UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Comprehensive Two-Dimensional Gas Chromatography (GC×GC) in the Analysis of Complex Chemical Mixtures

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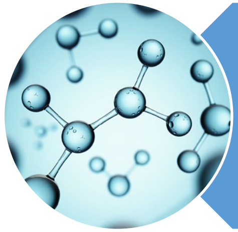
Chemistry & Biochemistry
California State University, Los Angeles

January 25, 2023

Overview

My Research Background



Complex Chemical Mixtures

Comprehensive Two-Dimensional Gas Chromatography (GC×GC)

Complex Chemical Composition Analysis Lab (C^3AL)

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

B.S. Chemistry and Chemical Technologies

M.S. Chemistry and Technology of Fuels and Environment

PURDUE UNIVERSITY

Ph.D., Chemistry of alternative aviation fuels

Post-Doctoral Researcher, Characterization of alternative aviation fuels

Office of Naval Research — ONR — Science & Technology

Naval Air Systems Command

Naval Research Laboratory — Washington, DC

Air Force Research Laboratory

Federal Aviation Administration

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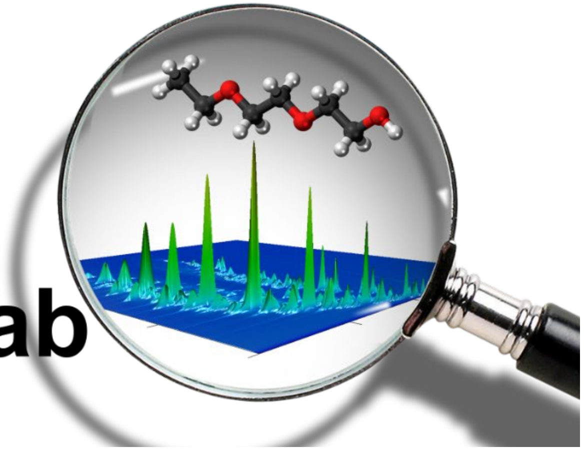
CALIFORNIA STATE UNIVERSITY, LOS ANGELES

Welcome to Dr. Vozka Research Lab



C^3AL

COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

GC×GC Training/Research Facility

LECO
EMPOWERING RESULTS
&
C3AL
COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

ChromaTOF®
ChromaTOF®|Tile

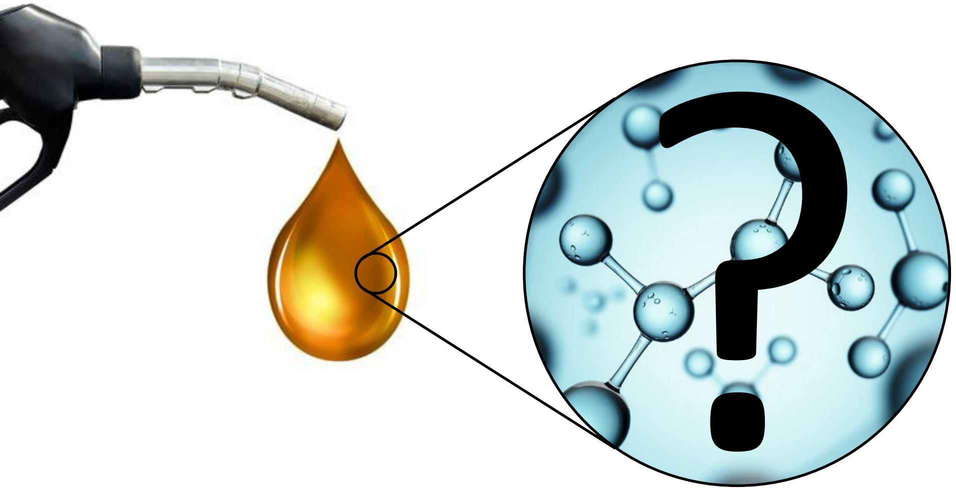
Pegasus BT GC-TOFMS
Benchtop GC Time-of-Flight Mass Spectrometer

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

Complex Chemical Mixtures

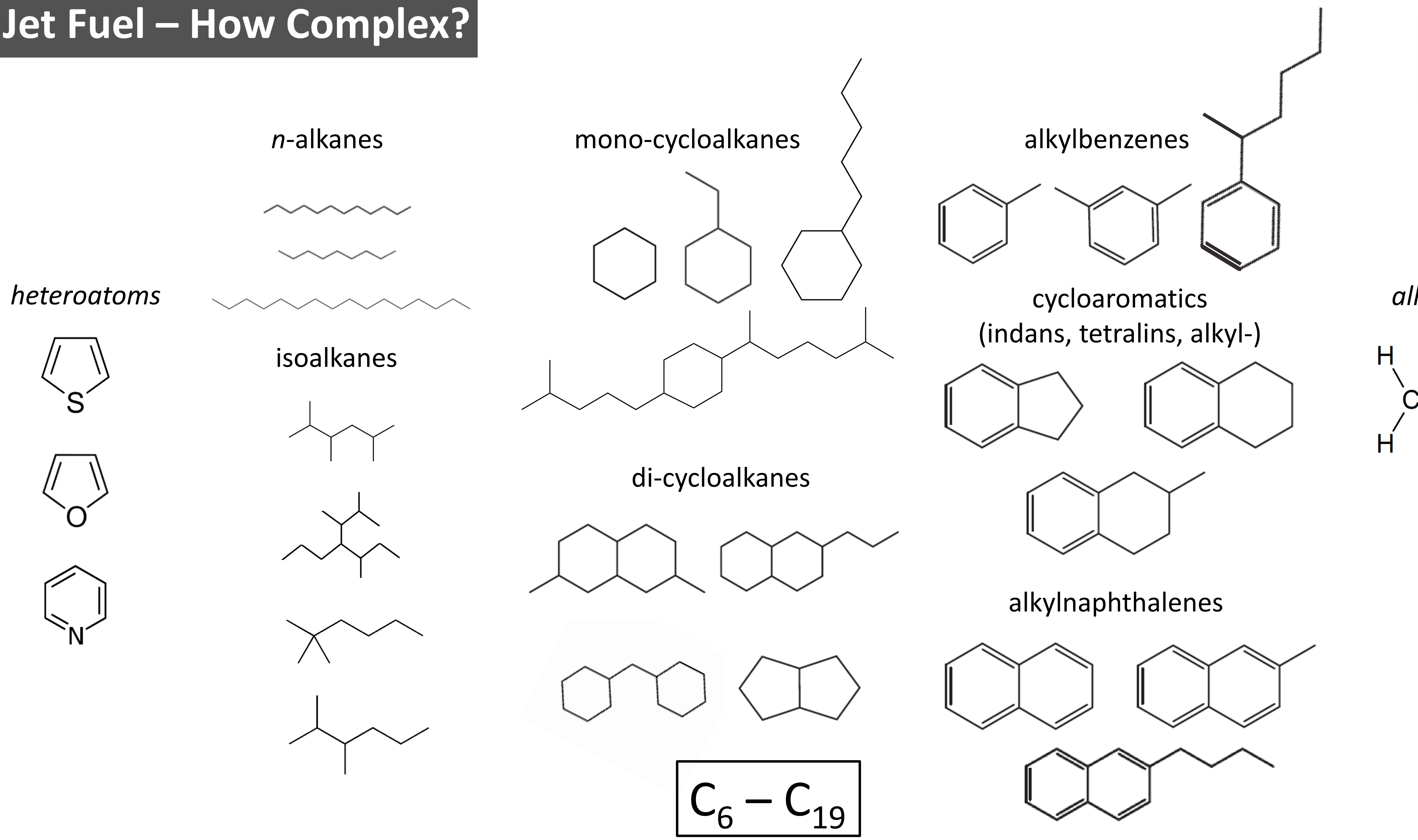
Example of a Complex Chemical Mixture



Left top: alibaba.com
Left bottom: es.123rf.com

Right top: oilprice.com
Right bottom: newsnation.in

Jet Fuel – How Complex?



Fuel Chemical Composition

Common:

Nuclear Magnetic Resonance

- aromatics and saturates carbon content

High-Pressure Liquid Chromatography

- aromatics content (mono-, di-, and poly-)

Gas Chromatography

- each *n*-paraffin content
- total contents of *n*-alkanes, isoalkanes, alkenes, naphthenes, aromatics, and oxygenates)

Left: prnewswire.com Middle: waters.com Right: agilent.com

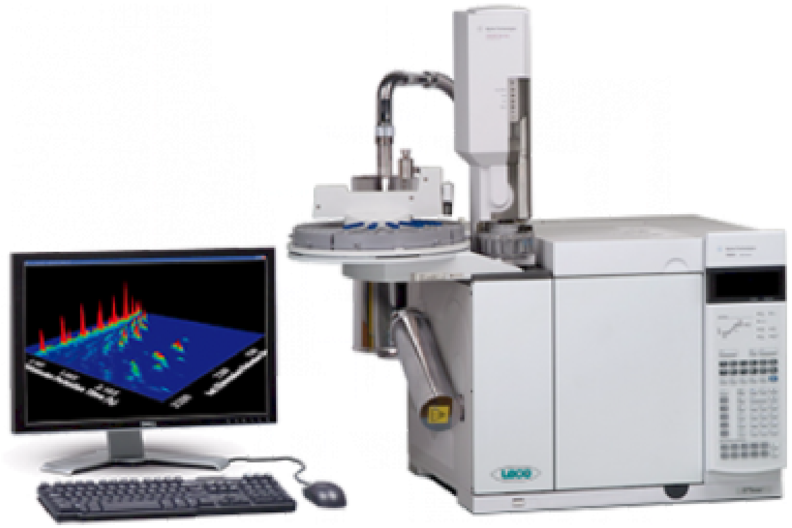
Comprehensive two-dimensional gas chromatography

Novel & Currently Growing:

Comprehensive two-dimensional gas chromatography (GC×GC) with various detectors

- each hydrocarbon class
- each carbon number
- each compound

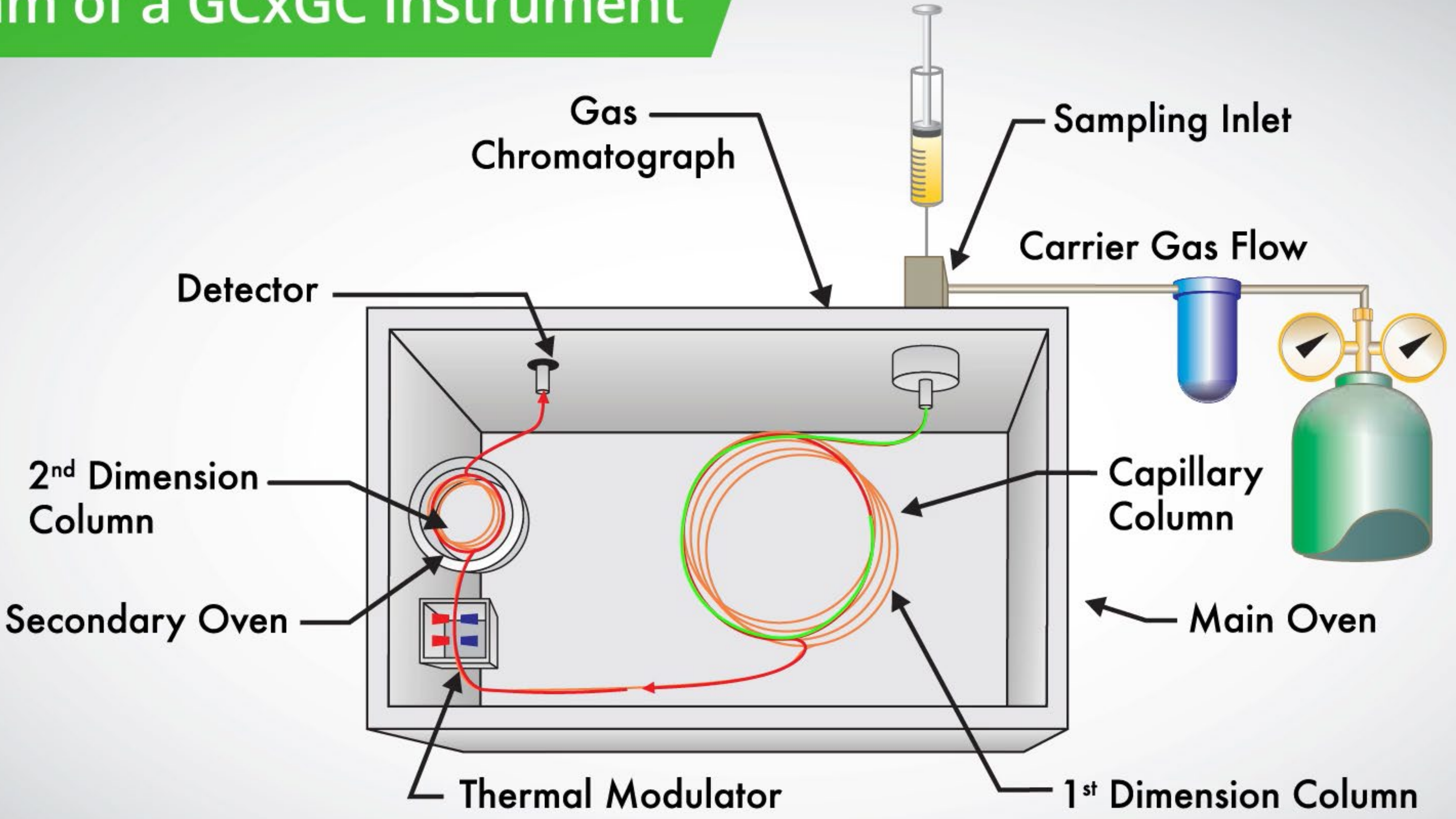
time-of-flight mass spectrometry (high-resolution)



flame ionization detector

Both: leco.com

Diagram of a GCxGC Instrument



The GCxGC hardware (modulator and secondary oven) are mounted inside the primary GC oven. Control of the GC autosampler, GC, LECO's GCxGC thermal modulator, and the selected detector are fully integrated within a single computer using LECO's ChromaTOF software.

Modulation

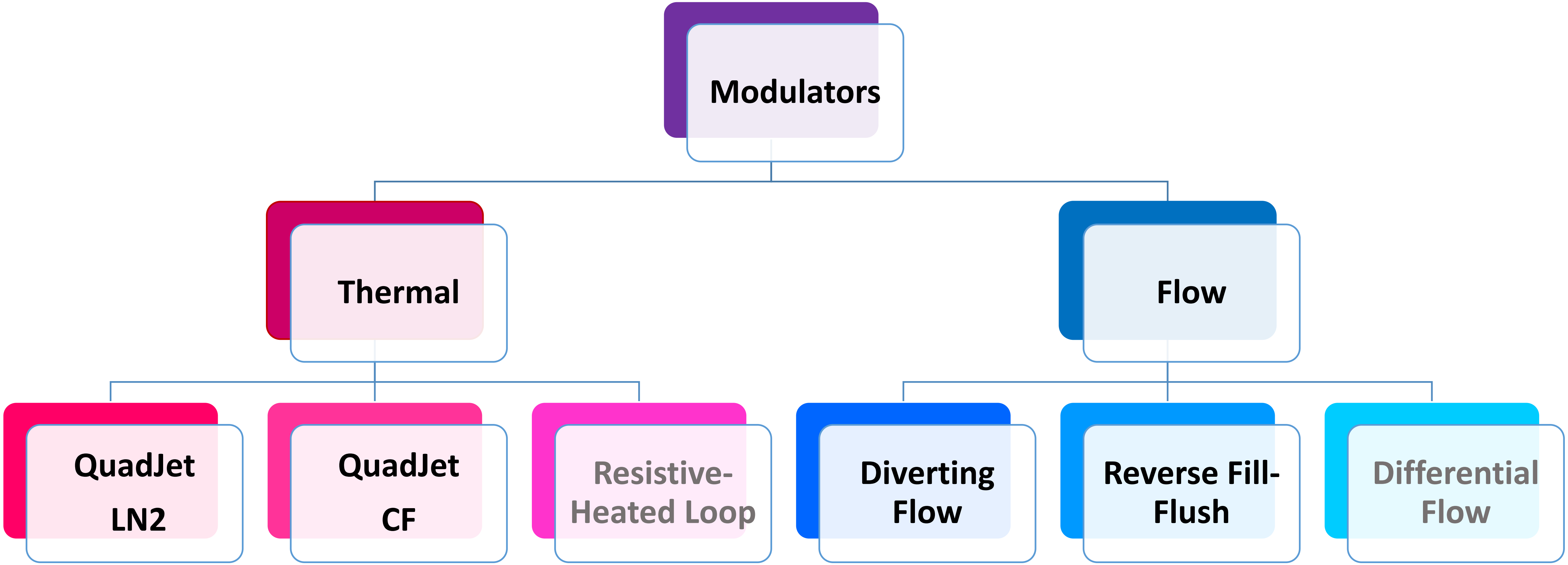
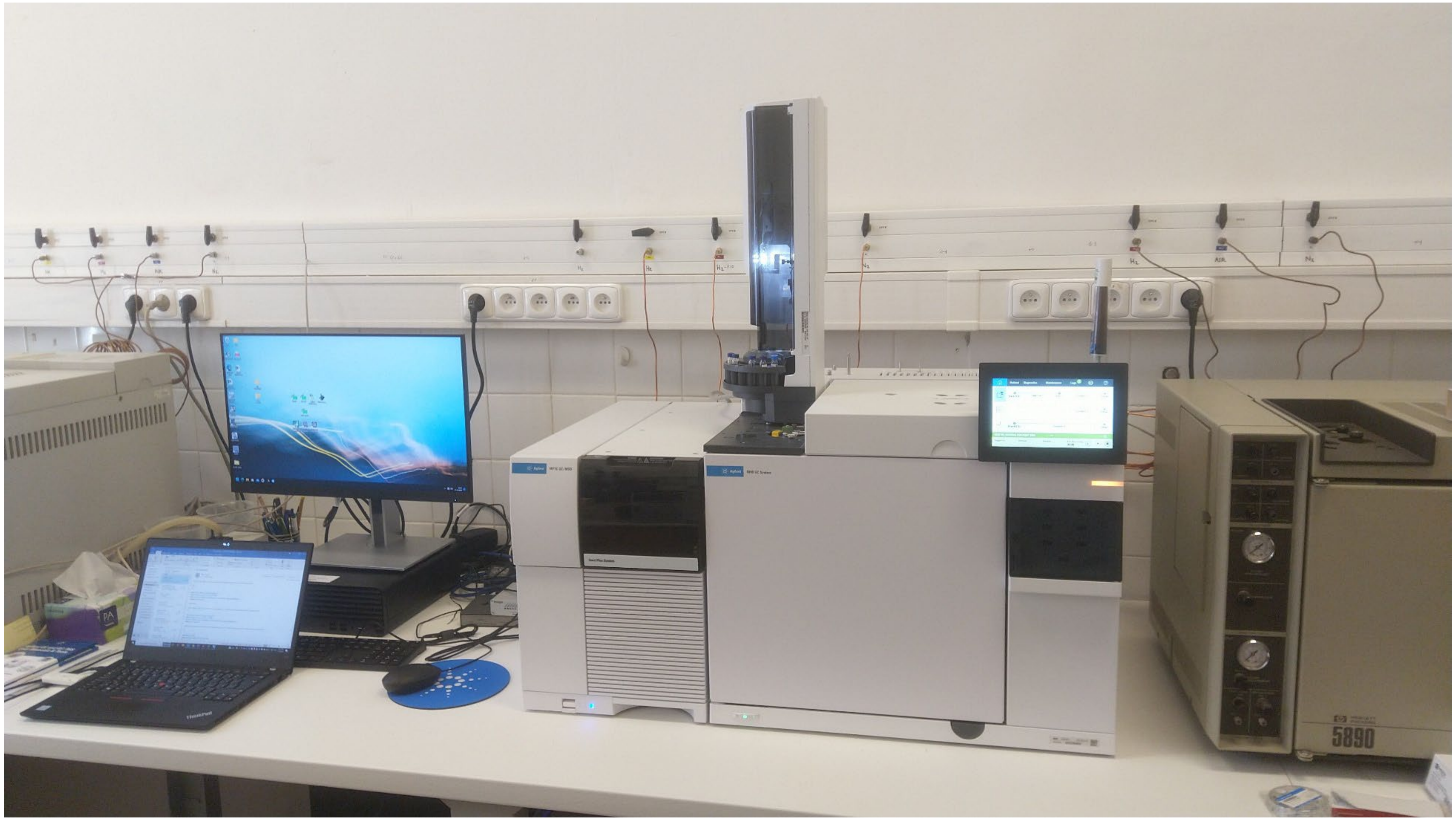


