14TH Multidimensional Chromatography Workshop

Quantitative Analysis of Aliphatic Olefins in Fuels made from Plastic Waste by Comprehensive Two-Dimensional Gas Chromatography

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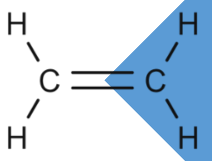
January 30, 2023

Overview

Comprehensive Two-Dimensional Gas Chromatography (GC×GC)



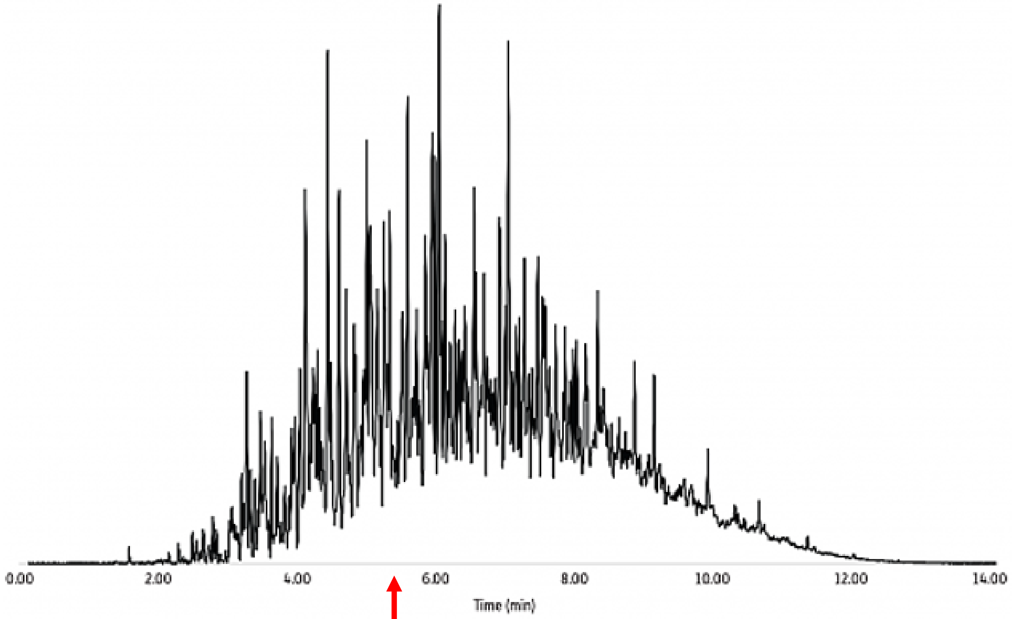
Quantitative Analysis of Aliphatic Olefins in Fuels made from Plastic Waste by GC×GC

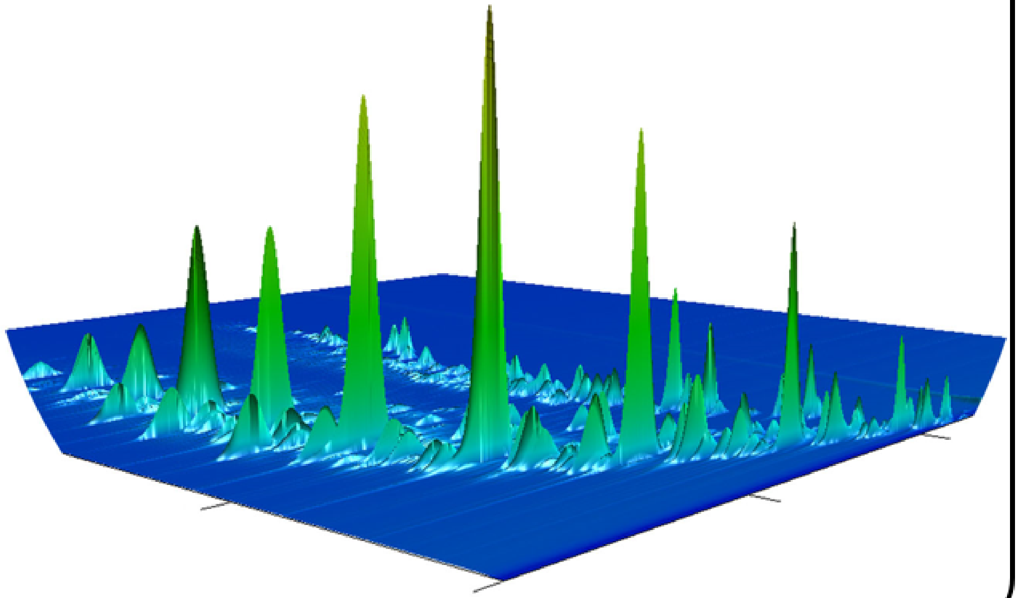
GC×GC in Academia/Teaching

1 D vs. 2 D

How it started:

How it's going:





peak capacity limited!

GC×GC Chromatogram

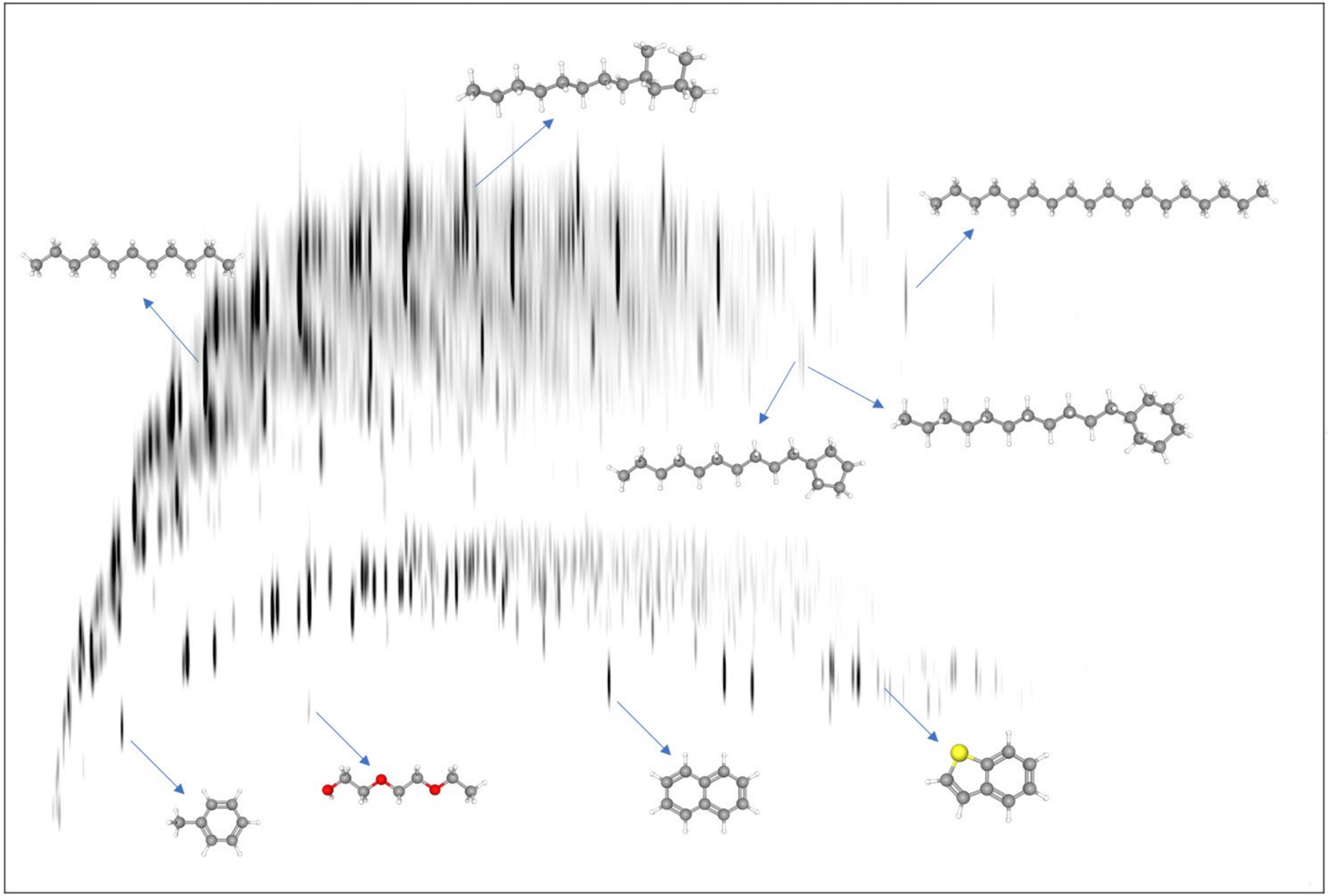
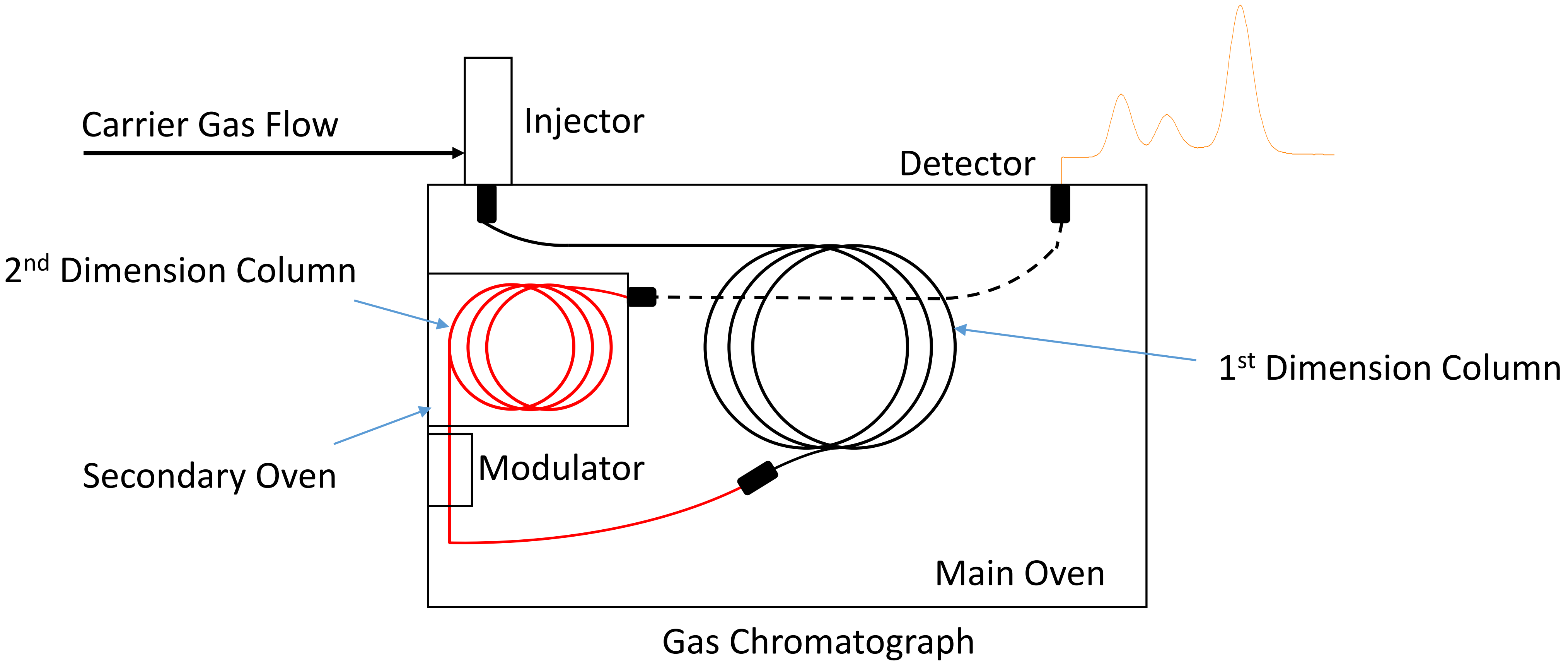


