Multidimensional Chromatography Workshop

C3AL
COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

COUNTING DOUBLE BONDS: GC×GC–FID FOR PLASTIC PYROLYSIS OILS

Genesis Barzallo, Hung Gieng, Ananya Sharma, Jyotika Patel, Nathan Venegas; Brenda Andrade Rounds; Miloš Auersvald, Petr Straka & Petr Vozka

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

Features | Recycling

Plastics recycling is in trouble

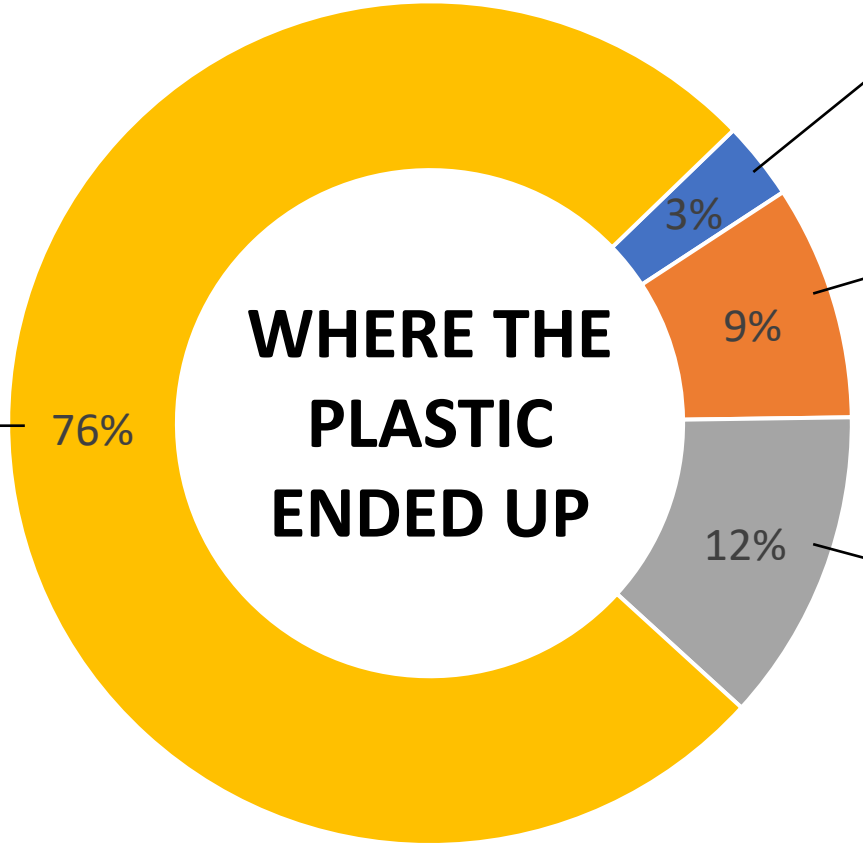
Consumer product companies have walked back their plastics sustainability goals, and many recyclers are closing their doors

by **Alexander Tullo**

November 4, 2025 • 12 min read

Plastic waste accumulation and recycling

Landfilled



Input to Oceans

Recycled in the US

Incinerated

Chemical conversion of plastic waste into fuels

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

PURDUE UNIVERSITY

TU Delft

Delft University of Technology

Pyrolysis

HTP

HTL

CalPoly Pomona

Chemical conversion of plastic waste into fuels

Fuel 273 (2020) 117726

Contents lists available at ScienceDirect

Fuel 294 (2021) 120505

Contents lists available at ScienceDirect

Chemical Engineering Journal 460 (2023) 141764

Journal of Environmental Chemical Engineering 12 (2024) 113836

Low-Pressure Hydrothermal Processing of Disposable Face Masks into Oils

by Cagri Un
Nien-Hwa Li

1 Davidson
2 Departme
Los Angel
* Author to

Processes 2(
Submission
Published: 2

(This article b
Industry (II))

Low-press
into oils

Clayton Gen

[a] Davidson School of
[b] Department of Chem

RSC Sustai

PAPER

Check f

Cite this: DOI: 10

ROYAL SOCIETY

Sustainable Chemistry for Climate Action

International Journal of Hydrogen Energy

Volume 200, 14 January 2026, 152882

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Octa

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Pilar Cua

Show mo

From waste COVID-19 face masks to fuel: Pyrolysis-oil/diesel blends with hydrogen enrichment in a CI engine

Ümit Ağbulut [a d e], Fikret Polat [b], Mustafa Karagöz [c], Suat Sarıdemir [b],

Full Length A

Conversic
hydrother

Kai Jin[a,b,1],

[a] Davidson School of
[b] School of Engineeri
[c] Department of Plast

Full Length Ar

Low-press
clean fuel

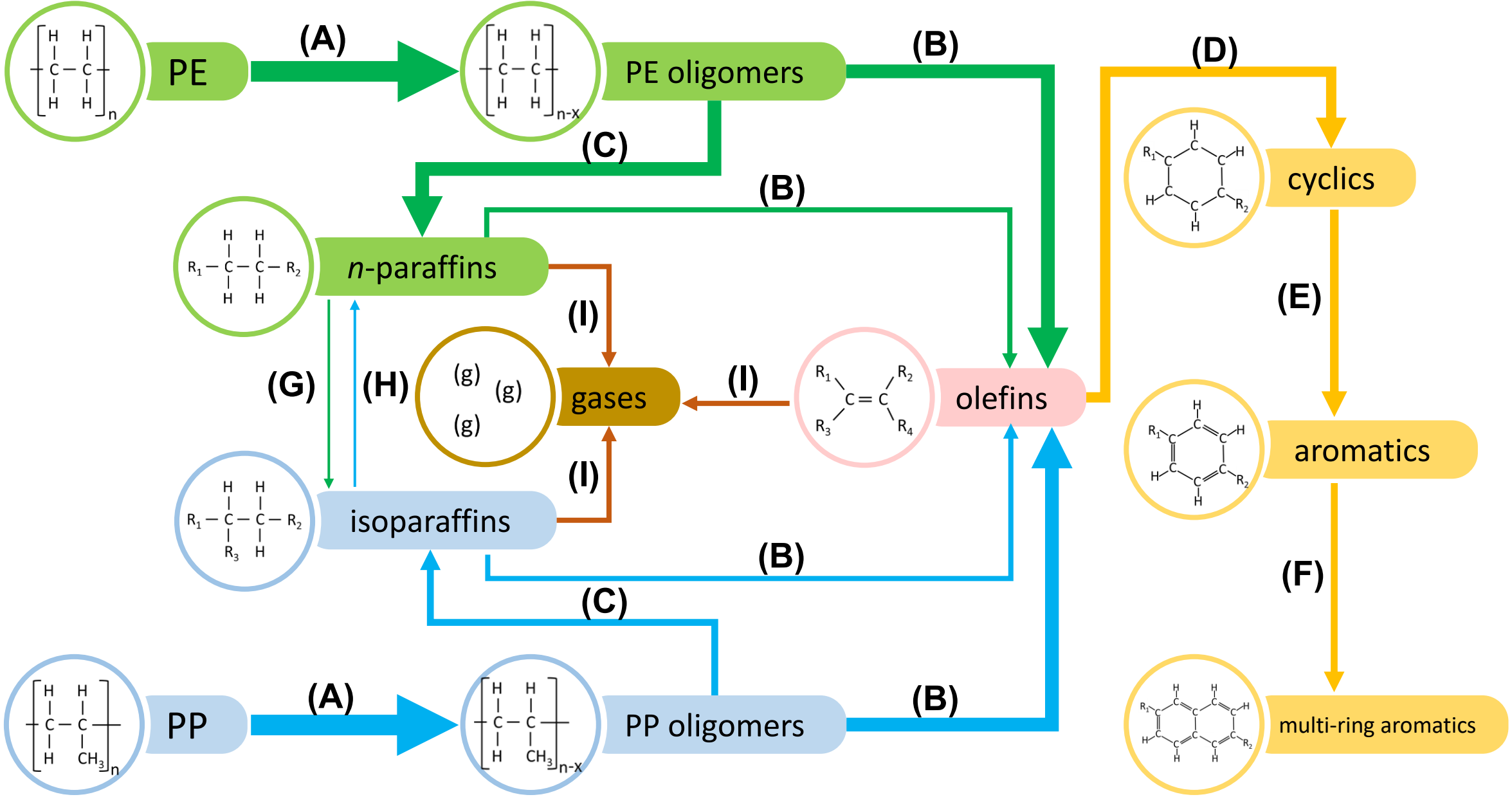
Kai Jin [a], Pet

[a] School of Engineerin
[b] Department of Chem
[c] Davidson School of

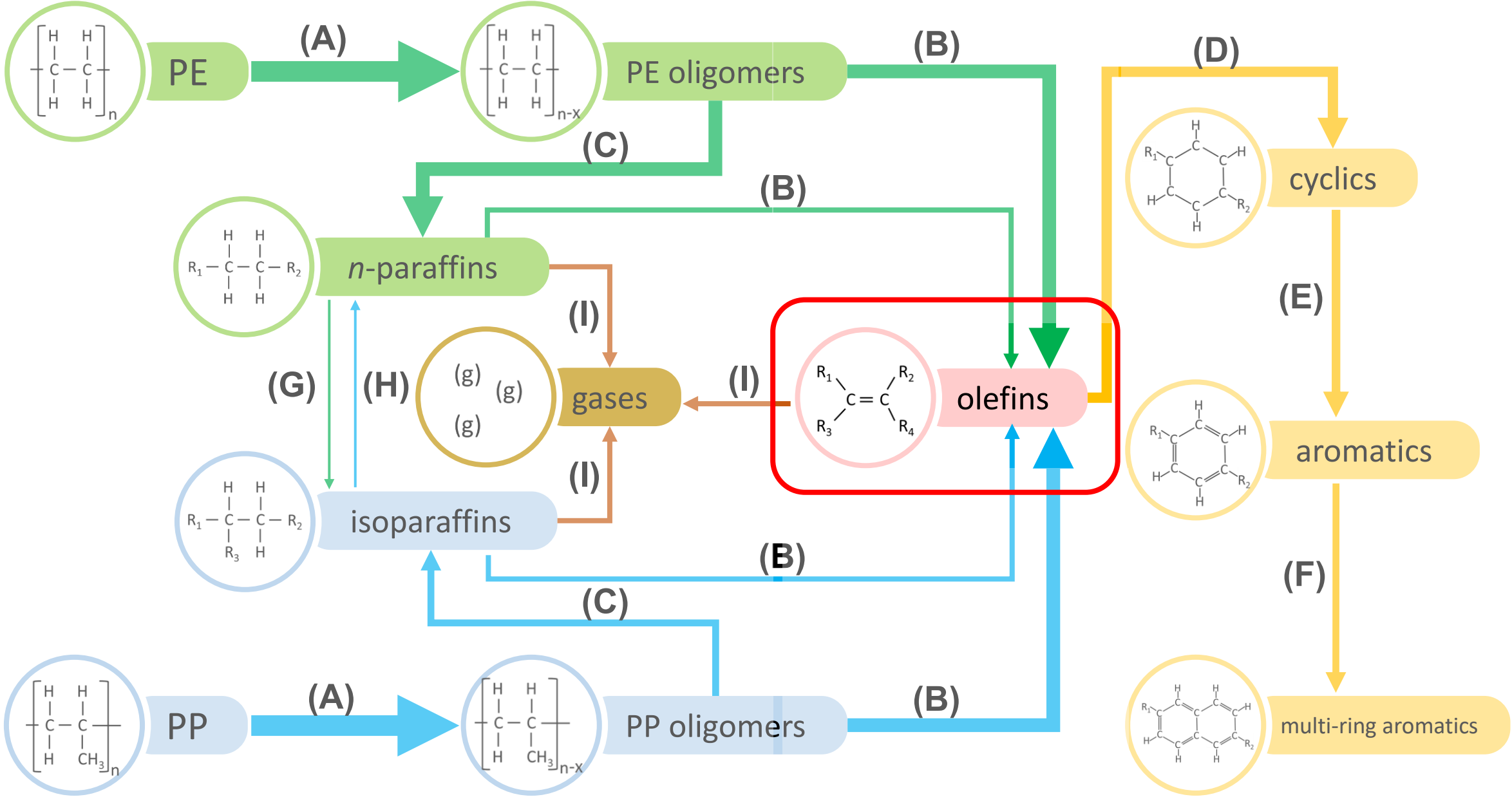
Productior
pyrolysis c

Petr Straka [a],

[a] University of Chemist
[b] California State Univ

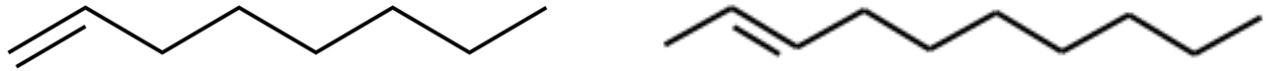


Potential reaction pathways of PE and PP co-processing under LP-HTP. (A) depolymerization, (B) β-scission, (C) hydrogen abstraction, (D) cyclization, (E) dehydrogenation, (F) formation of multi-ring aromatics, (G) isomerization, (H) formation of short *n*-paraffins (C_{6-7}), (I) further cracking to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

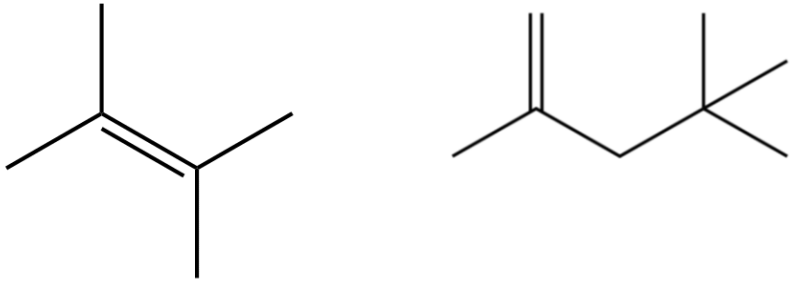


Potential reaction pathways of PE and PP co-processing under LP-HTP. (A) depolymerization, (B) β-scission, (C) hydrogen abstraction, (D) cyclization, (E) dehydrogenation, (F) formation of multi-ring aromatics, (G) isomerization, (H) formation of short *n*-paraffins (C_{6-7}), (I) further cracking to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

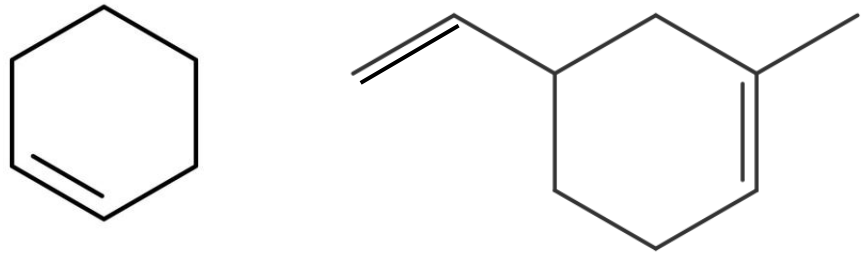
Olefins (alkenes)



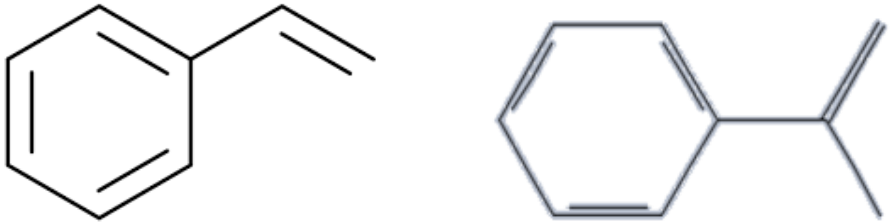
straight chain alkenes



branched alkenes



cyclo alkenes



aromatic alkenes

How to quantify olefins in complex samples as detailed as possible?

How to quantify olefins in complex samples as detailed as possible?

