15th Multidimensional Chromatography Workshop

Alkene Quantitation in Plastic Waste-Derived Alternative Fuels using GC×GC FID

Genesis Barzallo, Hung Gieng, Petr Vozka

Department of Chemistry and Biochemistry, California State University, Los Angeles

gbarzal@calstatela.edu

COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

Background

- California landfills enough plastic each day to fill 285 Olympic-size swimming pools (more than 12,000 tons).[1]

- In 2021, there were 2.3 billion units sold in the world's tire market, which amounted to 54.5 million tons of tires (2.7 billion units in 2027)[2].

Chemical Conversion Processes

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

- Pyrolysis (+ hydrotreating) of plastic foils and waste tires

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- Low Pressure Hydrothermal Processing of polyolefin plastic waste

Chemical Conversion Processes

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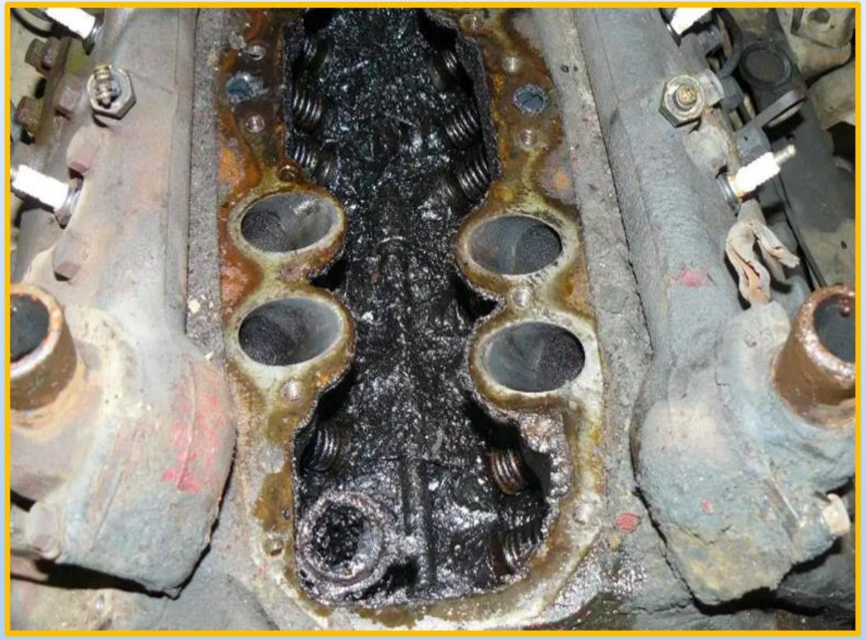
OLEFINS

Statement of the Problem

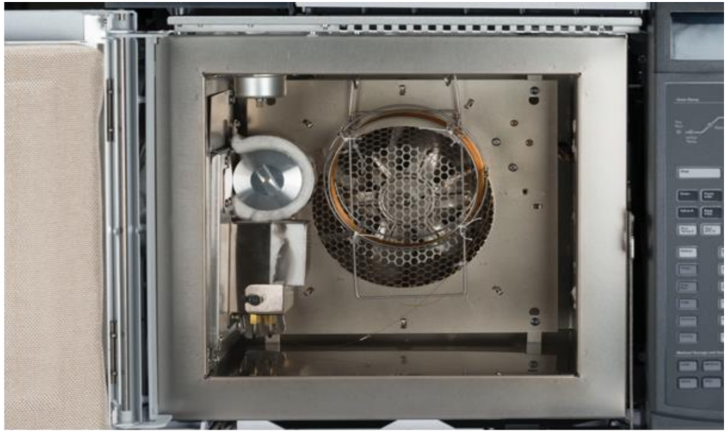
- High olefin content can be detrimental to engine cleanliness.
- Causes gum formations.

There are currently no methods for detailed quantitation of olefins, especially in high concentrations.



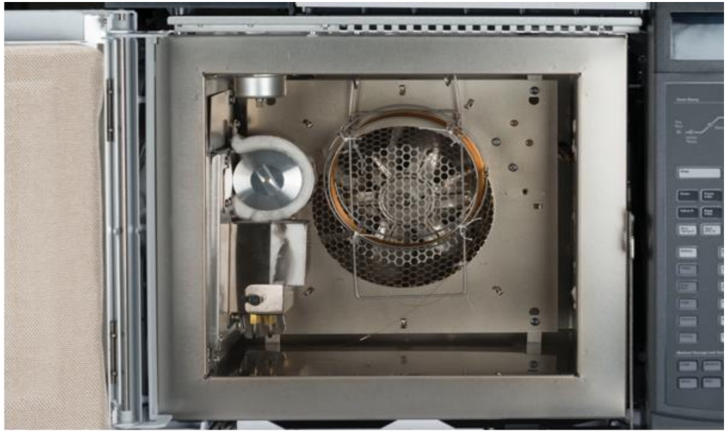
Methodology

- LECO's QuadJet GC×GC-FID with LN_2 thermal modulator
- Reversed-phase column configuration
    - (30 m × 0.25 mm × 0.25 μm Rxi-17 Sil MS, 0.9 m × 0.25 mm × 0.10 μm DB-1HT)
- Flame ionization detector (FID)

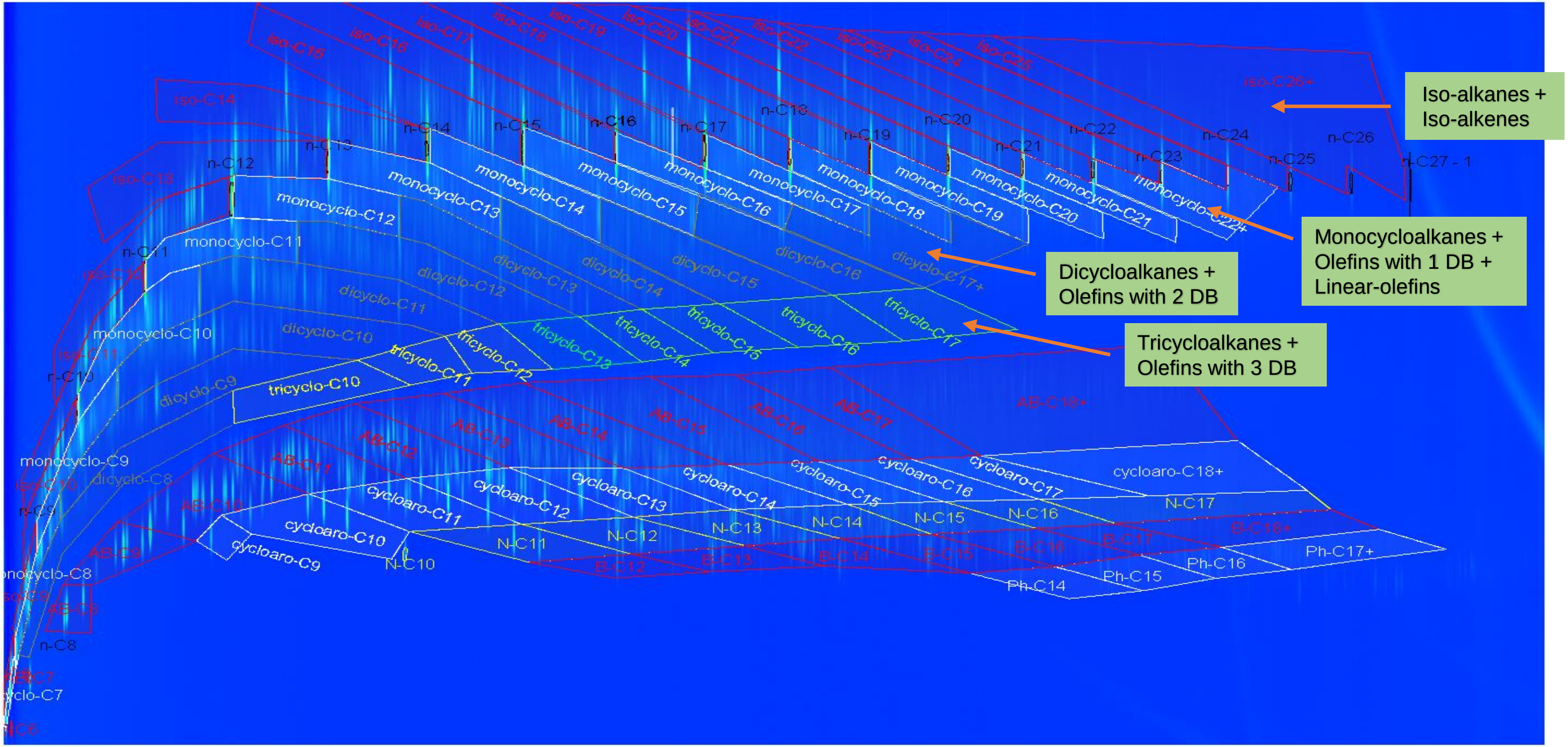


Methodology

- He flow rate of 1.5 mL/min
- Front inlet and FID temperatures: 275 and 280 ℃, respectively
- Second oven and modulator temperature offsets: 35 and 20 ℃, respectively
- Modulation period: 1.5 s (0.45 s hot pulse)
- Oven temperature program: from 40 ℃ (hold 0.2 min) to 200 ℃ (hold 1 min) with 3 ℃/min temperature ramp rate
- Split injection: 1:20



