tetrah	$C_{12}H_{16}$	160	842	852	31.79	42775-75-7	131	1362	12130.90	1570.0	
4207	1,2,3,6,7,8-Hexahydro-as-indacene	$C_{12}H_{14}$	158	856	888	55.54	1076-17-1	133	N.A.	42996.95	1800.0	
4224	1,2,3,6,7,8-Hexahydro-as-indacene	$C_{12}H_{14}$	158	851	885	51.30	1076-17-1	141	N.A.	10441.68	1800.0	
4321	Phenanthrene, 2,3,5-trimethyl-	$C_{17}H_{16}$	220	741	794	40.01	3674-73-5	220	2142	4268	0	
4439	Benzene, 1-methyl-4-(1-methylpro	$C_{11}H_{16}$	148	836	852	39.98	1595-16-0	118	1096	42411.89	1340.0	

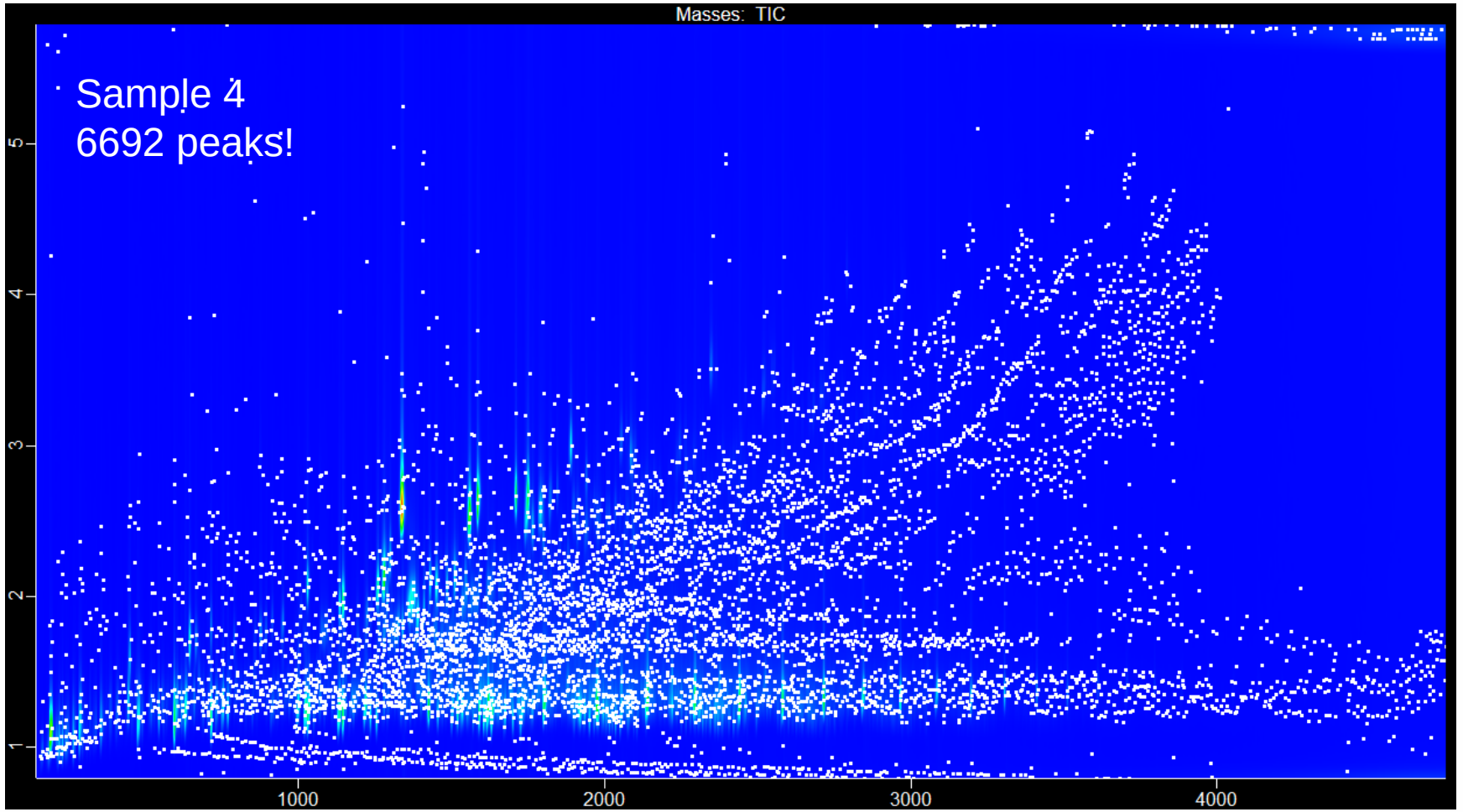
Heteroatomic Species Identification

Group-Type Analysis of Pyrolysis Oils



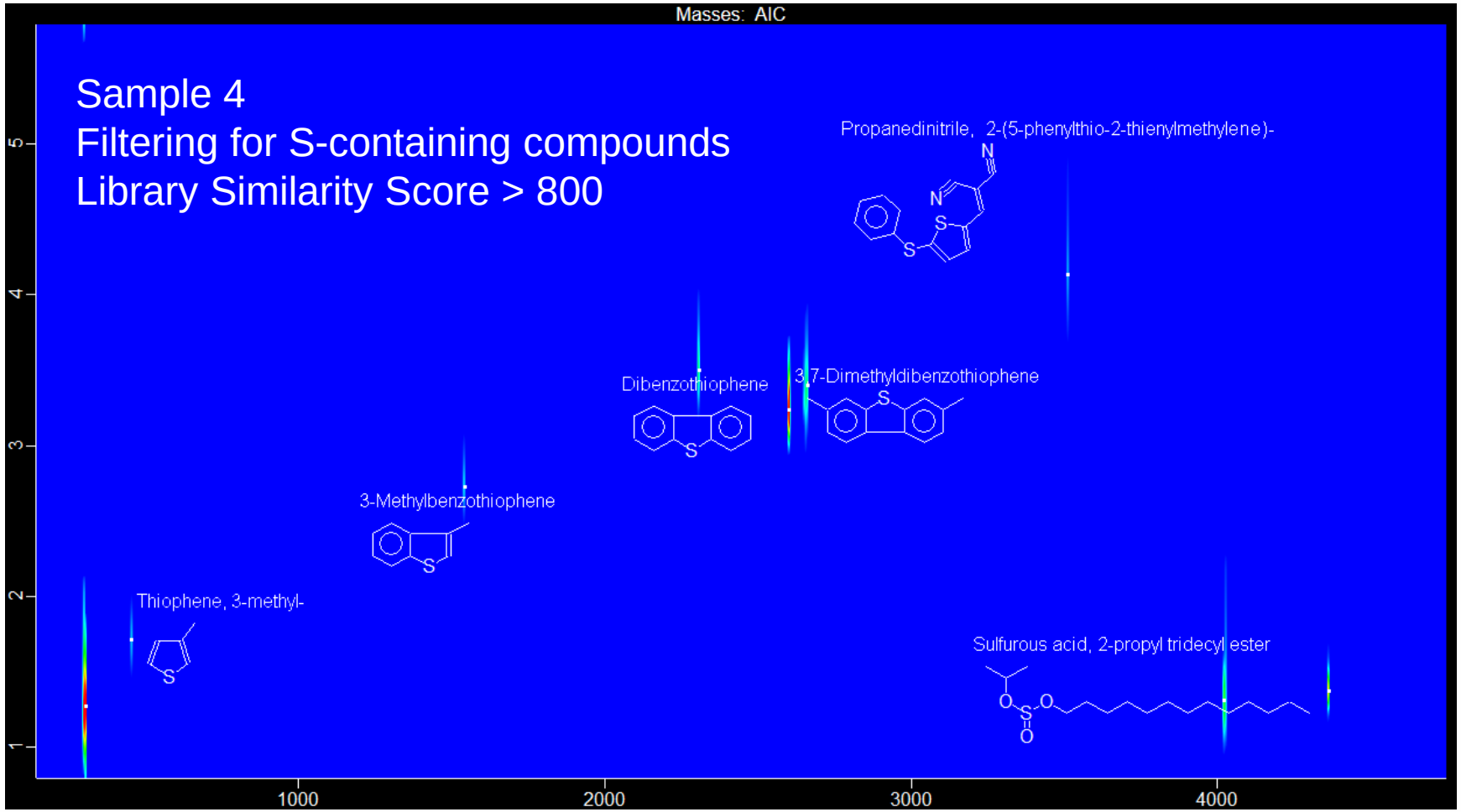
Heteroatomic Species Identification

Group-Type Analysis of Pyrolysis Oils



Heteroatomic Species Identification

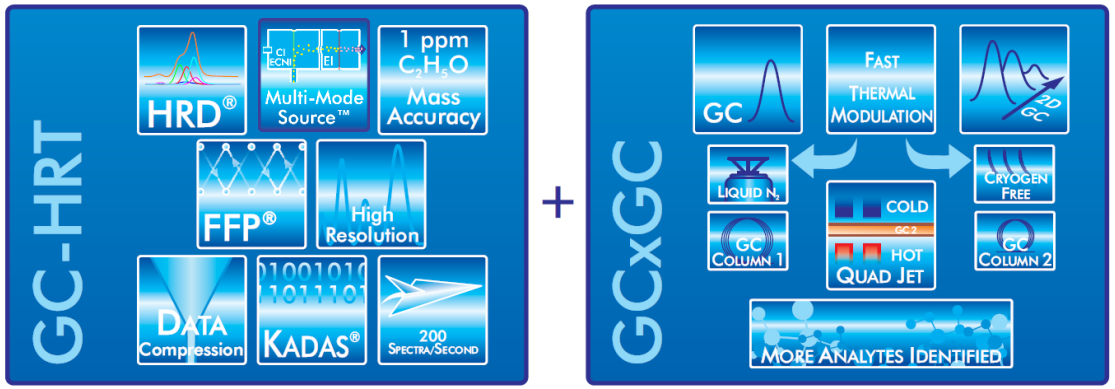
Group-Type Analysis of Pyrolysis Oils



GCxGC Options

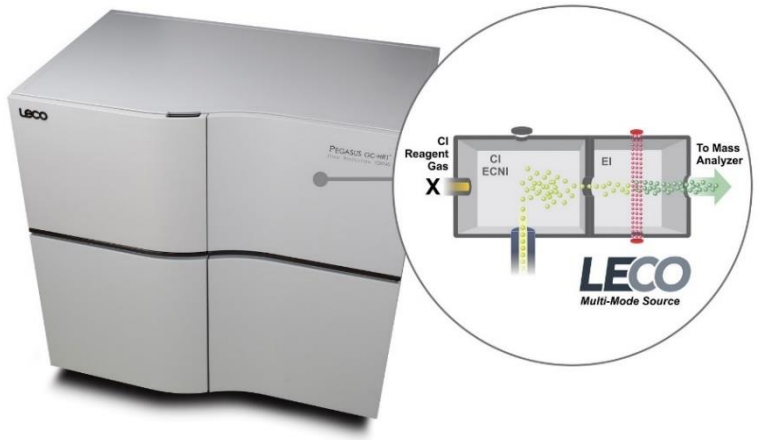
Benefits of the Pegasus HRT+ 4D

- High-resolution spectra
- Confident ID of compounds using complementary EI, PCI, and ECNI
- Unique Encoded Frequent Pushing increases sensitivity along folded flight path
- Mass accuracies calibrate to low ppm
- Combined with GCxGC separation power



GCxGC Options

Benefits of the Multi-Mode Source (MMS)



No hardware change between EI, PCI, and ECNI acquisitions, makes it easy to correlate peak retention times between modes:

