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Using GC×GC for monitoring biogenic components in renewable transportation fuel blends

*From **REALITY** to **DREAM***

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Natural Resources Canada

CanmetENERGY Devon

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Leadership in ecoInnovation

15th Multidimensional Chromatography (MDC) Workshop
Los Angeles, CA, USA – January 10-12, 2024

Canadä

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- Buildings and Communities
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- Renewable & Distributed Energy
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- Downstream & Renewables
- Upstream & Environment

Calgary and Hamilton

Advanced materials for:

- Energy end-use, production, and distribution (pipelines)
- Safety and Security

Ottawa

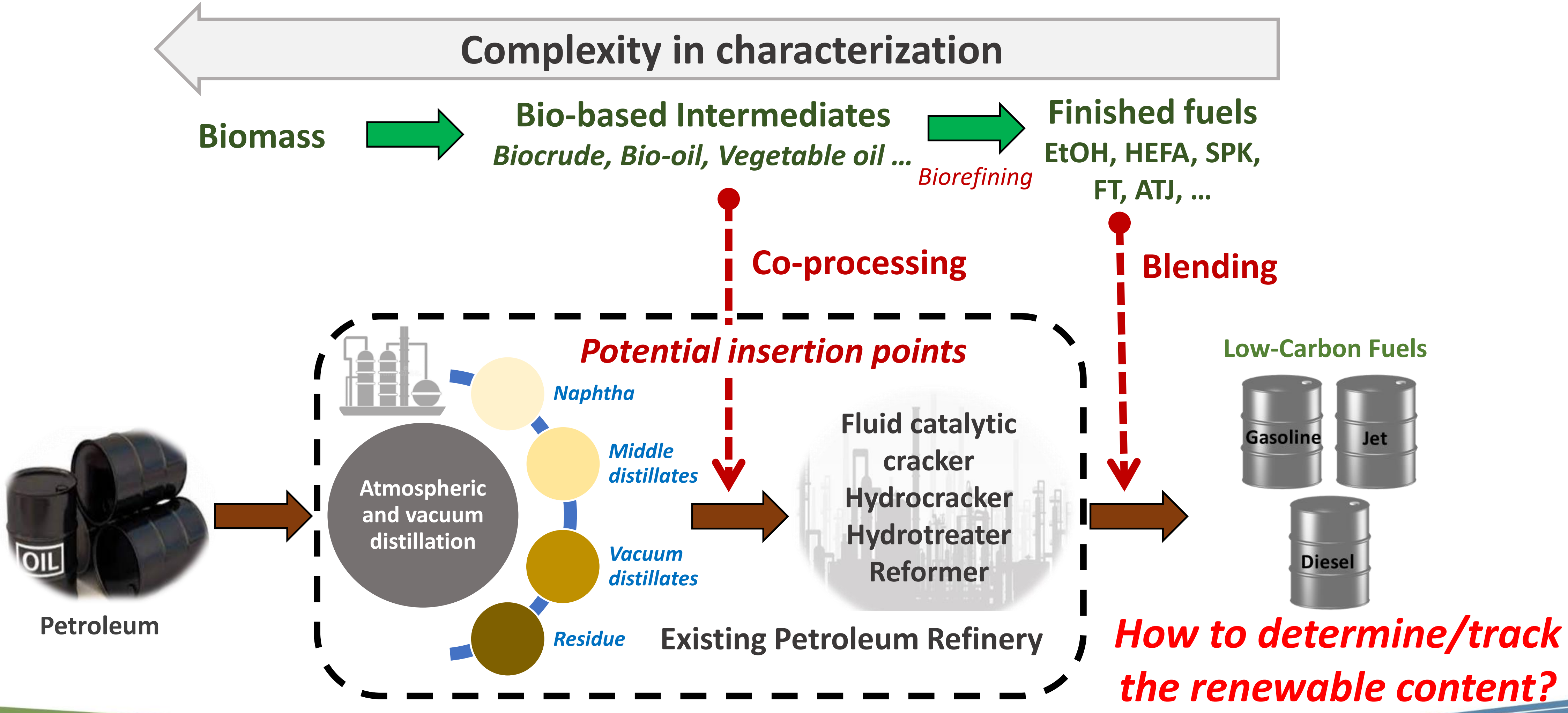
- Clean fossil fuels
- Renewables
- Energy end-use

Research Background

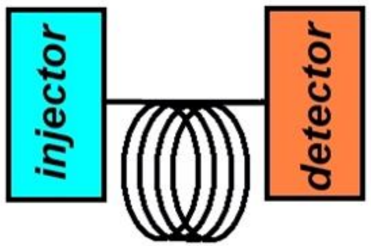
- Bioenergy is expected to play a significant role in achieving Canada's net zero emissions target by 2050.
- Renewable biomass biofuel production emits less GHG than fossil fuel production on a life cycle basis.
- Canada's federal regulation on renewables content in transportation fuels is: **5 vol% in gasoline and 2 vol% in diesel.**
- **Fuel blending and co-processing** - two strategies to incorporate renewable content mandates into transportation fuels.
- Quantifying **renewable carbon** content in transportation fuels is important for refiners to **obtain credits and financial incentives**.