GC×GC-FID Classification



Sample Preparation

Sample + Internal Standard + DMDS + I_2 solution

↓

70 °C oven for at least an hour

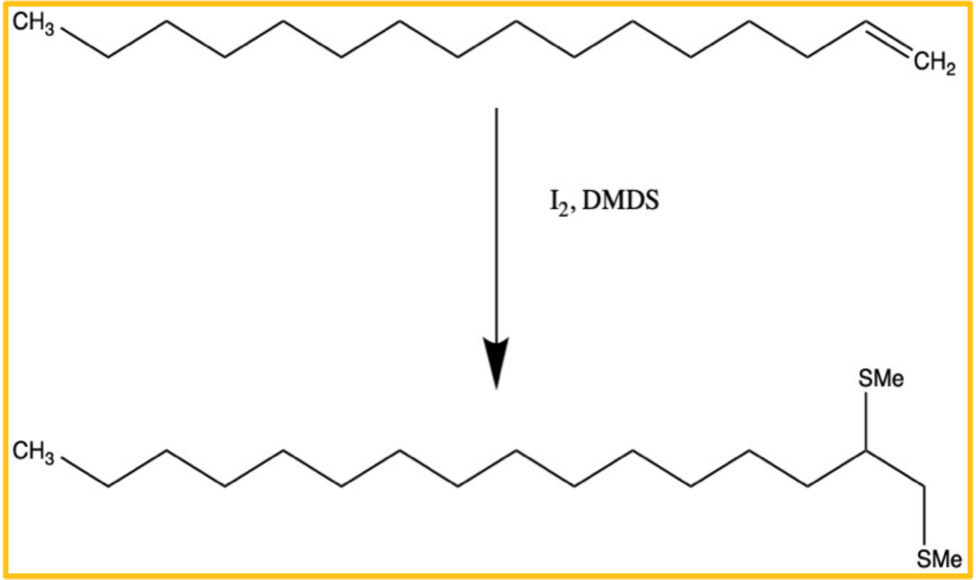
↓

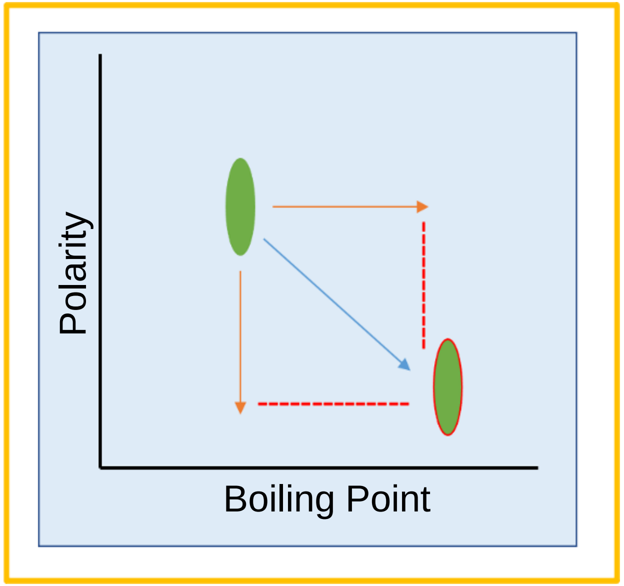
Sodium Thiosulfate

↓

Organic phase analyzed

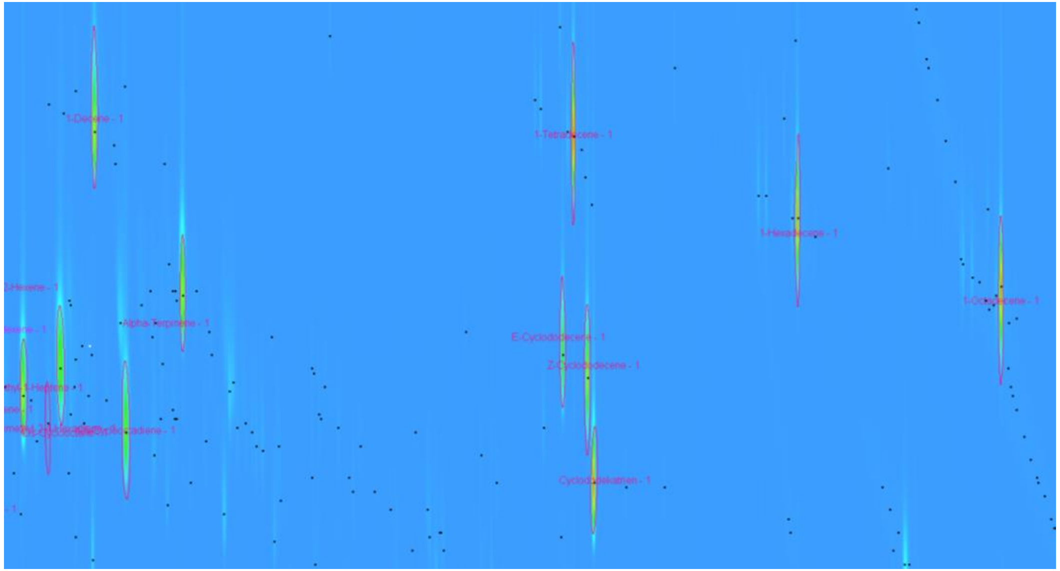
Theory





Model Compounds

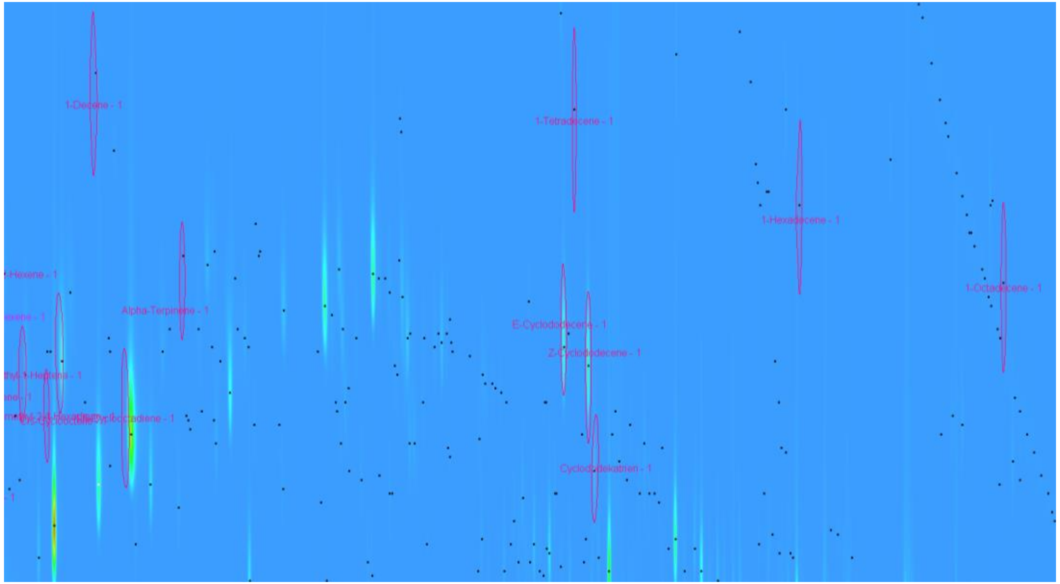
Before Derivatization



Standard Compounds			
1-Hexadecene	1-Octadecene	4-Methyl-1-Pentene	1-Tetradecene
2,4-Dimethyl-1-Heptene	1,7-Octadiene	Cycloheptene	1,5-Cyclooctadiene
Cyclo-dodecatriene	Alpha-terpinene	4,4-Dimethyl-1-Cyclohexene	1-Heptene
Cyclohexene	Cyclo-dodecene	Trans-2,2-Dimethyl-3-Hexene	3-Ethyl-5-Methyl-2-Hexene
2,4-Dimethyl-1,3-Pentadiene	1-Octene	2-Ethyl-1-Hexene	2,5-Dimethyl-2,4-Hexadiene
1-Decene	Cis-Cyclooctene	Cis-Trans-3-Heptene	