Figure: leco.com

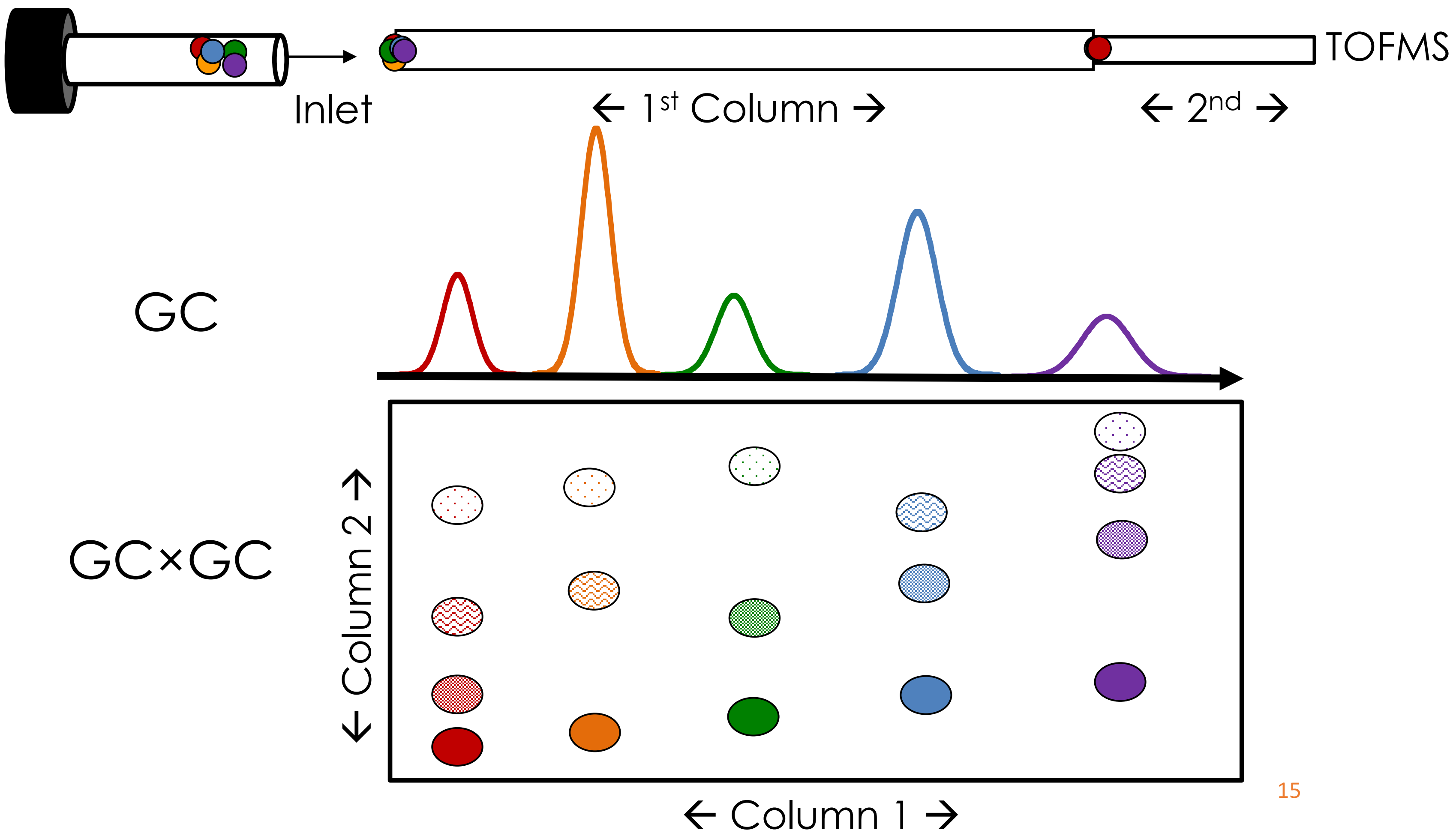
UCT Prague - Department of Petroleum Technology and Alternative Fuels



Picture: from Miloš Auersvald

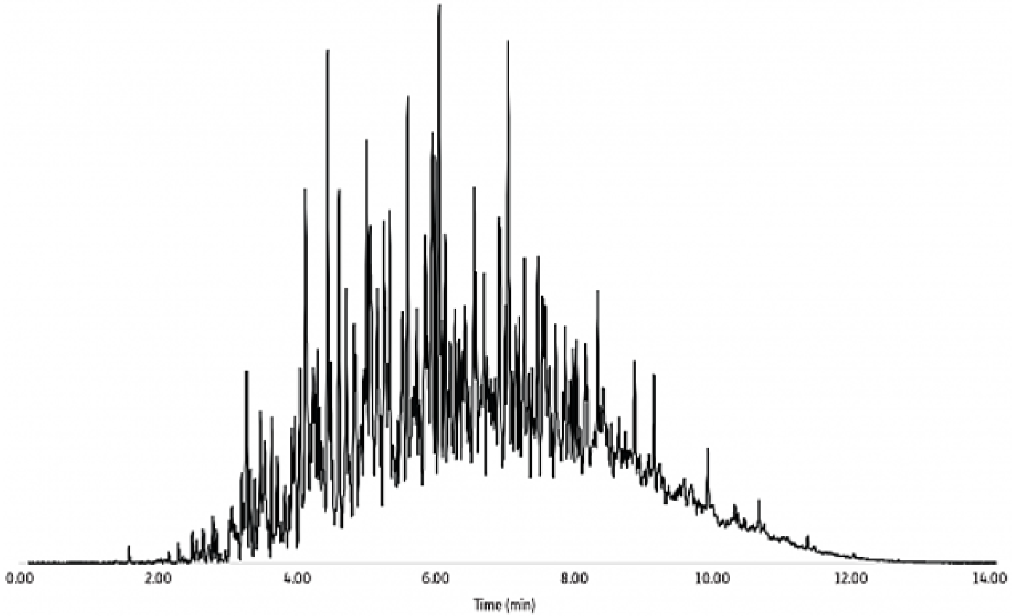
How GCxGC is achieved

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

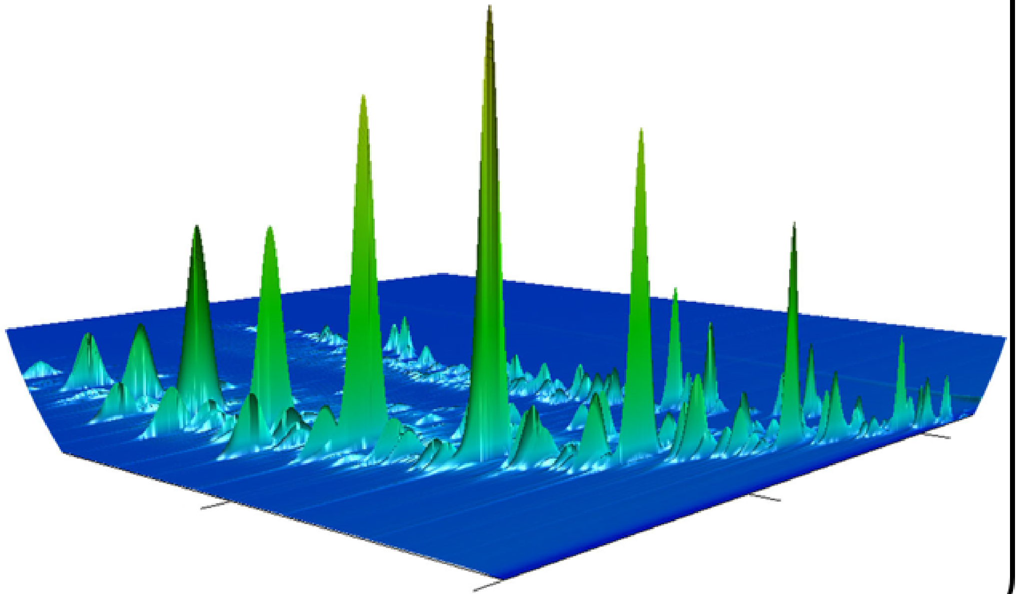


1 D vs. 2 D

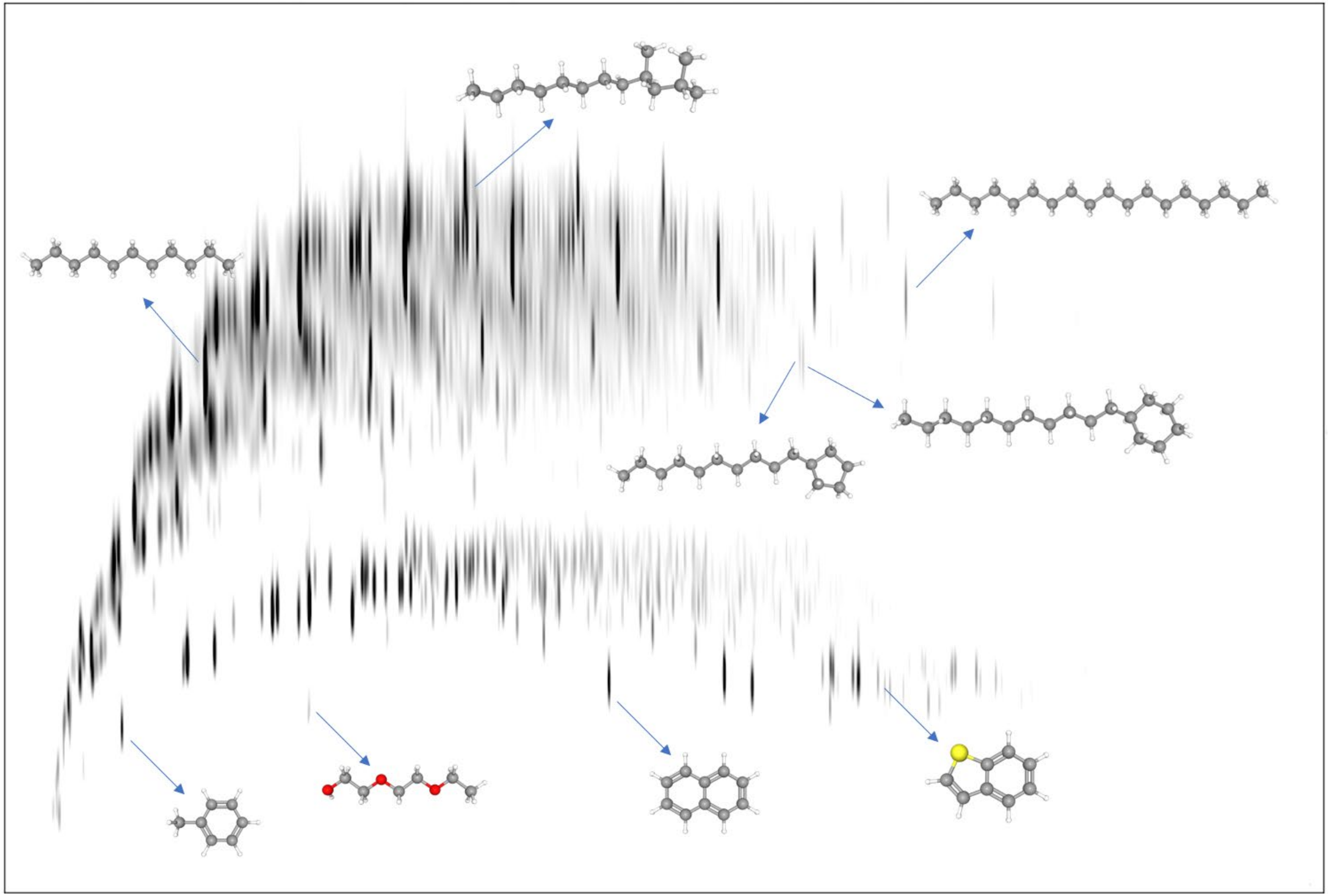
How it started:



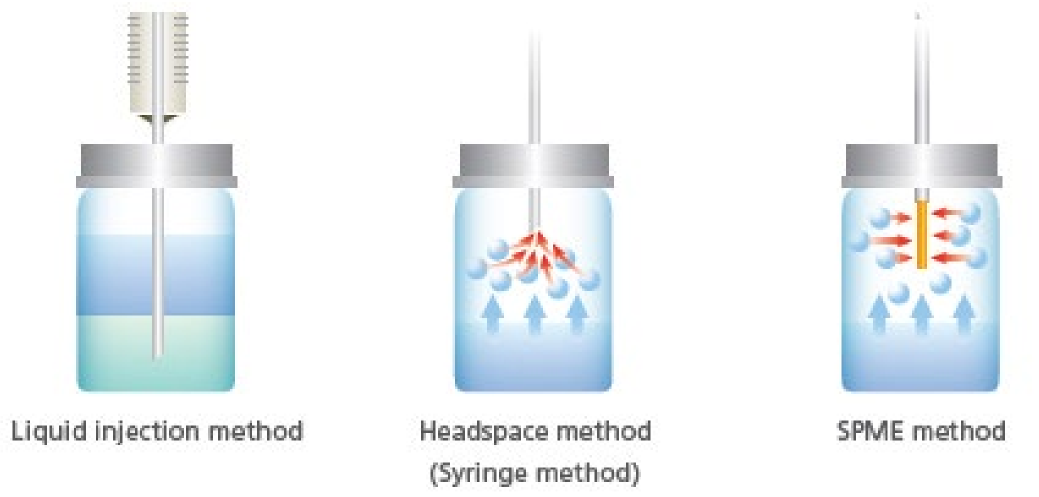
How it's going:



GC×GC Chromatogram



What can we analyze?



we can separate and detect compounds in the volatility range of C_5 to C_{40}

What do we do?