Diagram of a GC×GC Instrument



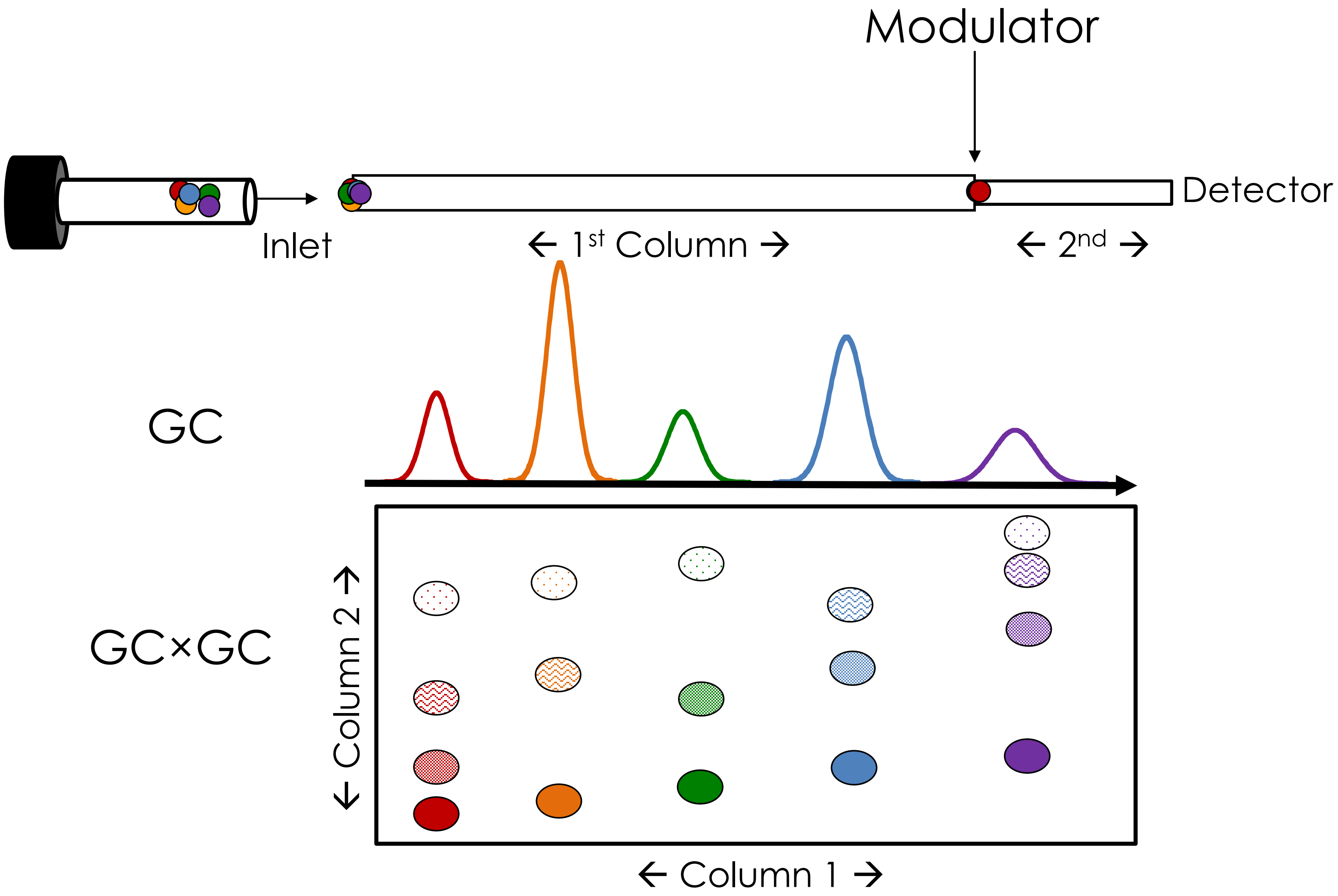
How GC×GC is achieved

1. Sample is injected on set of two columns connected in series

2. Primary column separates analytes in typical GC way

3. Analytes are modulated and then released onto secondary column

4. Secondary column separates analytes further with complementary phase chemistry



Slide: Christina Kelly, LECO

Modulation

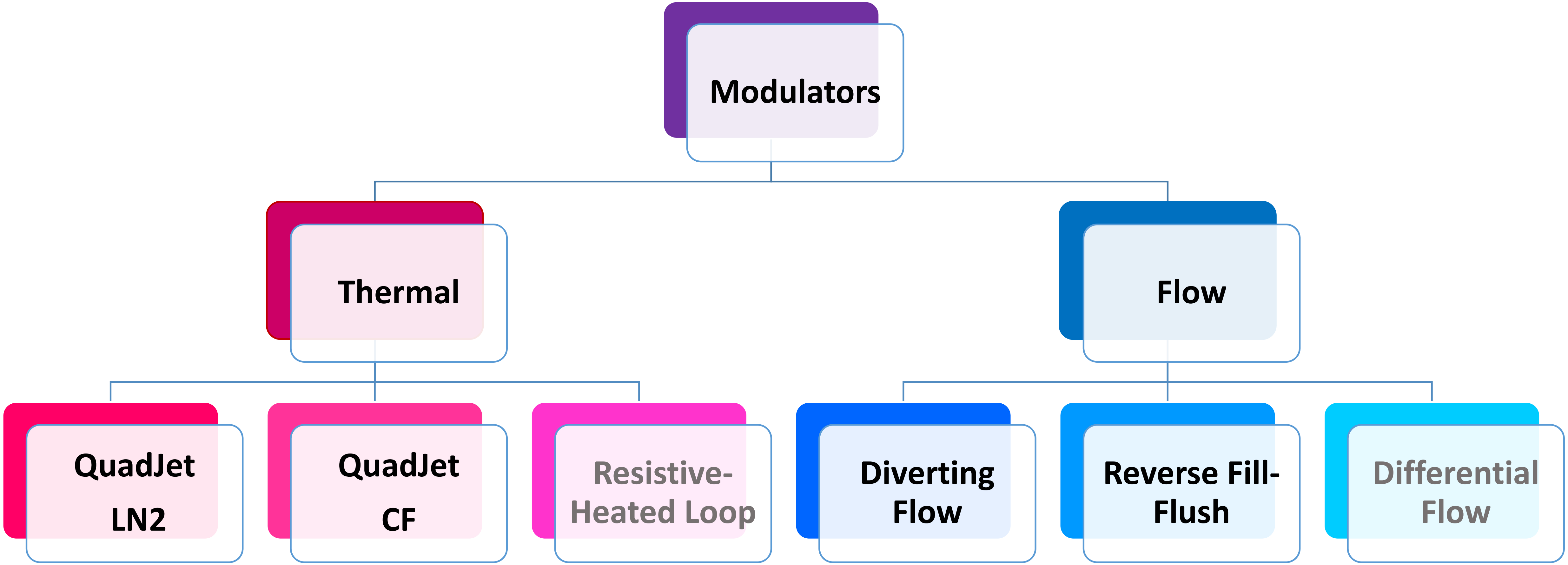
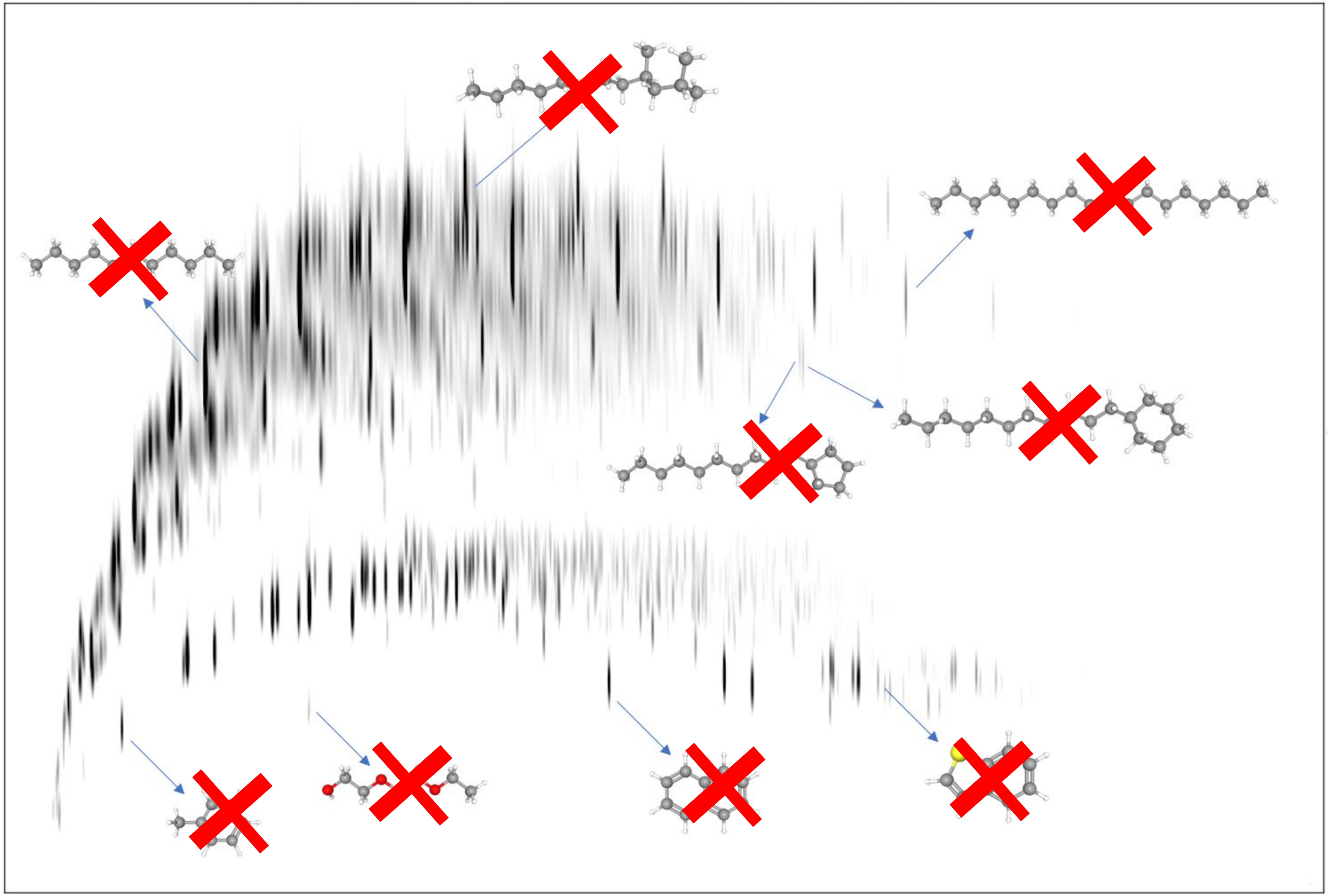
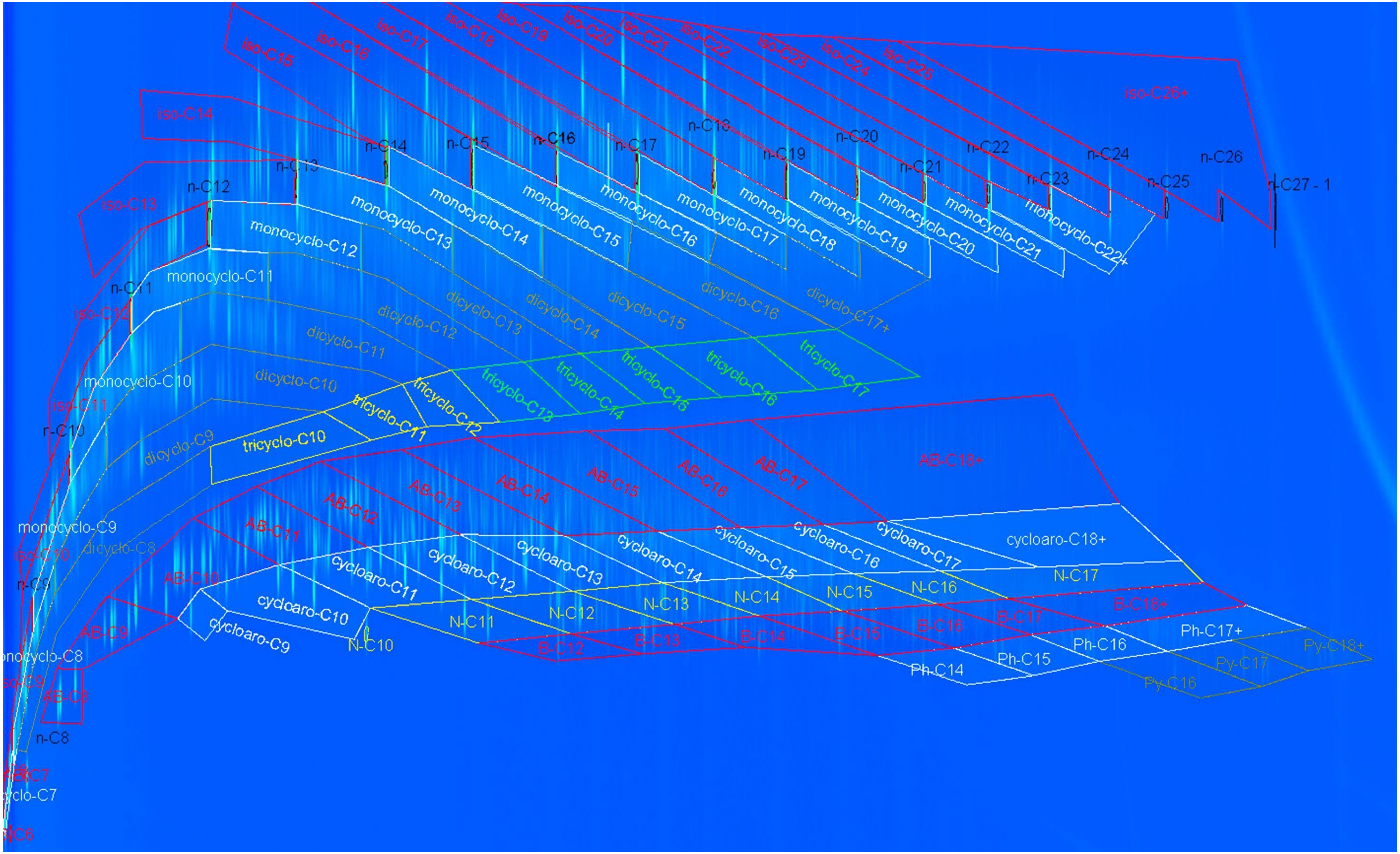