Trends in Analytical Chemistry 193 (2025) 118463

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

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

Toward accurate olefin quantification in plastic waste oils: Analytical strategies and future directions

Miloš Auersvald [a,b,*], Genesis Barzallo [c,d,e], Hung Gieng [c], Jyotika Patel [c], Ananya Sharma [c], Kevin M. Van Geem [b], Petr Straka [a], Petr Vozka [c,**]

[a] Department of Sustainable Fuels and Green Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b] Ghent University, Laboratory for Chemical Technology, Technologiepark 125, 9052, Ghent, Belgium
[c] Department of Chemistry and Biochemistry, California State University, Los Angeles, 5151 State University Dr., Los Angeles, CA, 90032, USA
[d] Herbert Wertheim School of Public Health, University of California San Diego, San Diego, CA, 92093, USA
[e] School of Public Health, San Diego State University, San Diego, CA, 92182, USA

Titration

- Bromine number
- Bromine index
- Iodine value

Spectroscopy

- FTIR
- Raman
- NMR

Chromatography

LC	GC
FIA	GC (*g*)
HPLC	GC (*l*)
SFC	GC×GC

Selective methods

- GC-VUV
- Soft ionization MS
- Derivatizations
- Adsorptions

Click a method to explore more details

Auersvald, M.; Barzallo, G.; Gieng, H.; Patel, J.; Sharma, A.; Van Geem, K. M.; Straka, P.; Vozka, P. Toward Accurate Olefin Quantification in Plastic Waste Oils: Analytical Strategies and Future Directions. TrAC Trends Anal. Chem. 2025.

Bromine Number

(BrN)

Application Range

Primarily in the light and middle distillate fractions boiling below ~327 °C, where it serves as a comparative rather than absolute measure of olefin unsaturation. ASTM D1159.

Advantages

Simple, standardized, and widely reported, providing a rapid comparative measure of olefinic unsaturation.

Limitations

Solubility and boiling range constraints, under- or overestimation due to olefin type, and interference from heteroatom- and aromatic species, making it unreliable as an absolute measure of total unsaturation.

g Br_2/100 g sample

Auersvald, M.; Barzallo, G.; Gieng, H.; Patel, J.; Sharma, A.; Van Geem, K. M.; Straka, P.; Vozka, P. Toward Accurate Olefin Quantification in Plastic Waste Oils: Analytical Strategies and Future Directions. TrAC Trends Anal. Chem. 2025.

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Comprehensive Two-Dimensional Gas Chromatography

(GC×GC)

Application Range

Applicable to detailed compositional and quantitative analysis of POs and hydrothermal products, resolving paraffins, olefins, diolefins, cycloparaffins, aromatics, and oxygenates across wide boiling ranges.

Advantages

Unparalleled resolution, reduced co-elution, and robust compound-level quantification (especially when coupled with FID, TOFMS, or HRMS), enabling accurate group-type and structural assignments in complex PO matrices.

Limitations

Labor-intensive, requires complex instrumentation and data processing, and struggles to fully distinguish olefins and cycloparaffins or diolefins and unsaturated naphthenes, absolute quantitation needs complementary methods.

Individual + group content (wt%)

Auersvald, M.; Barzallo, G.; Gieng, H.; Patel, J.; Sharma, A.; Van Geem, K. M.; Straka, P.; Vozka, P. Toward Accurate Olefin Quantification in Plastic Waste Oils: Analytical Strategies and Future Directions. TrAC Trends Anal. Chem. 2025.

Back

Total “olefin” content

Titration

- Bromine number
- Bromine index
- Iodine value

- g Br_2/100g
- mg Br/100 g
- g I/100g

Spectroscopy

- FTIR
- Raman
- NMR

Chromatography

LC	GC
FIA	GC (*g*)
HPLC	GC (*l*)
SFC	GC×GC

Selective methods

- GC-VUV
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- FIA reports some dienes and heteroatomic compounds as aromatics
- HPLC-RI overestimates monoaromatics, while underestimating polyaromatics

Titration

- Bromine number
- Bromine index
- Iodine value

Spectroscopy

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¿Detailed olefin content?

Titration

- Bromine number
- Bromine index
- Iodine value

Spectroscopy

- FTIR
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- NMR

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LC	GC
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- GC-VUV
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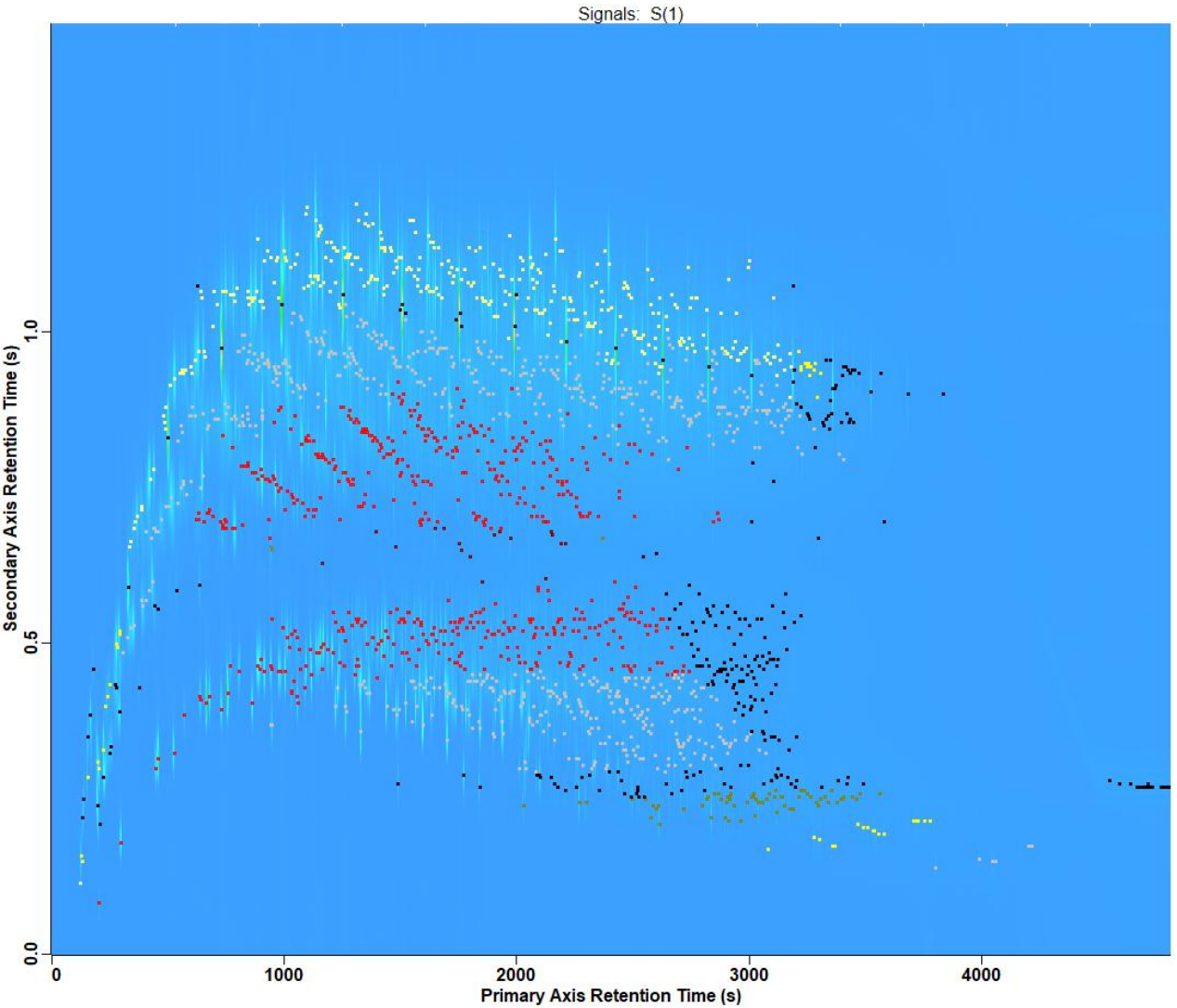
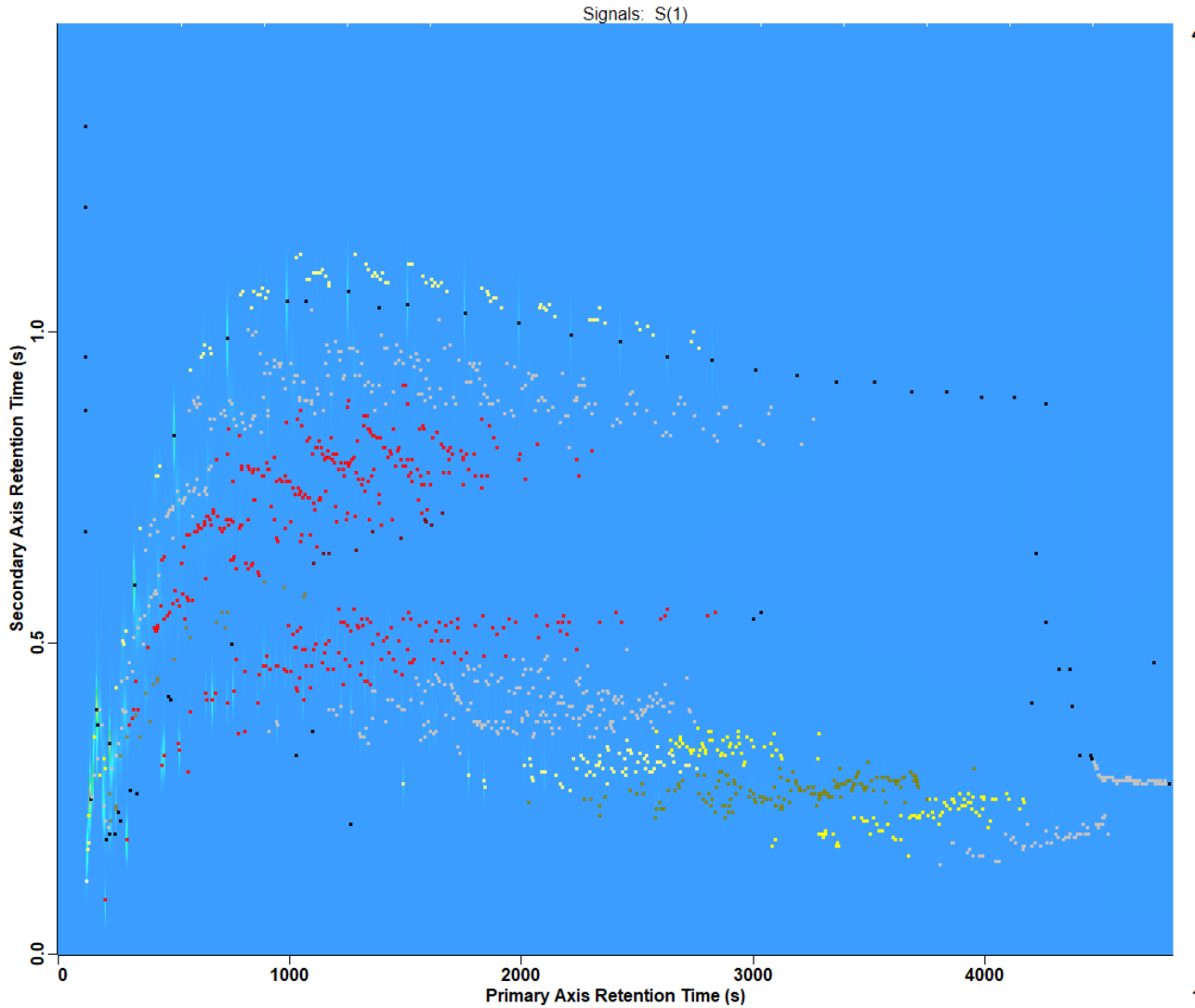
¿Detailed olefin content?