- EI (electron impact ionization) provides universal, reproducible fragmentation that matches NIST library spectra with high fidelity
- PCI (positive chemical ionization) provides softer ionization than EI, allowing selective formation of molecular ions and adducts that allow for identification of chemical formula for most hydrocarbon species
- ECNI (electron-capture negative ionization) provides exceptional sensitivity for electronegative species (compounds with halogens like F, Cl, I, Br)

1) Primary ion formation: $CH_4 + e^{\ominus} \rightarrow CH_4^{\oplus\bullet} + CH_3^{\oplus} + CH_2^{\oplus\bullet} + CH^{\oplus} + C^{\oplus\bullet} + H_2^{\oplus\bullet} + H^{\oplus}$

2) Reagent ion formation:
$CH_4^{\oplus\bullet} + CH_4 \rightarrow CH_5^{\oplus} + CH_3^{\bullet}$
$CH_3^{\oplus} + CH_4 \rightarrow C_2H_5^{\oplus} + H_2$
$CH_4 + C_2H_3^{\oplus} \rightarrow C_3H_5^{\oplus} + H_2$

3) Adduct Formation:
$M + CH_5^{\oplus} \rightarrow [MH]^{\oplus} + CH_4$
$M + C_2H_5^{\oplus} \rightarrow [M+C_2H_5]^{\oplus}$
$M + C_3H_5^{\oplus} \rightarrow [M+C_3H_5]^{\oplus}$
$AH + CH_5^{\oplus} \rightarrow A^{\oplus} + CH_4 + H_2$

Formation of Thermal Electrons ($*e^-$):
CH_4 (buffer gas)$+ e^- \rightarrow + CH_4^{+\bullet} + *e^- + e^-$
CH_4 (buffer gas)$+ e^- \rightarrow + CH_3^+ + H^\bullet + *e^- + e^-$