Figure: leco.com

GC×GC Chromatogram



GC×GC Classification



Quantitative results (some)

n-paraffins	F-76	Jet A	FT-IPK	Green diesel
C8	0.13	0.83	0.00	0.13
C9	0.42	5.05	0.00	0.20
C10	1.54	4.96	0.10	0.18
C11	2.32	3.36	0.00	0.00
C12	2.22	2.37	0.10	0.18
C13	2.21	1.90	0.08	0.23
C14	2.13	1.27	0.04	0.40
C15	1.93	0.76	0.03	0.88
C16	1.71	0.36	0.01	2.84
C17	1.58	0.10	0.00	1.76
C18	1.32	0.02	0.00	4.40
C19	1.10	0.00	0.00	0.04
C20	0.95	0.00	0.00	0.08
C21	0.72	0.00	0.00	0.00
C22	0.45	0.00	0.00	0.01
C23	0.24	0.00	0.00	0.00
C24	0.11	0.00	0.00	0.00
C25	0.05	0.00	0.00	0.00
C26	0.02	0.00	0.00	0.00
C27	0.00	0.00	0.00	0.00
Total n-paraffins	21.15	20.97	0.35	11.33

	F-76	Jet A	FT-IPK	Green diesel
Alkylbenzenes				
C7	0.06	0.07	0.00	0.03
C8	0.26	1.79	0.01	0.00
C9	1.30	4.86	0.07	0.00
C10	1.75	3.27	0.08	0.00
C11	1.33	2.15	0.04	0.00
C12	0.94	1.72	0.00	0.00
C13	0.63	1.04	0.00	0.00
C14	0.33	0.35	0.00	0.00
C15	0.25	0.19	0.00	0.00
C16	0.20	0.02	0.00	0.00
C17	0.19	0.00	0.00	0.00
C18 +	0.14	0.00	0.00	0.00
Total alkylbenzenes	7.40	15.46	0.20	0.03
Cycloaromatics				
C9	0.05	0.14	0.00	0.00
C10	0.44	0.78	0.00	0.00
C11	1.29	1.73	0.01	0.00
C12	1.68	2.24	0.05	0.00
C13	1.52	1.26	0.01	0.00
C14	1.19	0.73	0.00	0.00
C15	1.02	0.01	0.00	0.00
C16	0.36	0.00	0.00	0.00
C17	0.03	0.00	0.00	0.00
C18 +	0.00	0.00	0.00	0.00
Total Cycloaromatics	7.58	6.89	0.08	0.00

Vozka, P., Mo, H., Šimáček, P., Kilaz, G. (2018). Talanta, 186C, p. 140-146.

Detailed Analysis of Complex Chemical Mixtures

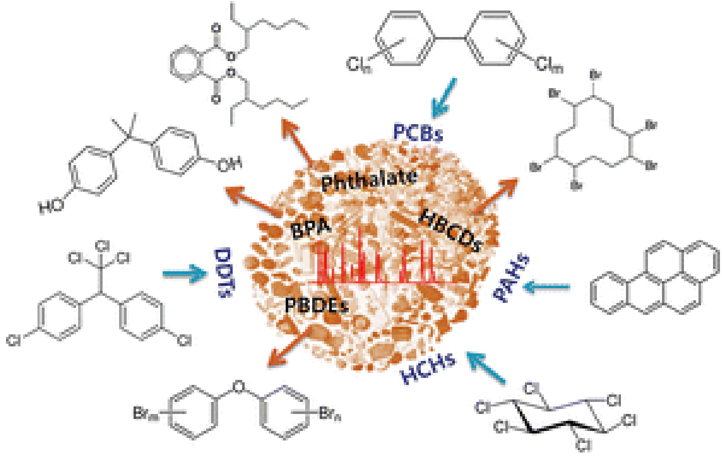
Such as:

- Petroleum products

- Beach Oil spills

- Microplastics analysis

  (Organic compounds)