PURDUE UNIVERSITY

Commercial Diesel fuel

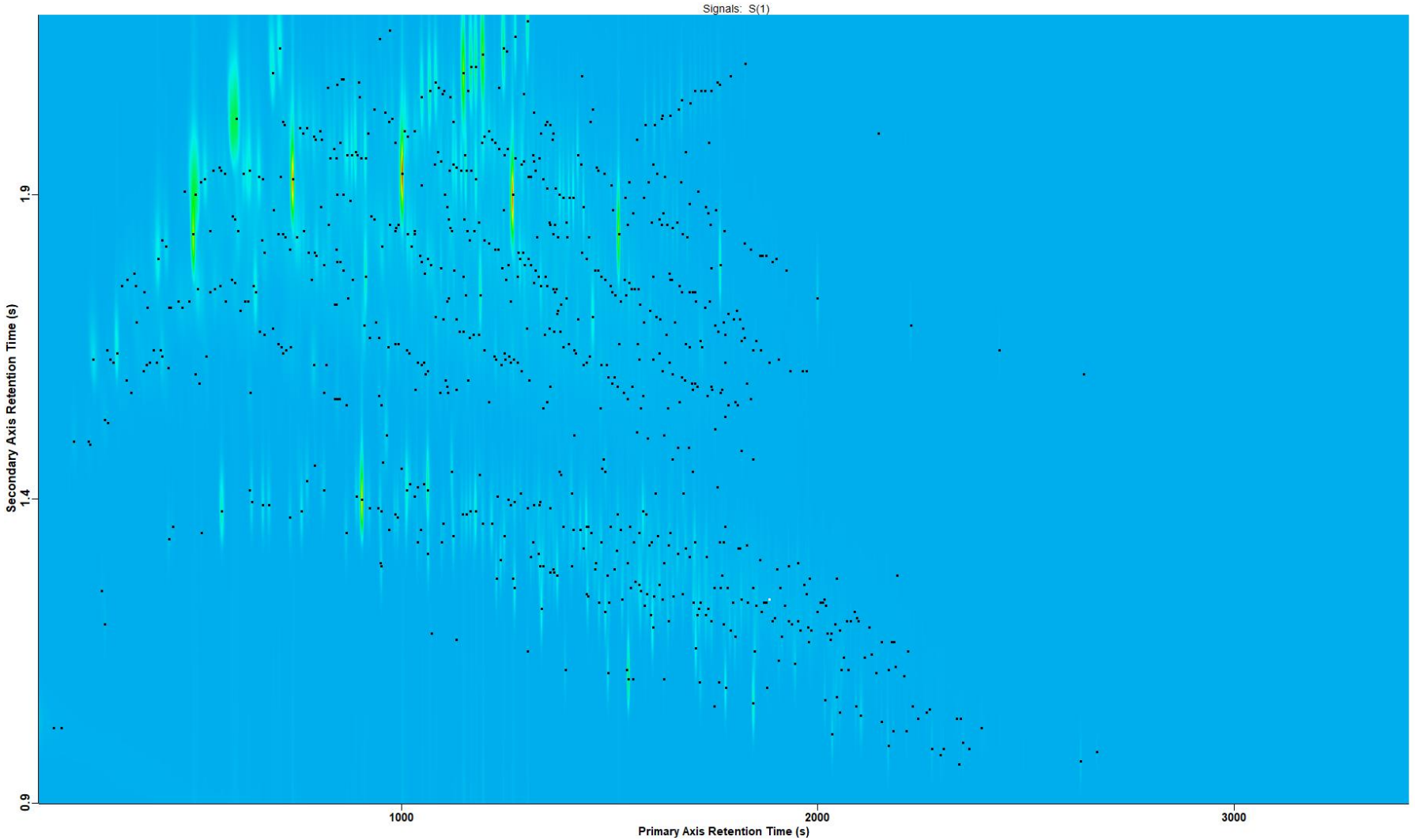


HTP Diesel fuel

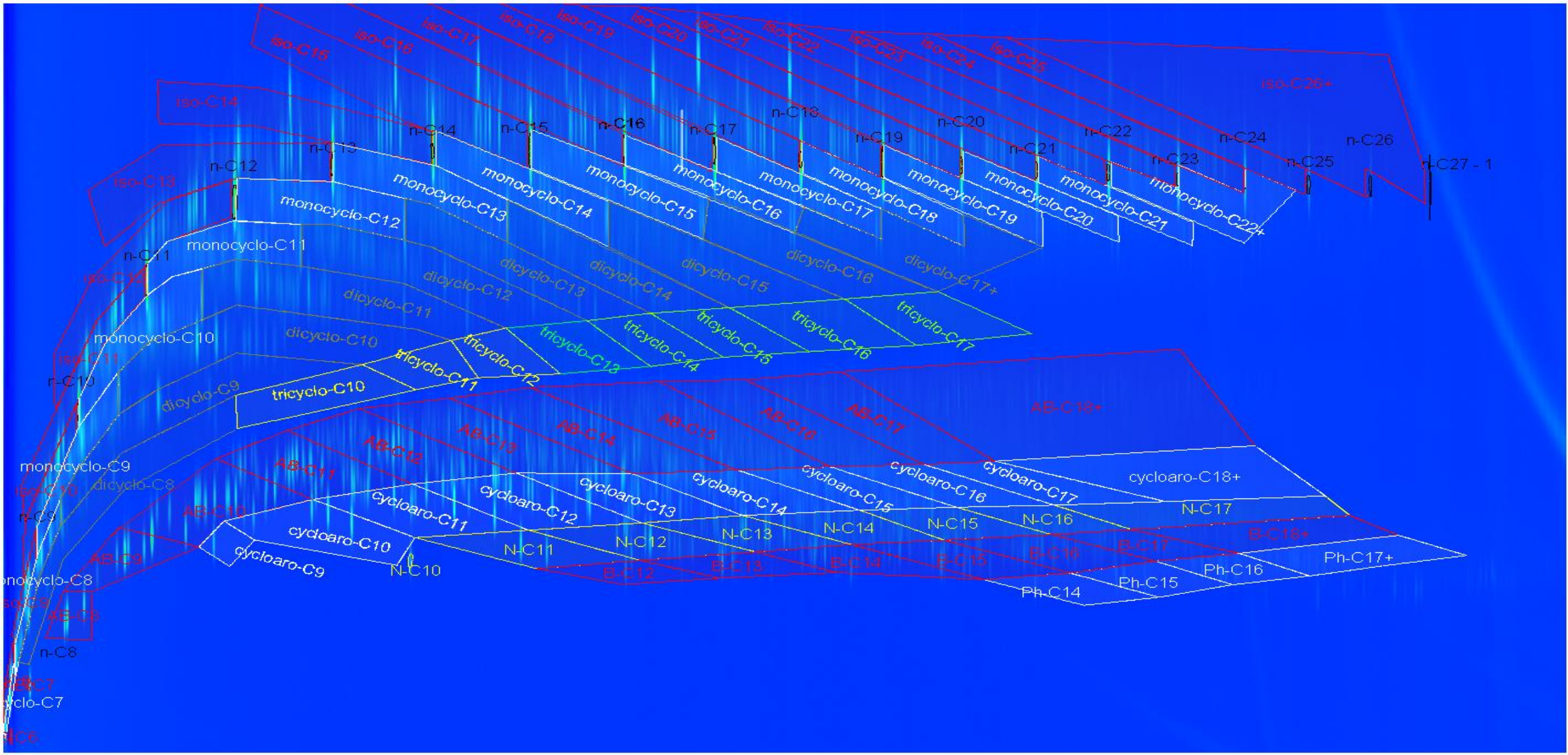


UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

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



Where do alkenes elute?



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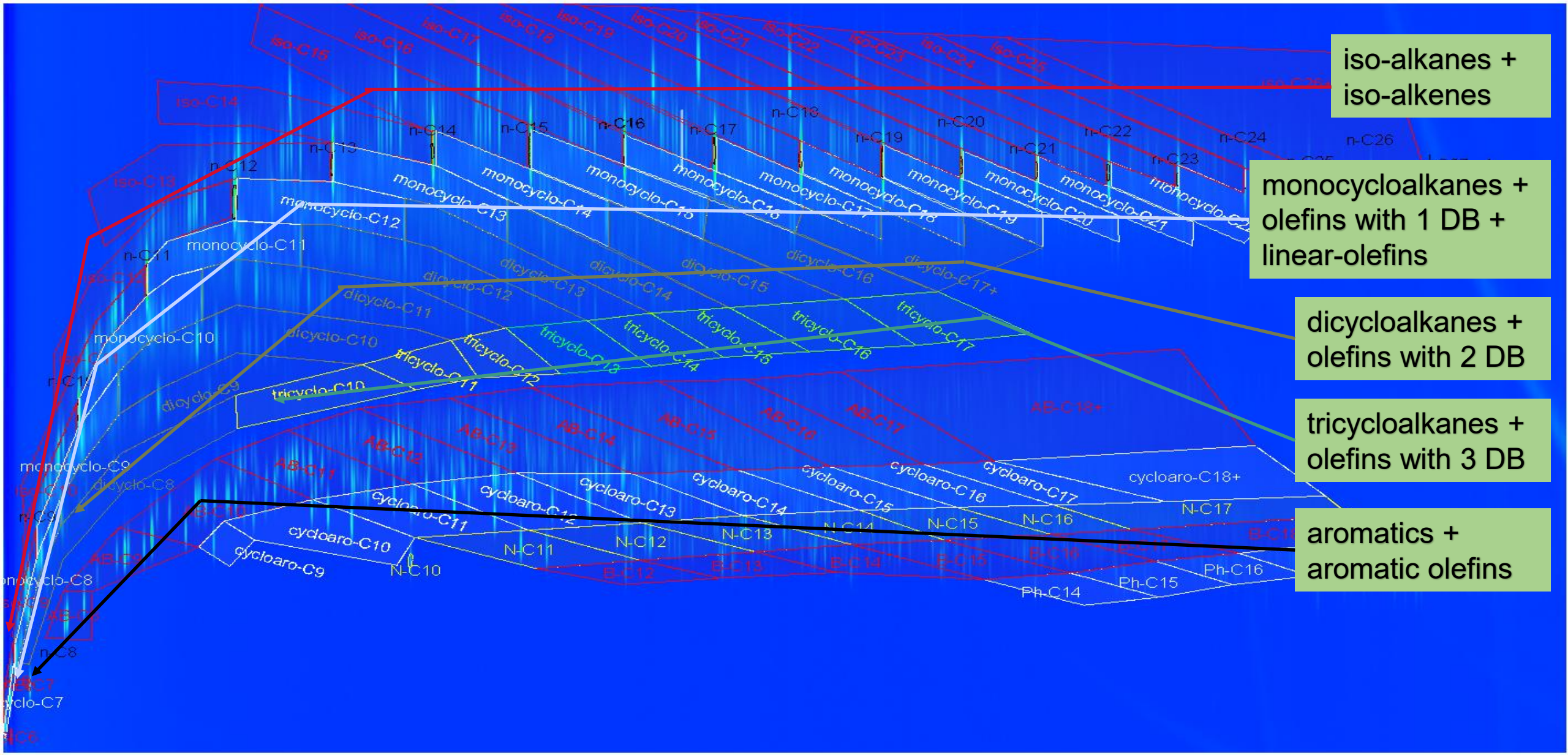

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¿Detailed olefin content?

GC×GC-FID and adsorption by Ag-SiO_2

Talanta 281 (2025) 126792

Contents lists available at ScienceDirect

Talanta

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

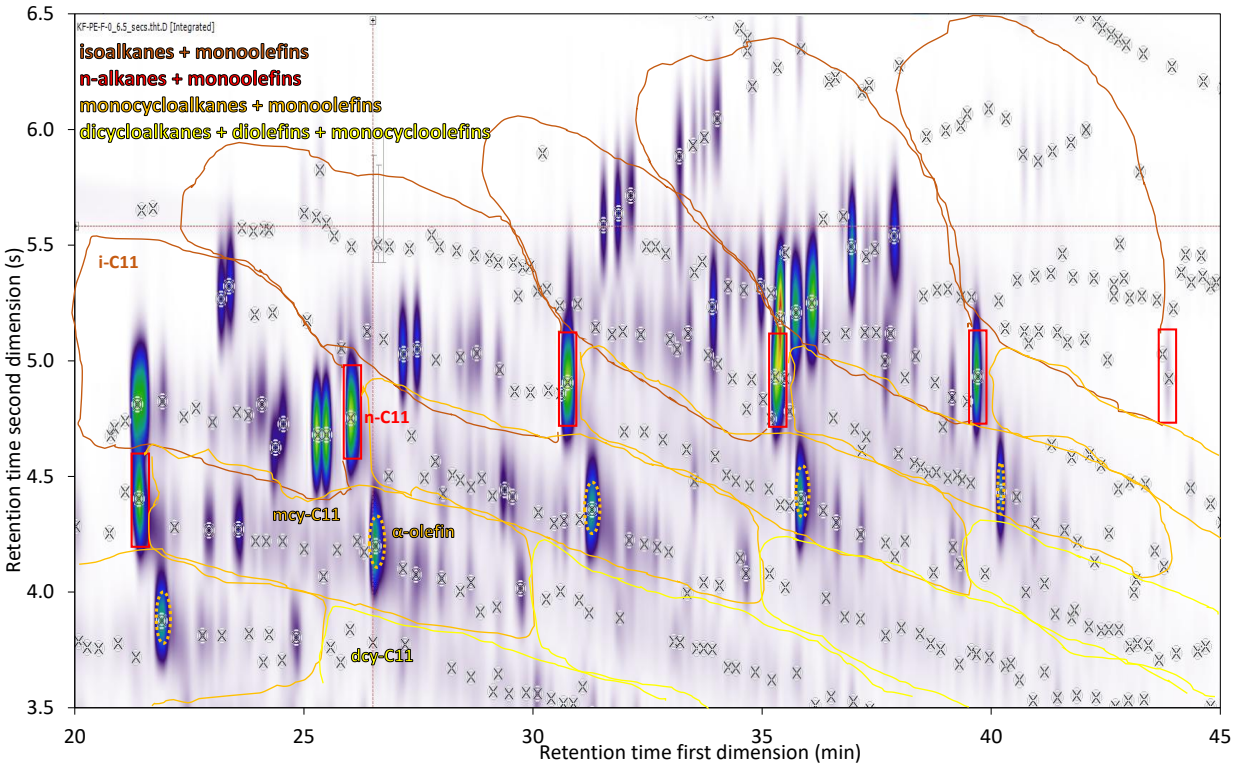
Quantitative determination of olefins in pyrolysis oils from waste plastics and tires using selective adsorption by Ag–SiO_2 followed by GC×GC-FID

Miloš Auersvald [a,**], Michal Šiman [a], Petr Vozka [b,*], Petr Straka [a]

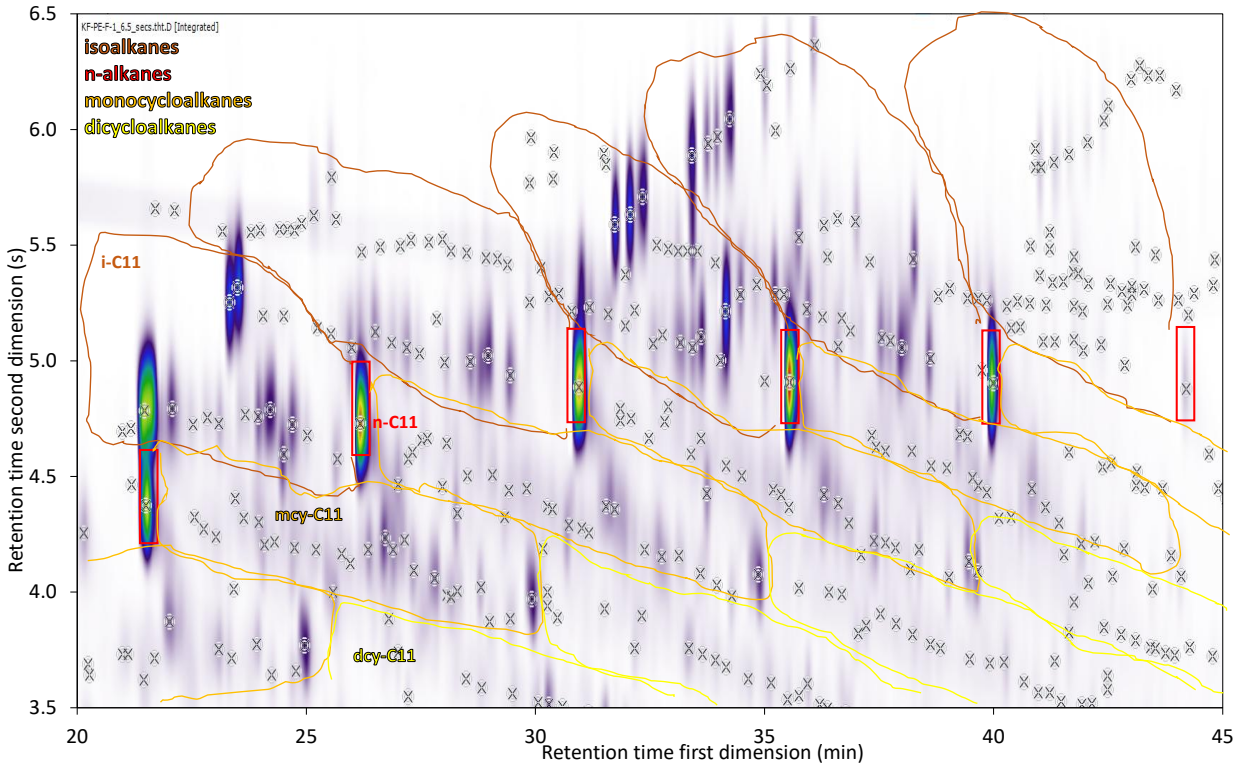
[a] Department of Sustainable Fuels and Green Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b] California State University, Los Angeles, State University, Drive 5151, CA, 90032, Los Angeles, United States

At least *n*-alkanes are safe..., right?

Neat sample



After alkene adsorption



Auersvald, M., Šiman, M., Vozka, P., Straka, P. (2025). Quantitative determination of olefins in pyrolysis oils from waste plastics and tires using selective adsorption by Ag-SiO_2 followed by GC×GC-FID, *Talanta*, 281, 126792.