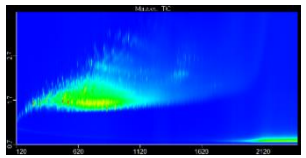
1) Associative Resonance Capture: $M + *e^- \rightarrow M^{-\bullet}$

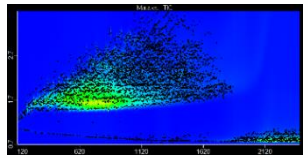
2) Dissociative Resonance Capture: $M\text{-}X + *e^- \rightarrow M^- + X^\bullet$

3) Ion-Pair Formation: $M\text{-}X + *e^- \rightarrow M^+ + X^- + e^-$

GCxGC Options

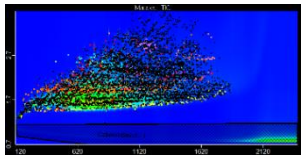
Pegasus HRT+ 4D Data Processing Workflows





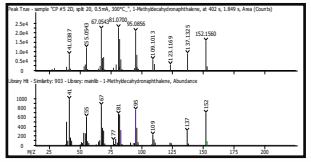
Acquire data

Peak Find with HRD®



Filter and Classify Peak(s)

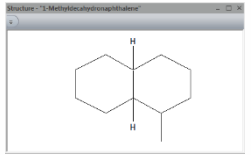
Library Search Peak True Spectra



Generate Peak Classification Summary

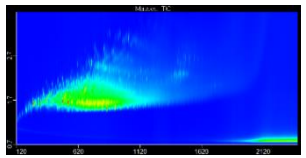
#	Class	Abundance (TIC)	Color
1*	Benzenes	7.308	
2	Cycloparaffins	9.661	
3	Paraffins	73.559	
4	Steranes	0.139	
5	Benzothiophenes	0.308	
6	Bicyclic	2.116	
7	Hopanes	0.547	
8	Diaromatics	1.131	
9	Monoaromatics	7.308	
10	Triaromatics	0.901	
11	Benzenes C1+C2	0.121	
12	Column Bleed	0.000	
	Unclassified	54.392	
	Total	100.000	

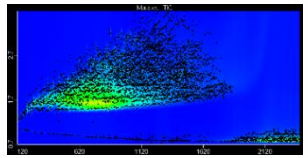
Identify Specific Peak



GCxGC Options

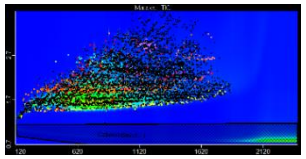
Pegasus HRT+ 4D Data Processing Workflows





Acquire data

Peak Find with HRD®



Filter and Classify Peak(s)

Library Search Peak True Spectra

Generate Peak Classification Summary

#	Class	Abundance (TIC)	Color
1*	Benzenes	7,308	
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	Unclassified	54,392	
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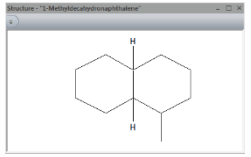
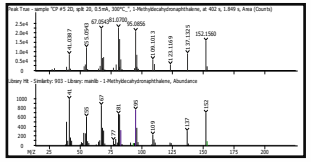
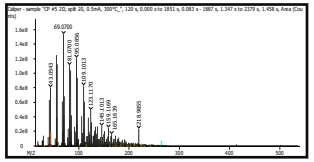
Identify Specific Peak

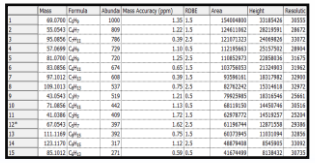




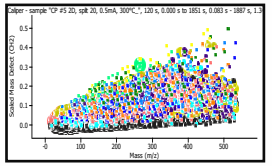
Create Composite Spectra



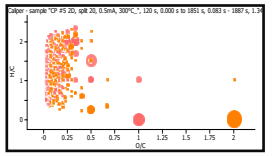
Calculate Mass Formula(e)