Plastic Waste in Oceans

Plastic Waste in Oceans

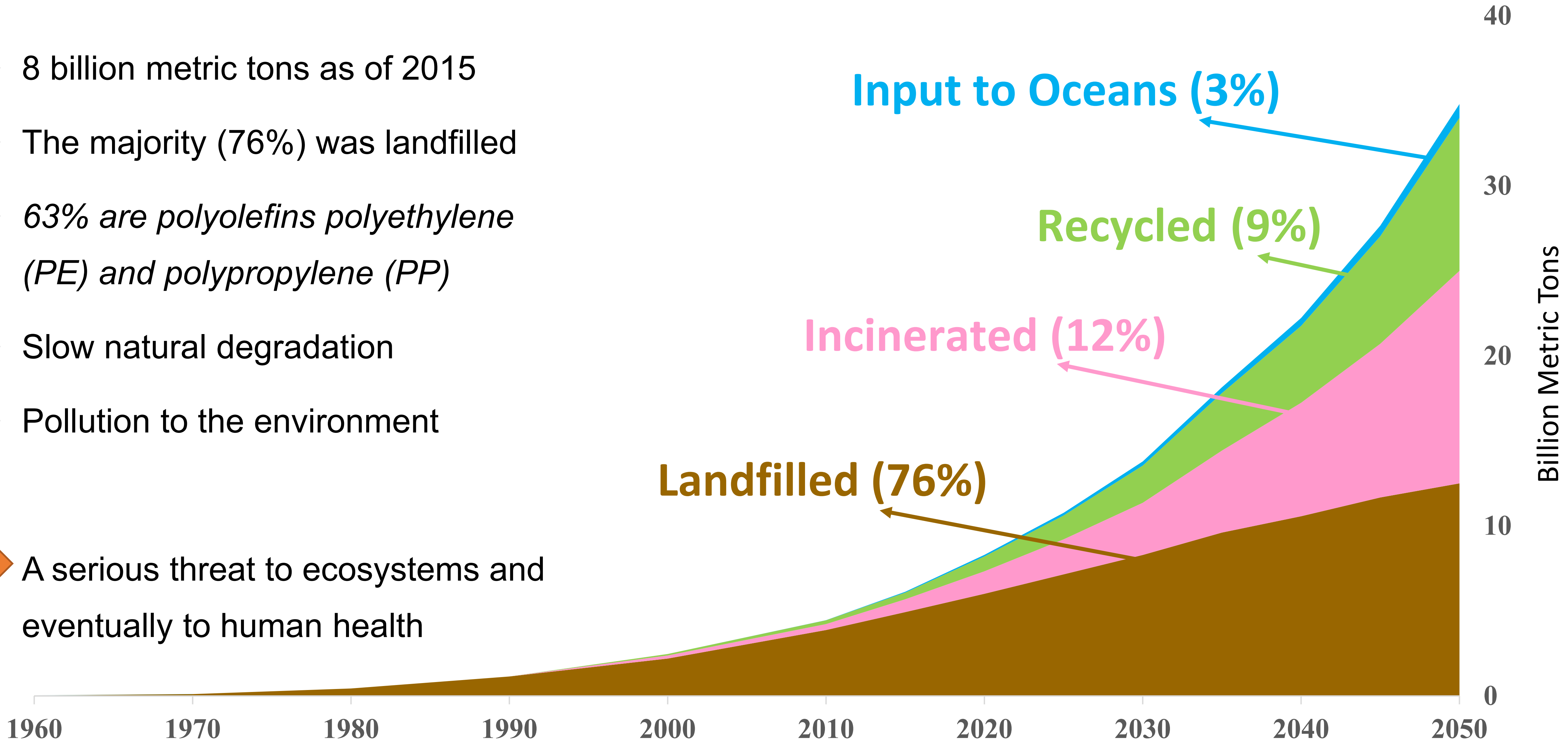

Experts say that by 2050 there may be more plastic than fish in the ocean, or perhaps only plastic left.

Plastic Waste - Landfill

The growing plastic waste problem

- 8 billion metric tons as of 2015
- The majority (76%) was landfilled
- *63% are polyolefins polyethylene (PE) and polypropylene (PP)*
- Slow natural degradation
- Pollution to the environment

A serious threat to ecosystems and eventually to human health



Global Plastic Waste Accumulation/Disposal and Projection

Chemical conversion of plastic waste into fuels

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

PURDUE UNIVERSITY

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

- Hydrothermal Processing of: polyolefin plastic waste

Chemical conversion of plastic waste into fuels

Collaboration with:

PURDUE UNIVERSITY

Fuel 273 (2020) 117726

Contents lists available at ScienceDirect

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Full Length Article

Conversion of polyethylene waste into clean fuels and waxes via hydrothermal processing (HTP)

Kai Jin[a,b,1], Petr Vozka[b,1], Gozdem Kilaz[b], Wan-Ting Chen[c], Nien-Hwa Linda Wang[a,*]

[a] Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN, 47907, USA
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[c] Department of Plastic Engineering, University of Massachusetts Lowell, Lowell, MA, 01854, USA

Fuel 294 (2021) 120505

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

ELSEVIER

Full Length Article

Low-pressure hydrothermal processing of mixed polyolefin wastes into clean fuels

Kai Jin[a], Petr Vozka[b], Clayton Gentilcore[c], Gozdem Kilaz[a], Nien-Hwa Linda Wang[c,*]

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Chemical conversion of plastic waste into fuels

Collaboration with:

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Production of Transportation Fuels Via Hydrotreating of Scrap Tires Pyrolysis Oil

22 Pages • Posted: 1 Nov 2022

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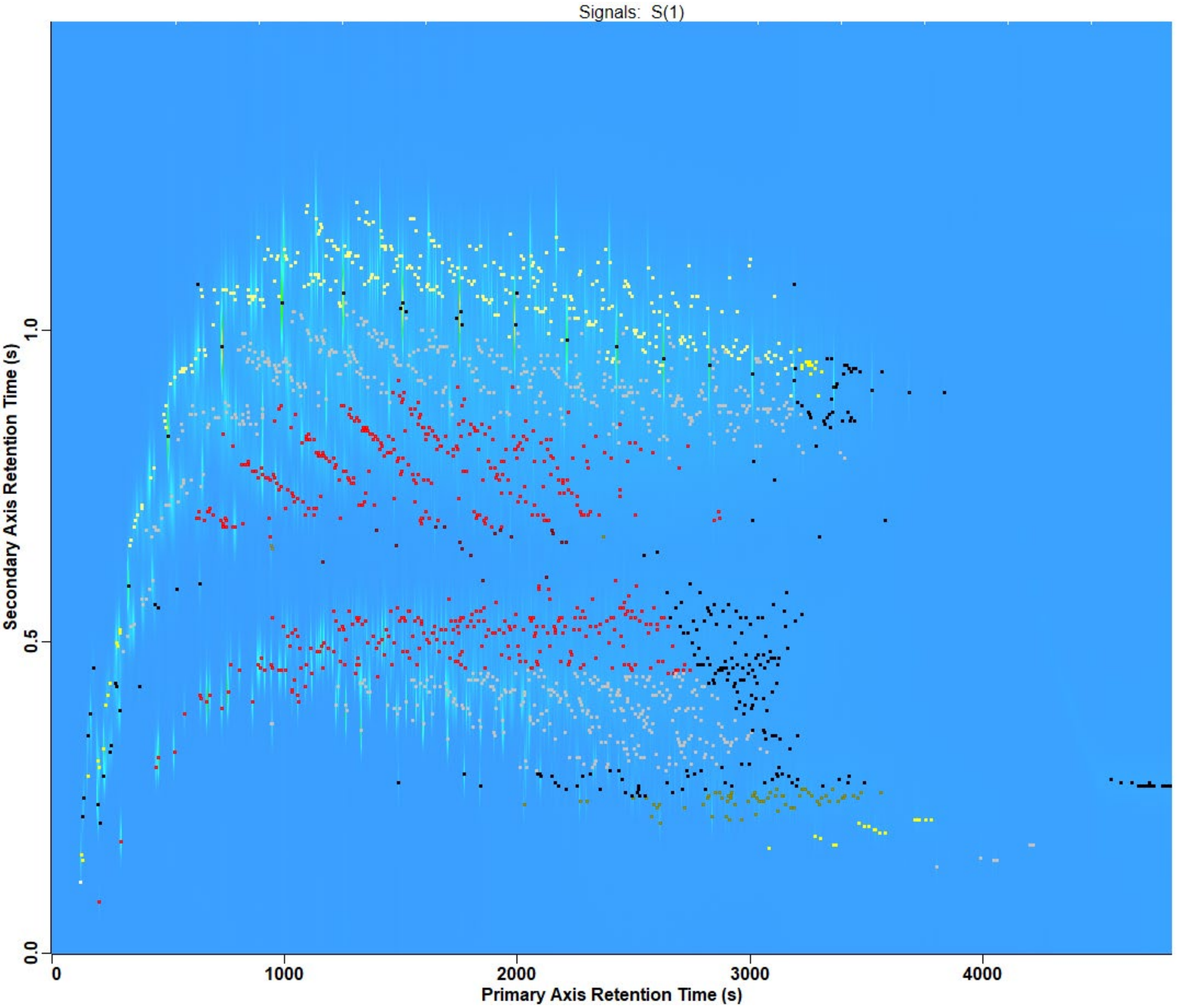
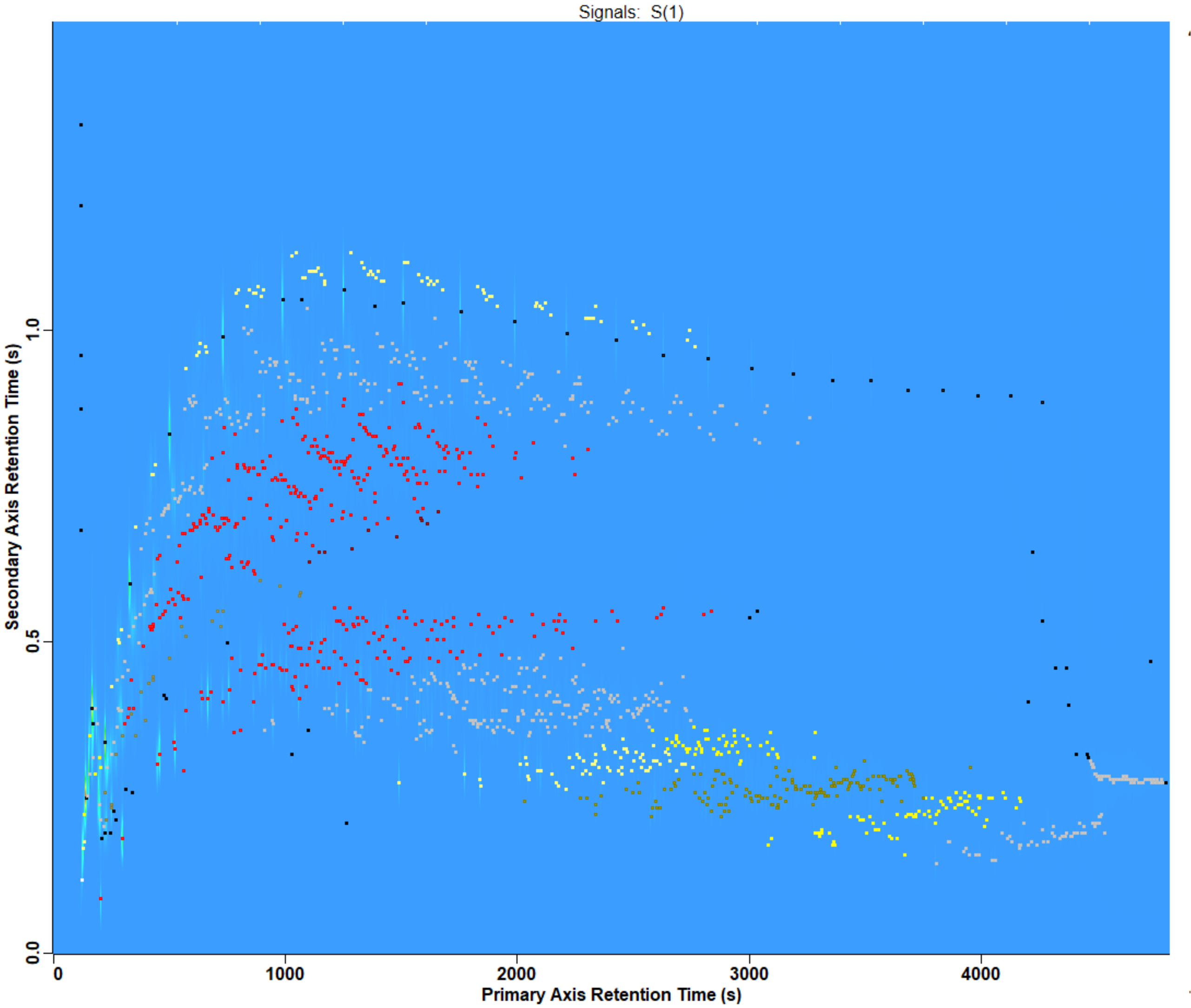
Commercial Diesel fuel