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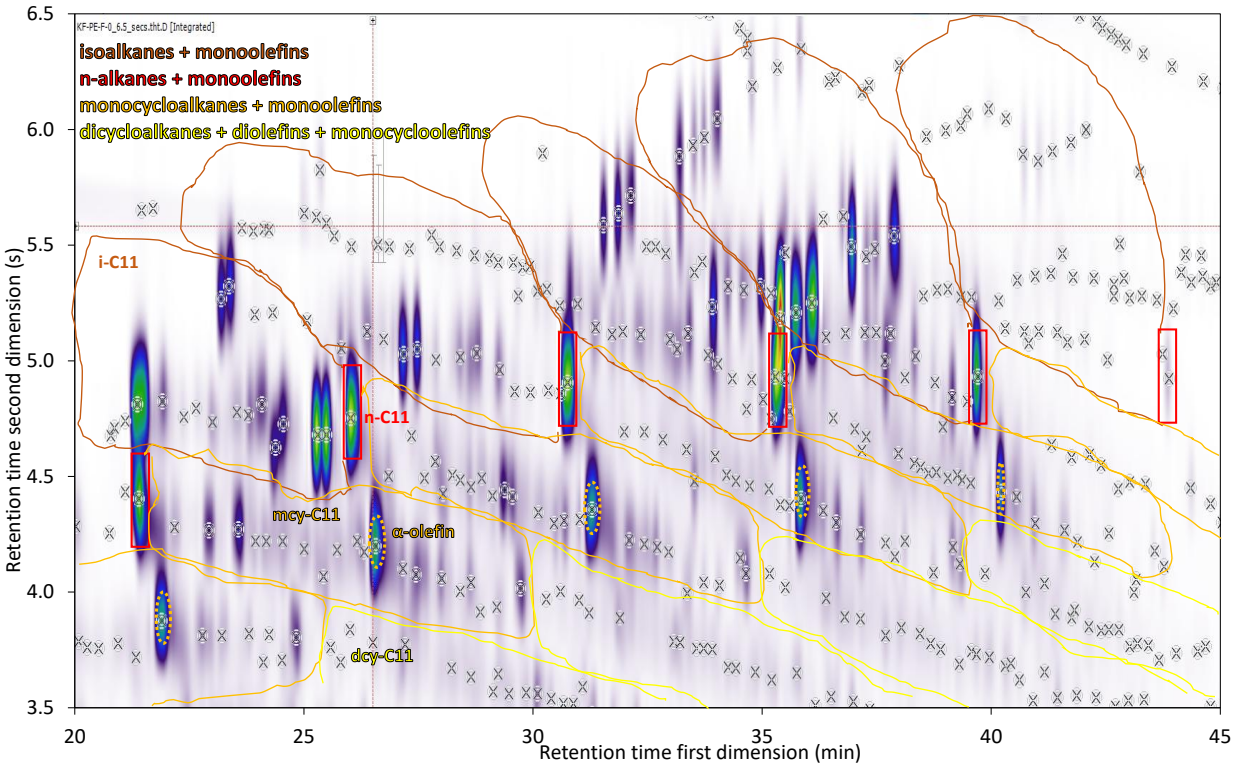
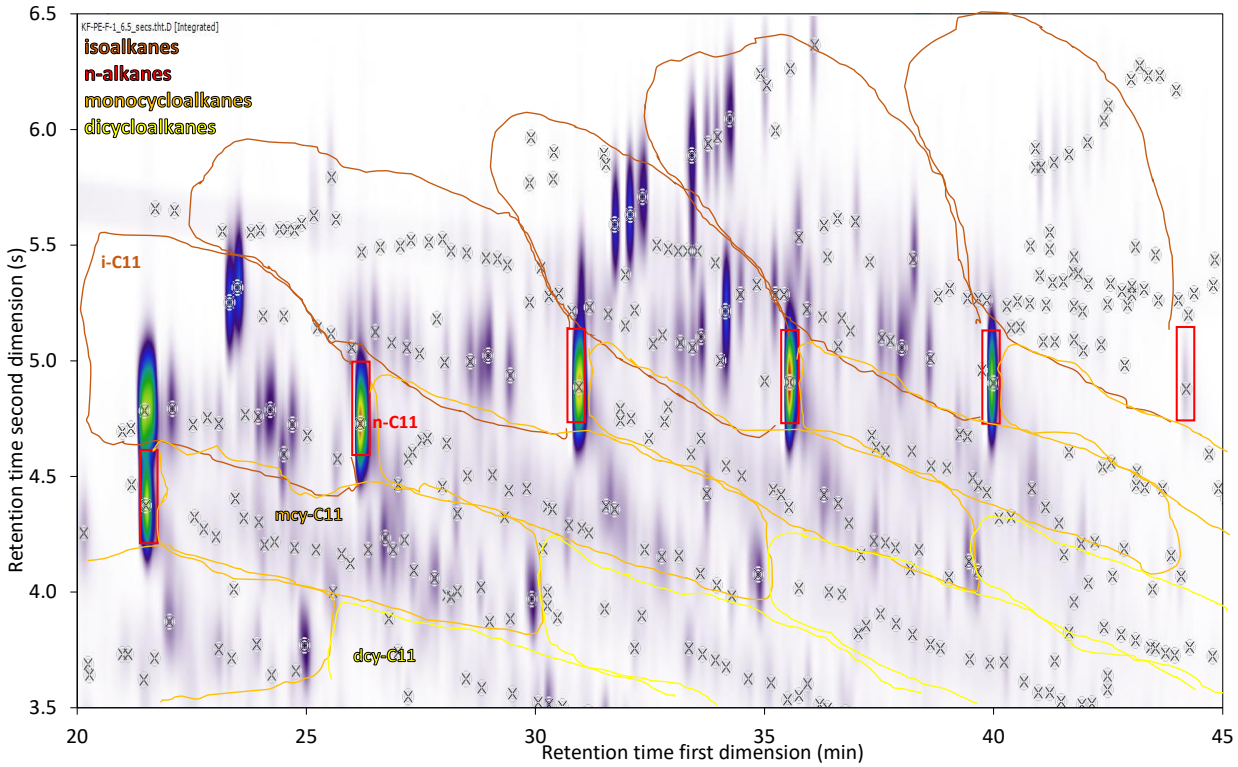


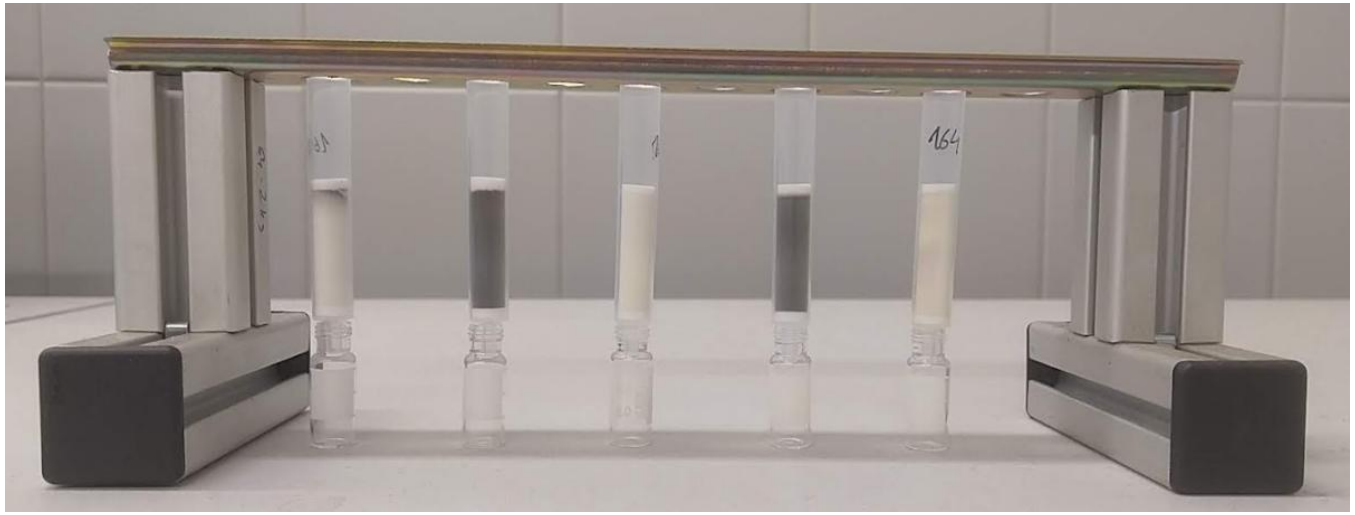
After alkene adsorption



n-alkane content (wt%)	C10	C11	C12	C13	C14	C15
apparent with olefins (A)	2.65	3.16	3.34	5.05	1.86	0.07
real without olefins (B)	2.12	3.00	3.24	3.27	1.84	0.06

Auersvald, M., Šiman, M., Vozka, P., Straka, P. (2025). Quantitative determination of olefins in pyrolysis oils from waste plastics and tires using selective adsorption by Ag-SiO_2 followed by GC×GC-FID, *Talanta*, 281, 126792.

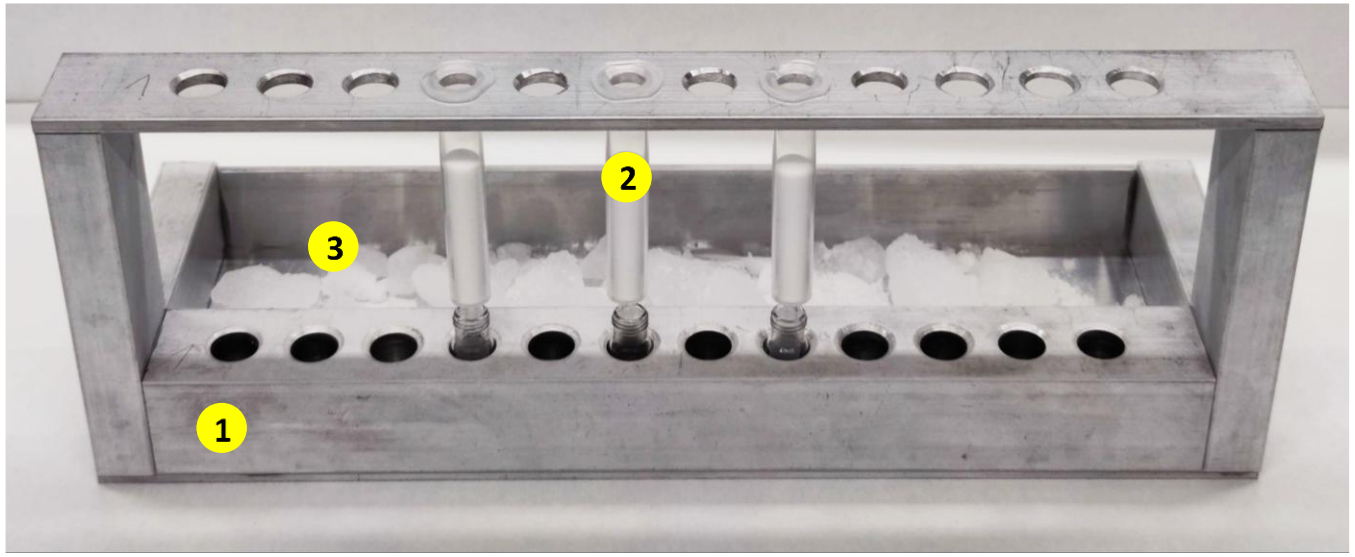
Olefins separation over $Ag\text{-}SiO_2$



SPE cartridge

loading 1.45 ± 0.03 g

particle size 0.040–0.063 mm



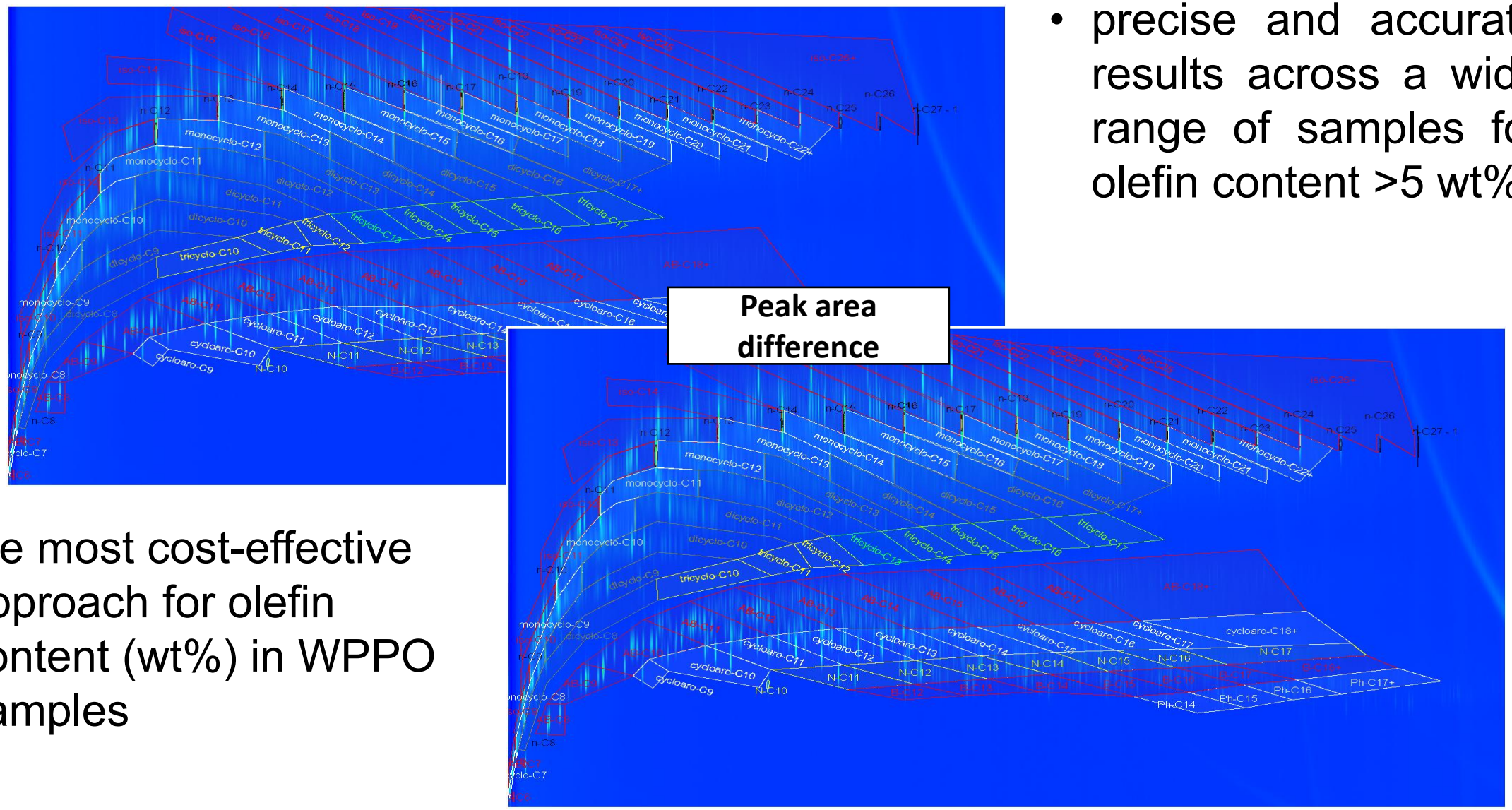
Method

50 µL of sample

15 min for separation

(**1** - cooled block with 2 mL vials, **2** - SPE column filled with $Ag\text{-}SiO_2$, **3** - reservoir with dry ice)

Olefins separation over Ag-SiO_2



- precise and accurate results across a wide range of samples for olefin content >5 wt%
- the most cost-effective approach for olefin content (wt%) in WPPO samples

Auersvald, M., Vozka, P., & Straka, P. (2025). Quantitative determination of olefins in pyrolysis oils from waste plastics and tires using **selective adsorption** by Ag-SiO_2 followed by GC×GC-FID, *Talanta*, 281, 126792.

Titration

- Bromine number
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- FTIR
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LC	GC
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HPLC	GC (*l*)
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Selective methods

- GC-VUV
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- Derivatizations
- Adsorptions

¿Detailed olefin content?

Quantitation of aliphatic and aromatic alkenes (up to 50 wt. %)