Model Compounds

1 hr Post Derivatization



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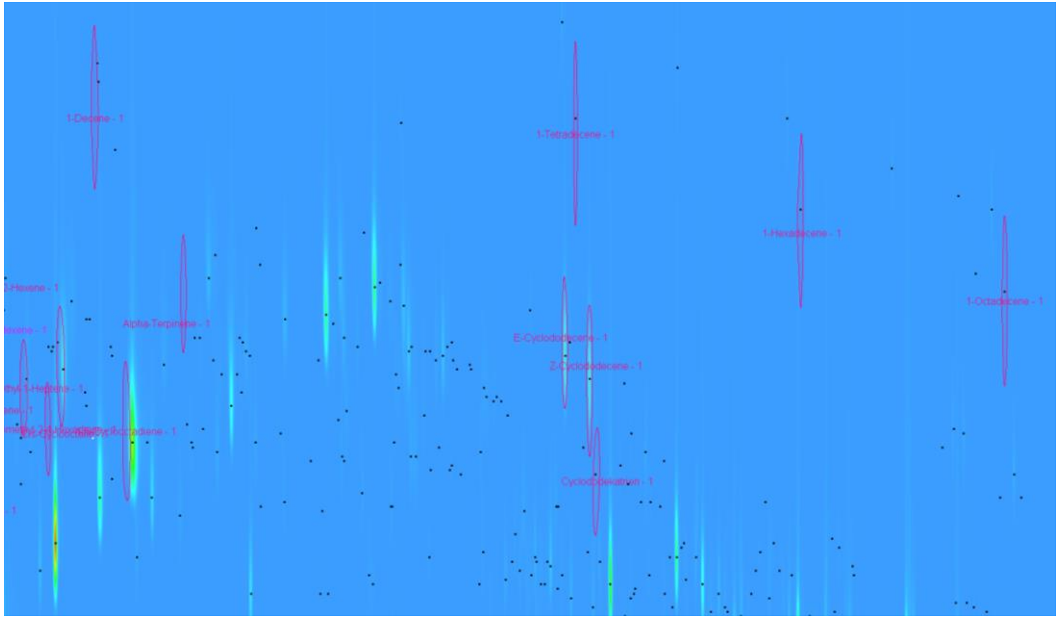
Model Compounds

2 hr Post Derivatization



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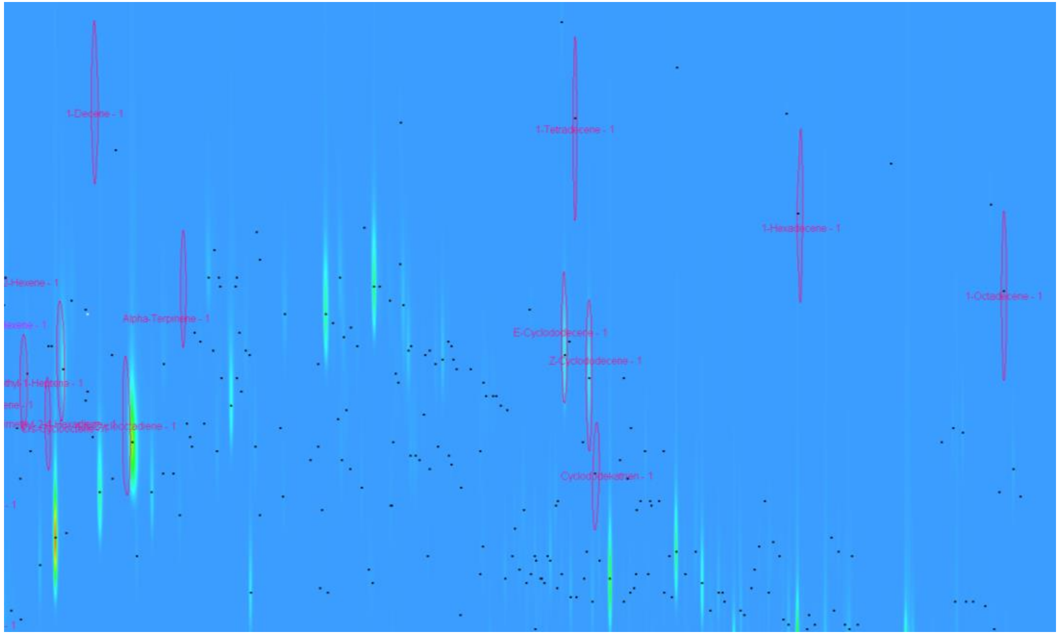
Model Compounds

3 hr Post Derivatization



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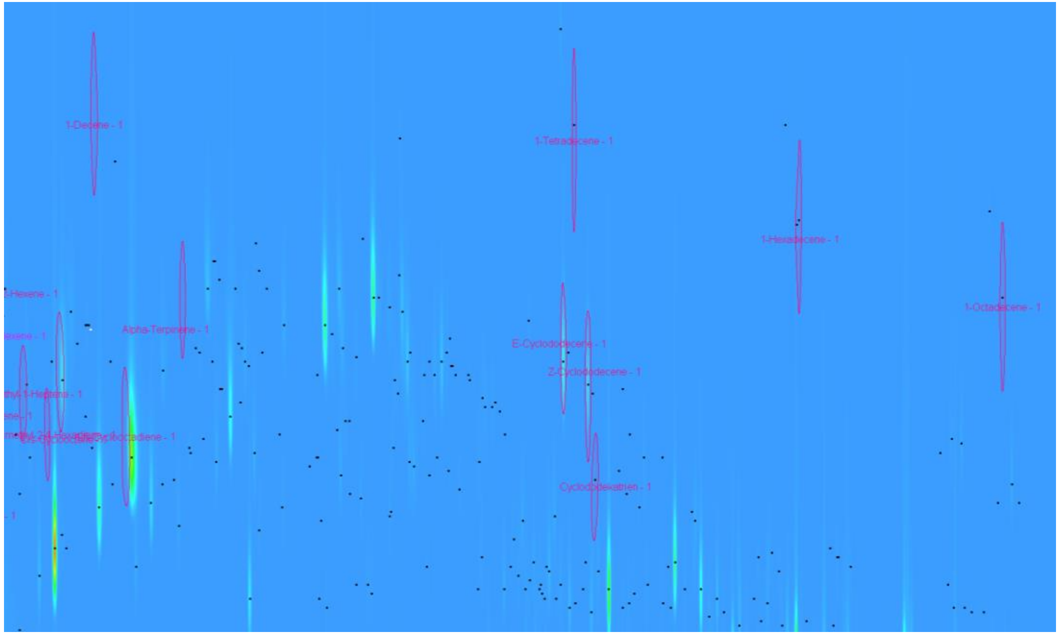
Model Compounds

4 hr Post Derivatization



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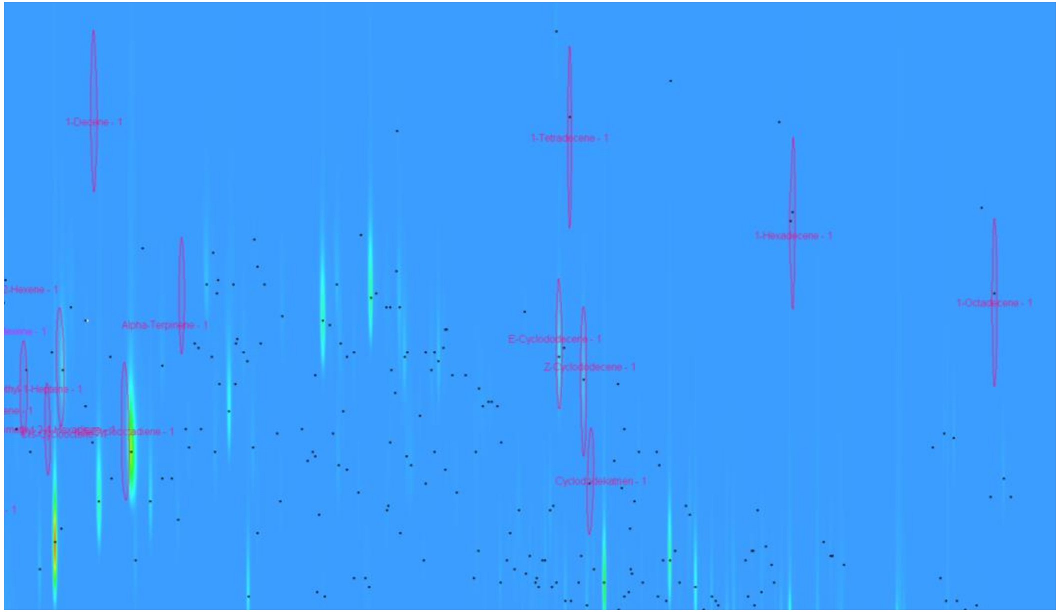
Model Compounds