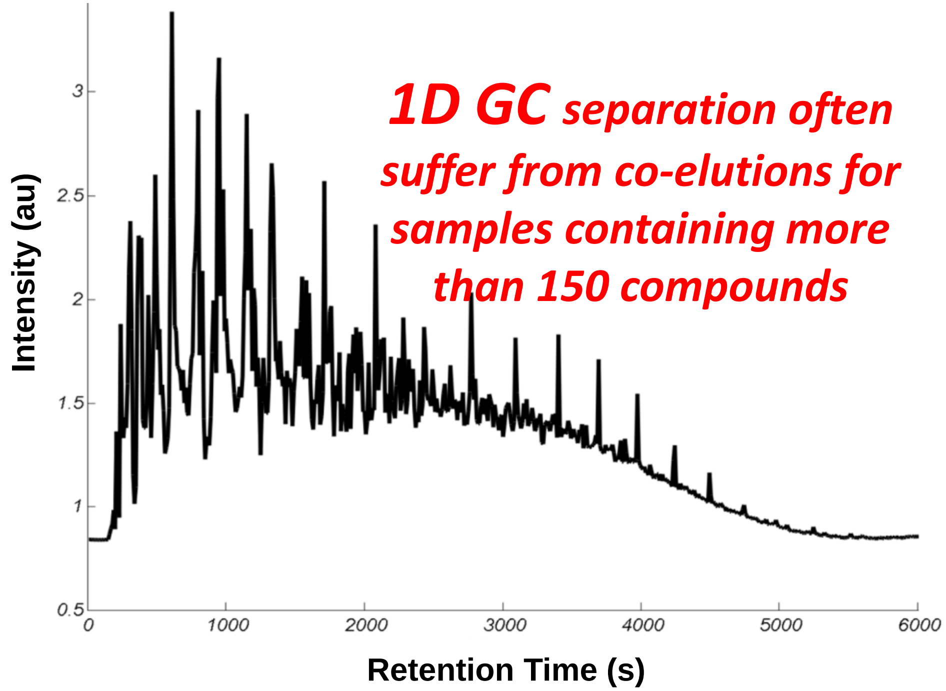
How to Increase the % of Biogenic Carbon in Fuels