HTP Diesel fuel



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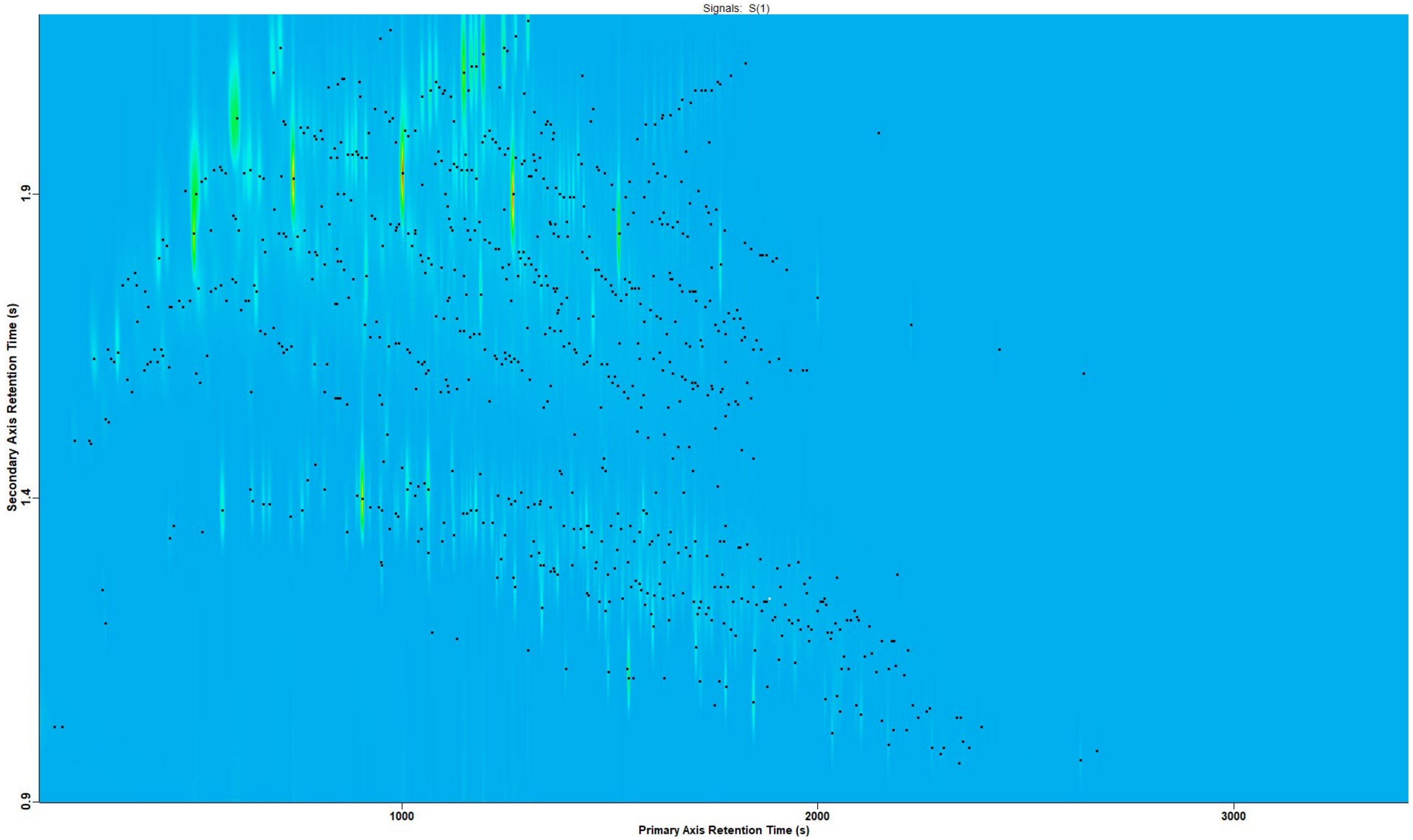
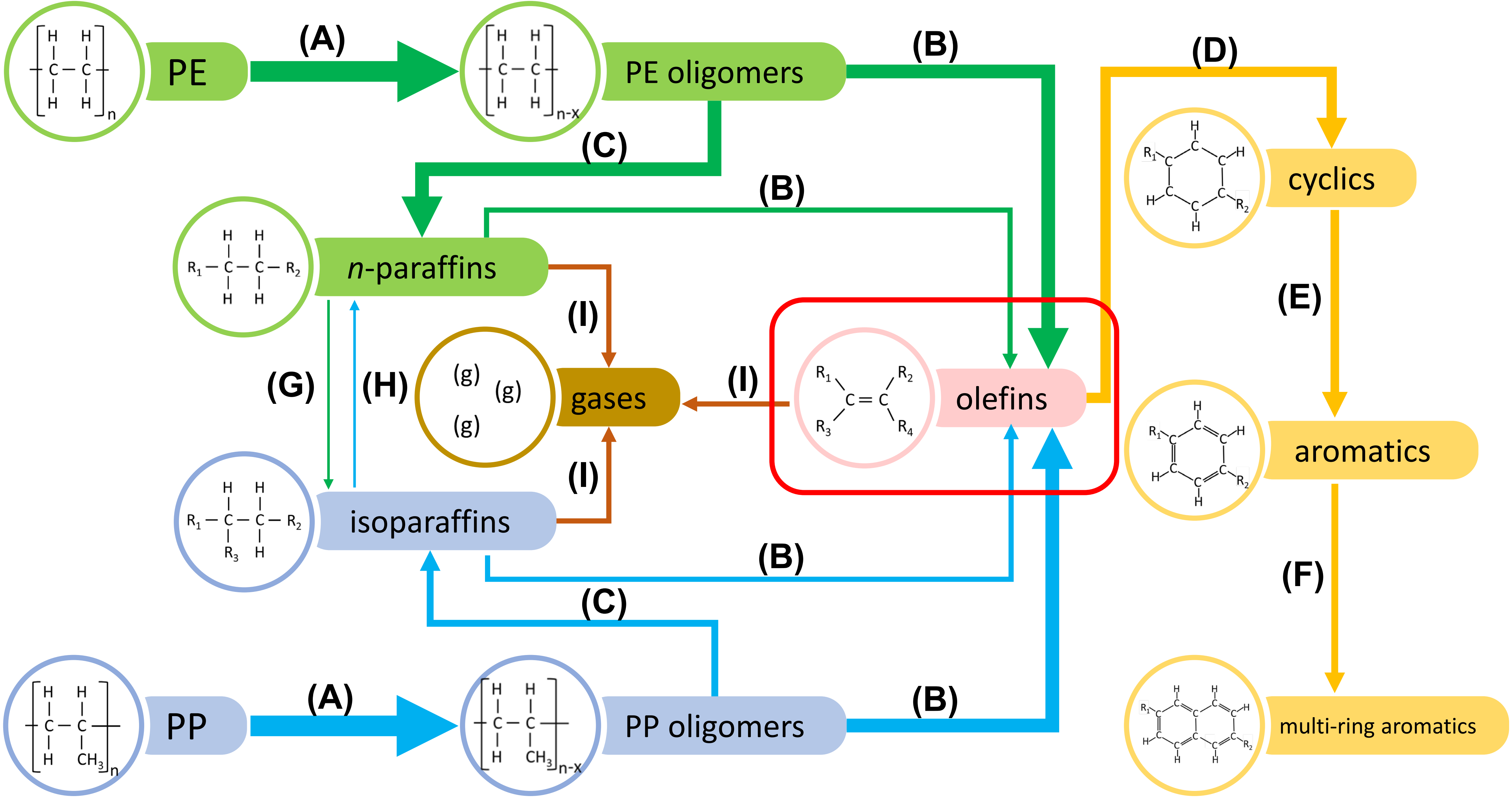
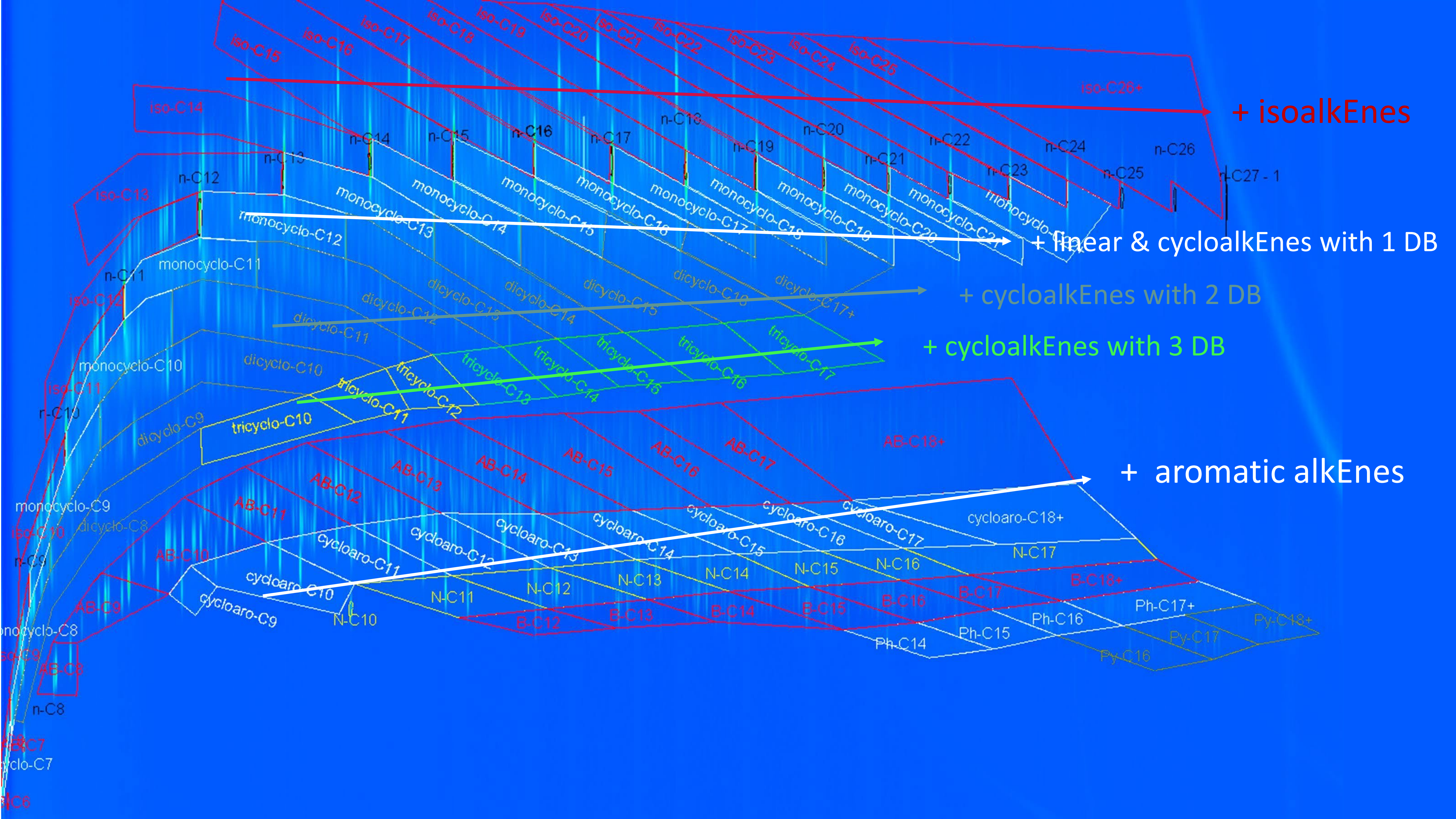
Diesel fuel distillation range pyrolysis oil after hydrotreating (270 °C and 6 MPa)





Potential reaction pathways of PE and PP co-processing under LP-HTP. (A) depolymerization, (B) β-scission, (C) hydrogen abstraction, (D) cyclization, (E) dehydrogenation, (F) formation of multi-ring aromatics, (G) isomerization, (H) formation of short *n*-paraffins ($C_{6\text{-}7}$), (I) further cracking to gases. The thickness of the arrows indicates the relative amounts of products.