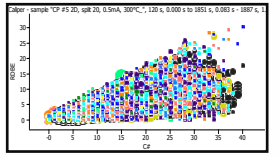
Generate Mass Defect Plot



Generate Van Krevelen Plot



Generate C# vs RDBE Plot

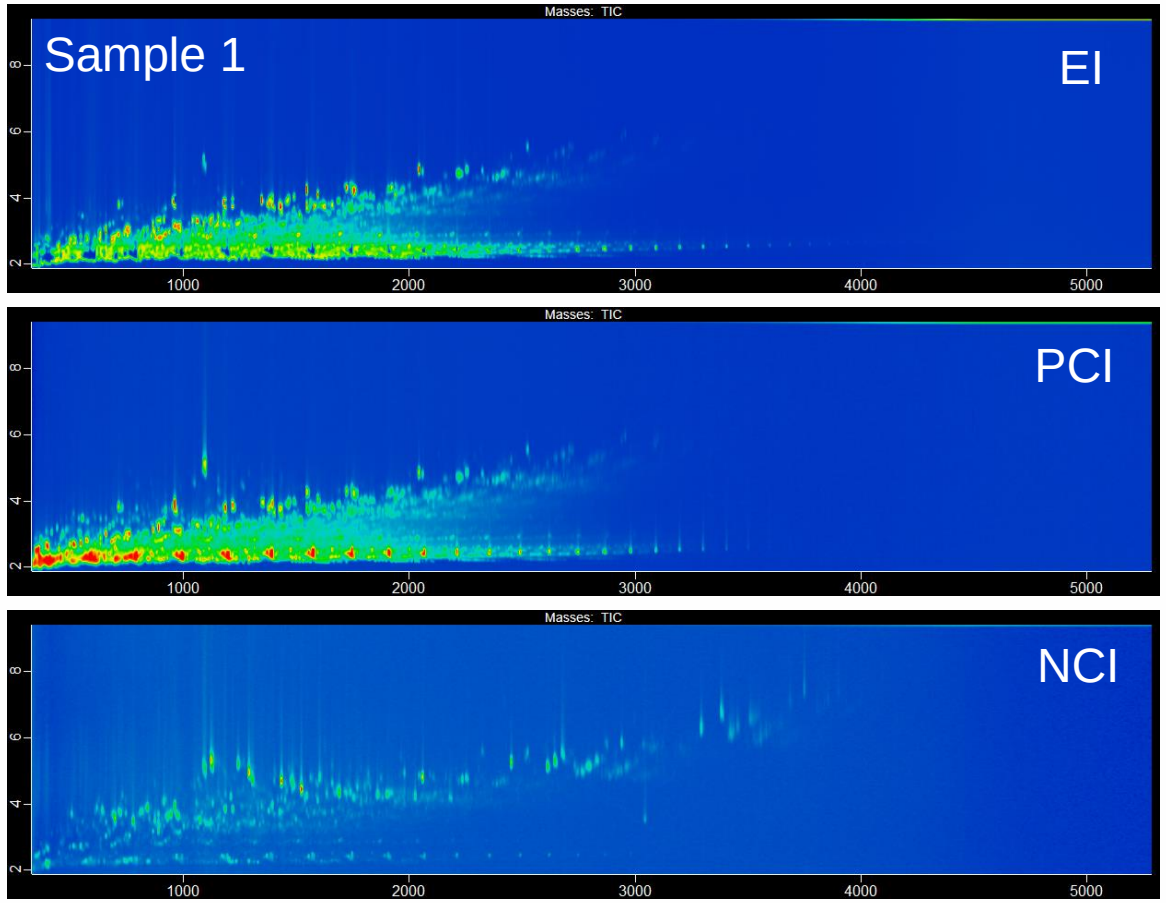


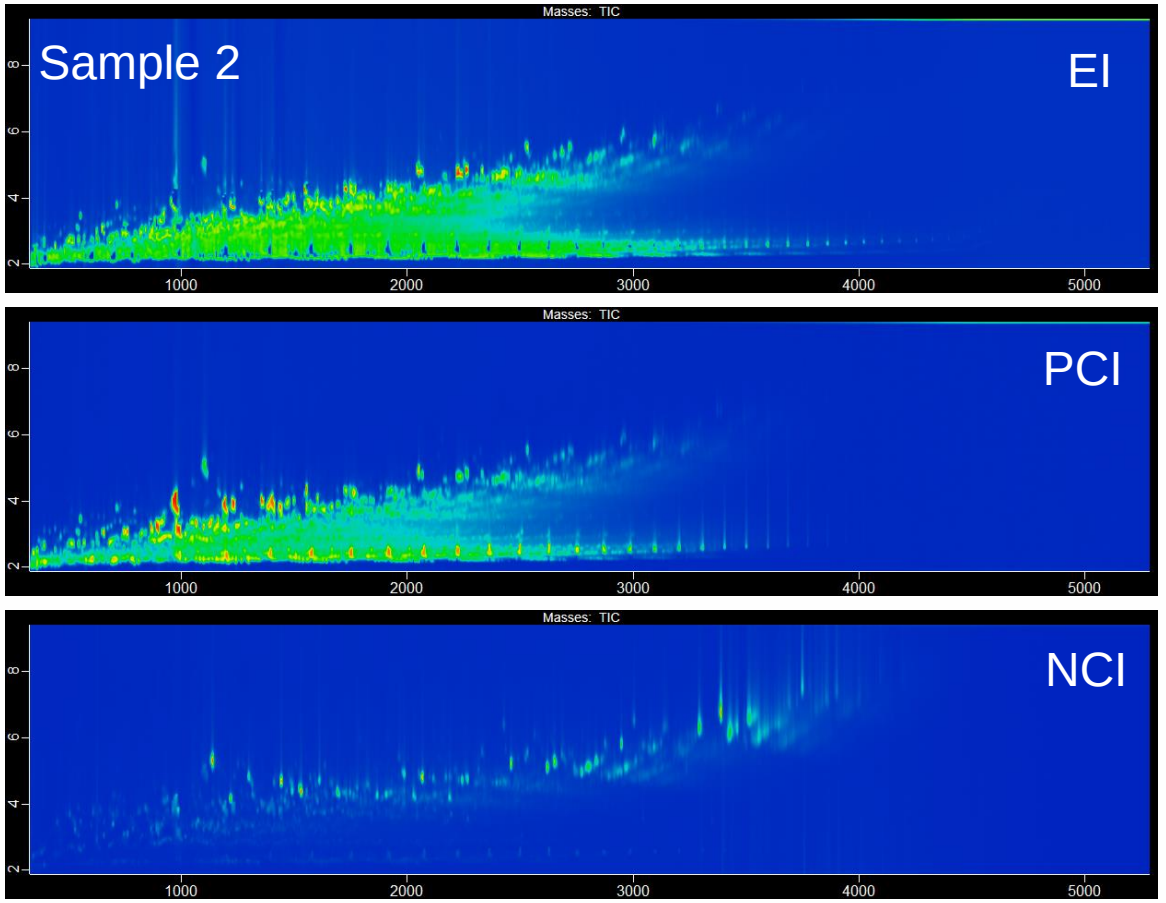
Generate Mass Classification Summary

#	Class	Region	Area	Area % In-Class	Area % In-Sample
1	HC		18813759	100.00	3.16
2		Region 2	18813759	100.00	3.16
3	HC		23165770	100.00	3.89
4		Region 1	14471642	62.47	2.43
5		Region 2	8694128	37.53	1.46
6	N		526432	100.00	0.09
7		Region 2	526432	100.00	0.09
8	N		578841	100.00	0.09
9		Region 1	76867	13.28	0.01
10		Region 2	501974	86.72	0.08
11	O		510288	100.00	0.09