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COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

Detailed Analysis of Complex Chemical Mixtures

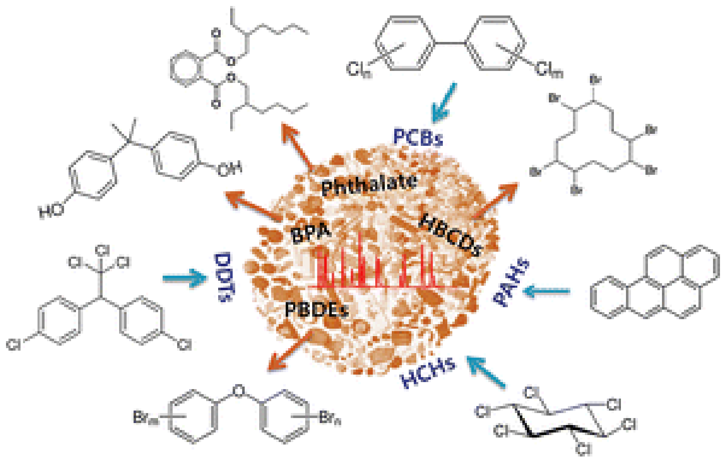
Such as:

- Petroleum products

- Beach Oil spills

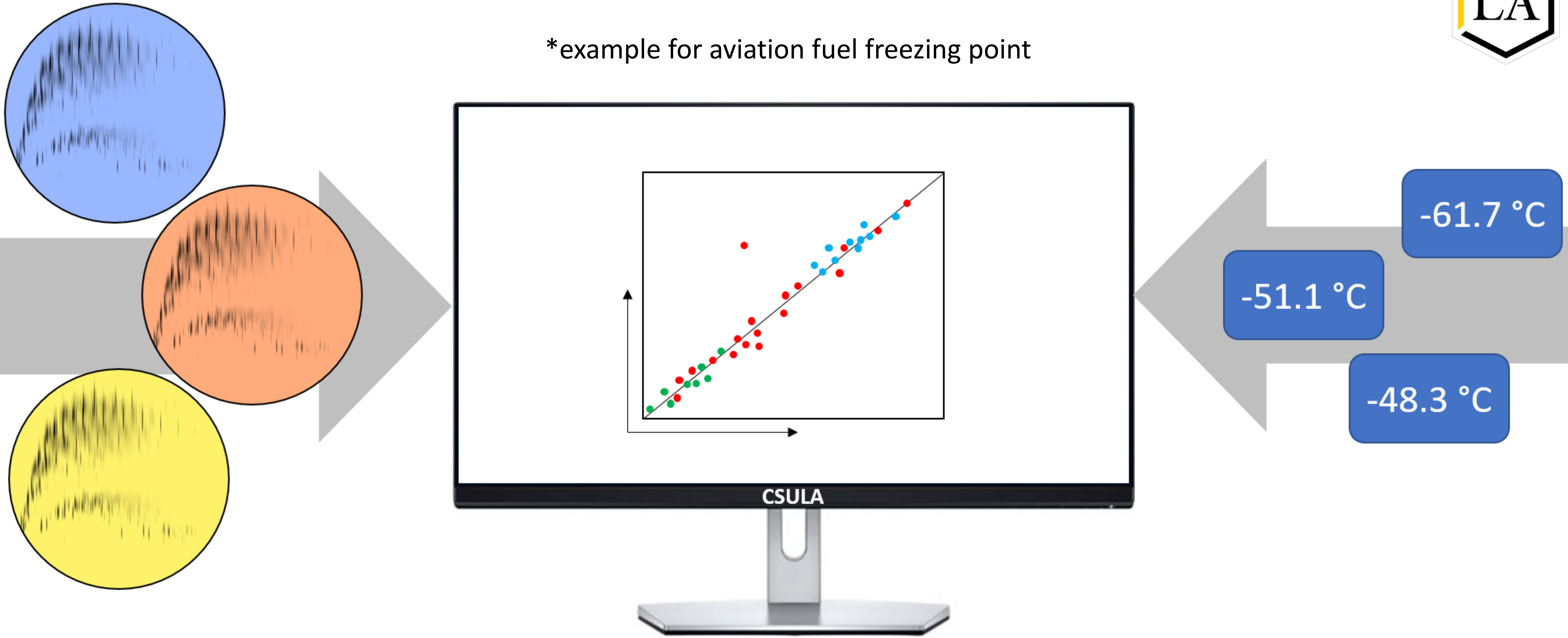
- Microplastics analysis

  (Organic compounds)



Chemometrics

*example for aviation fuel freezing point



Research project: Relationship between aviation fuel chemical composition and its freezing point

Plastic Waste in Oceans

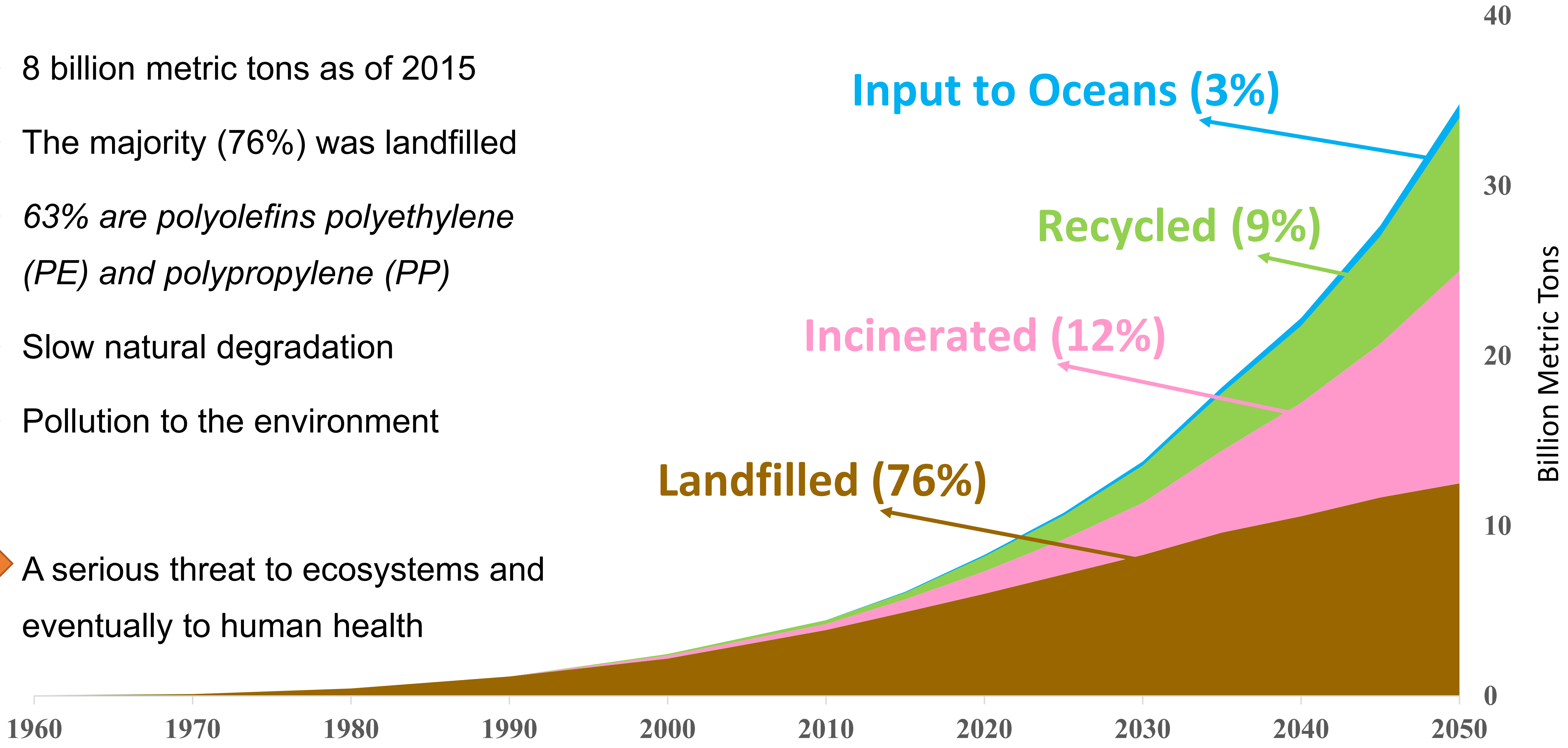
Plastic Waste in Oceans

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


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

Research projects

plastic waste → **microplastics**

Chemical conversion of plastic waste into fuels

Analysis of compounds adsorbed on microplastics

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Chemical conversion of plastic waste into fuels

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- 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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ELSEVIER

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*

[b] *School of Engineering Technology, Fuel Laboratory of Renewable Energy (FLORE), Purdue University, West Lafayette, IN,*

[c] *Department of Plastic Engineering, University of Massachusetts Lowell, Lowell, MA, 01854, USA*

Fuel 294 (2021) 120505

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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,*]

[a] *School of Engineering Technology, Fuel Laboratory of Renewable Energy (FLORE), Purdue University, West Lafayette, IN 47907, USA*

[b] *Department of Chemistry and Biochemistry, California State University, Los Angeles, CA 90032, USA*