5 hr Post Derivatization



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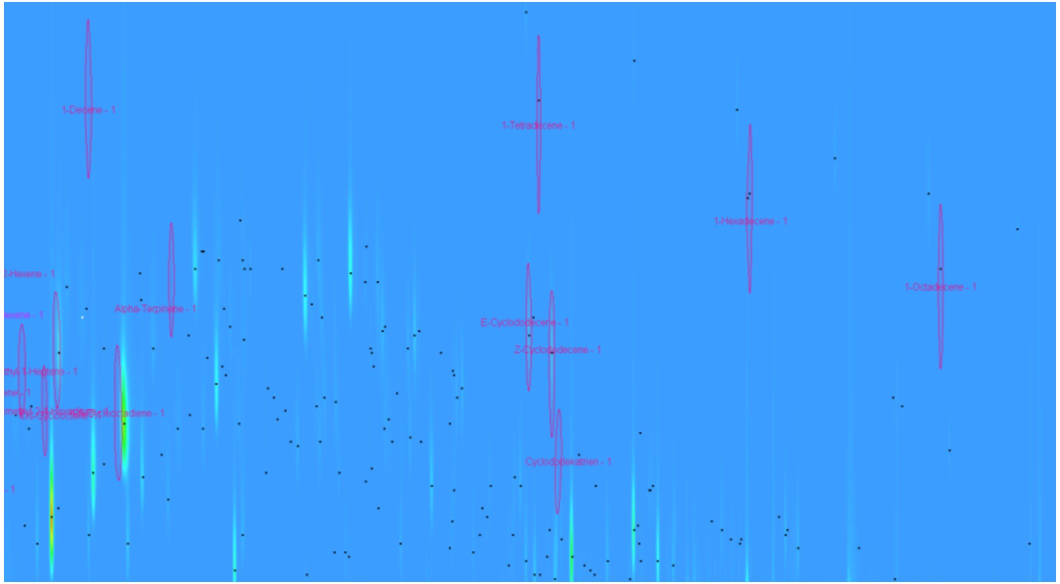
Model Compounds

24 hr Post Derivatization



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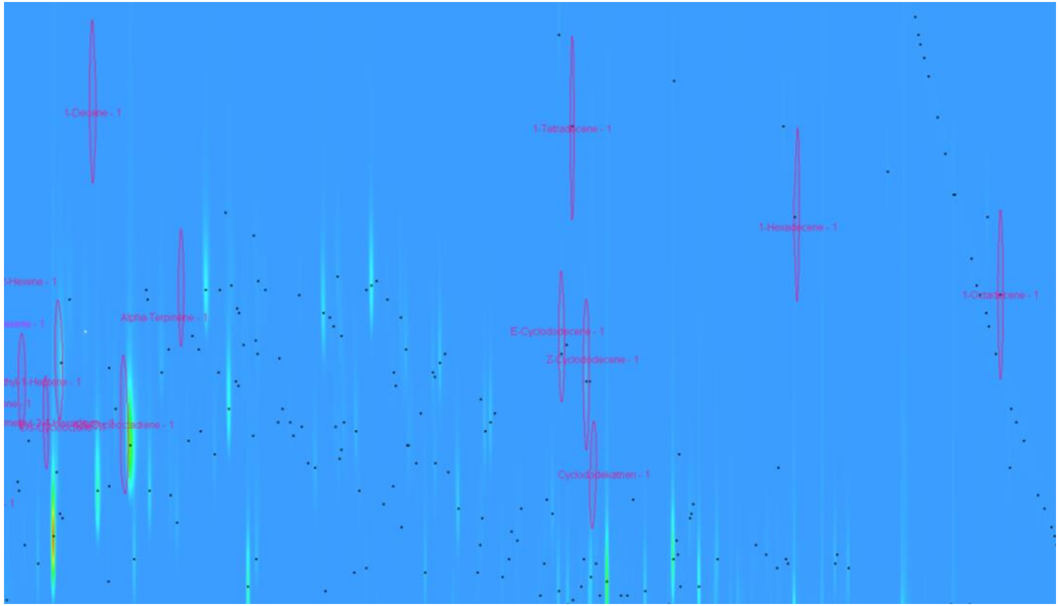
Model Compounds

36 hr Post Derivatization



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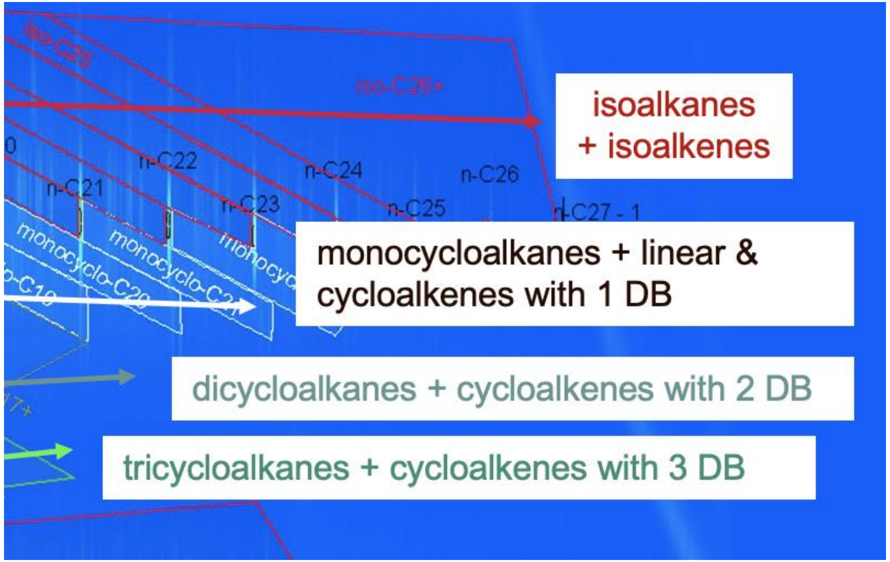
Calculations

Olefins in sample

- Iso-alkenes
- Olefins with 1 double bond + Linear-alkenes
- Olefins with 2 double bonds
- Olefins with 3 double bonds



Equation

$$Wt.\%_{Olefin,\,C\#} = P.A._{Pre-Derivatization,\,C\#} - P.A._{Post-Derivatization\ and\ Normalization,\,C\#}$$

Example

$$Wt.\%_{Iso-alkene,\,C11} = P.A._{Pre-Derivatization,\,C11} - P.A._{Post-Derivatization\ and\ Normalization,\,C11}$$