Heteroatomic Species Identification

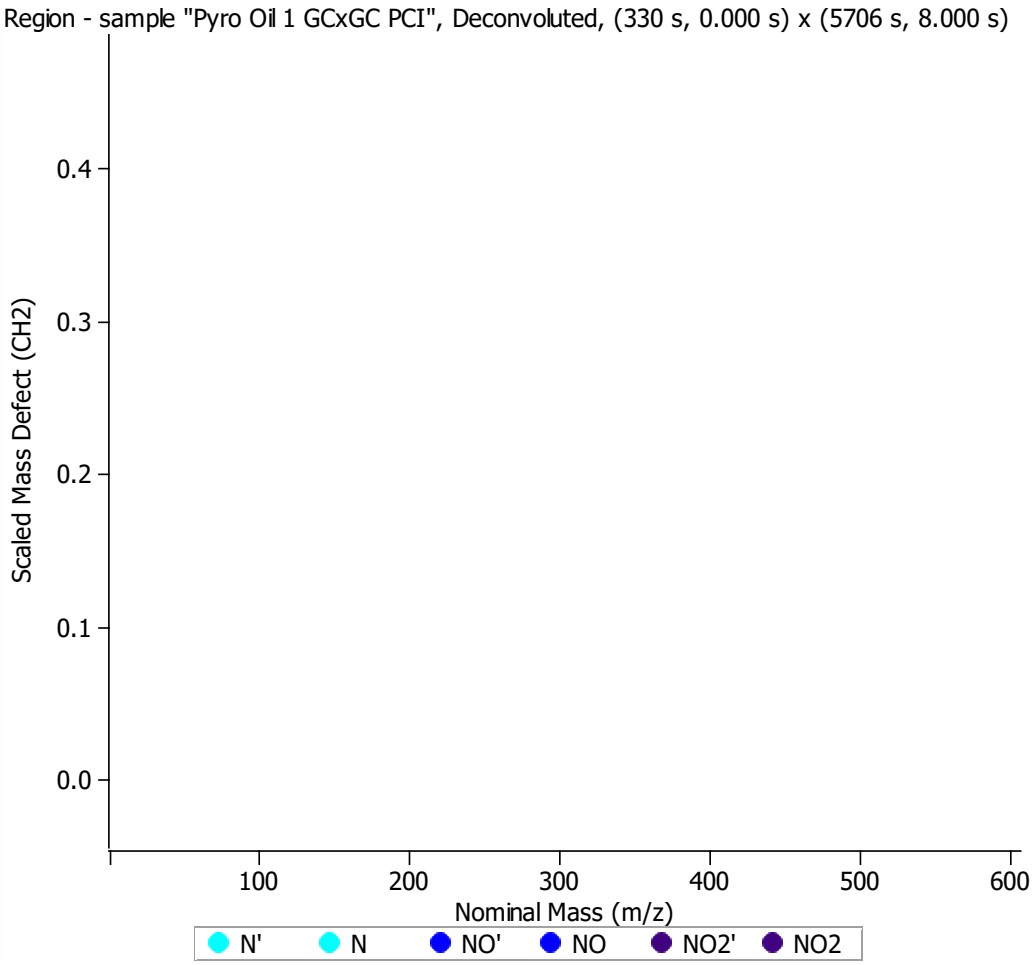
High-Resolution, Accurate Mass Data

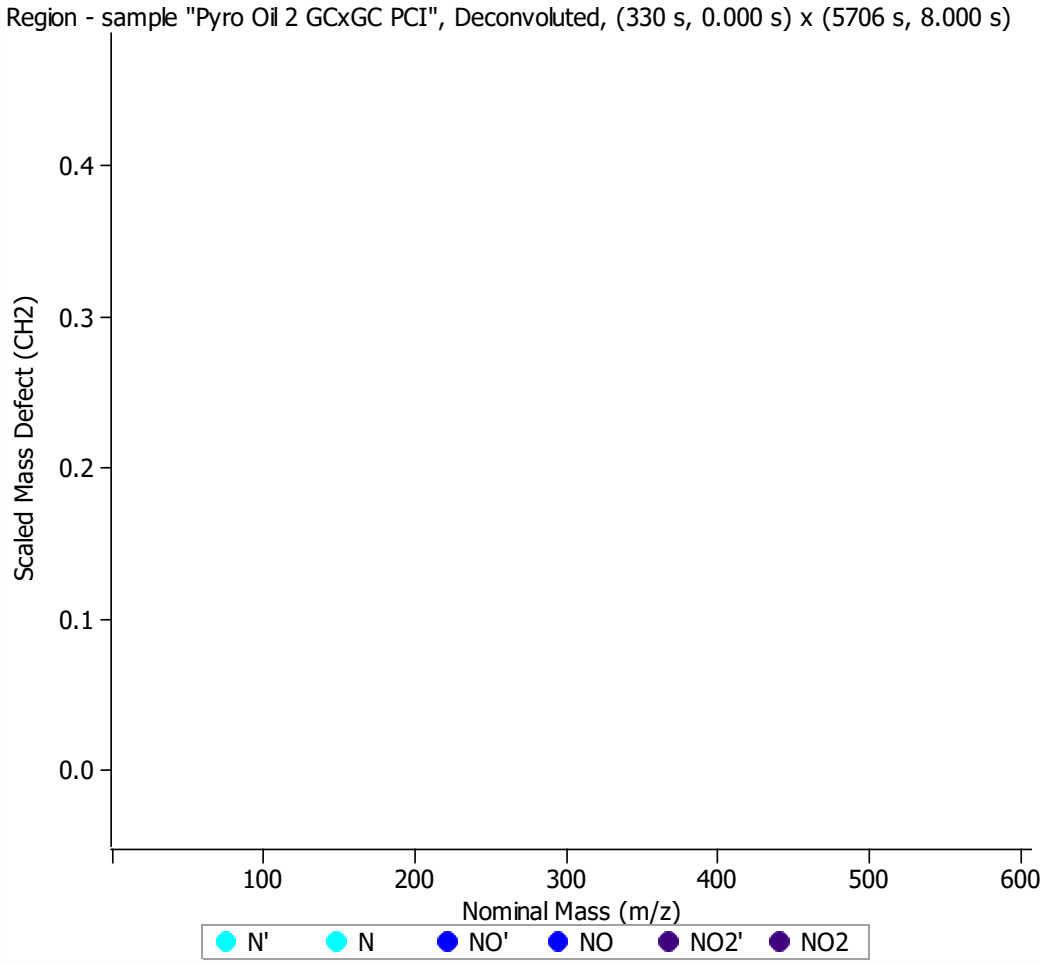




Heteroatomic Species Identification

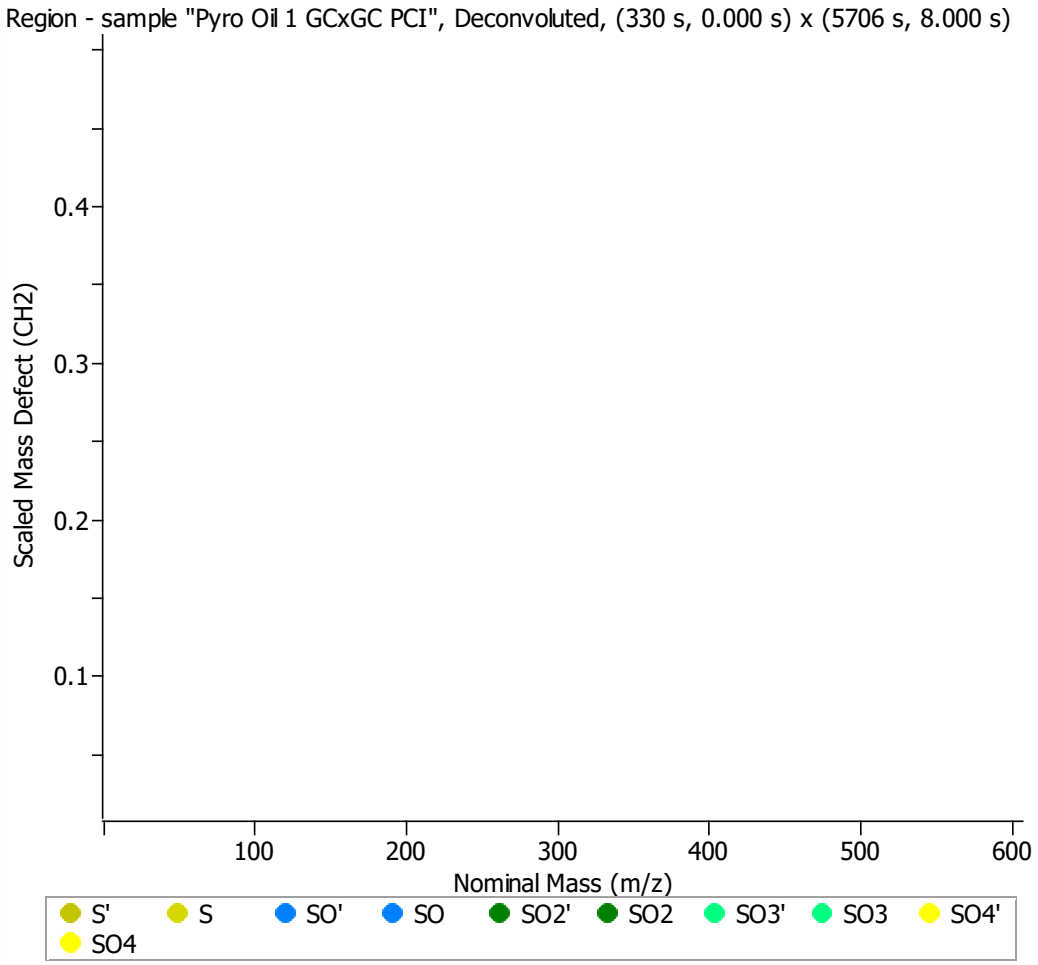
Mass Defect: Nitrogen-Containing Species