Sample + Internal Standard + DMDS + I_2 solution

↓

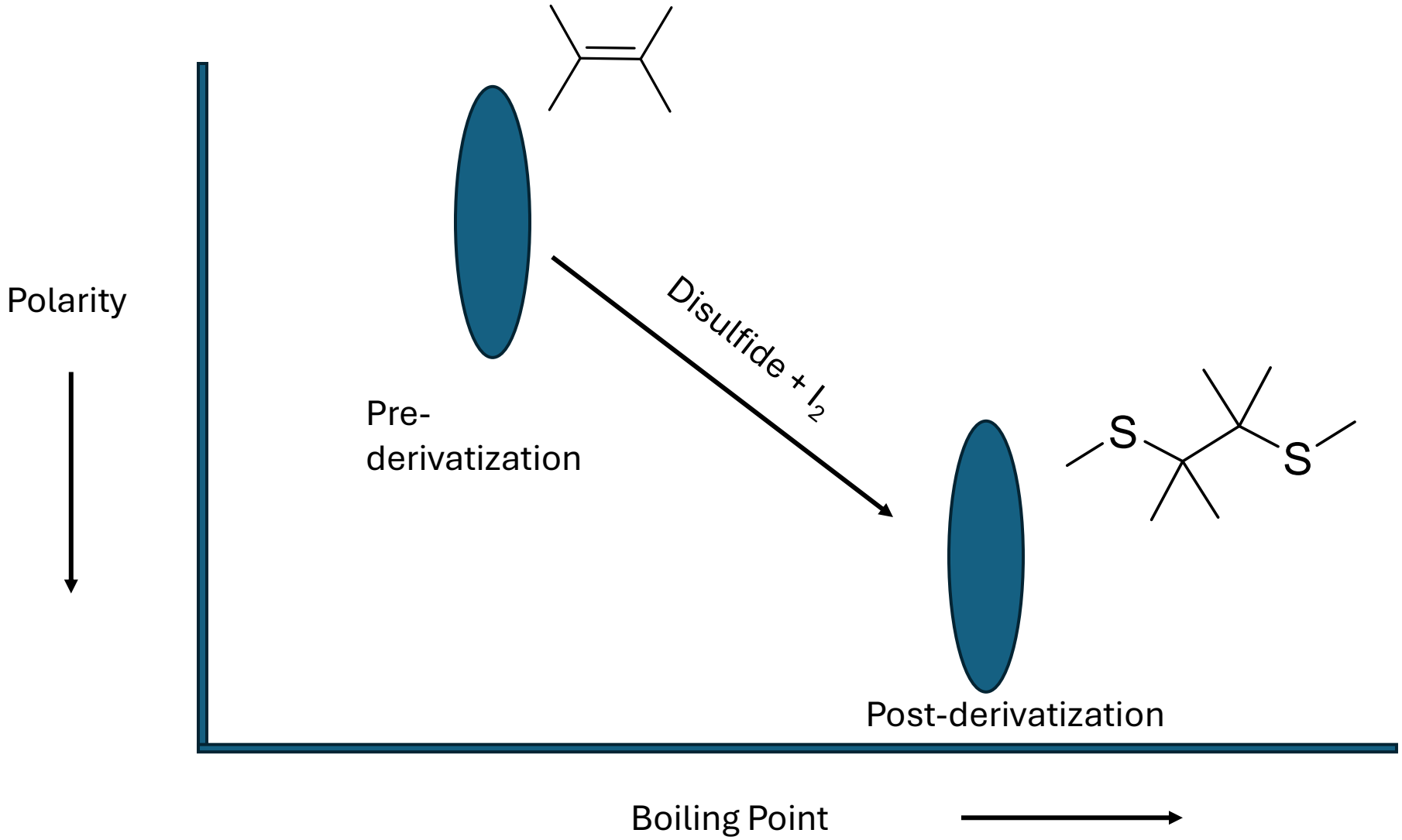
70 °C oven for at least an hour

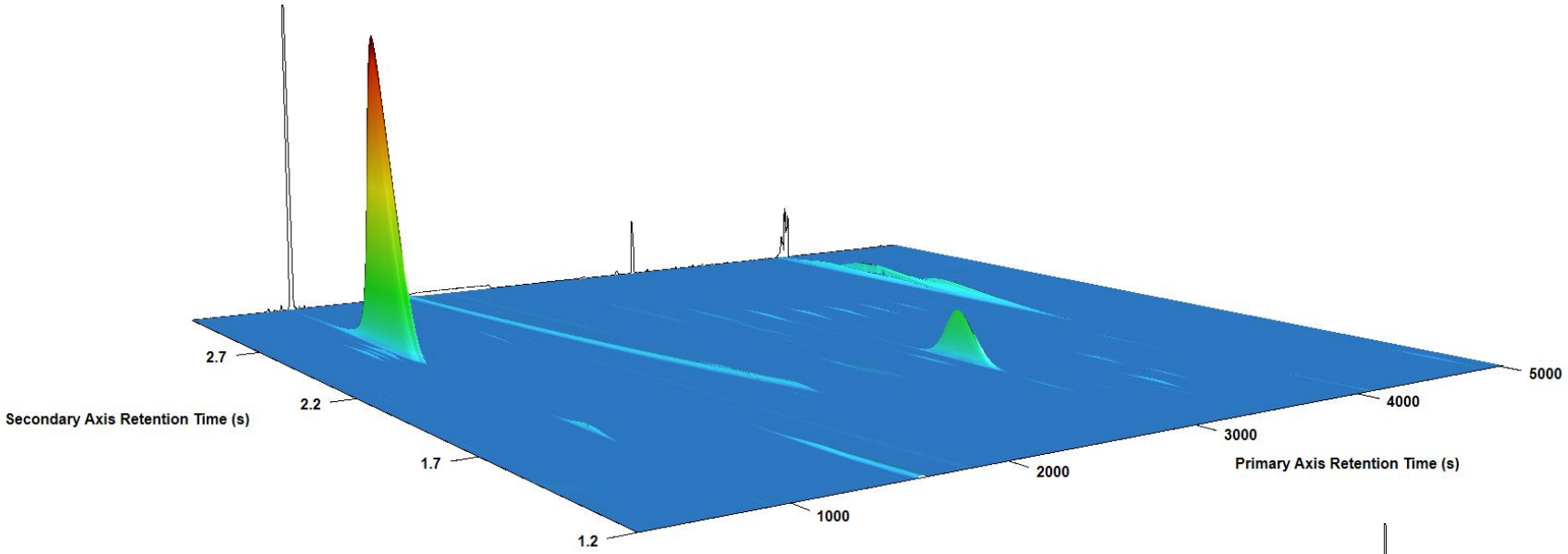
↓

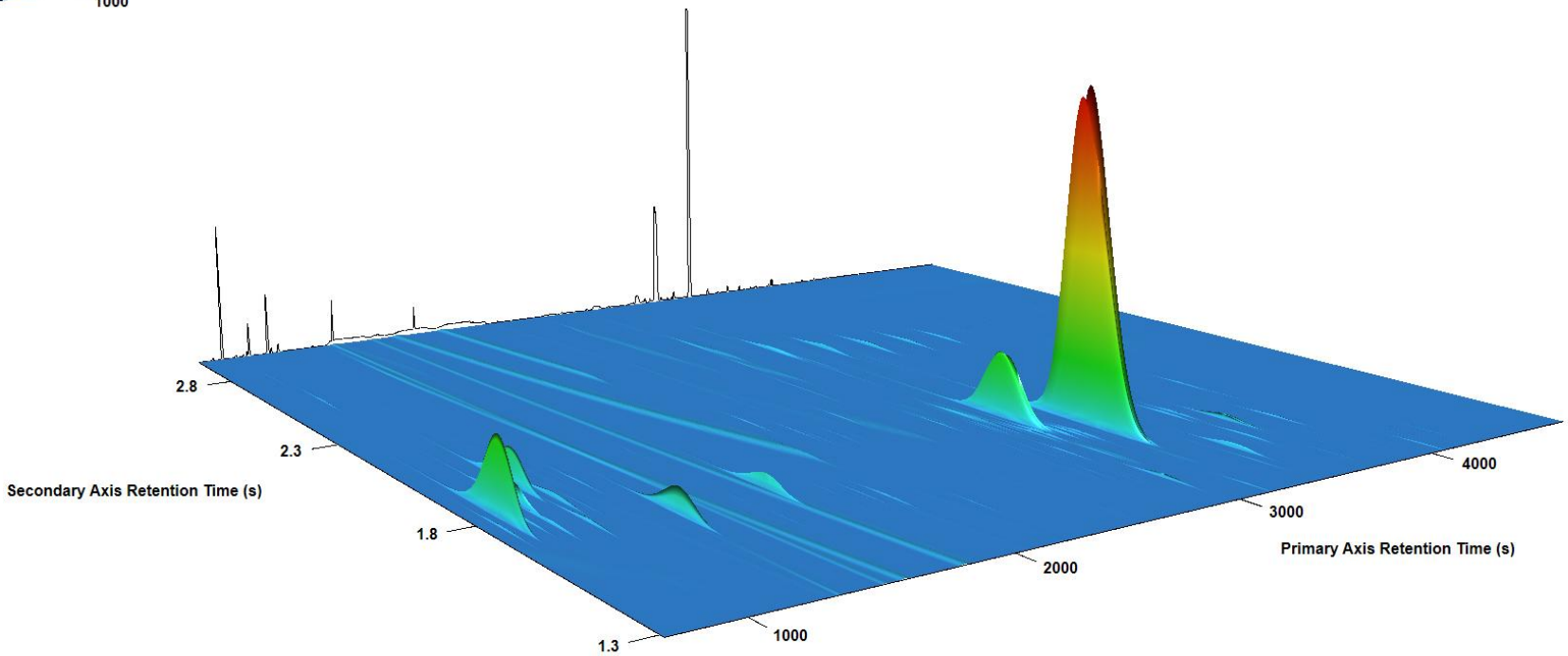
Sodium Thiosulfate

↓

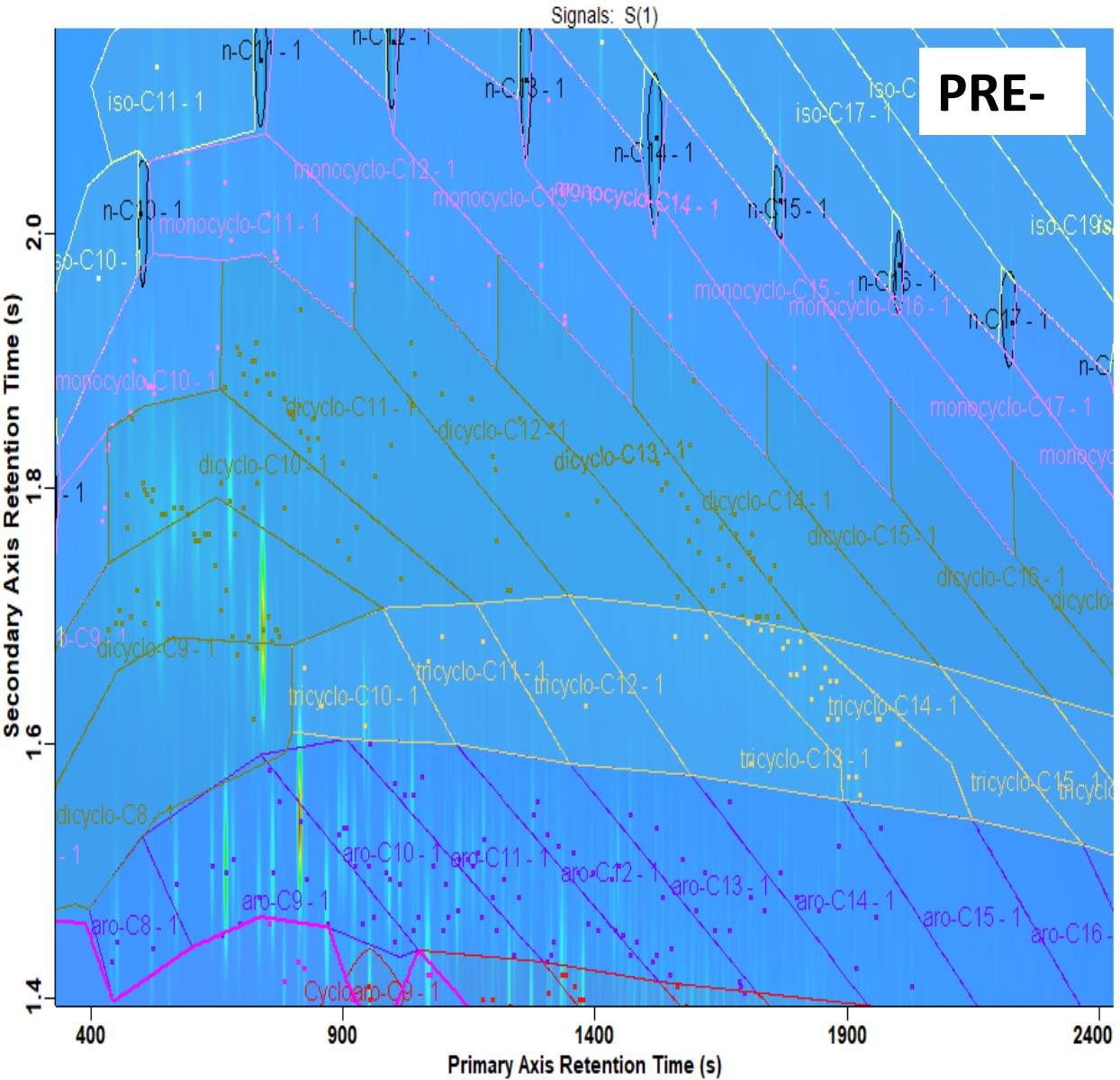
Organic phase analyzed

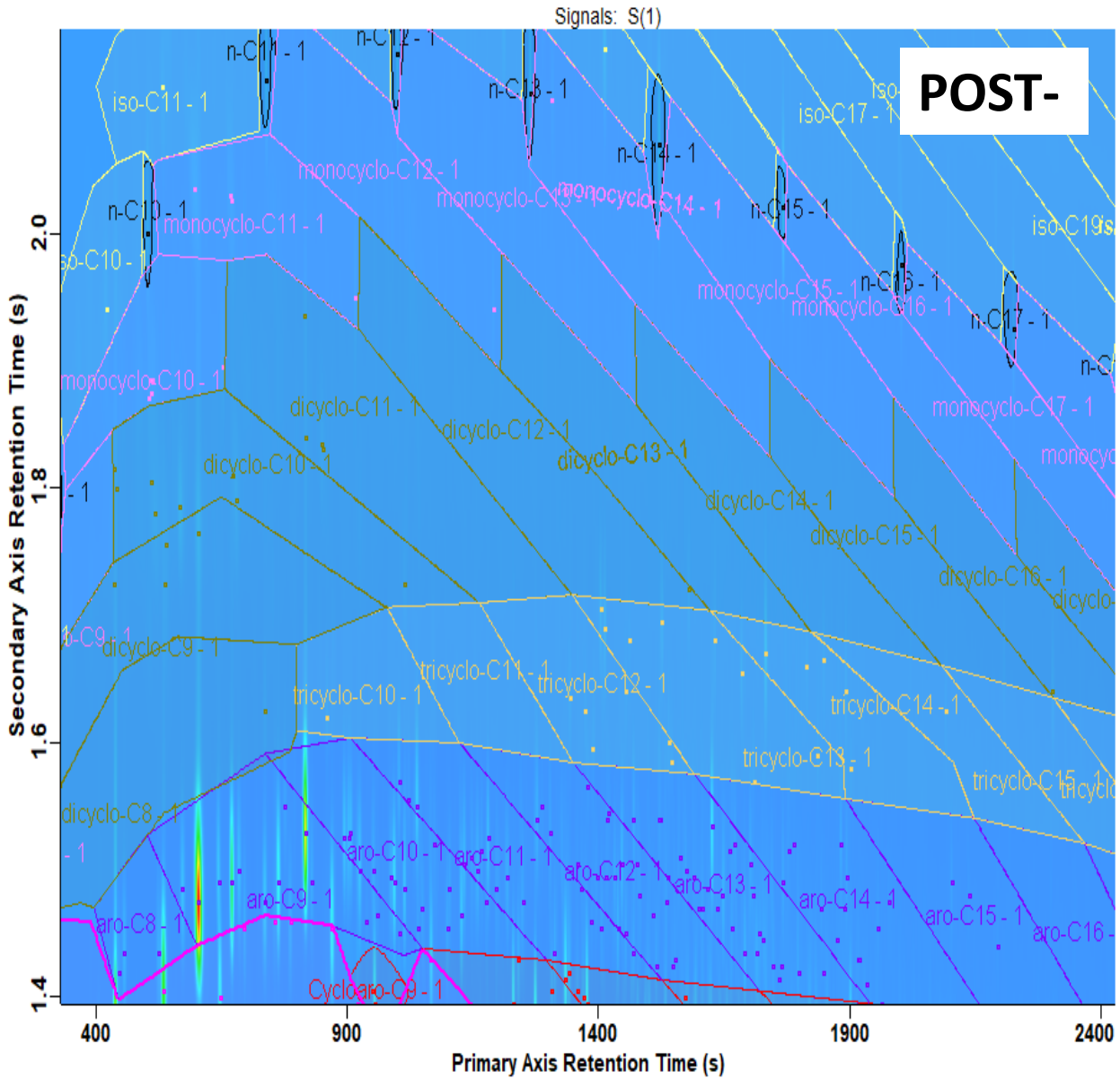

Polarity
Pre-
derivatization
Disulfide + I_2
S
S
Post-derivatization
Boiling Point