[c] *Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA*

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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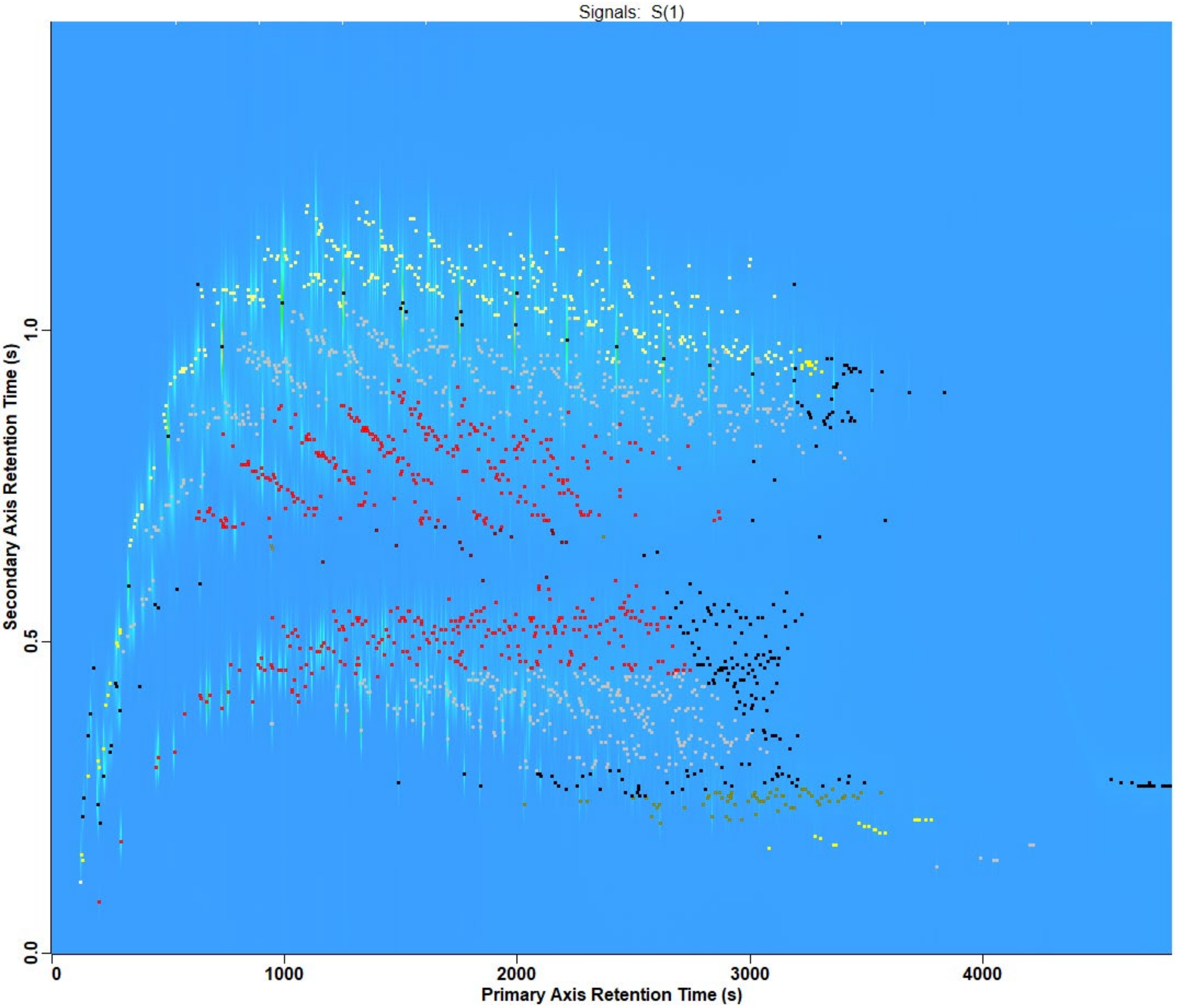
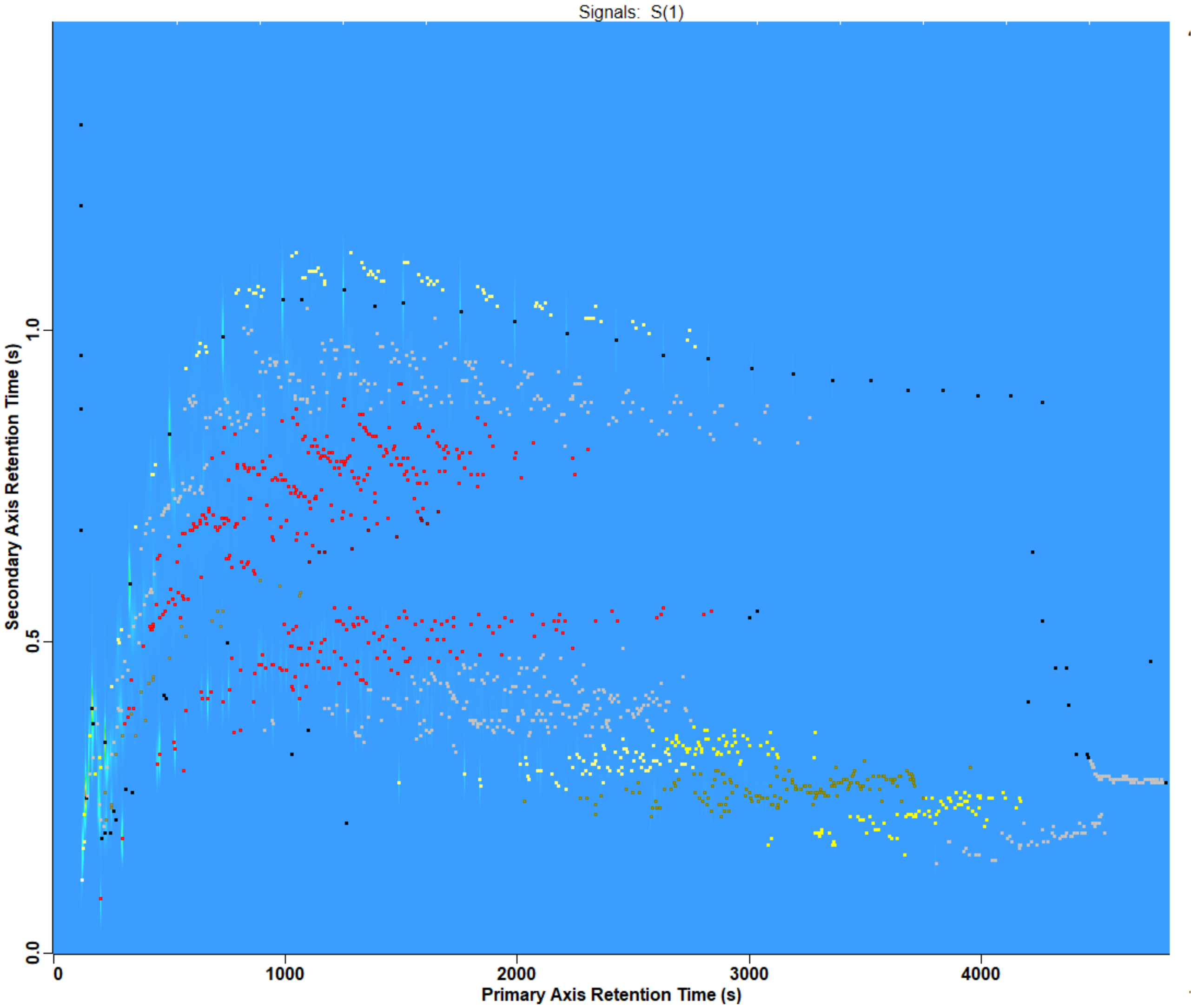
Commercial Diesel fuel



HTP Diesel fuel



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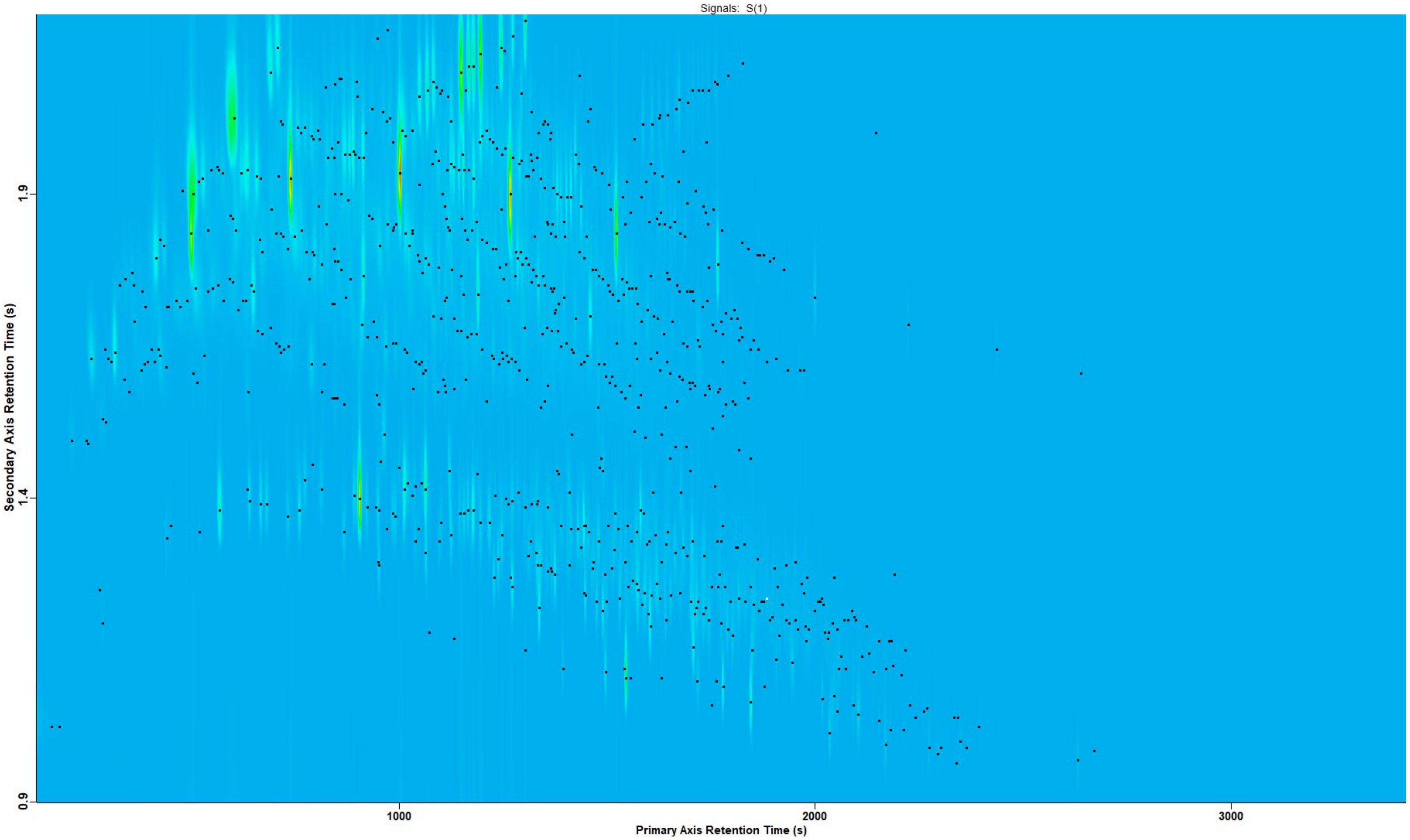
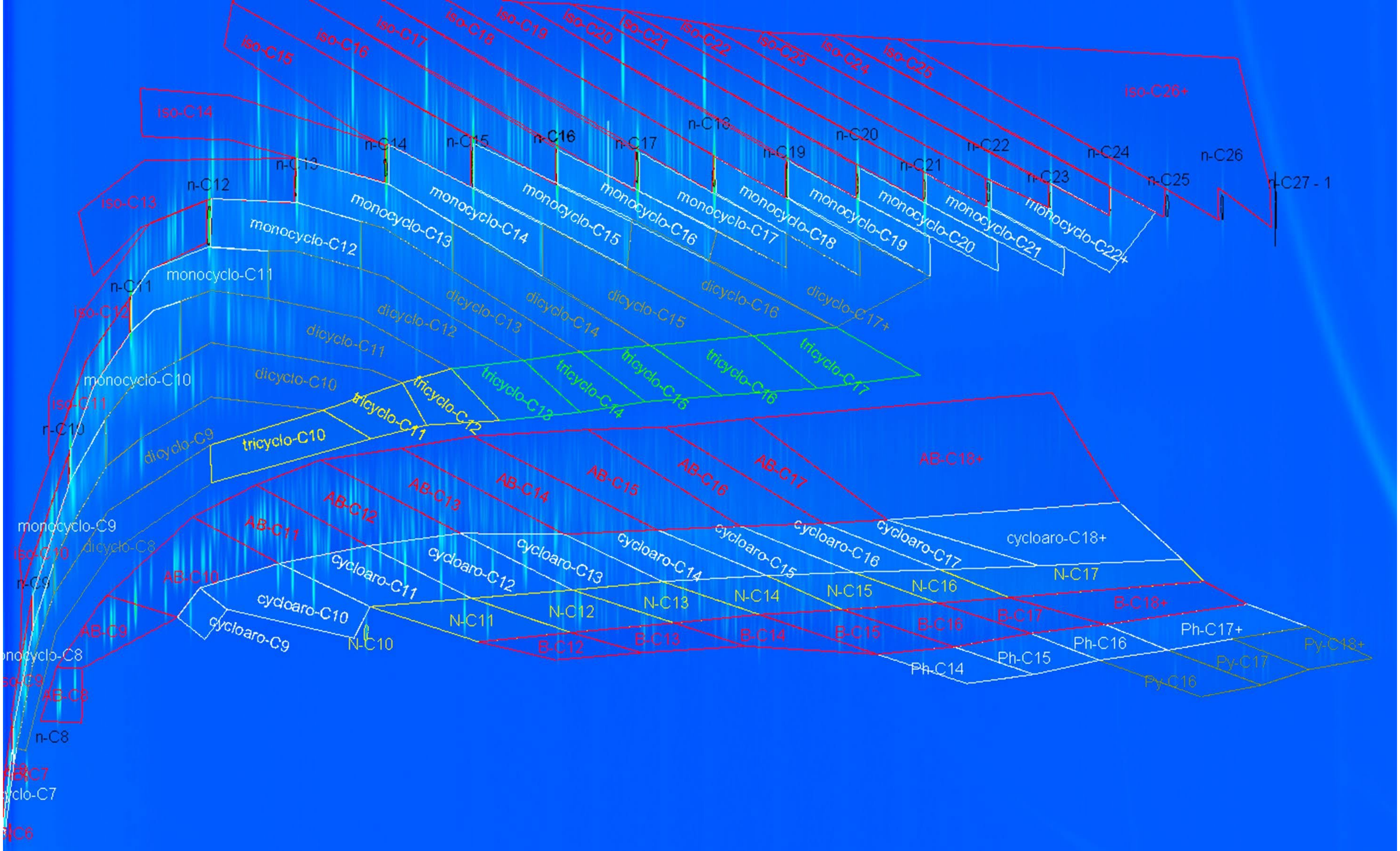
Diesel fuel distillation range pyrolysis oil after hydrotreating (270 °C and 6 MPa)