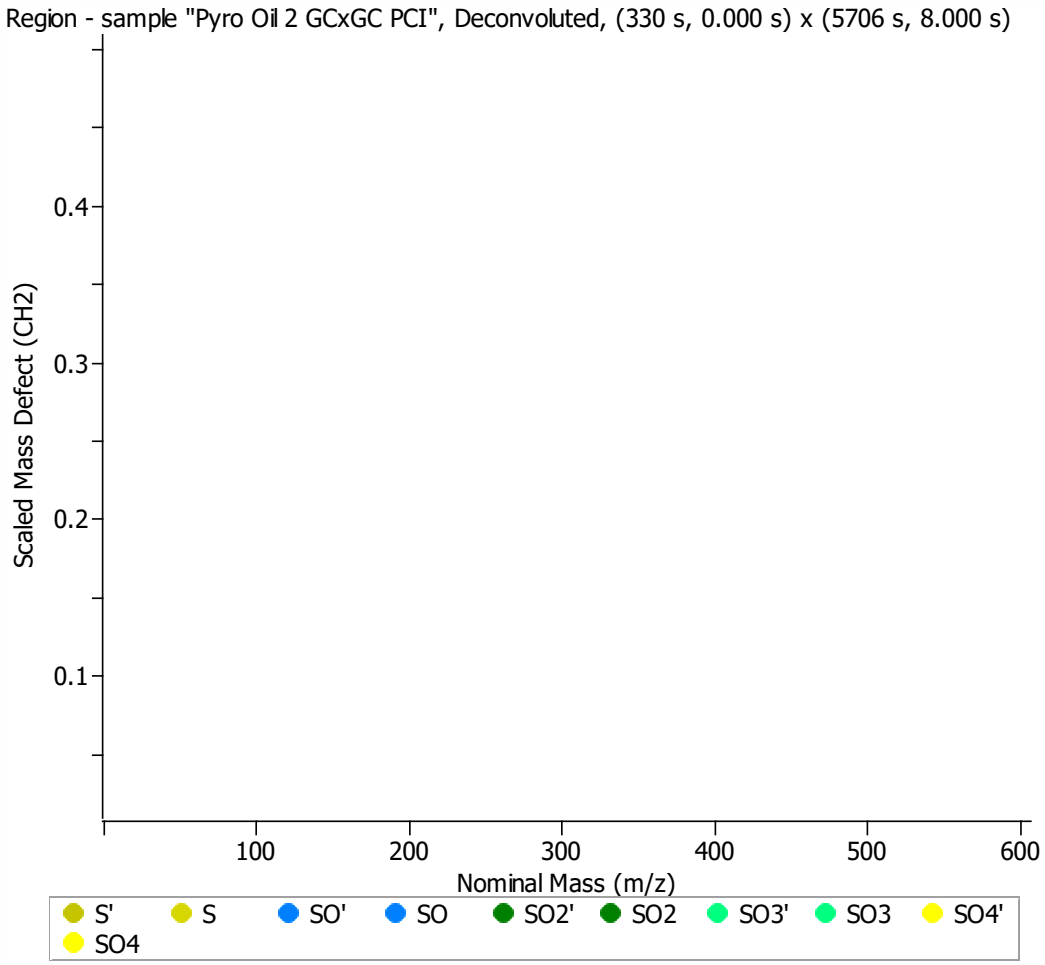




Heteroatomic Species Identification

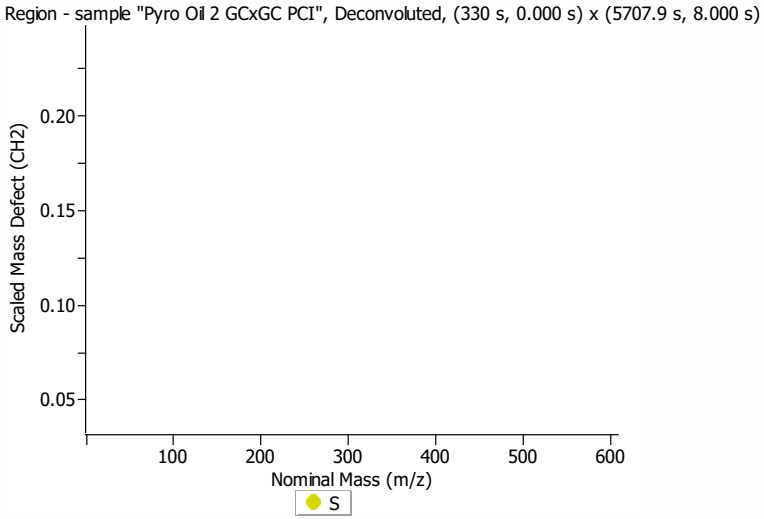
Mass Defect: Sulfur-Containing Species





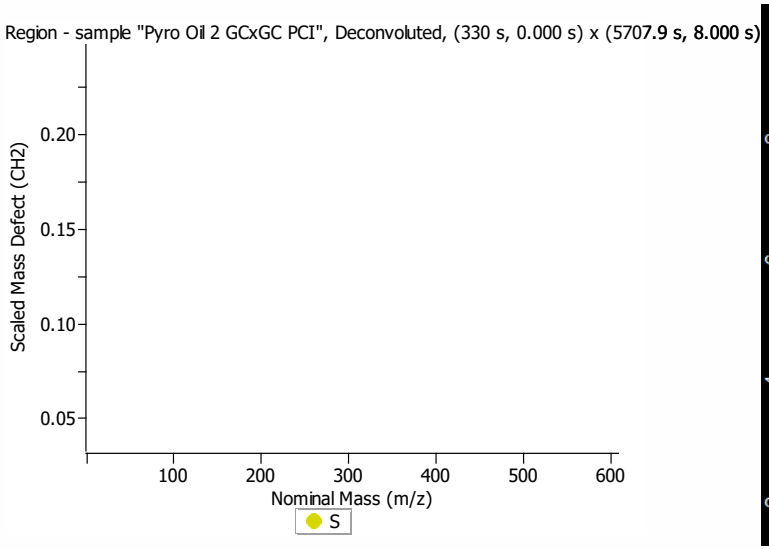
Heteroatomic Species Identification

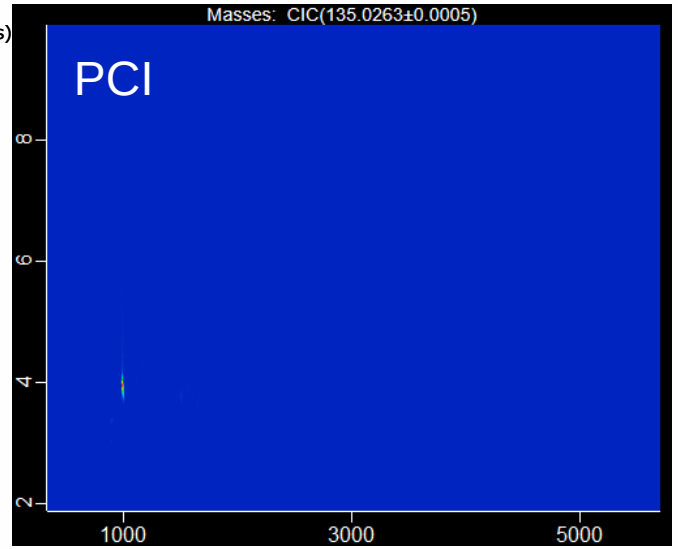
Leveraging High Resolution Mass Accuracy