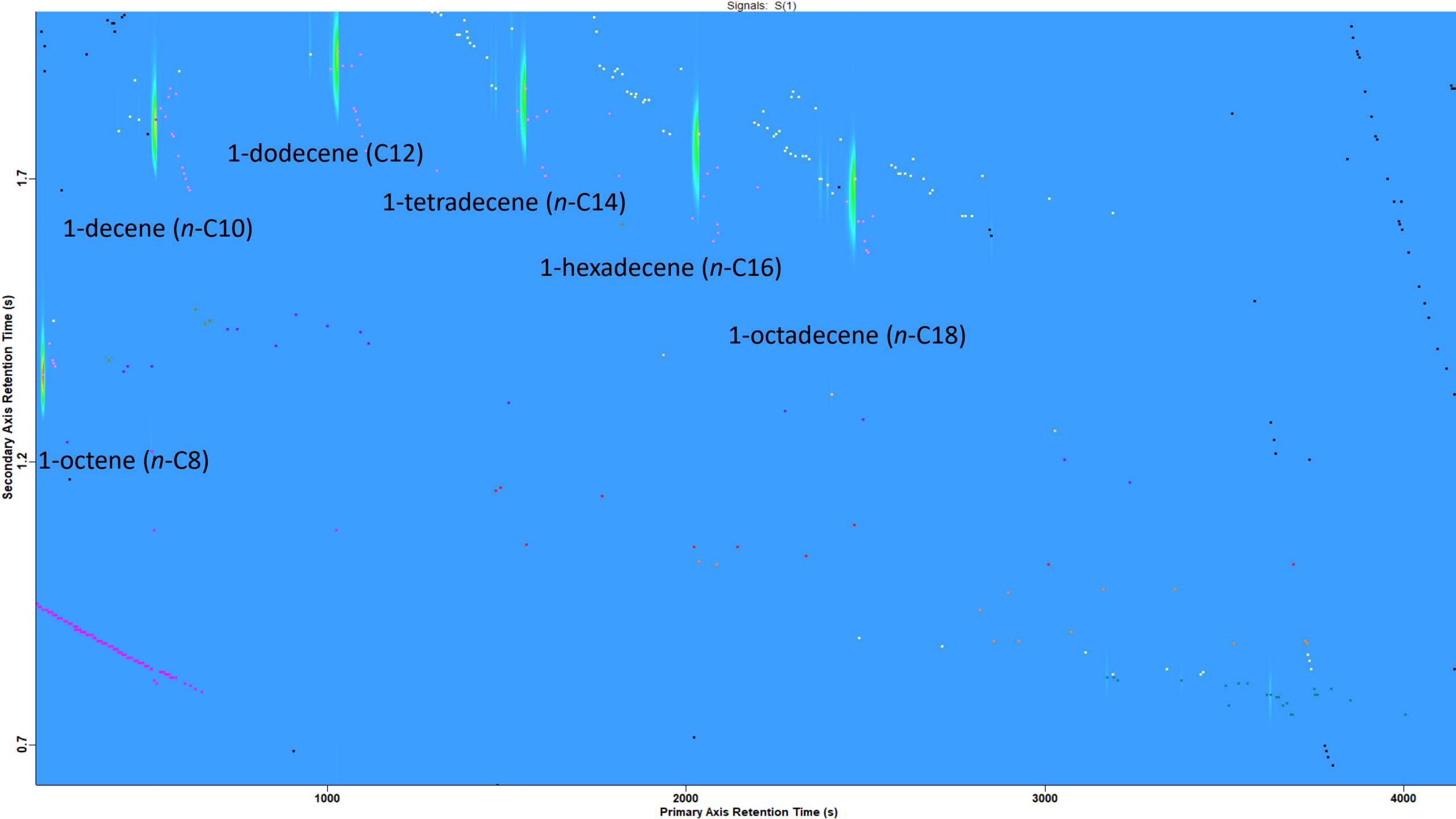

2.7
2.2
1.7
1.2
Secondary Axis Retention Time (s)
1000
2000
3000
4000
5000
Primary Axis Retention Time (s)

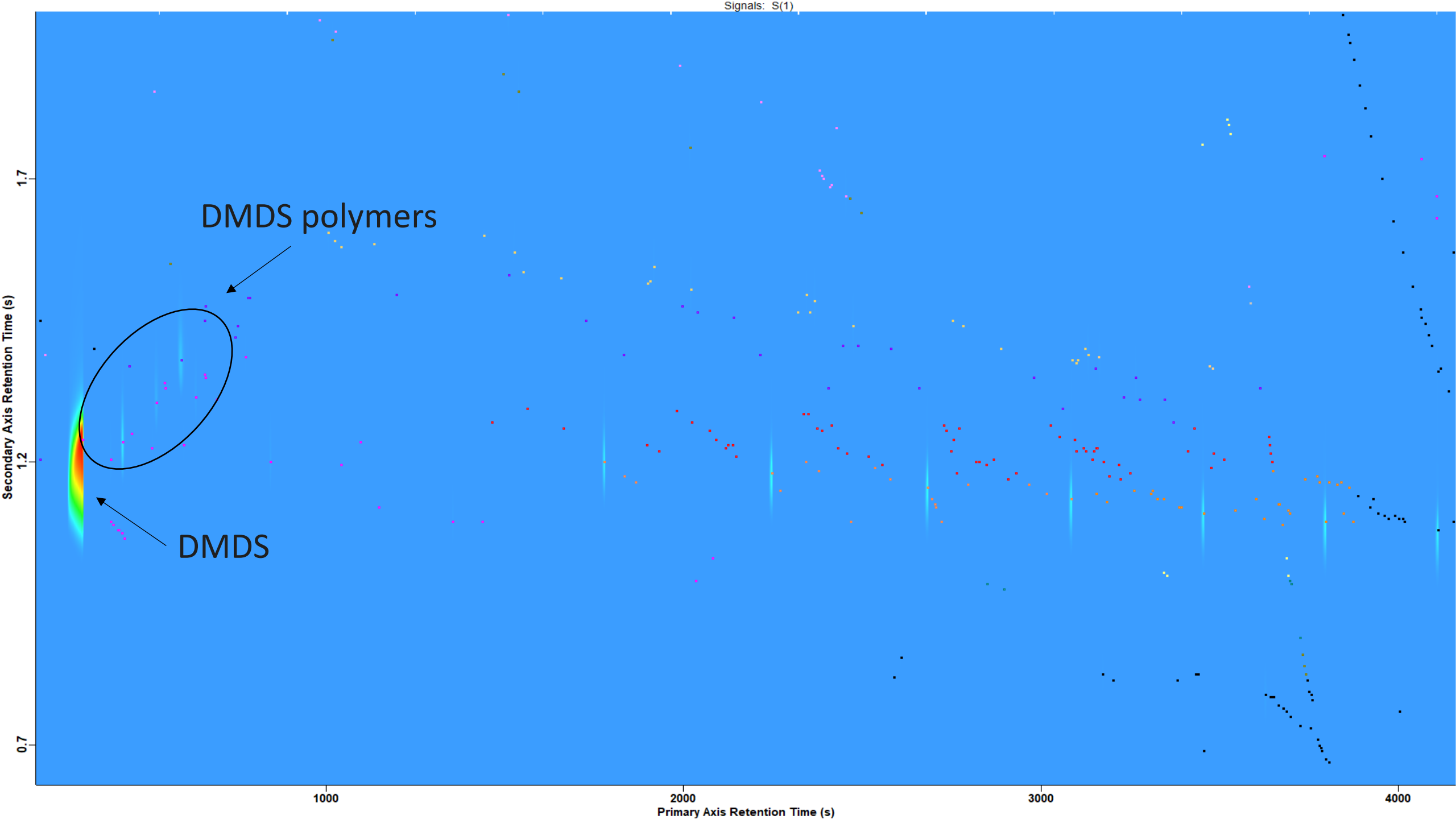

2.8
2.3
1.8
1.3
Secondary Axis Retention Time (s)
1000
2000
3000
4000
Primary Axis Retention Time (s)

Fuels in jet-fuel boiling point



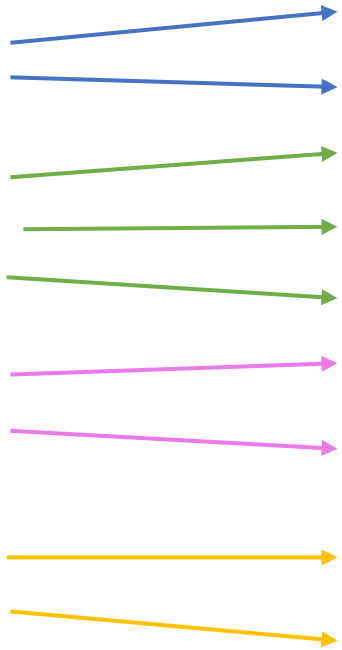



Signals: S(1)
1-dodecene (C12)
1-tetradecene (n-C14)
1-decene (n-C10)
1-hexadecene (n-C16)
1-octadecene (n-C18)
1-octene (n-C8)
Secondary Axis Retention Time (s)
1.7
1.2
0.7
1000
2000
3000
4000
Primary Axis Retention Time (s)


Signals: S(1)
DMDS polymers
DMDS
Secondary Axis Retention Time (s)
1.7
1.2
0.7
1000
2000
3000
4000
Primary Axis Retention Time (s)

Quantitative data – group totals

Before	wt. %
n-Alkanes	1.54
Isoalkanes	0.86
Monocycloalkanes	4.43
Dicycloalkanes	27.01
Tricycloalkanes	4.60
Aromatics	53.66
Light hydrocarbons	7.90



After	wt. %
n-Alkanes	1.54
Isoalkanes	0.64
Isoalkenes	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

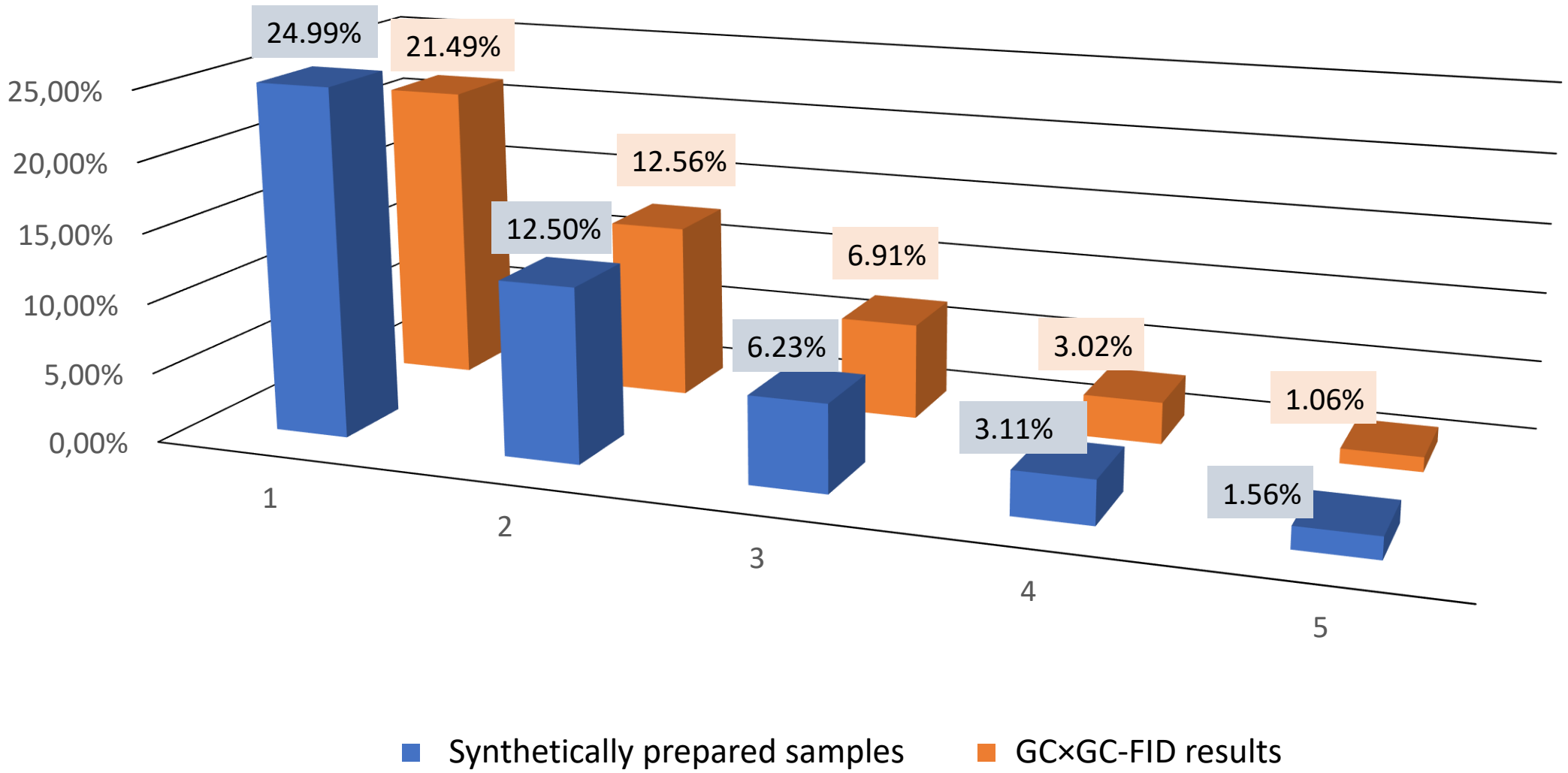
Quantitative data – detailed (Waste Tire Pyrolysis Gasoline)

Monocycloalkane region (example)

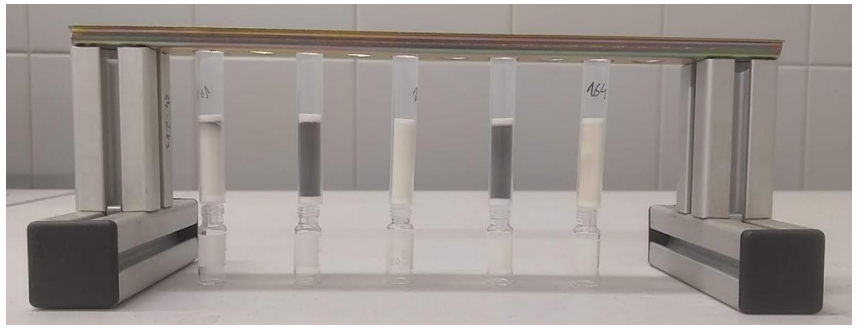
	Pre-derivatization		Post-derivatization			True results	
Carbon number	"Monocyclo" (p.a.)	"Monocyclo" (wt. %)	"Monocyclo" (p.a.)	"Monocyclo" (p.a. after norm.)	Olefins (p.a.)	Olefin (wt.%)	Monocyclo (wt.%)
C5	52883.75	6.00	38374.69	31454.66	21429.09	2.32	3.68
C6	81707.23	9.27	65393.26	53601.03	28106.20	3.04	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
Total	329874.53	37.44	236177.58	193588.18	136286.35	14.77	22.67

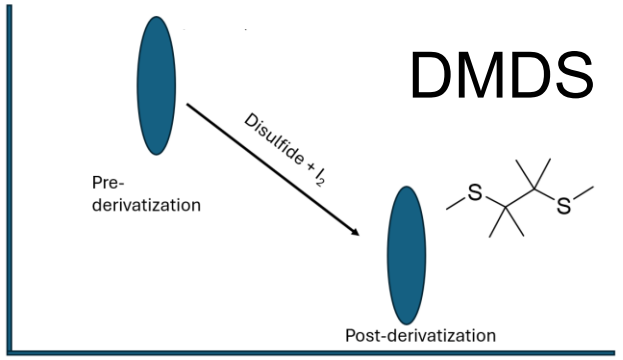
Quantitation of aliphatic and aromatic alkenes (up to 50 wt. %)

Barzallo, G., Gieng, H., Sharma, A., Patel, J., Auersvald, M., Straka, P., Vozka, P. Quantitative Analysis of Aliphatic Olefins in Alternative Fuels (in gasoline distillation range) Made from the Conversion of Plastic Waste via GCxGC-FID, *J. Chromatogr. A*, **in preparation**

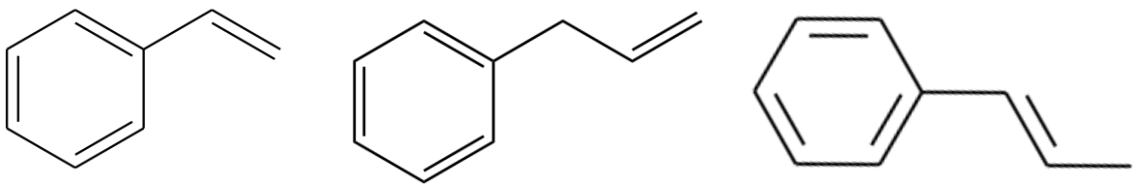


Drawbacks of the methods



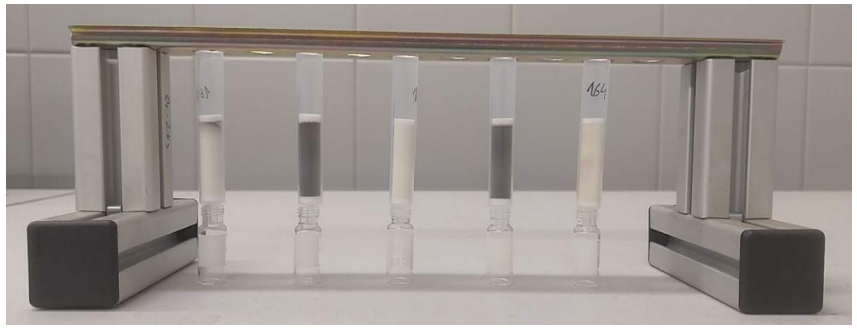


- precise and accurate results across a wide range of samples for olefin content >5 wt%
- works (“only”) for aliphatic olefins and alkenylbenzenes, and alkenyl-substituted alkylbenzenes



- iodine is DEA-regulated at many places
- DMDS….