+ isoalkEnes
+ linear & cycloalkEnes with 1 DB
+ cycloalkEnes with 2 DB
+ cycloalkEnes with 3 DB
+ aromatic alkEnes

DMDS Derivatization

Sample Preparation

IS, DMDS, and I_2 solution

↓

70 °C oven for at least an hour

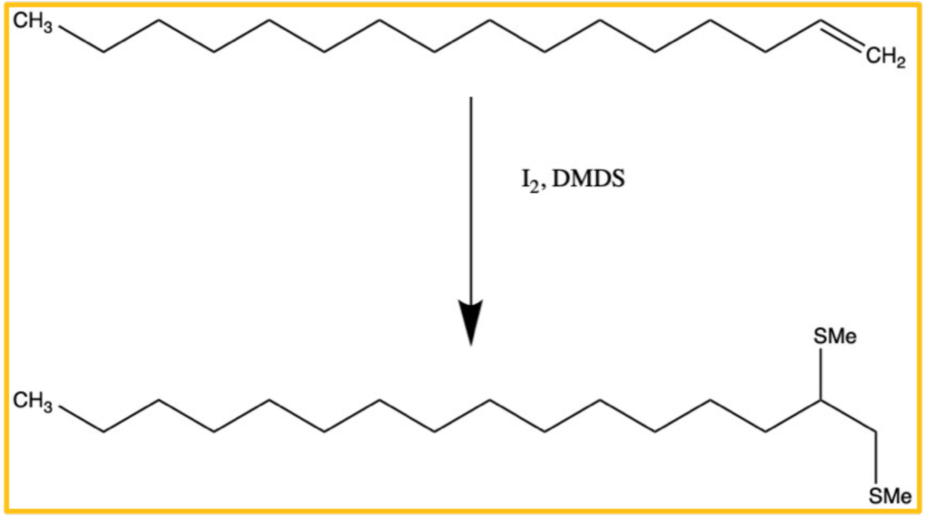
↓

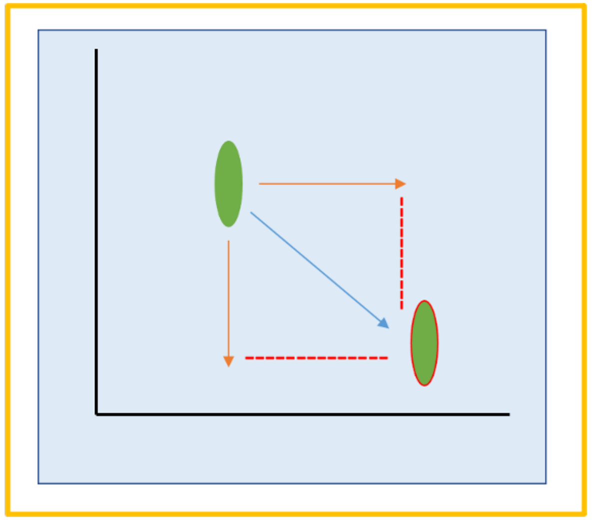
Sodium Thiosulfate

↓

Organic phase analyzed via GC×GC-FID

Theory

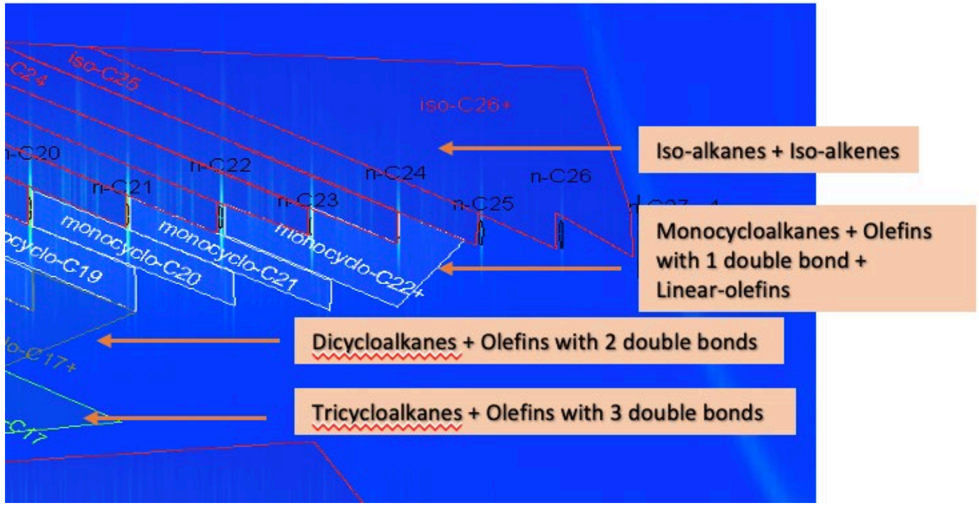




Calculations

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

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

Calculations

Olefins in sample

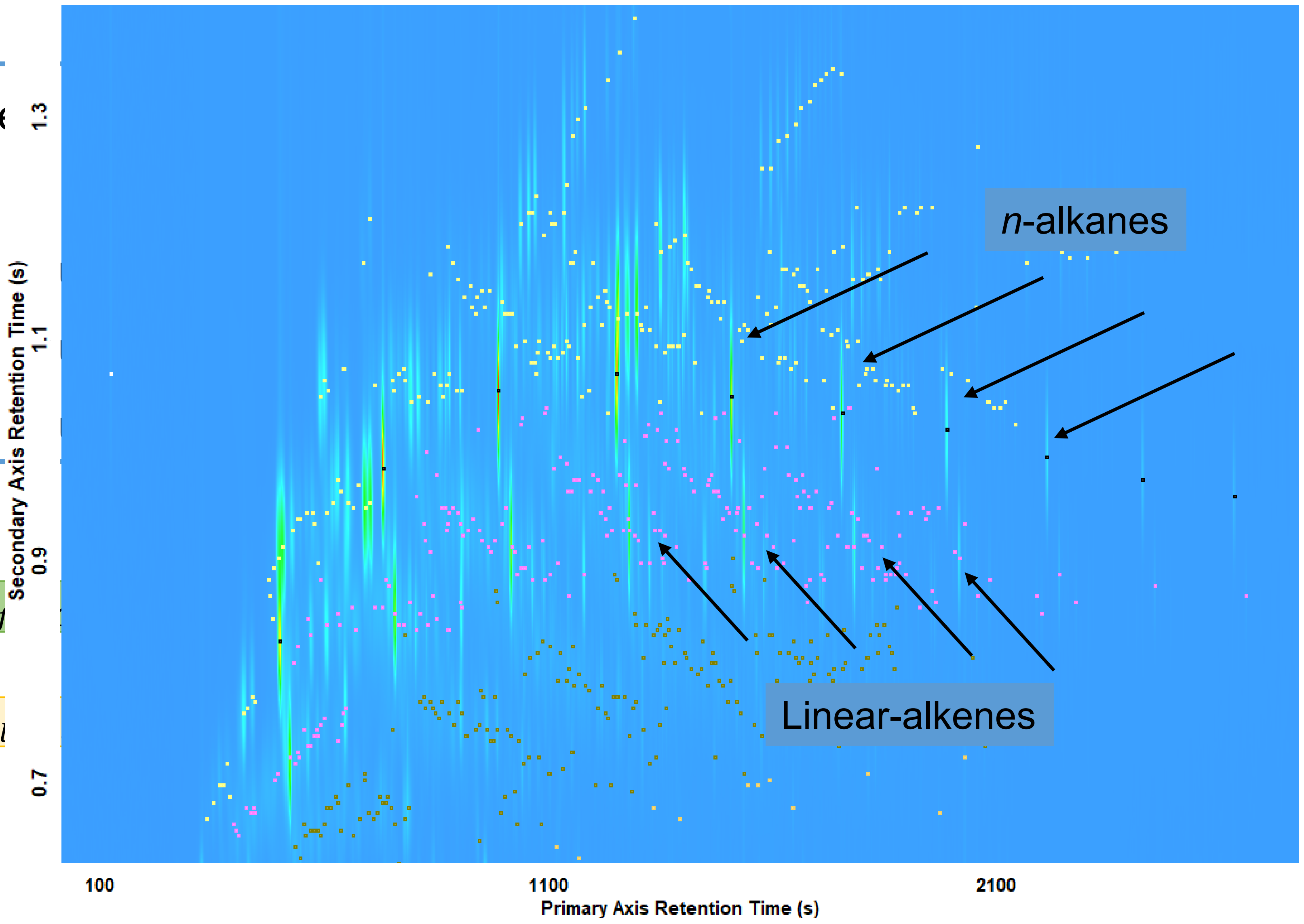
- Iso-alkenes
- Olefins with 1
- Olefins with 2
- Olefins with 3