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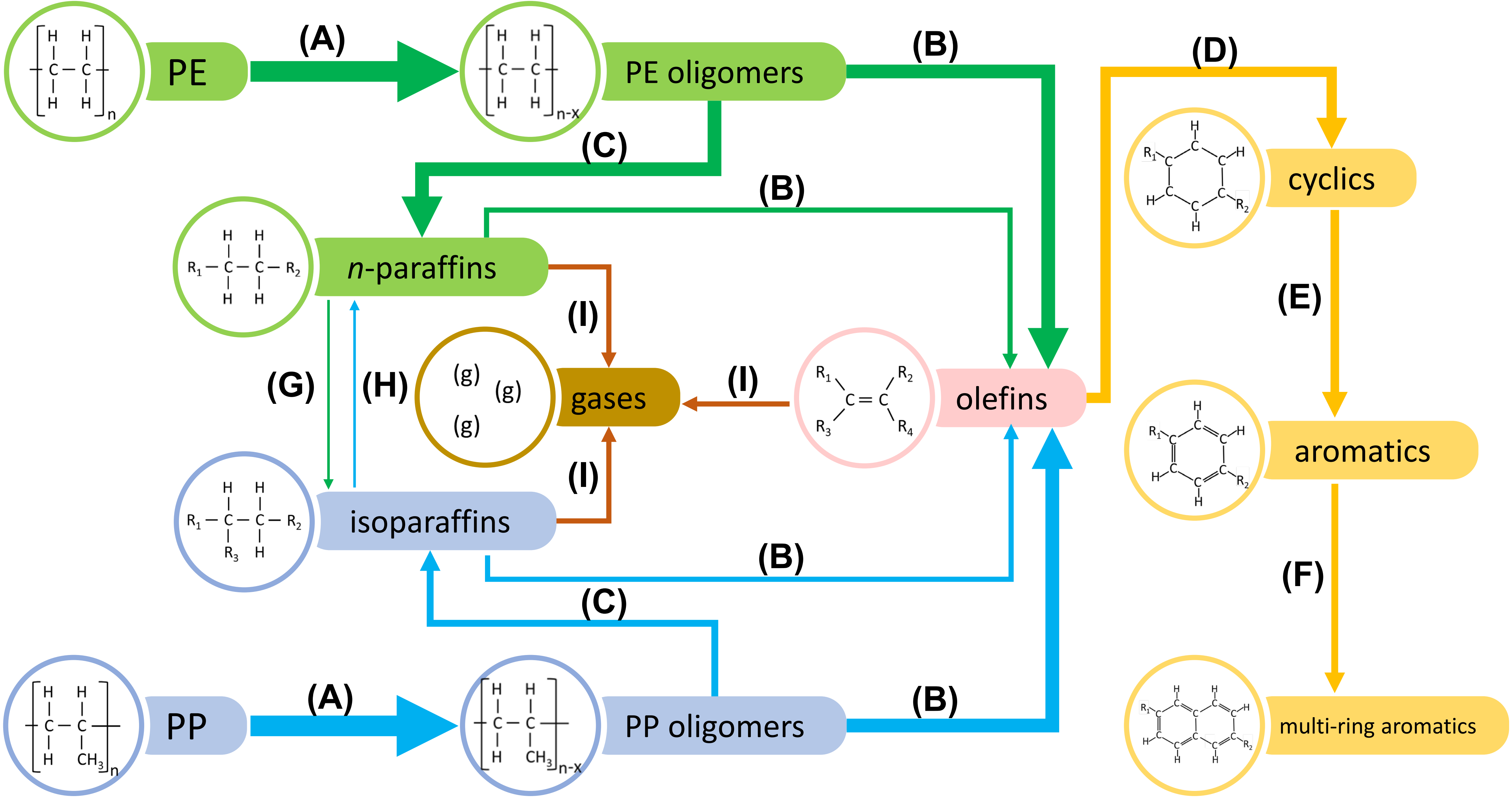
B-C18+
Ph-C14
Ph-C15
Ph-C16
Ph-C17+
Py-C16
Py-C17
Py-C18+

Quantitative results (some)

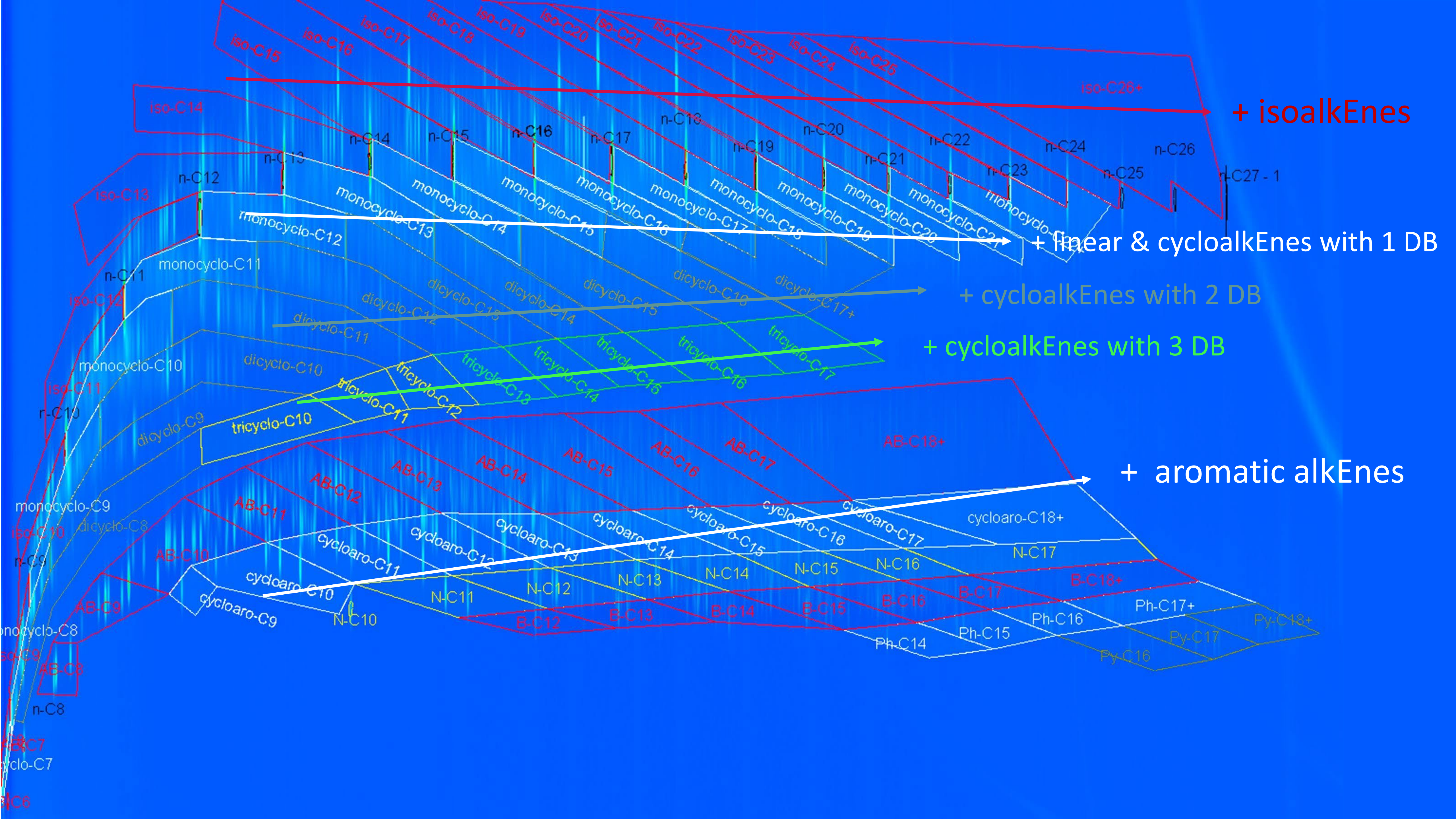
n-paraffins	F-76	Jet A	FT-IPK	Green diesel
C8	0.13	0.83	0.00	0.13
C9	0.42	5.05	0.00	0.20
C10	1.54	4.96	0.10	0.18
C11	2.32	3.36	0.00	0.00
C12	2.22	2.37	0.10	0.18
C13	2.21	1.90	0.08	0.23
C14	2.13	1.27	0.04	0.40
C15	1.93	0.76	0.03	0.88
C16	1.71	0.36	0.01	2.84
C17	1.58	0.10	0.00	1.76
C18	1.32	0.02	0.00	4.40
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.