Drawbacks of the methods



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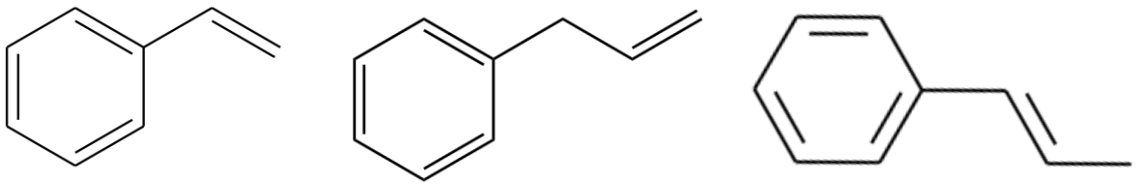
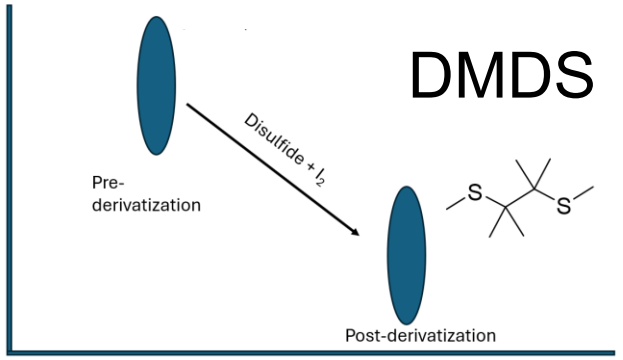
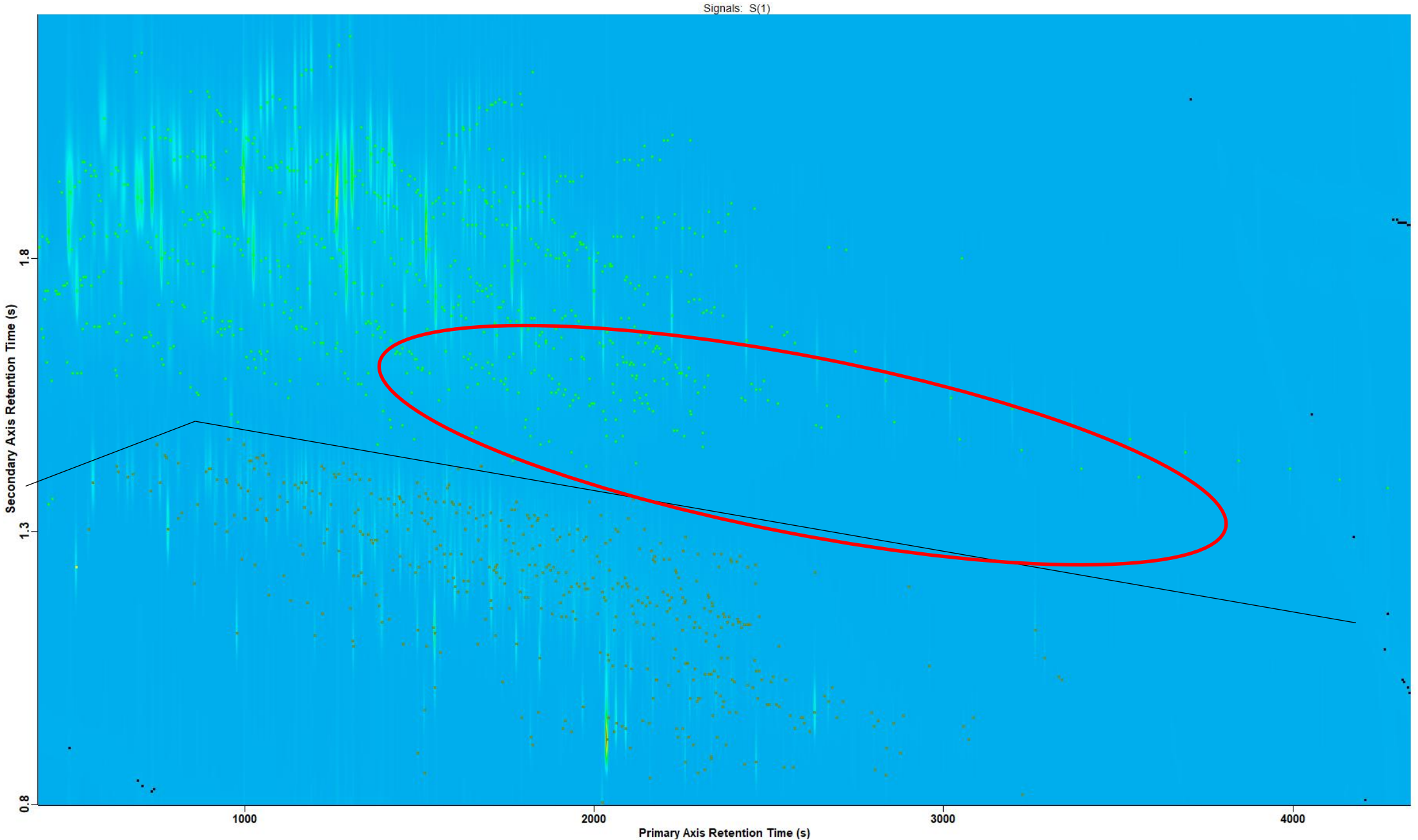




- iodine is DEA-regulated at many places
- DMDS….
- 70 °C – gasoline-like samples
- works only for aliphatic olefins
- main problem – heavier iso-alkenes are not shifting to the aromatic region

Chromatogram – diesel-like sample pre-derivatization



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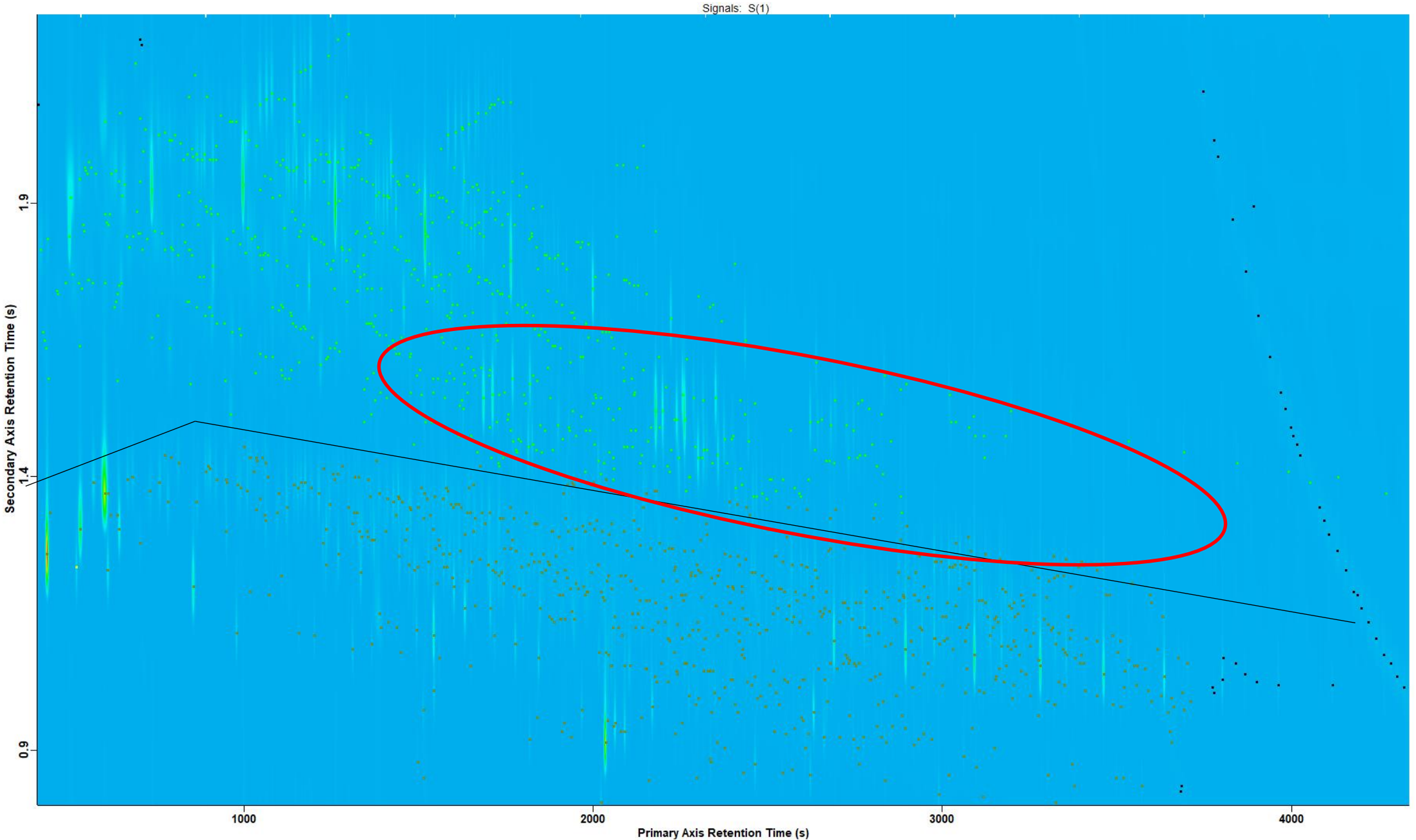
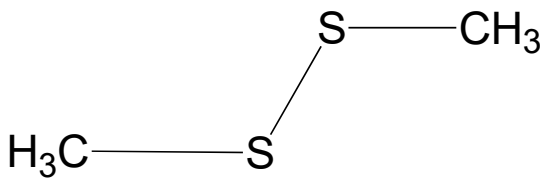


Potential solutions

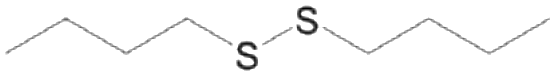
- Iodine – hard to buy in some places (like CA) → TPO (photoinitiator)
- DMDS → DBDS, DPhDS, DBzDS, …
- 70 °C → room temperature

- Main problem – heavier iso-alkenes → not shifting to the aromatic region

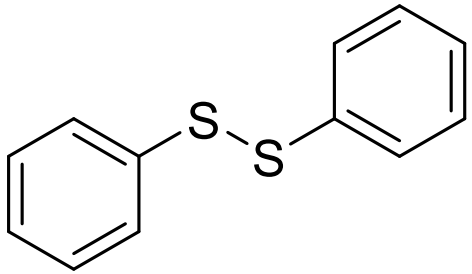
Disulfides



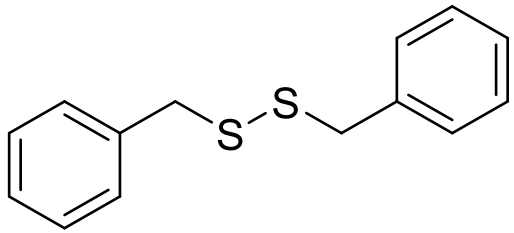
Dimethyl Disulfide ($C_2H_6S_2$)



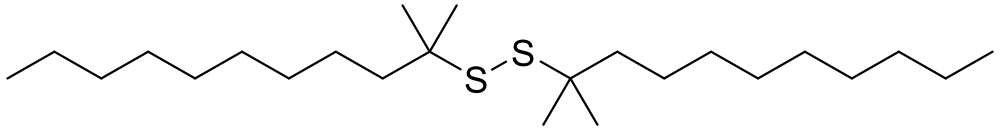
Dibutyl Disulfide ($C_8H_{18}S_2$)



Diphenyl Disulfide ($C_{12}H_{10}S_2$)



Dibenzyl Disulfide ($C_{14}H_{14}S_2$)



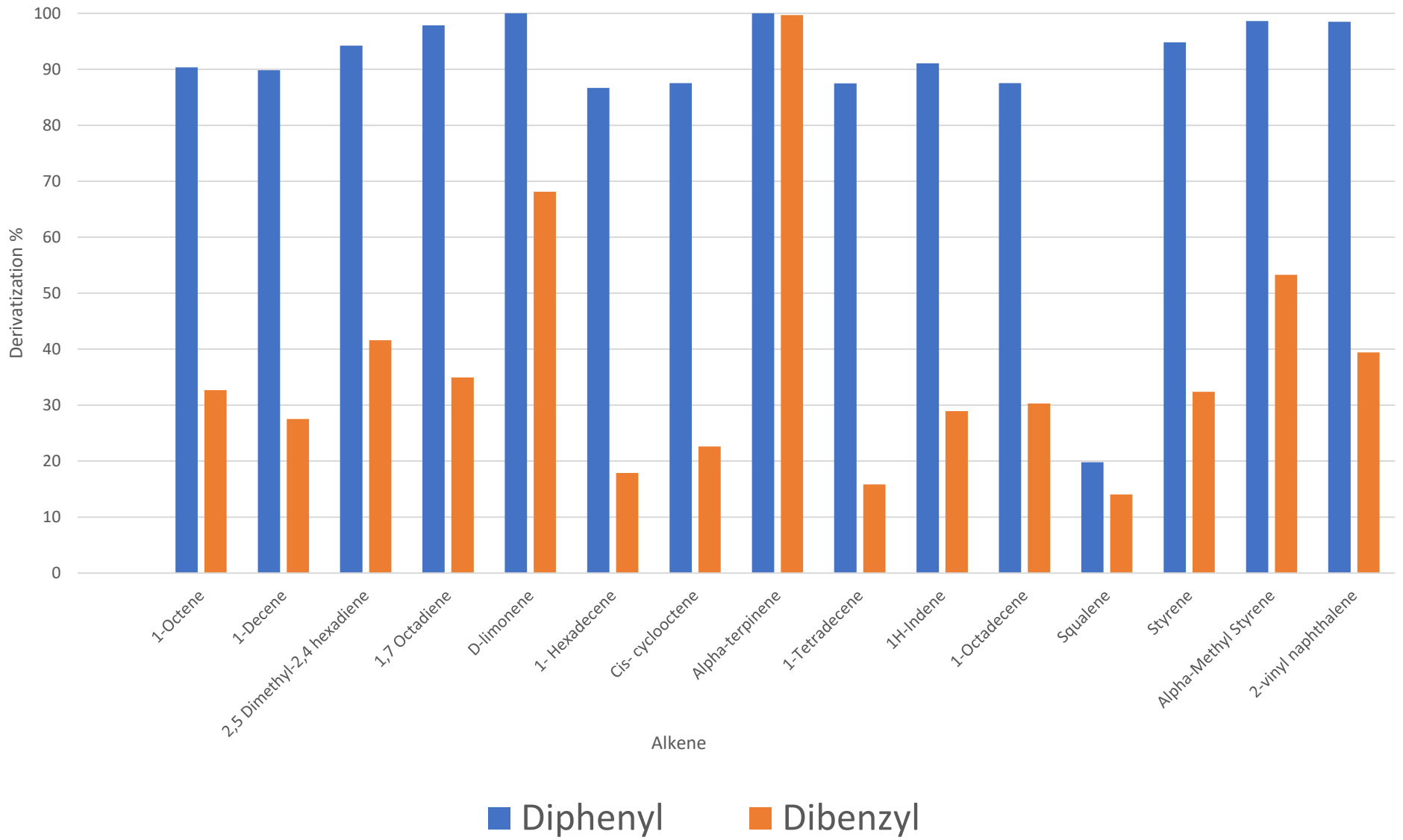
Di-tert-dodecyl Disulfide ($C_{24}H_{50}S_2$)

(. . .)