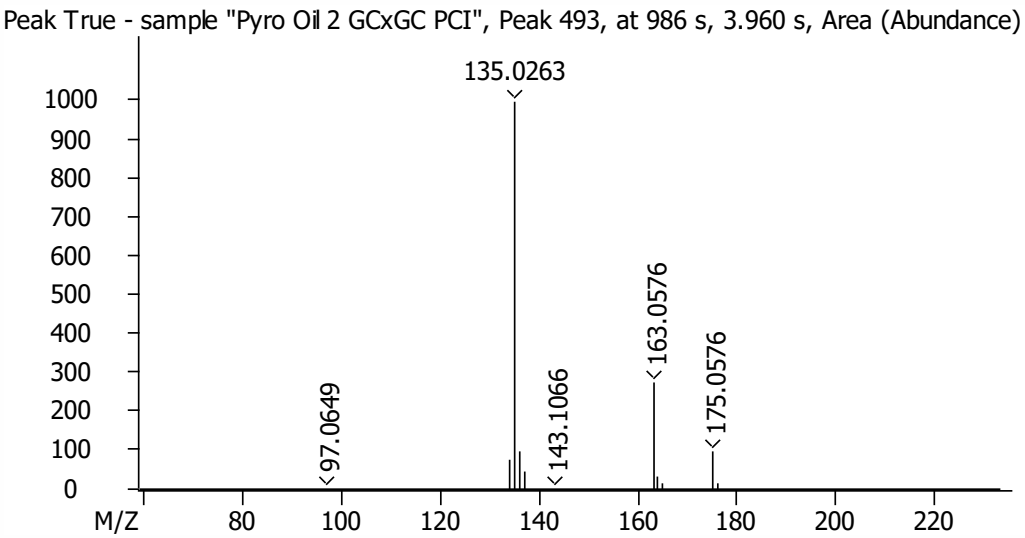


Heteroatomic Species Identification

Leveraging High Resolution Mass Accuracy



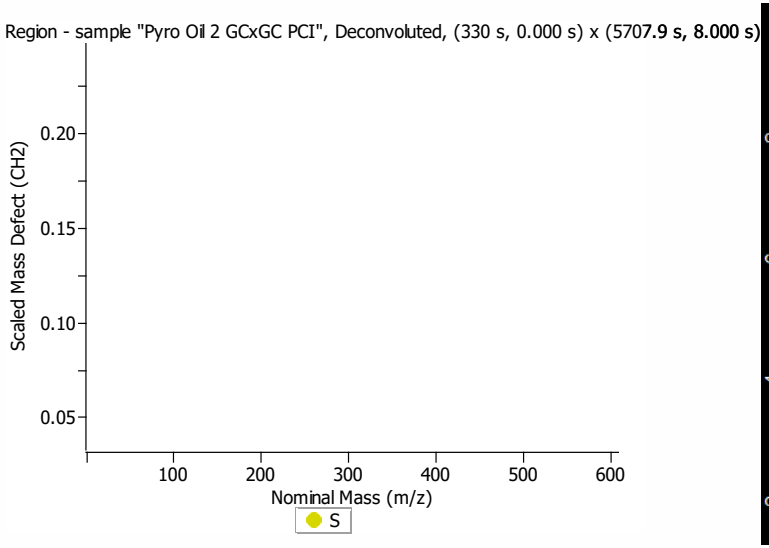


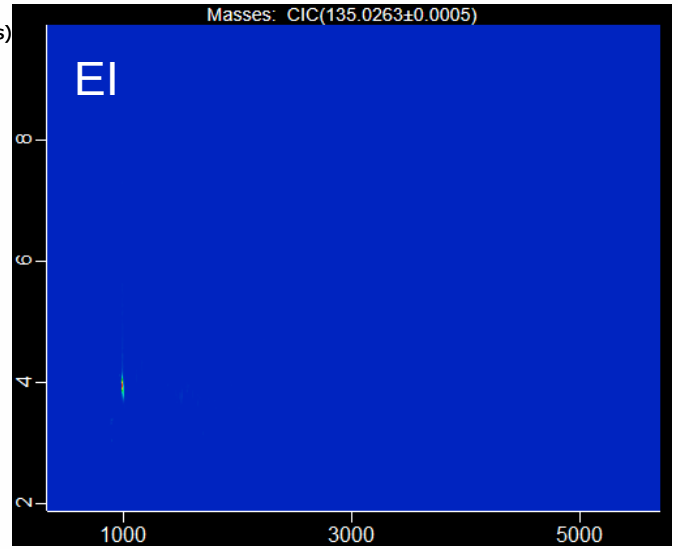


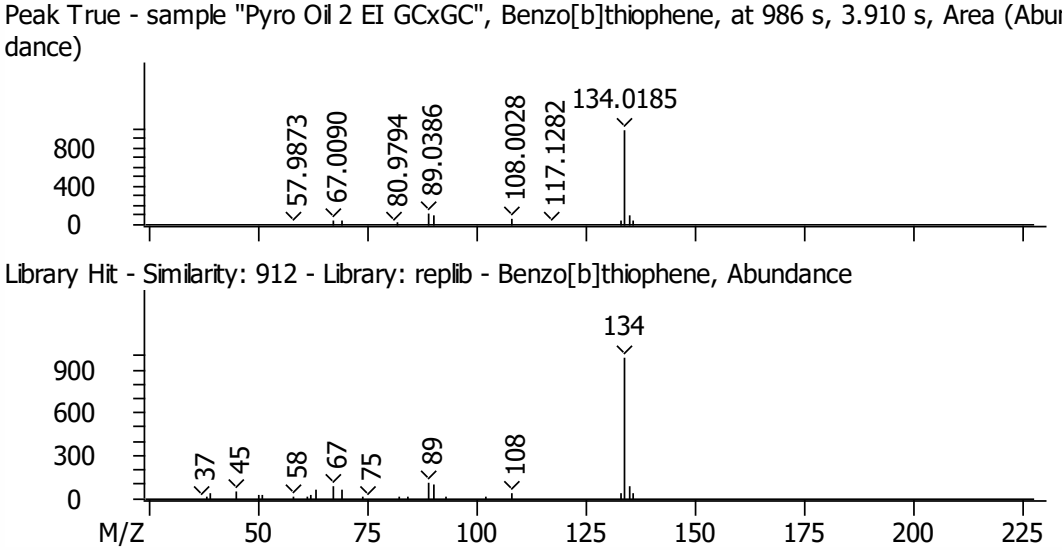
Mass	Formula	Mass Accuracy (ppm)	Species	Abundance
135.0263	C_8H_7S	-0.08	$[M+H]^+$	1000
163.0576	$C_{10}H_{11}S$	0.26	$[M+C_2H_4]^+$	274
175.0576	$C_{11}H_{11}S$	-0.23	$[M+C_3H_5]^+$	97

Heteroatomic Species Identification

High-Resolution, Accurate Mass Data



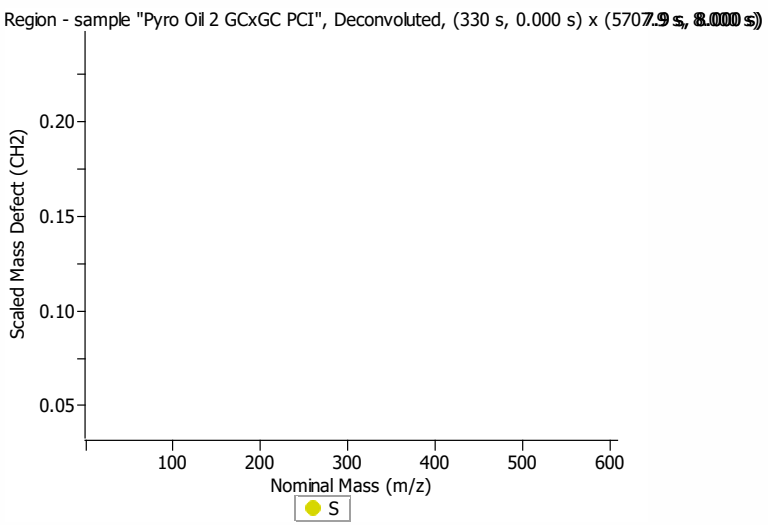


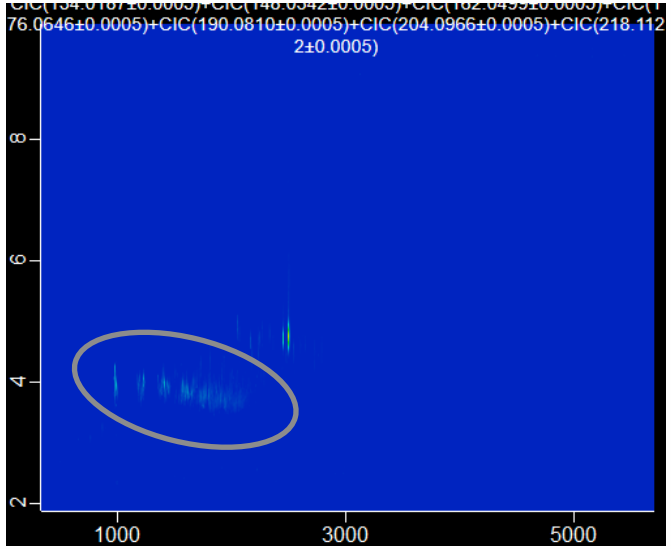


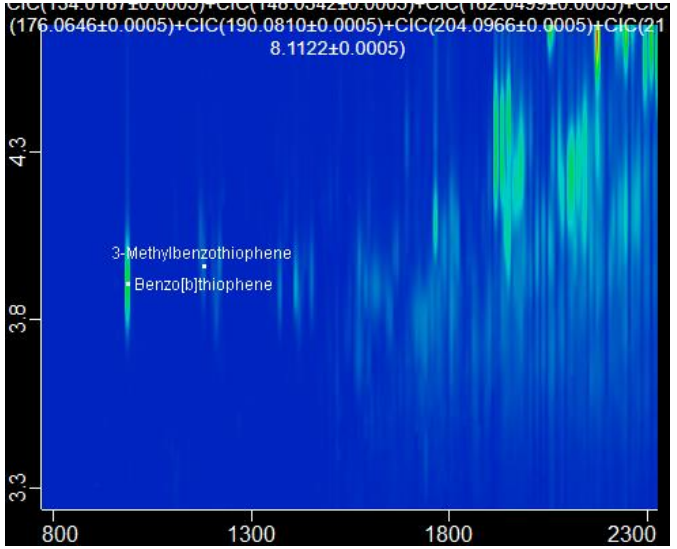
Mass	Formula	Mass Accuracy (ppm)	Abundance
134.0185	C_8H_6S	-0.08	1000
89.0386	C_7H_5	0.26	111
135.0218	$^{13}C_7CH_6S$	-0.23	100
90.0464	C_7H_6	0.05	91

Heteroatomic Species Identification

High-Resolution, Accurate Mass Data







Elution band signifies the low-level presence of clusters of C1-, C2-, C3- and possibly C4- benzothiophene isomers

Plotting back to EI tells us where to look; some were already properly identified!

Combination of high-resolution and GCxGC resolves the mass split!

Conclusion

- The variety of LECO GCxGC options provides high-quality data for both quantitative and qualitative characterization of plastics-derived pyrolysis oils
  - Group-type bulk composition
  - Statistical analysis of differences between samples
  - Detailed identification of heteroatomic species