Scrap Tire Pyrolysis Oil Results

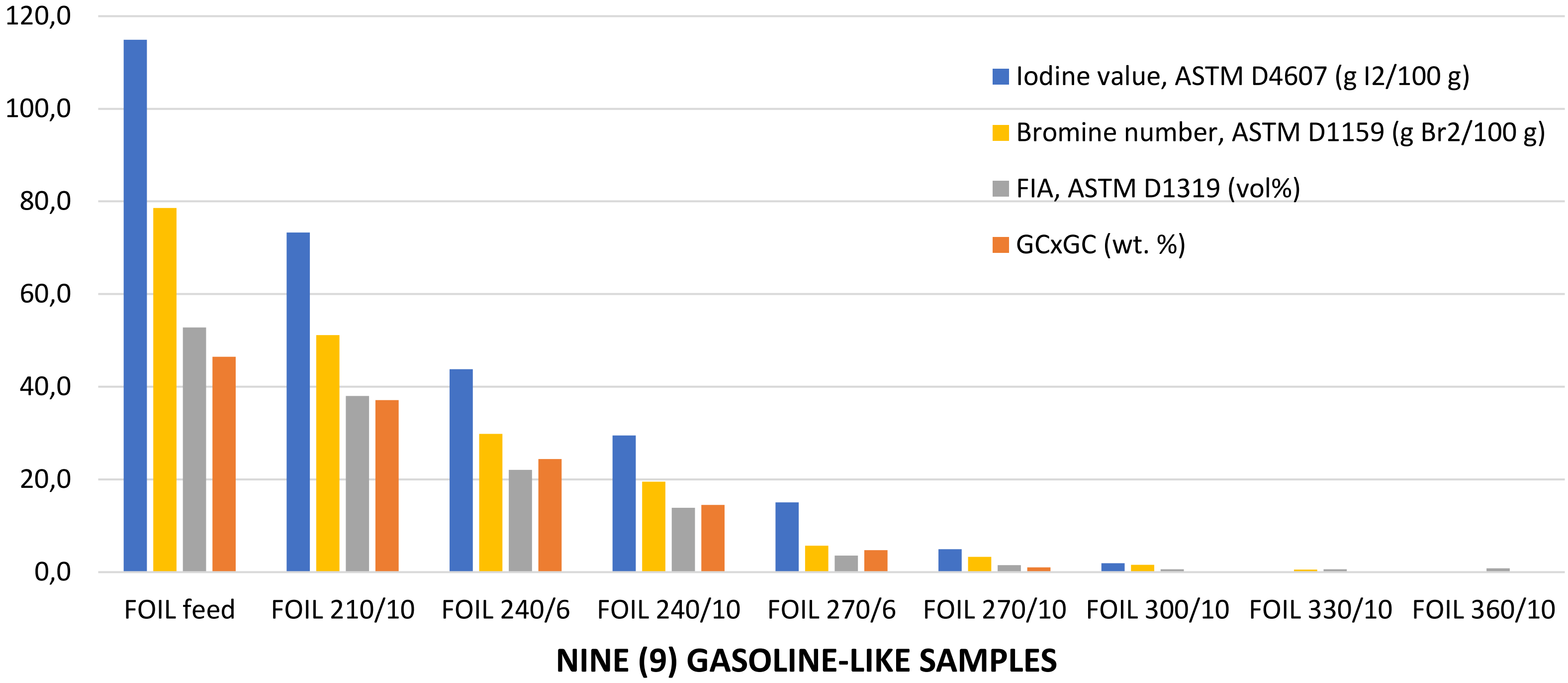
Before	wt. %
n-alkanes	1.54
Iso-alkanes + Iso-alkenes	0.86
Monocycloalkanes + Olefins with 1 Double Bond + Linear-alkenes	4.43
Dicycloalkanes + Olefins with 2 Double Bonds	27.01
Tricycloalkanes + Olefins with 3 Double Bonds	4.60
Aromatics	53.66
Light Hydrocarbons	7.90

After	wt. %
n-alkanes	1.54
Iso-alkanes	0.64
Iso-alkenes	0.22
Monocycloalkanes	0.96
Linear alkenes	1.04
Olefins with 1 Double Bond	2.43
Dicycloalkanes	1.80
Olefins with 2 Double Bonds	25.20
Tricycloalkanes	1.10
Olefins with 3 Double Bonds	3.50
Aromatics	53.66
Light Hydrocarbons	7.90

Results

	Waste Tire Pyrolysis, Gasoline		Post Derivatization				
Monocycloalkanes	p.a.	wt. %	p.a.	After Norm p.a.	Olefins (p.a.)	Olefin (wt.%)	Real Cyclo (wt.%)
C5	52883.75	6.00	38374.69	31454.66	21429.09	2.32	3.68
C6	81707.23	9.27	65393.26	53601.03	28106.20	3.05	6.23
C7	86175.05	9.78	64515.59	52881.63	33293.42	3.61	6.17
C8	50744.41	5.76	50393.38	41306.05	9438.36	1.02	4.74
C9	56524.36	6.41	16947.64	13891.51	42632.85	4.62	1.80
C10	1839.73	0.21	553.02	453.30	1386.43	0.15	0.06
C11	0	0.00	0	0	0	0	0.00
C12	0	0.00	0	0	0	0	0.00
C13	0	0.00	0	0	0	0	0.00
C14	0	0.00	0	0	0	0	0.00
C15	0	0.00	0	0	0	0	0.00
C16	0	0.00	0	0	0	0	0.00
Total	**329874.53**	**37.44**	**236177.58**	**193588.18**	**136286.35**	**14.77**	**22.67**

Validation (Compared to other ASTM methods)



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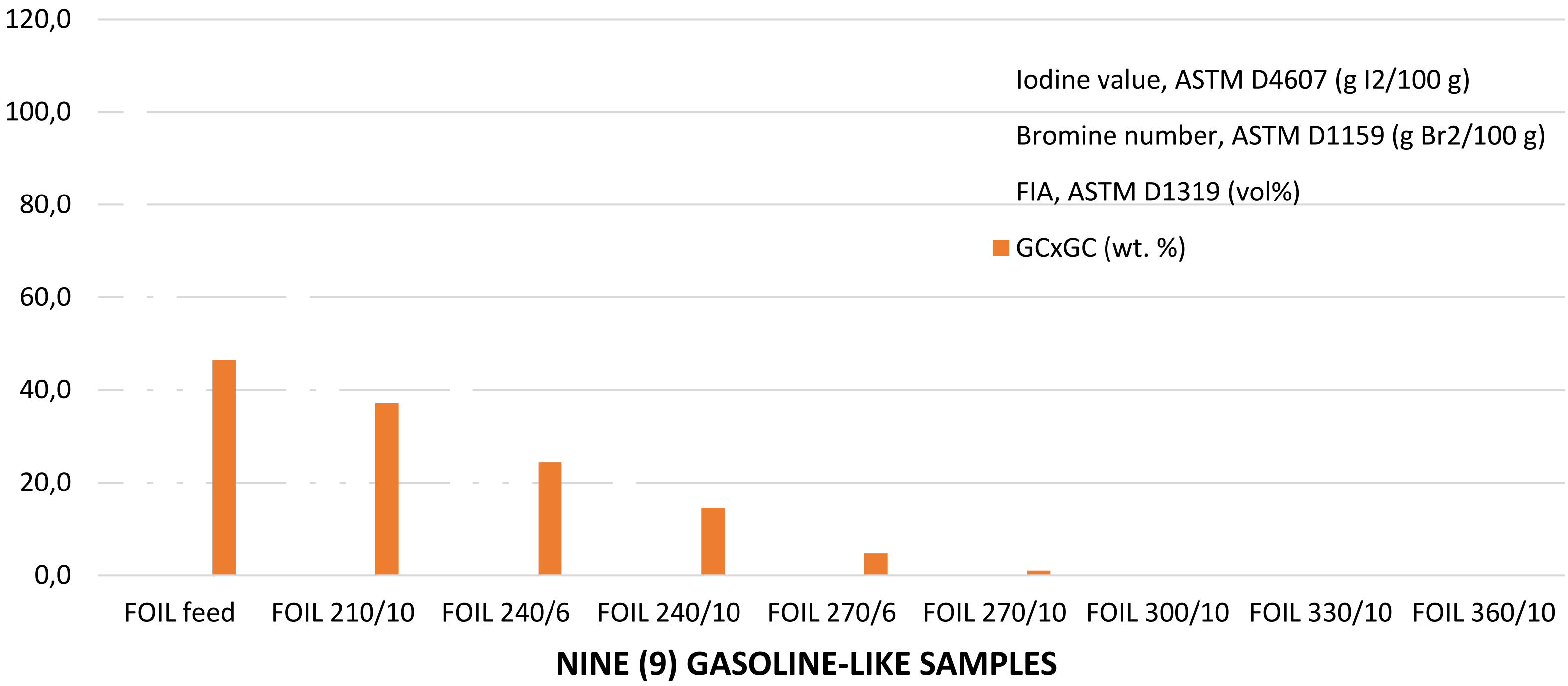