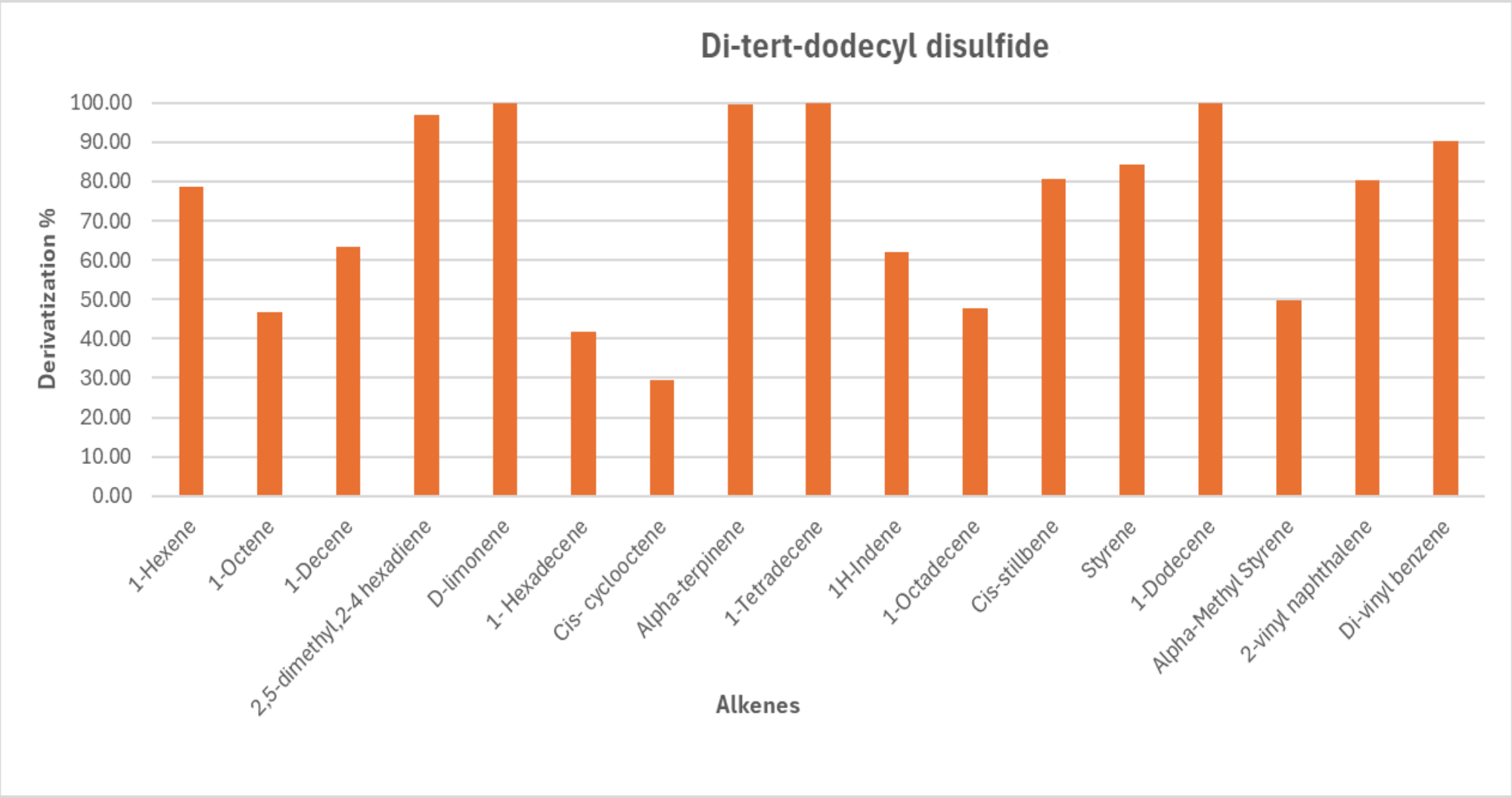
Derivatization conditions

Reagents	Time (hours)	Temperature (°C)	Solvent	Ratio (Equivalent)
Dimethyl Disulfide	1	RT	-	1,1.5
	12	40		
	24	70		
Diphenyl Disulfide	1	RT	Diethyl ether	1,1.5
	12	40		
	24	70		
Dibenzyl Disulfide	1	RT	-	1,1.5
	12	40		
	24	70		
Dibutyl Disulfide	1	70	Diethyl ether	1, 1.5
	24	70		
Di-tert-dodecyl Dis.	1	RT	Diethyl ether	1,1.5
	12	40		
	24	70		

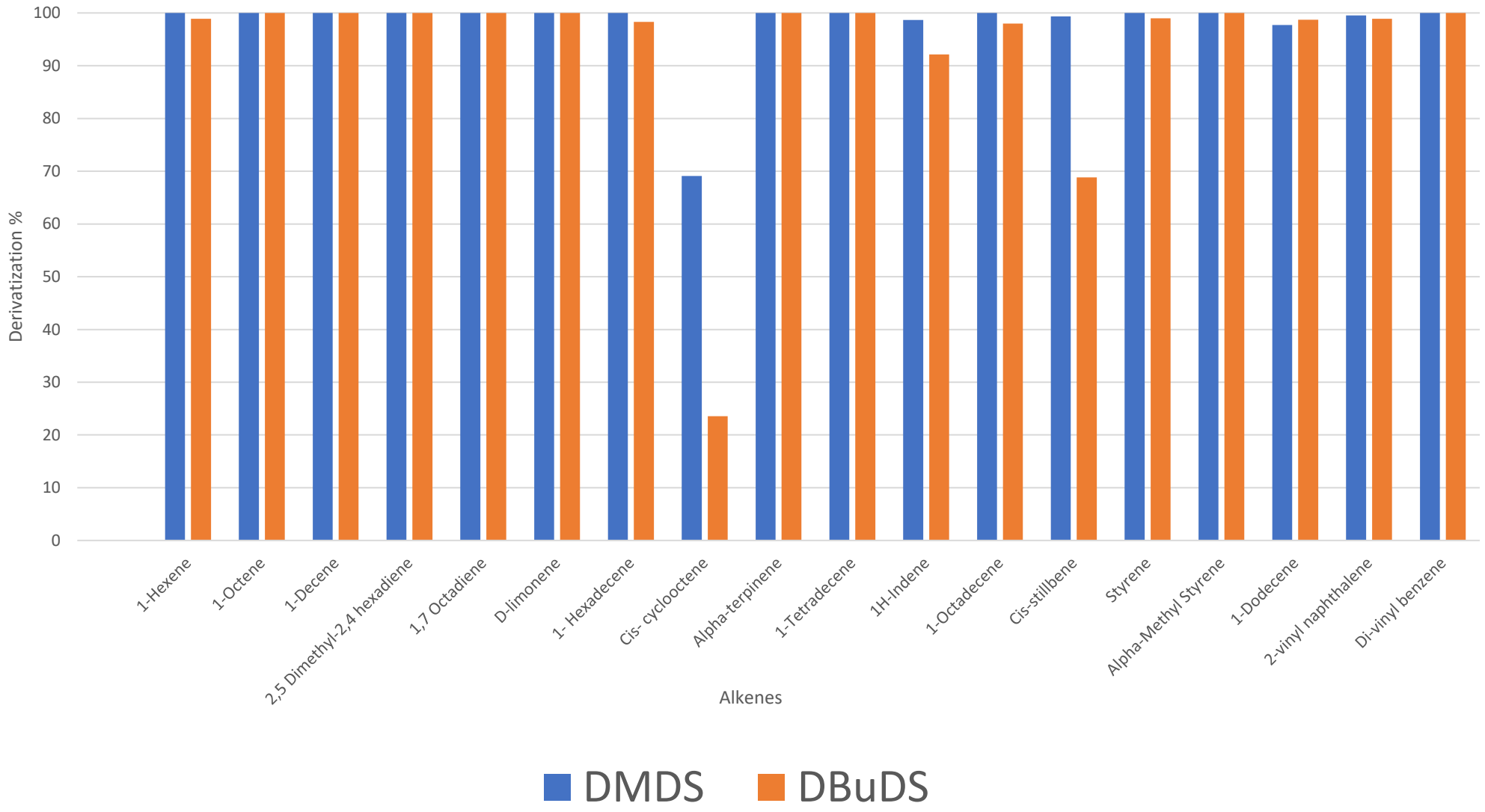
Results – 12 hours & RT



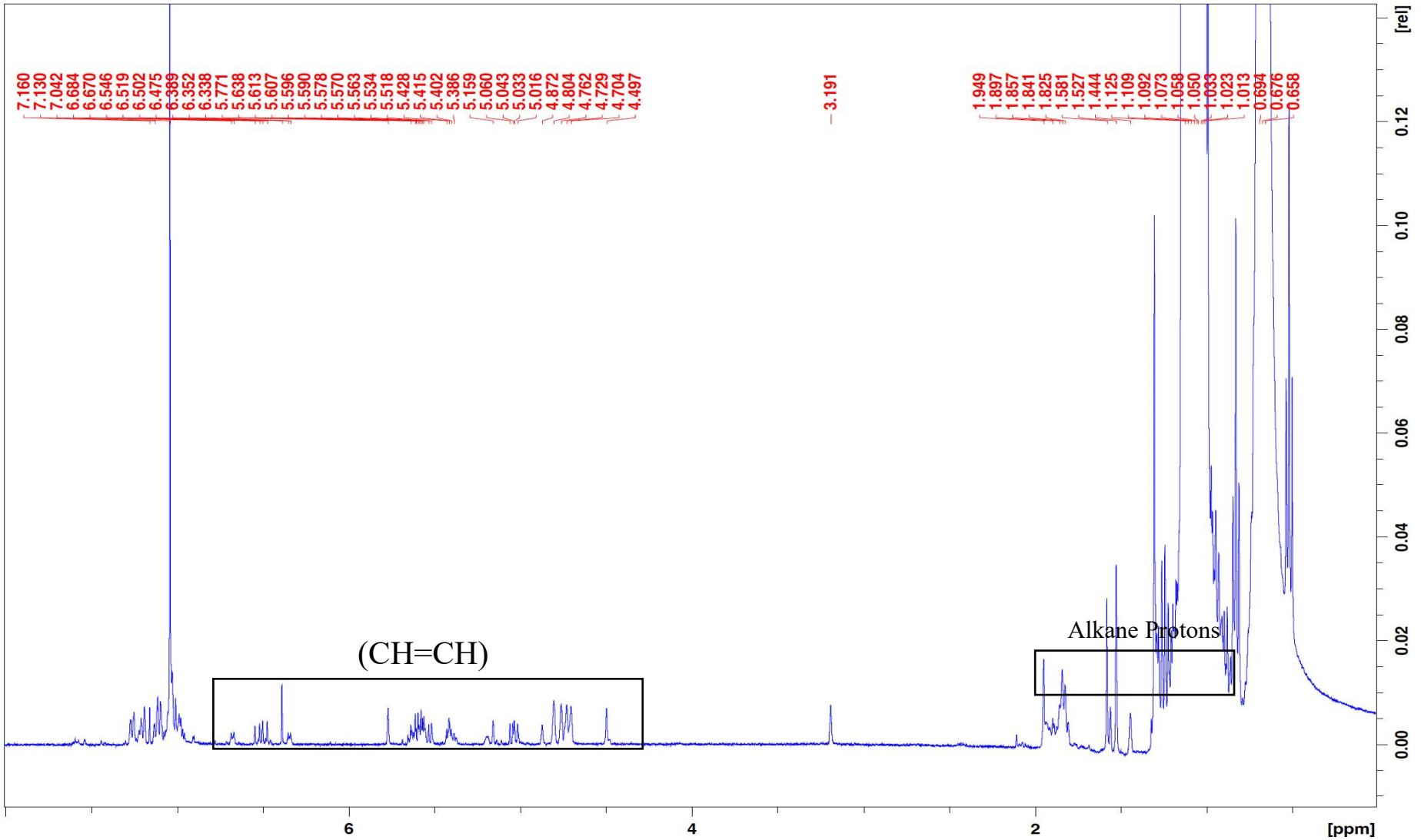
Results – 12 hours & 70 °C



Results – 24 hours & 70 °C



Did we find it? ^{1}H NMR of pre-derivatized alkene mix



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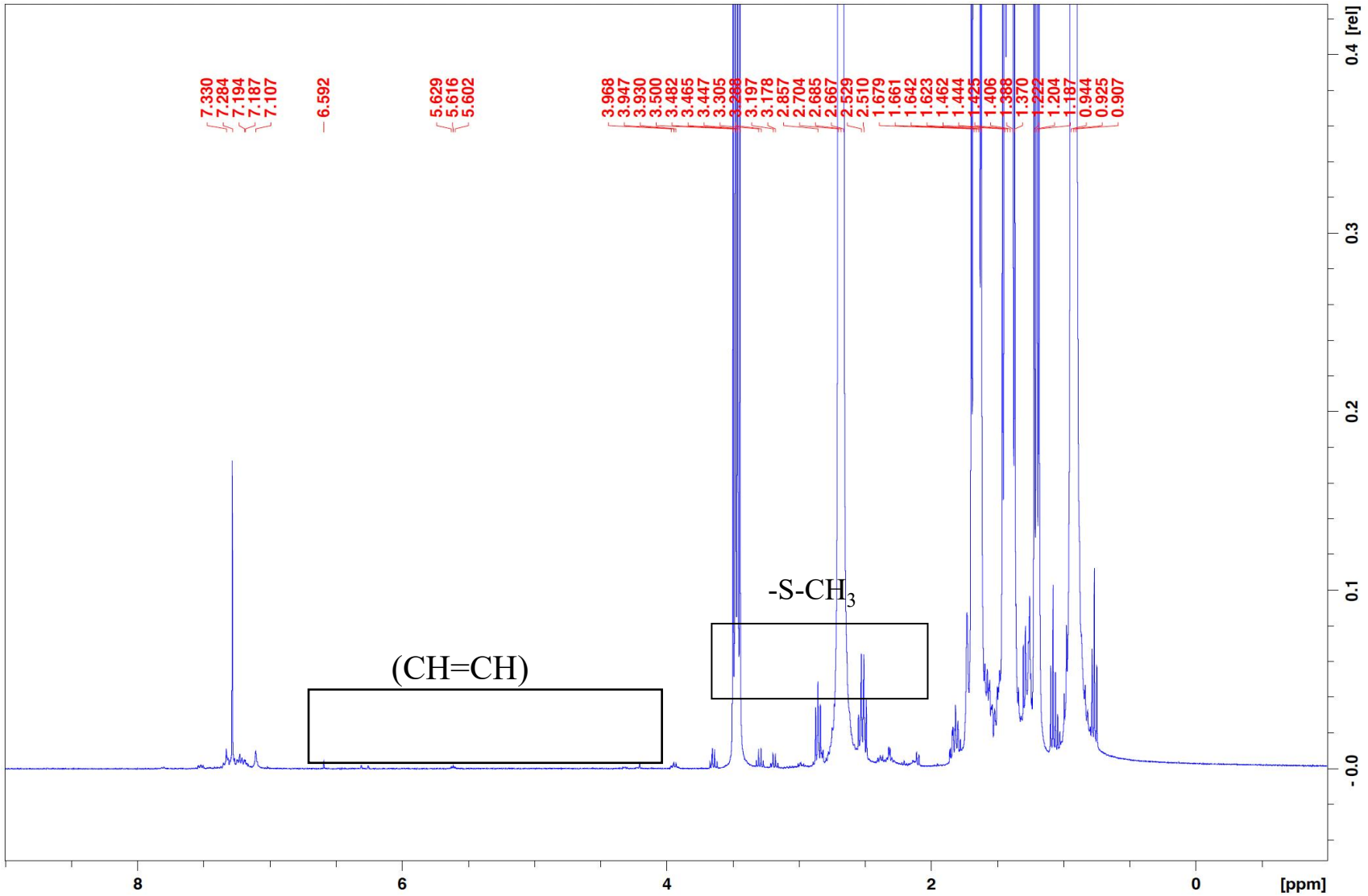

Conclusion

Previous work

- Dimethyl Disulfide effective at 70 °C for 24 hours for gasoline (C_6 to C_{12})
- Unsuitable for heavier fuels – jet and diesel

Current work

- Testing additional ("heavier") disulfides: DBuDS, Ph_2S_2, DBDS, Di-tert-dodecyl DS, …
- Exploring reaction conditions for complete derivatization

Validation

- ^{1}H-NMR Spectroscopy: confirmed successful derivatization with consistent spectral shifts
- Next: analyzing synthetic mixtures with known olefin content + TOFMS

Acknowledgements

C3AL
COMPLEX CHEMICAL COMPOSITION ANALYSIS LAB

LECO
EMPOWERING RESULTS

VICI DBS

RESTEK

NXT POWER

CATSUS
NSF CREST

My students