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_{6-7}), (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
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B-C16
B-C17
B-C18+
Ph-C14
Ph-C15
Ph-C16
Ph-C17+
Py-C16
Py-C17
Py-C18+

DMDS Derivatization

Sample Preparation

IS, DMDS, and I_2 solution

↓

70 °C oven for at least an hour

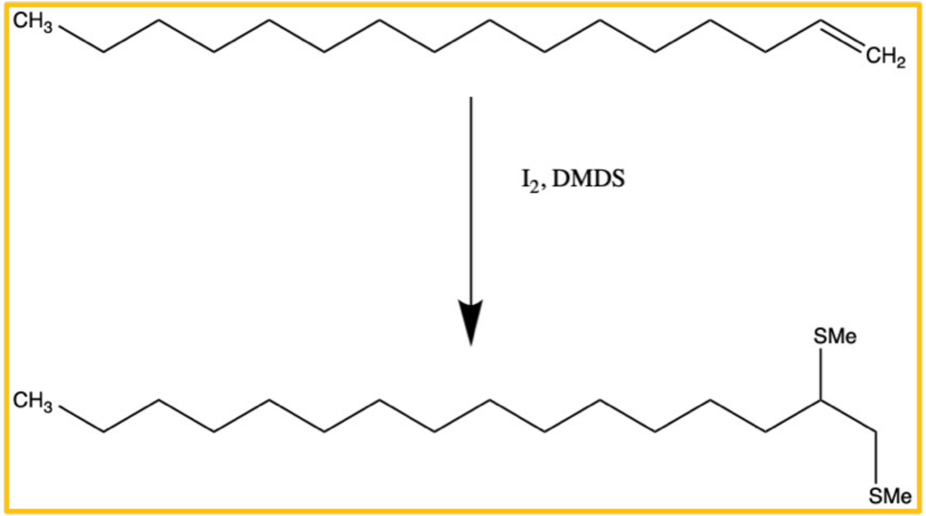
↓

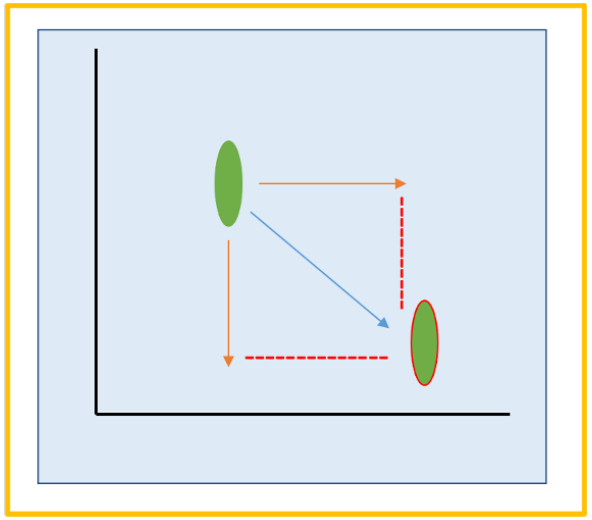
Sodium Thiosulfate

↓

Organic phase analyzed

Theory

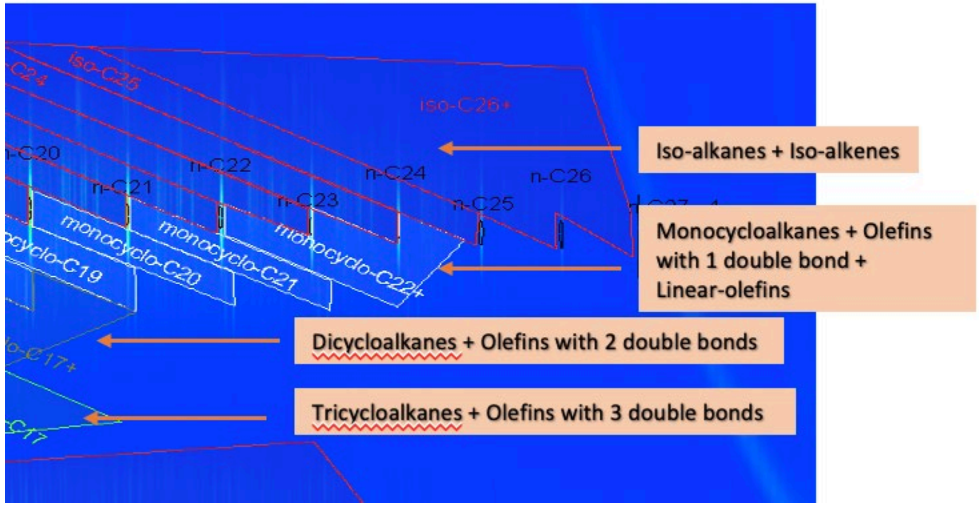




Calculations

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

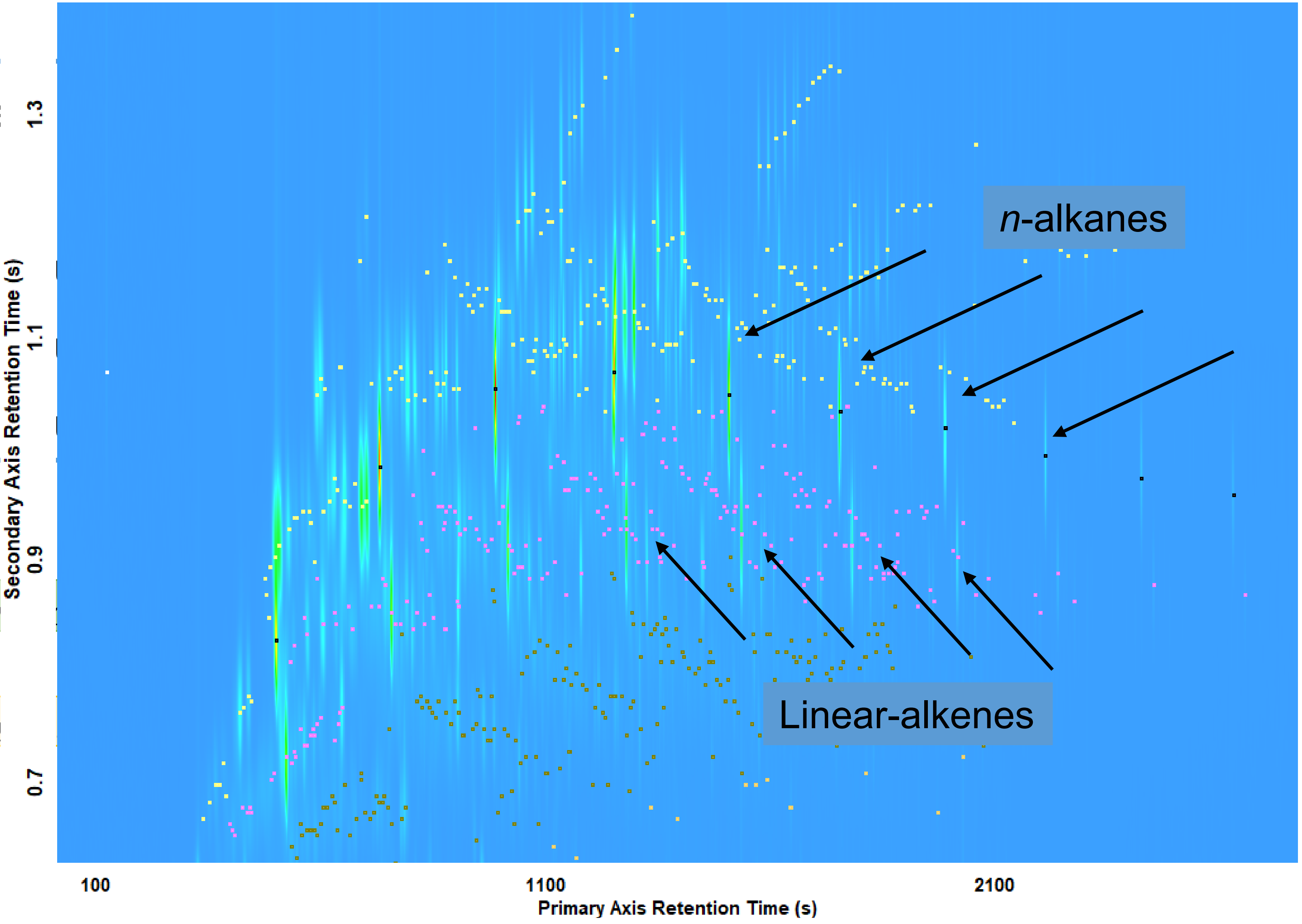
- Iso-alkenes
- Olefins with 1
- Olefins with 2
- Olefins with 3