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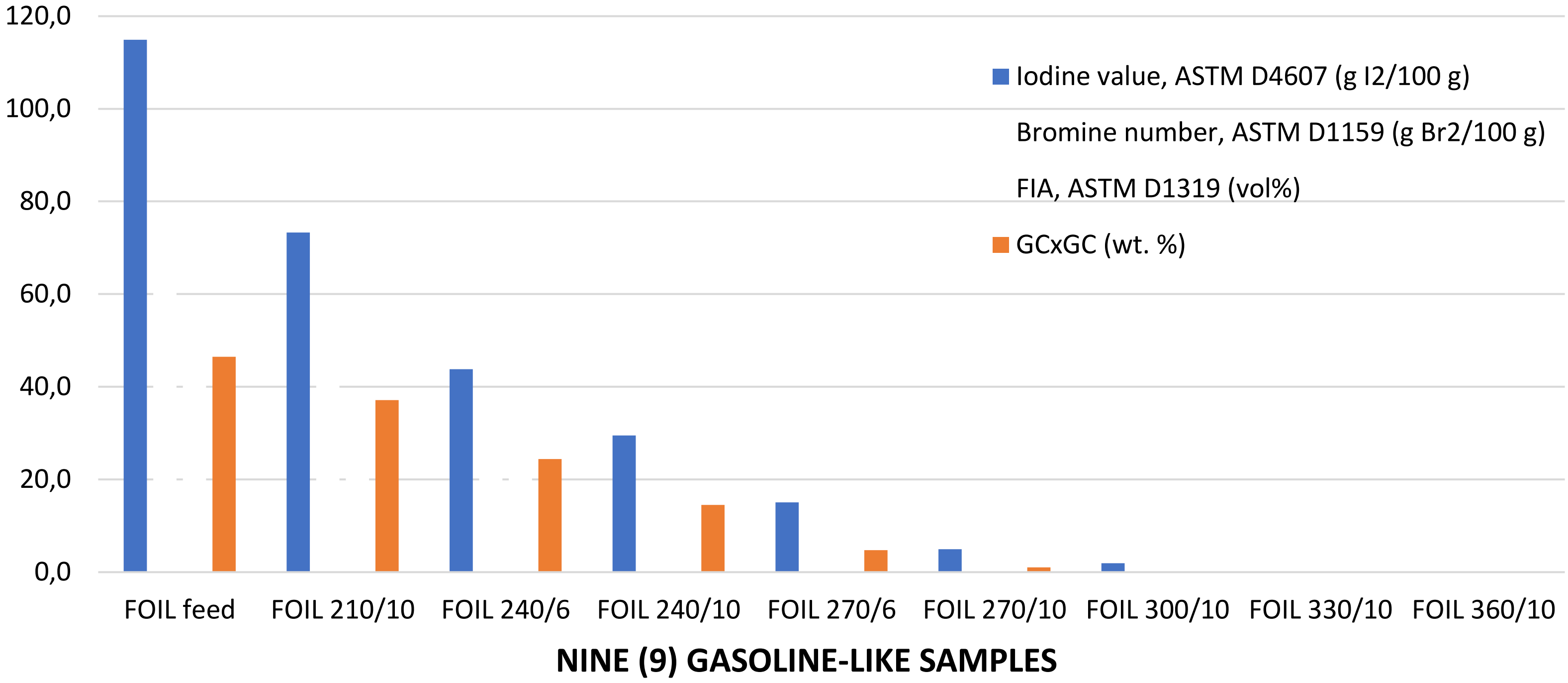

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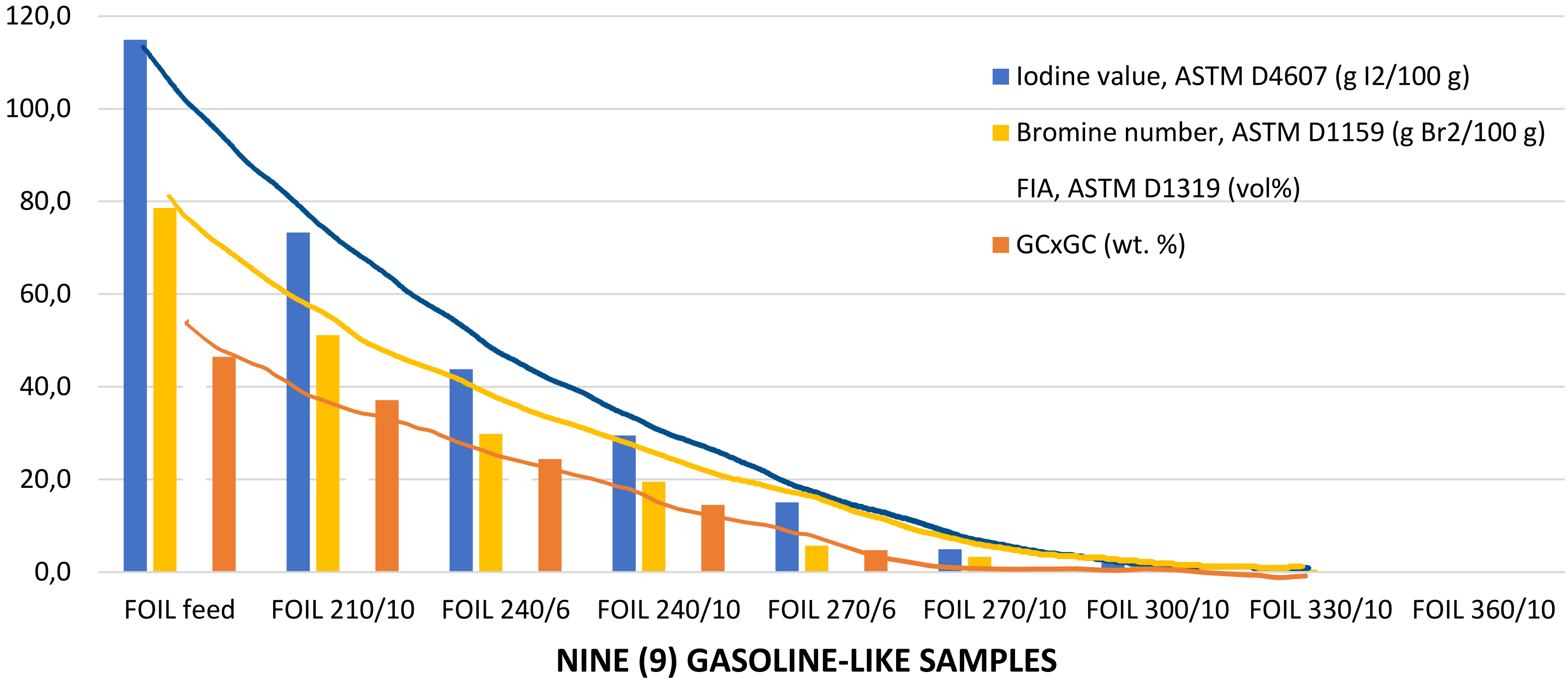

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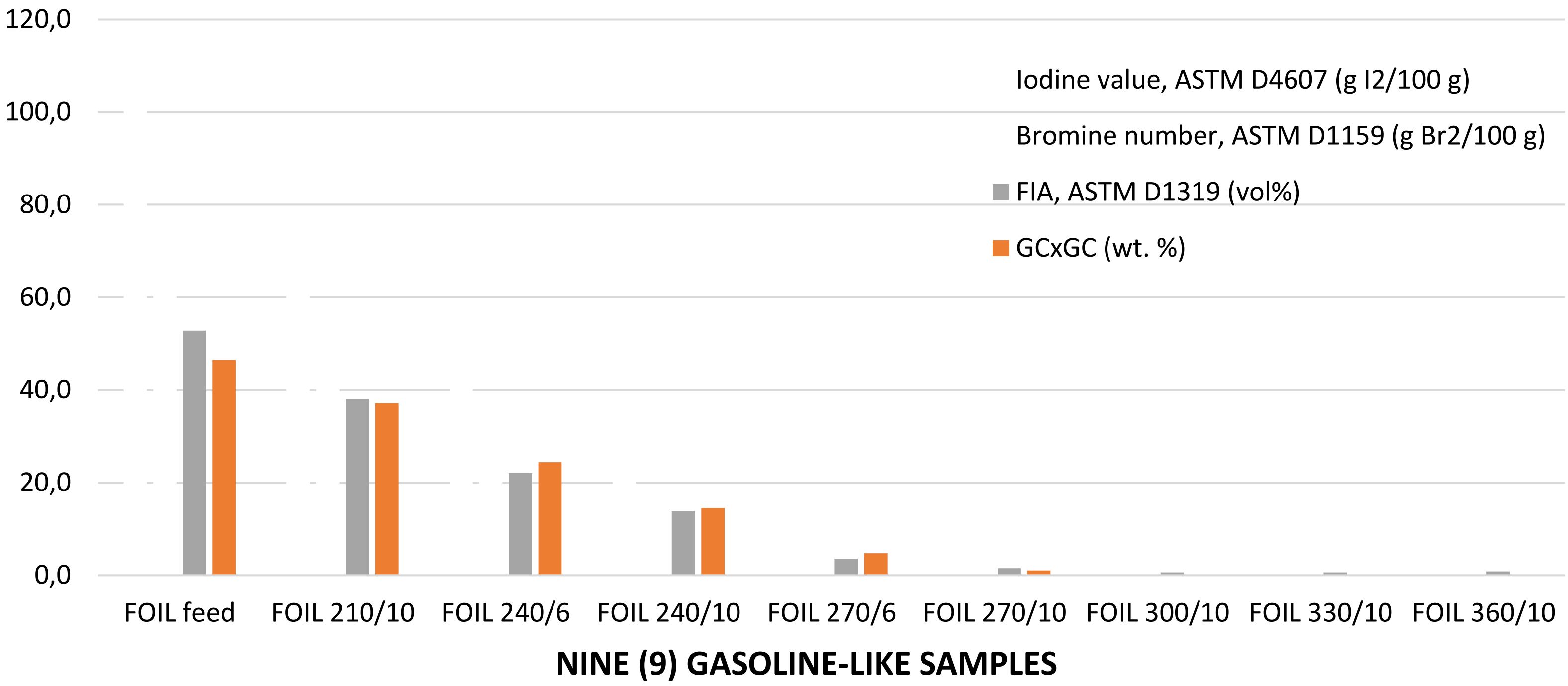