Equation

$Wt.\%_{Olef}$

Example

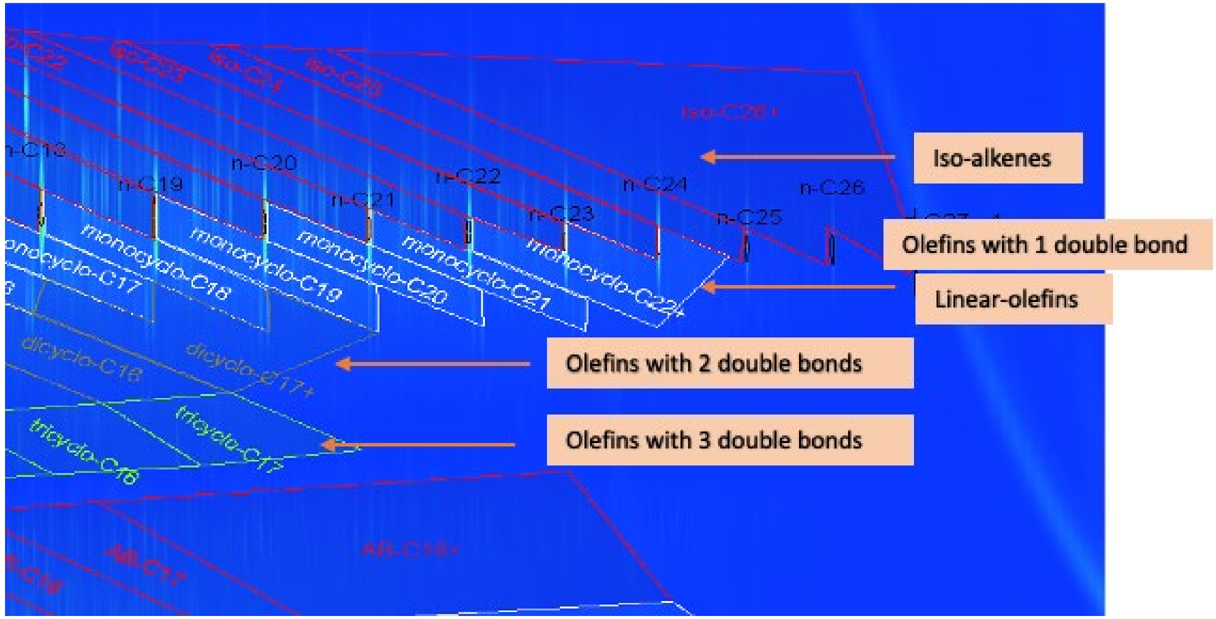
$Wt.\%_{Iso-al}$ … $C11$



Calculations

Olefins in sample

- Linear-alkenes
- Iso-alkenes
- Olefins with 1 double bond
- 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

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

Results (selected)

Example

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

UCT Prague sample; diesel fraction obtained from the pyrolysis of scrap tires

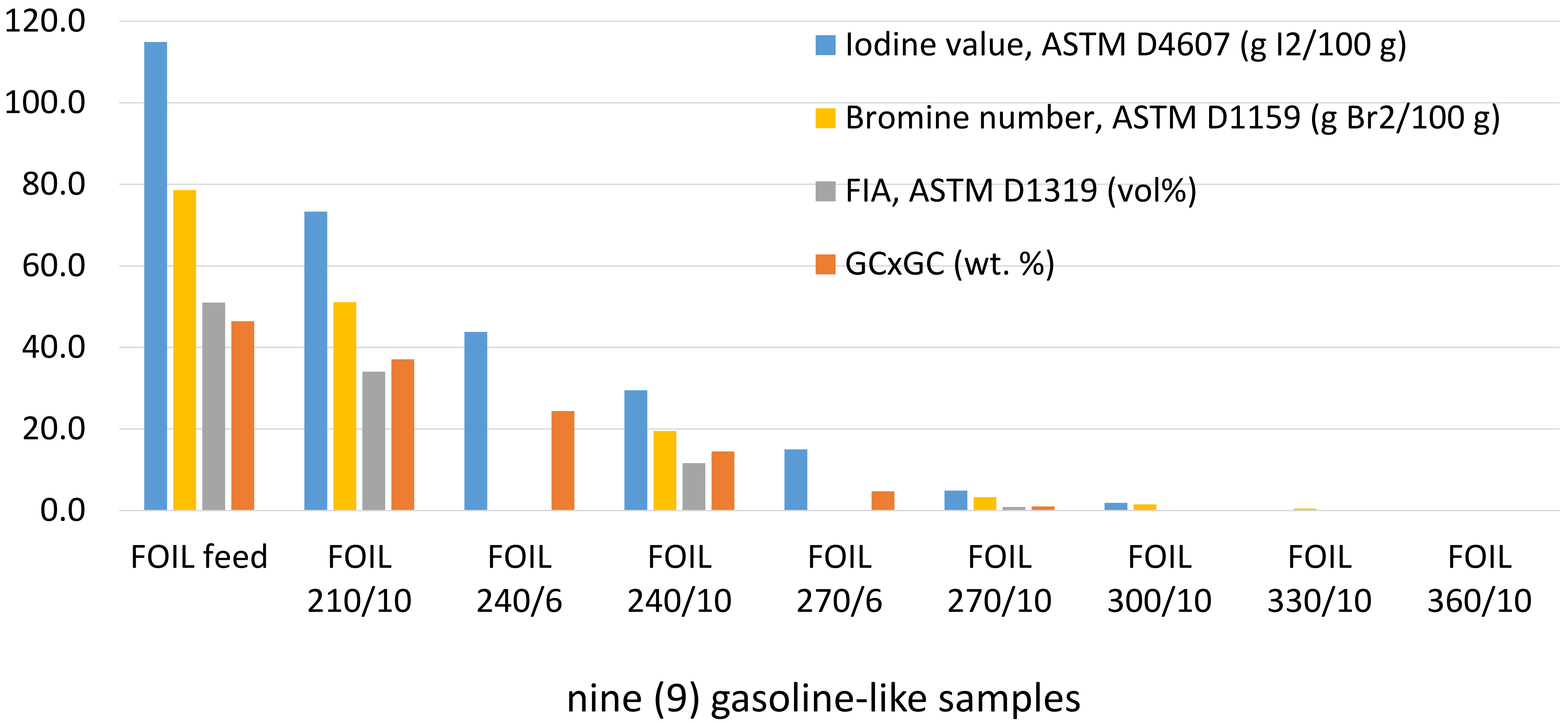
Cycloalkanes	Surovina PNEU PE (area)	Surovina PNEU PE (wt. %)	Post-Der. (area)	Post-Der. Normalization (area)	Olefins (area)	Olefin (wt. %)	Real Cyclo (wt. %)
monocyclo-alkane C5	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C6	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C7	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C8	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C9	2457.75	0.46	525.59	417.13	2040.62	0.38	0.08
monocyclo-alkane C10	5073.85	0.94	4278.24	3395.43	1678.42	0.31	0.63
monocyclo-alkane C11	8531.58	1.59	6142.81	4875.25	3656.33	0.68	0.91
monocyclo-alkane C12	3023.63	0.56	1665.03	1321.45	1702.18	0.32	0.25
monocyclo-alkane C13	2498.03	0.46	1307.33	1037.56	1460.47	0.27	0.19
monocyclo-alkane C14	1658.46	0.31	510.81	405.40	1253.06	0.23	0.08
monocyclo-alkane C15	382.18	0.07	0	0	382.18	0.07	0.00
monocyclo-alkane C16	201.36	0.04	0	0	201.36	0.04	0.00
monocyclo-alkane C17	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C18	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C19	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C20	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C21	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C22	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C23	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C24	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C25	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C26	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C27	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C28	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C29	0	0.00	0	0	0	0.00	0.00
monocyclo-alkane C30+	0	0.00	0	0	0	0.00	0.00
total monocyclo-alkanes	**23826.84**	**4.43**	**14429.81**	**11452.23**	**12374.61**	**2.30**	**2.13**

Results (totals)

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
Olefins with 1 Double Bond + Linear alkenes	3.47
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

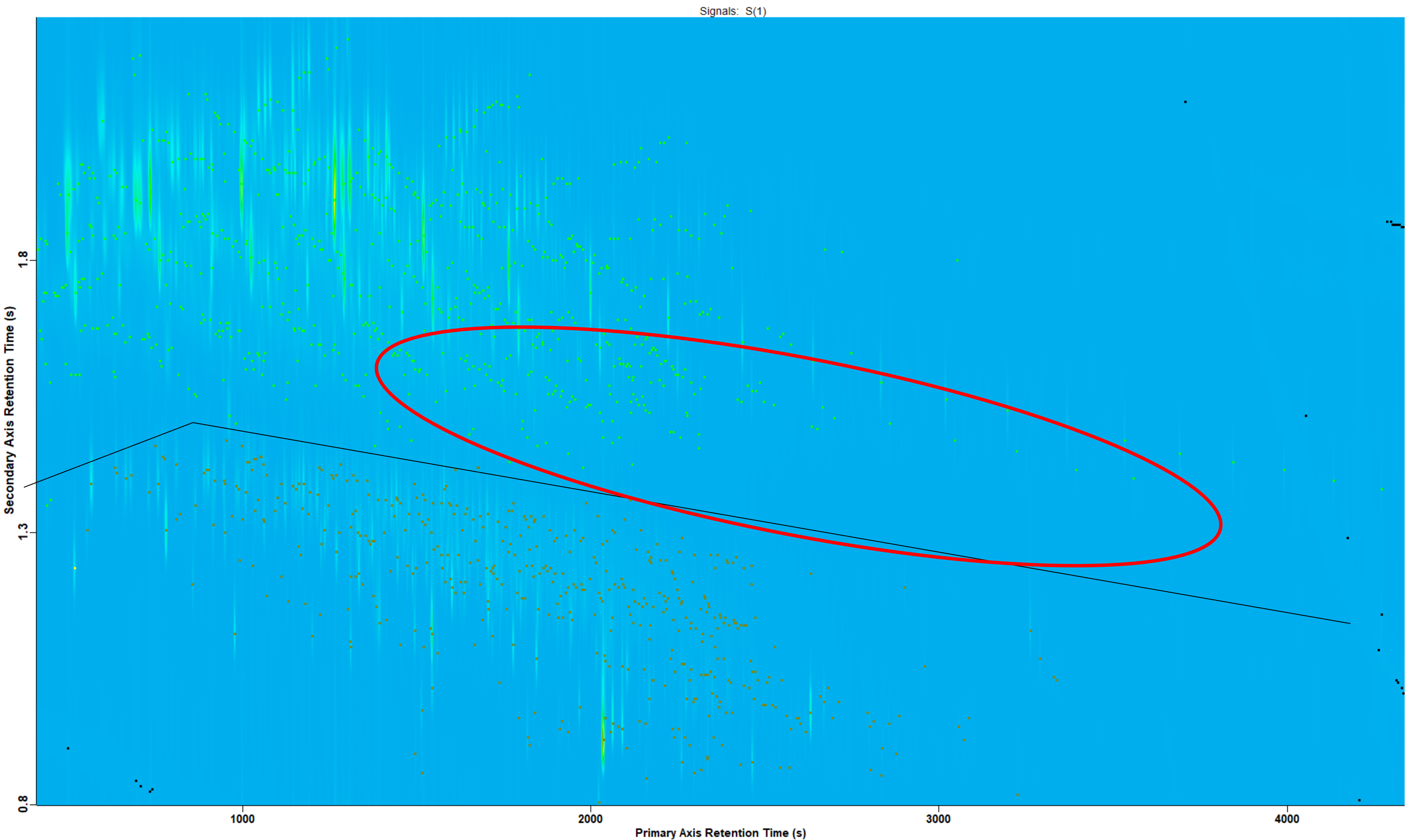
Validation → comparison to other ASTM methods