Equation

$Wt.\%_{Olef}$

Example

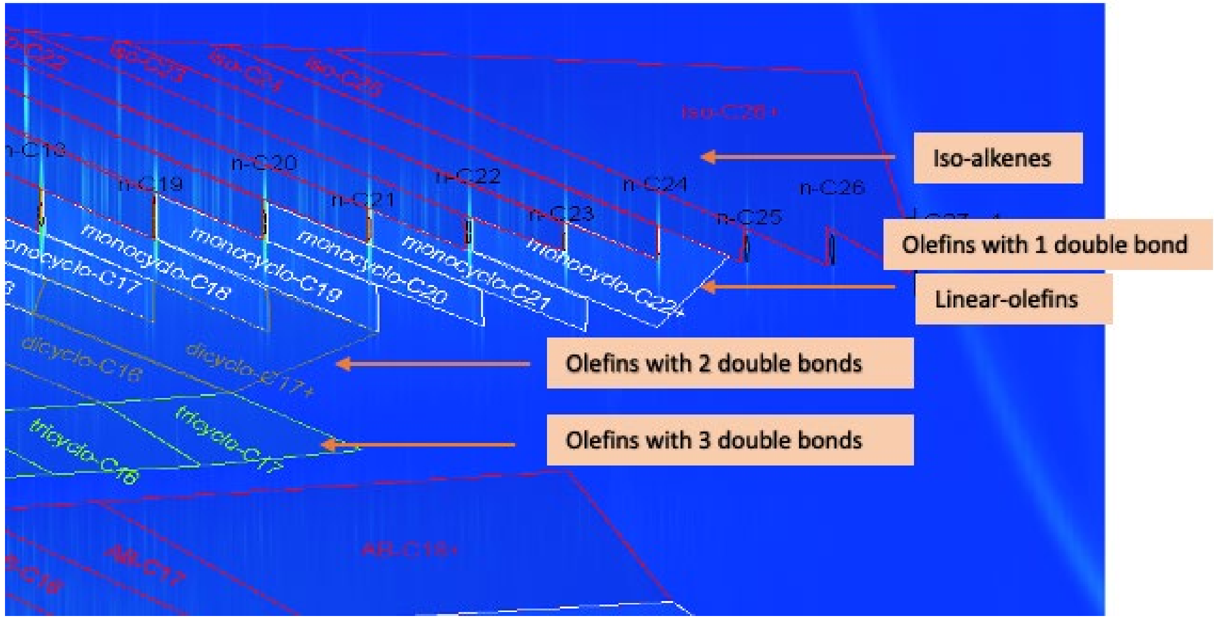
$Wt.\%_{Iso-al}$ … $C11$



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

Research projects

plastic waste → **microplastics**

Chemical conversion of plastic waste into fuels

Analysis of compounds adsorbed on microplastics

PURDUE UNIVERSITY

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

Microplastics

https://graphics.reuters.com/ENVIRONMENT-PLASTIC/0100B4TF2MQ/index.html

Every week

5 grams of plastic

https://graphics.reuters.com/ENVIRONMENT-PLASTIC/0100B4TF2MQ/index.html

Every year

250 grams of plastic

https://graphics.reuters.com/ENVIRONMENT-PLASTIC/0100B4TF2MQ/index.html

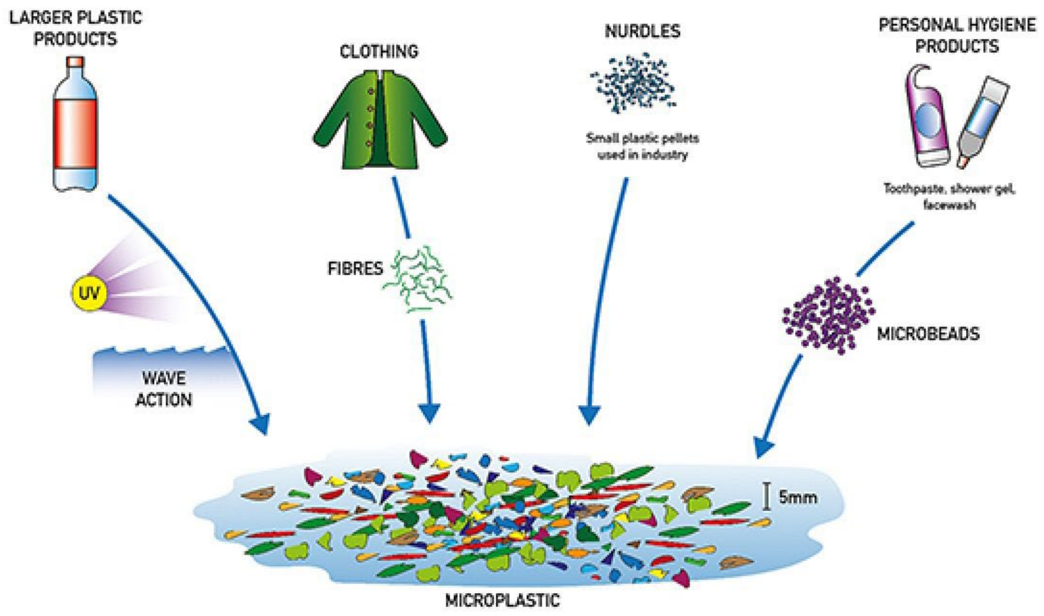
In our lifetime

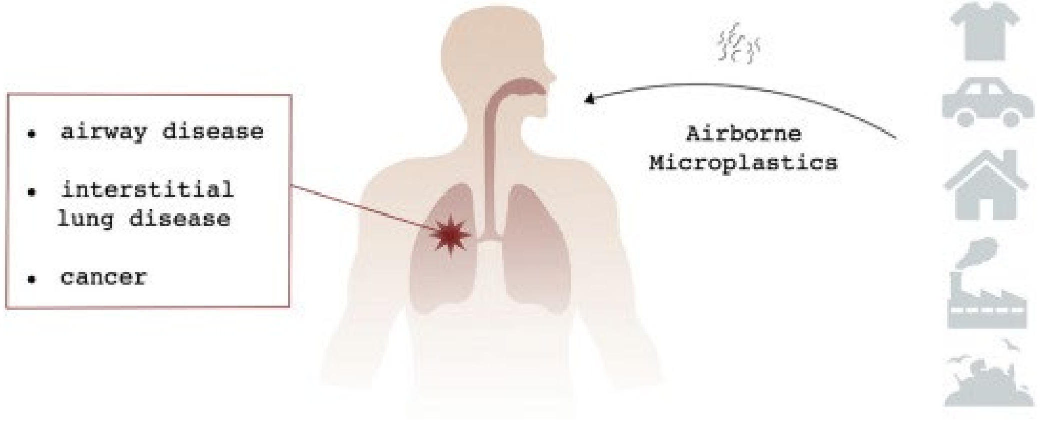
20 kg of plastic

https://graphics.reuters.com/ENVIRONMENT-PLASTIC/0100B4TF2MQ/index.html

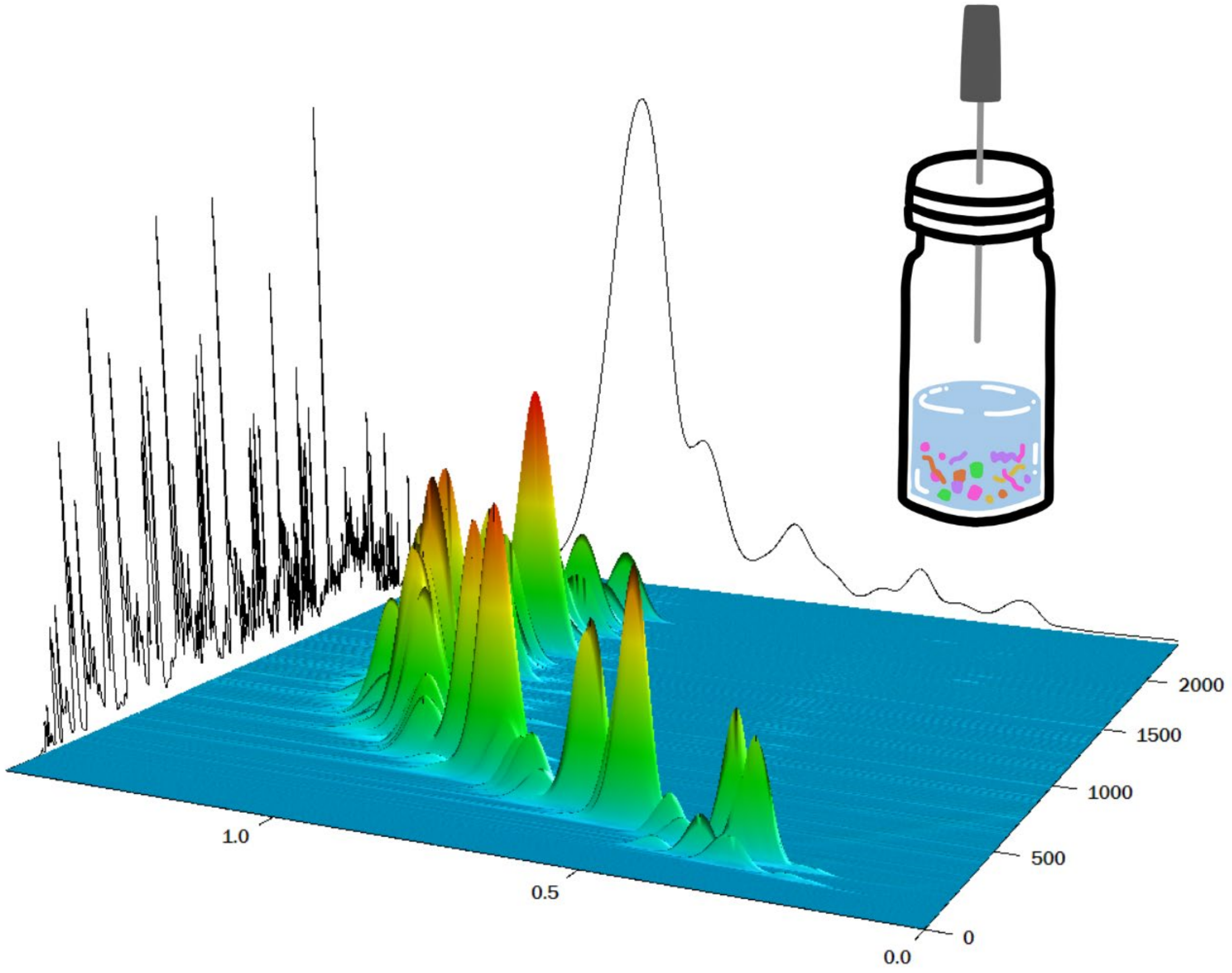
Interactions between microplastics and organic compounds

?





Interactions between microplastics and organic compounds



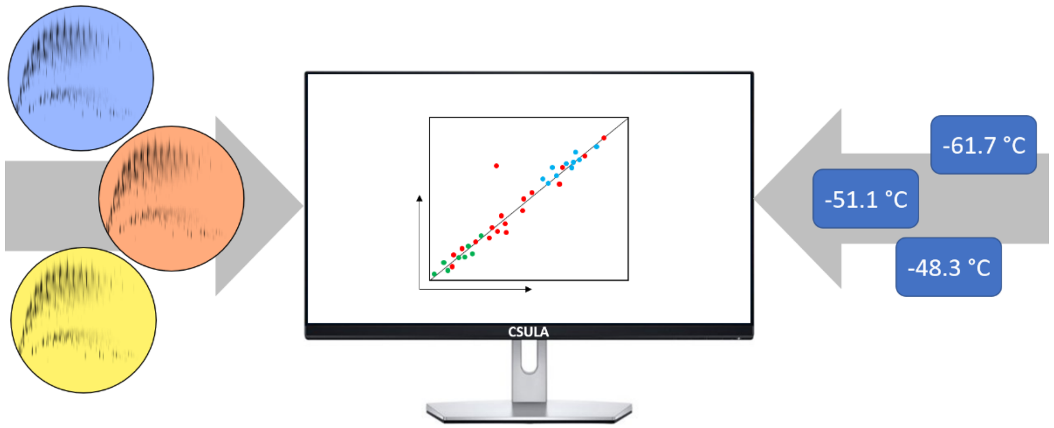
Interactions between microplastics and organic compounds

Pegasus BT 4D GC×GC-TOFMS

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

with thermal desorption/pyrolysis unit with a LN2 trap

Examples of our other projects



Fundamental Understanding of the chemical composition - freezing point relationship in aviation fuels

Mapping biodegradation of subsurface oil in Huntington Beach Sands

Time Since Deposition/Aging Studies for Latent Fingerprints

My awesome students…

C^{3}AL

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Thank you!

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- Dr. Petr Straka
- Ing. Ivo Novotný (LabRulez s.r.o)
- Dr. Pavel Jiroš (LECO Czech)
- All of you for coming today…