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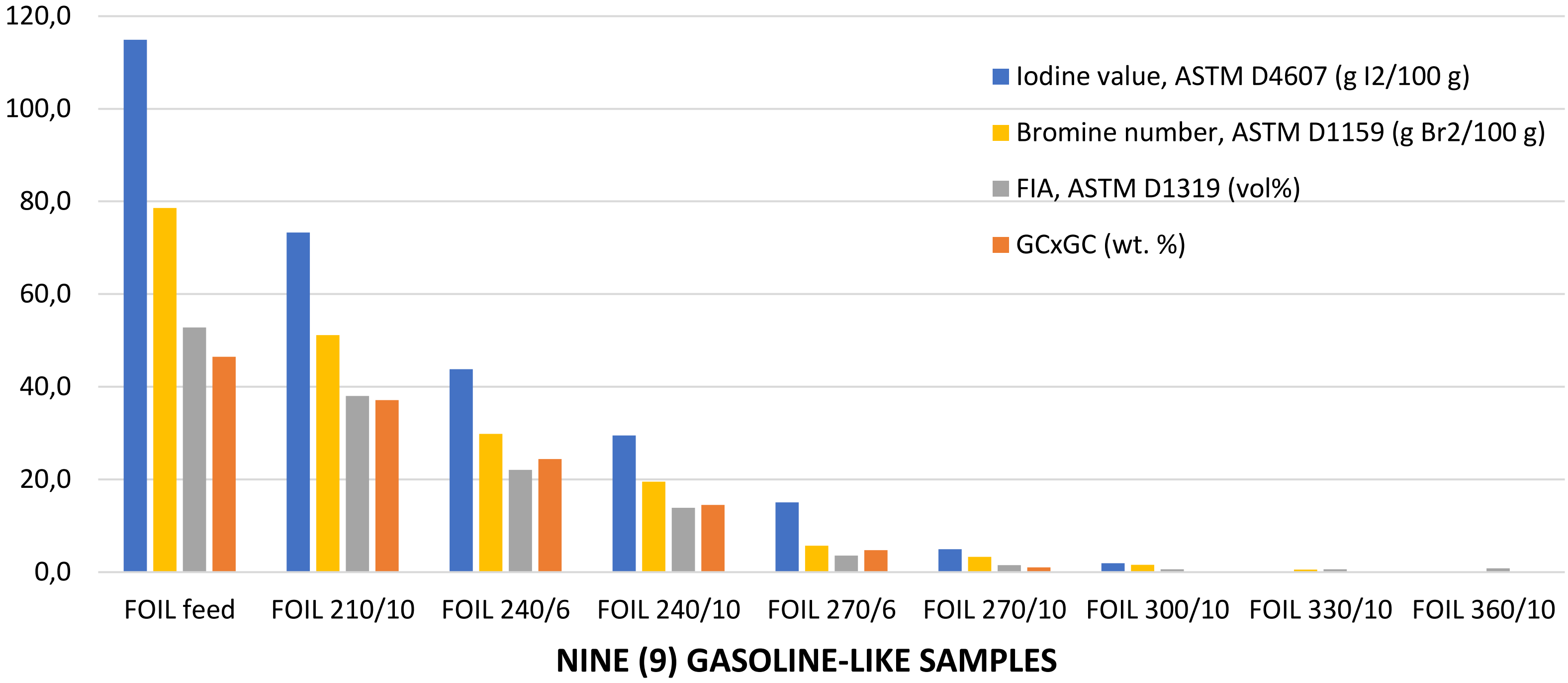


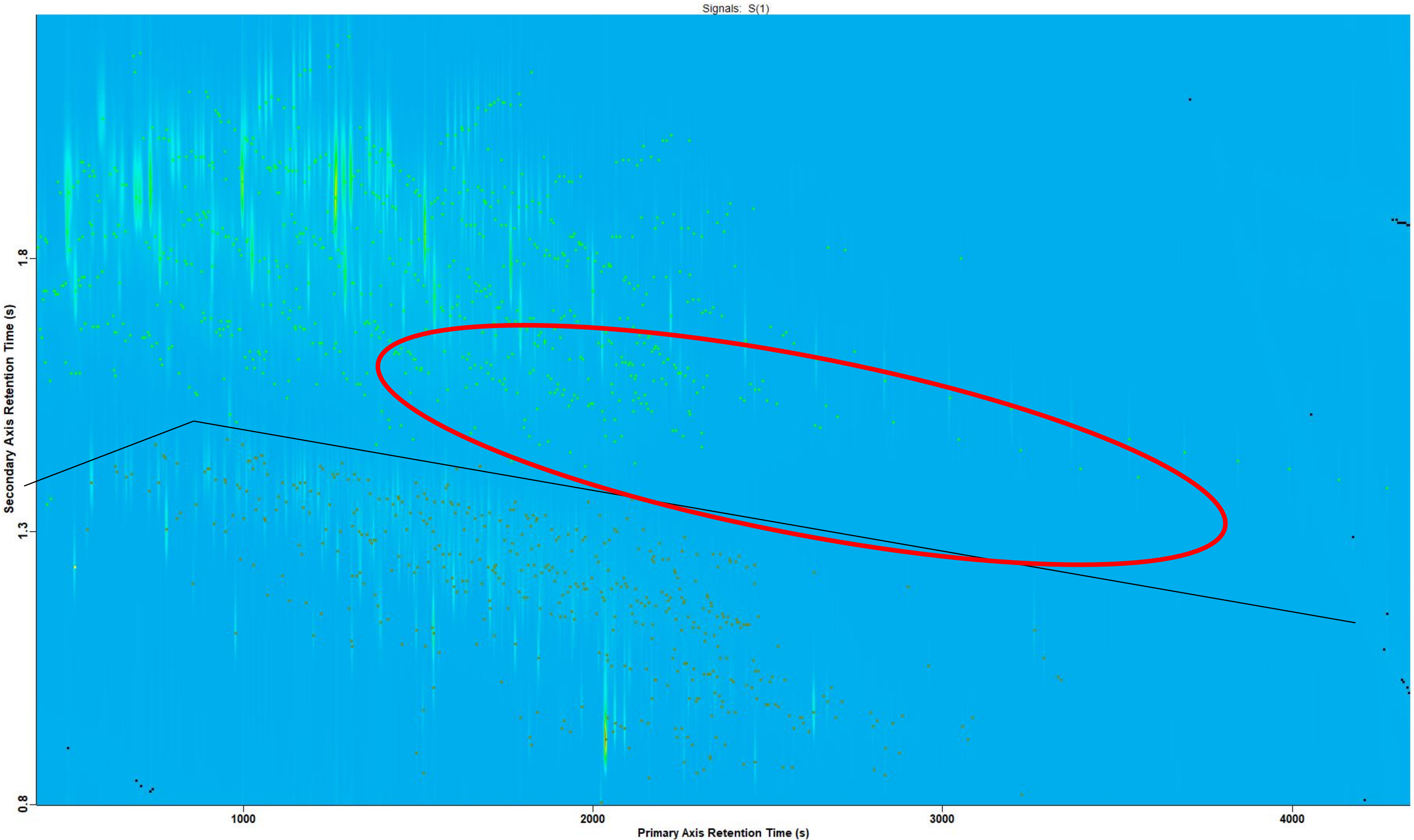
Conclusion

- We introduced a possible method for olefin quantitation in complex alternative fuels made from the conversion of plastic waste.