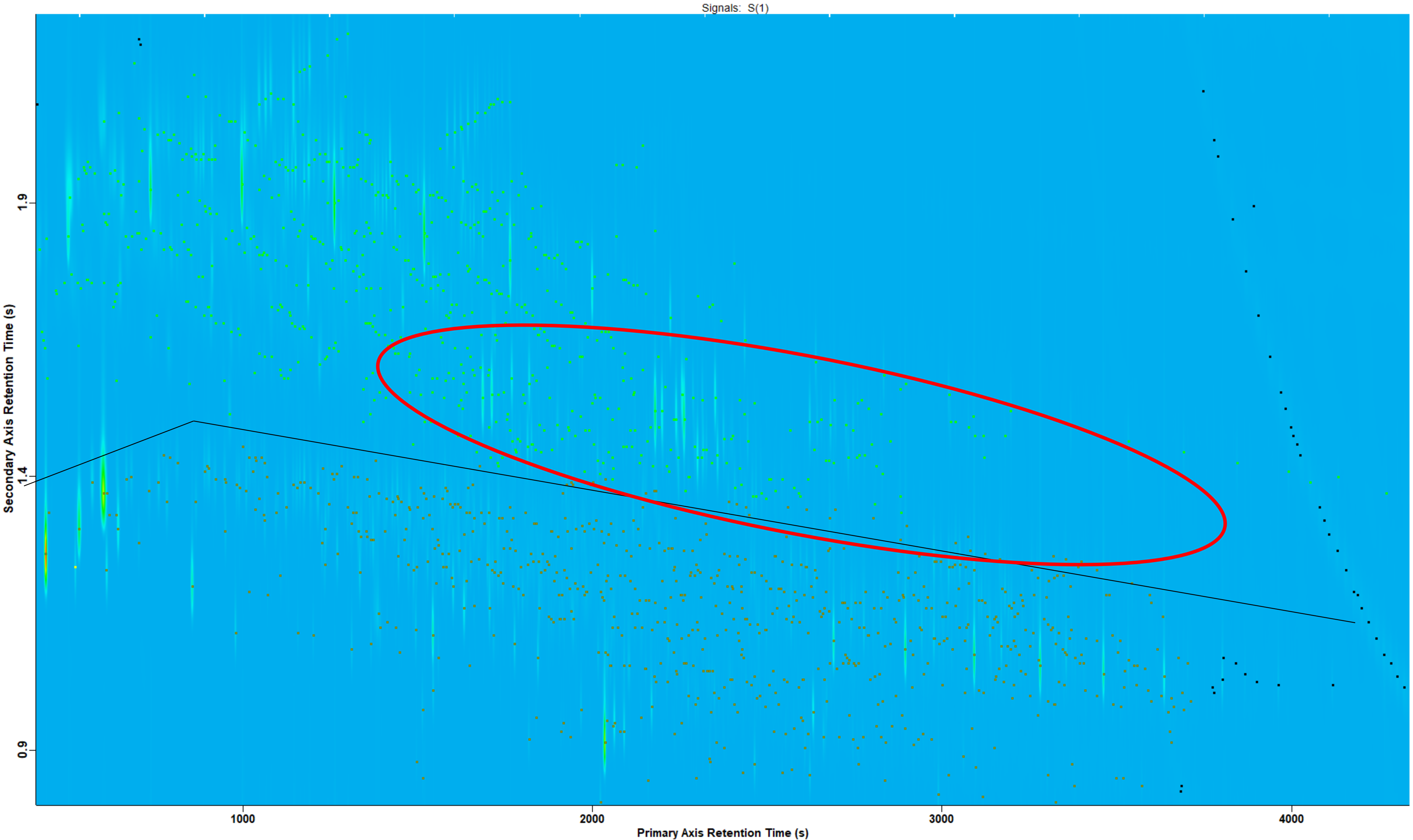
Methods - disadvantages

- Iodine – hard to buy in some places
- DMDS – ….
- Main problem – heavier isoalkenes → not shifting to aromatic region

Chromatogram – diesel-like sample pre-derivatization



Chromatogram – diesel-like sample post-derivatization



Future work

- Validate the results using GC×GC-TOFMS

Pegasus BT 4D GC×GC-TOFMS

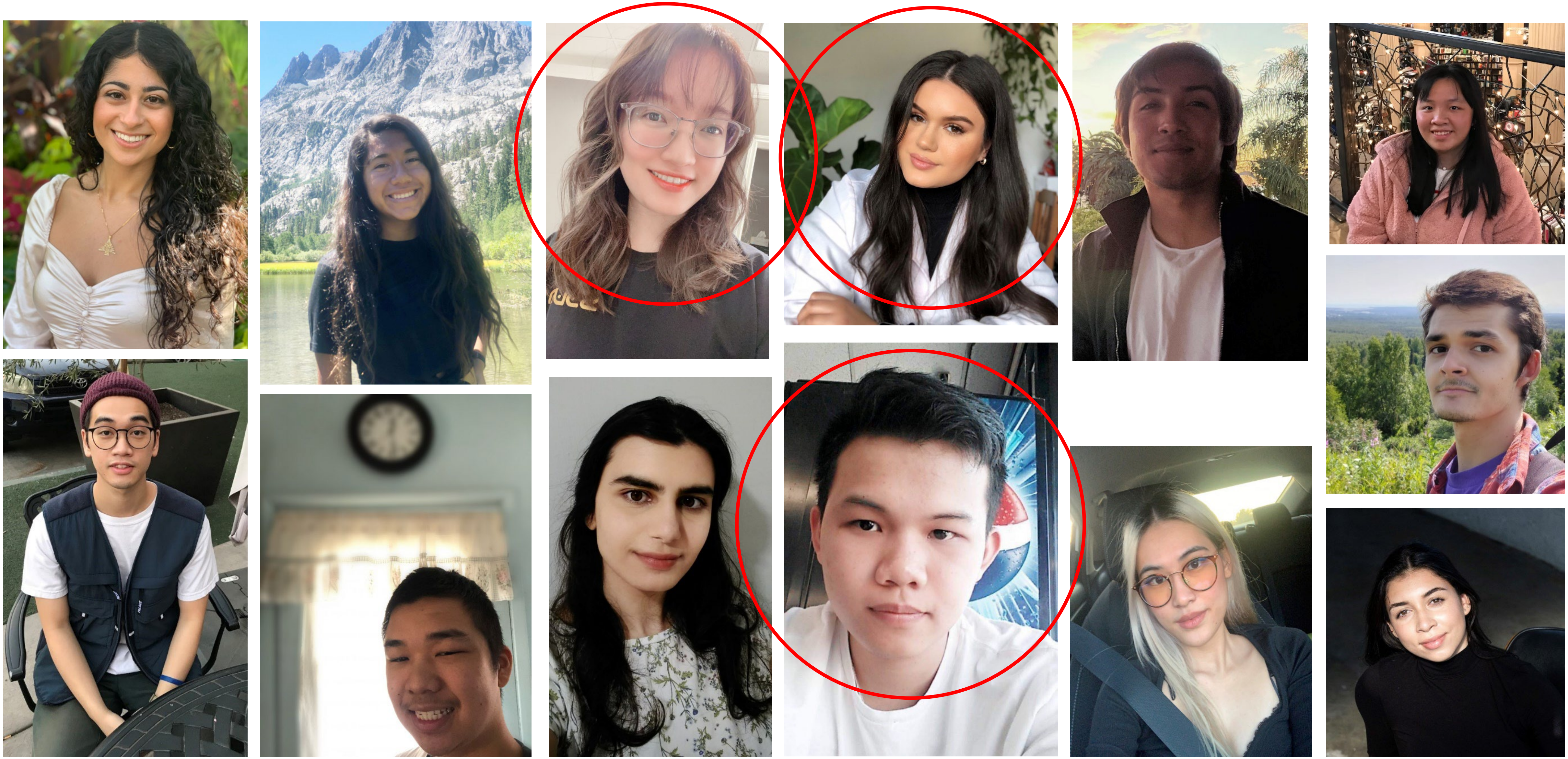
Benchtop GC-MS with high-performance GC×GC modulation

with thermal desorption/pyrolysis unit with a LN2 trap

Future work

- Validate the results using GC×GC-TOFMS
- Attempt to use ChromaTOF Tile
  (or beg Dr. Synovec group for their help)
- Use different derivatization methods (e.g., oxidative derivatizations, such as ozonolysis and single oxygen)

My awesome students…



GC×GC Training/Research Facility

LECO
EMPOWERING RESULTS
&
C3AL
COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

ChromaTOF®
ChromaTOF® | Tile

Pegasus BT GC-TOFMS
Benchtop GC Time-of-Flight Mass Spectrometer

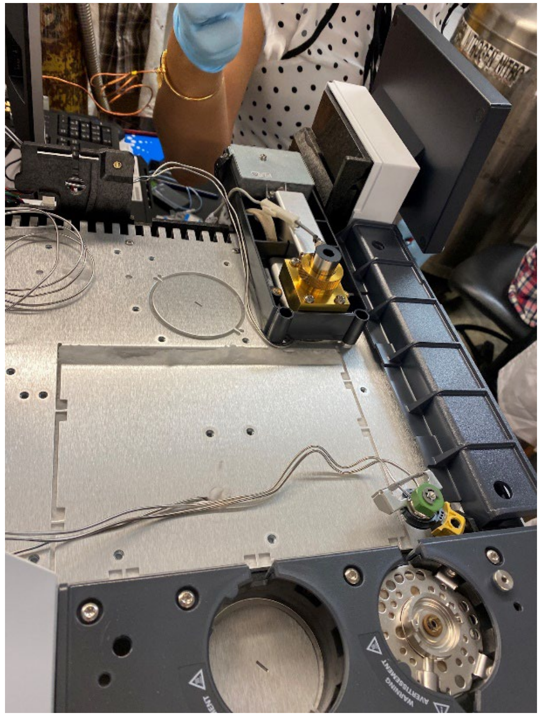
QuadJet SD
GC×GC modulation system with Flame Ionization Detection

Pegasus BT 4D GC×GC-TOFMS
Benchtop GC-MS with high-performance GC×GC modulation

Course: Analytical Separations and Mass Spectrometry

What I did:

- asked for free (broken/used) stuff from the vendors
- redesigned the curriculum by including MDC instruments
- let students practice on real instruments/parts



C^{3}AL

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Thank you, thank you….!

Dr. Pierre-Hugues Stefanuto

Dr. Katelynn A. Perrault

Dr. Dwight Stoll

14TH Multidimensional Chromatography Workshop