- Validate the results using GC×GC with time-of-flight mass spectrometry (TOFMS).

Pegasus BT 4D GC×GC-TOFMS

Chromatogram – diesel-like sample pre-derivatization



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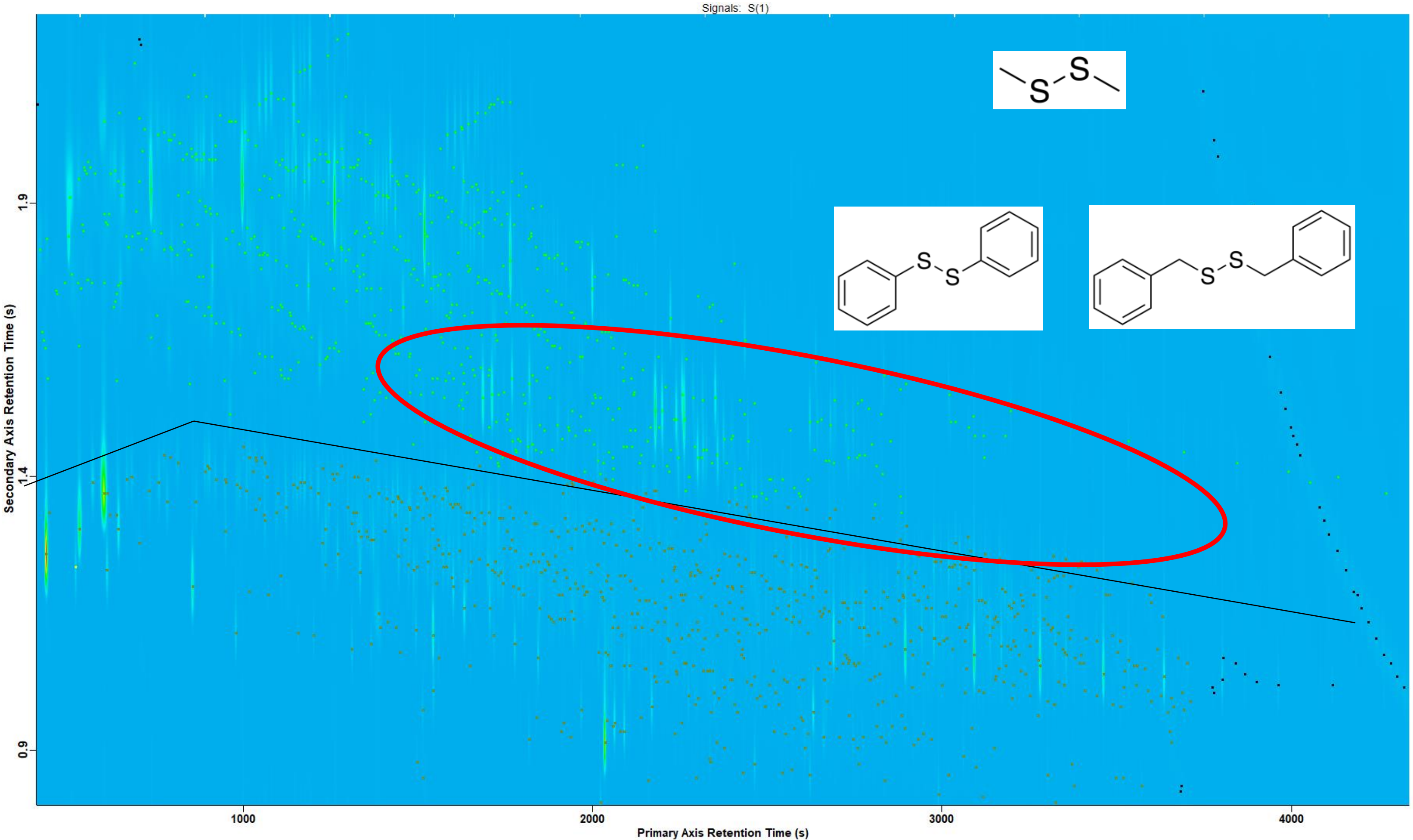

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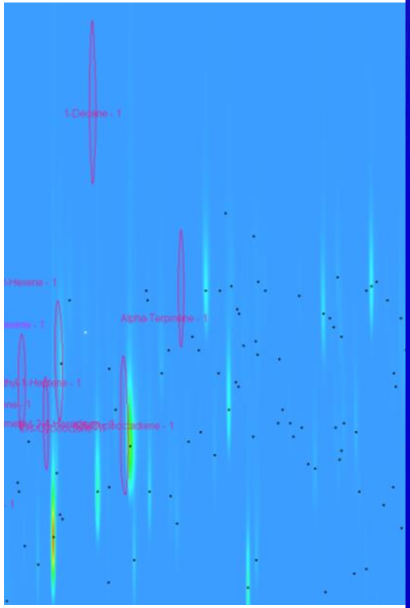

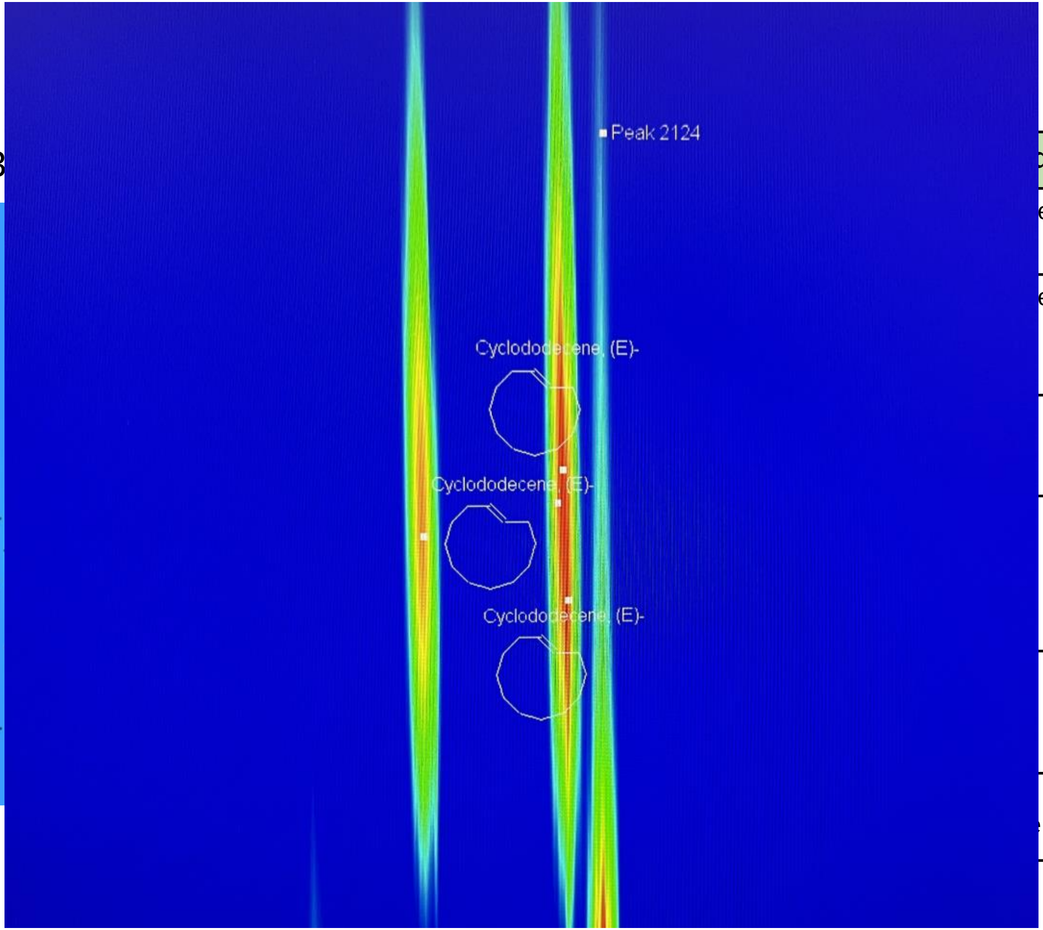

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	2-Ethyl-1-Hexene	2,5-Dimethyl-2,4-Hexadiene
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References

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Dr. Vozka's Research Lab

calstatela.edu/research/c3al

pvozka@calstatela.edu

www.linkedin.com/in/genesis-b-042363b3

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