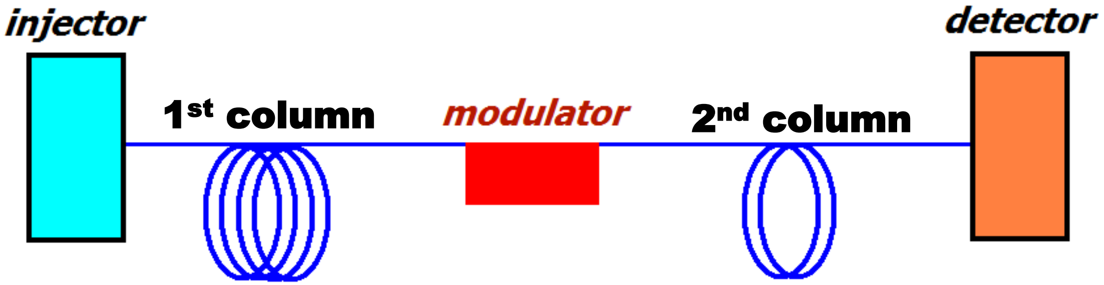
Fuel Blending and Co-Processing

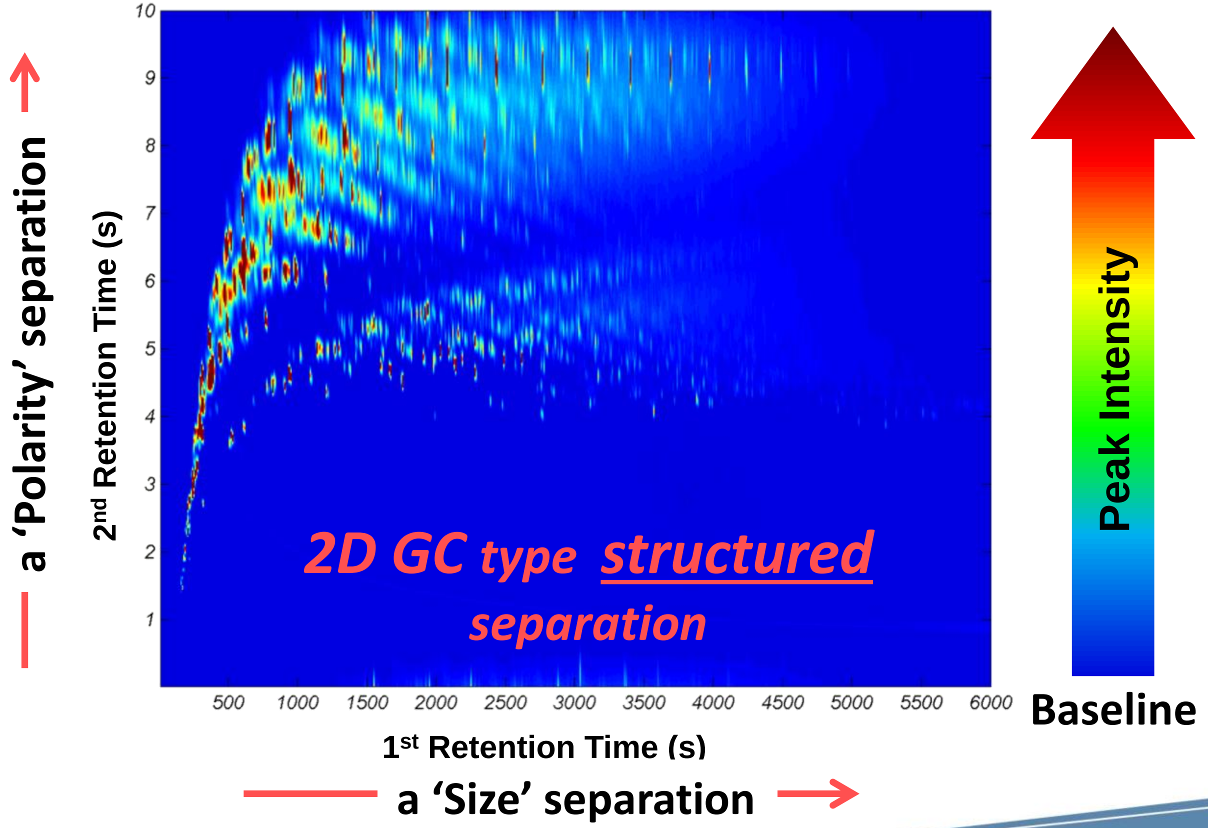


Two-Dimensional Gas Chromatography (GC×GC or 2D GC)

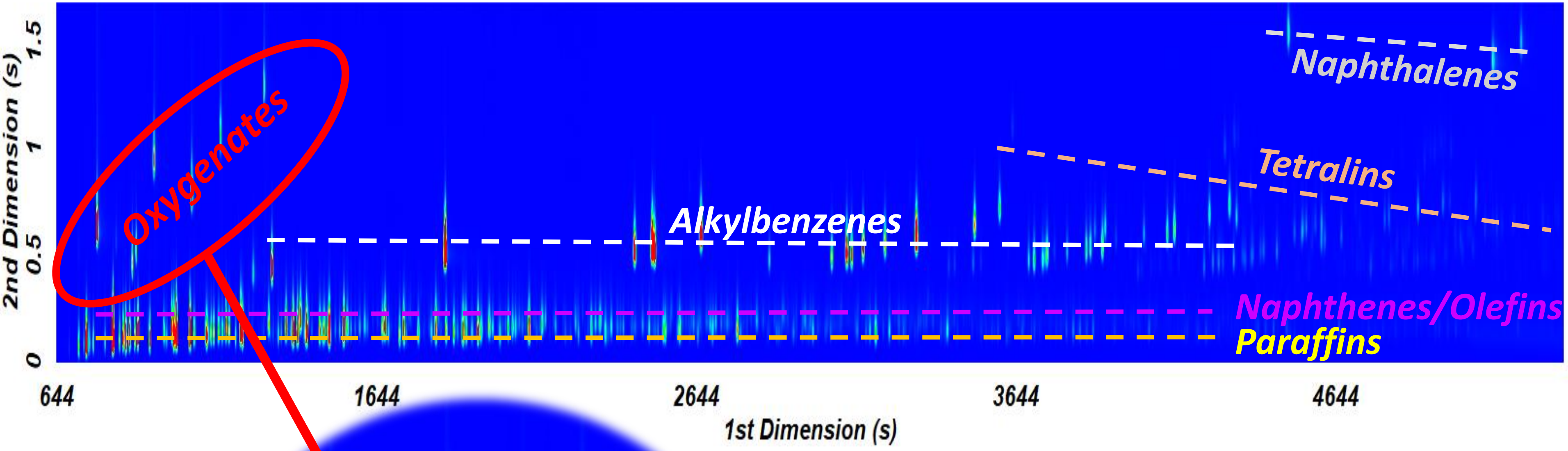




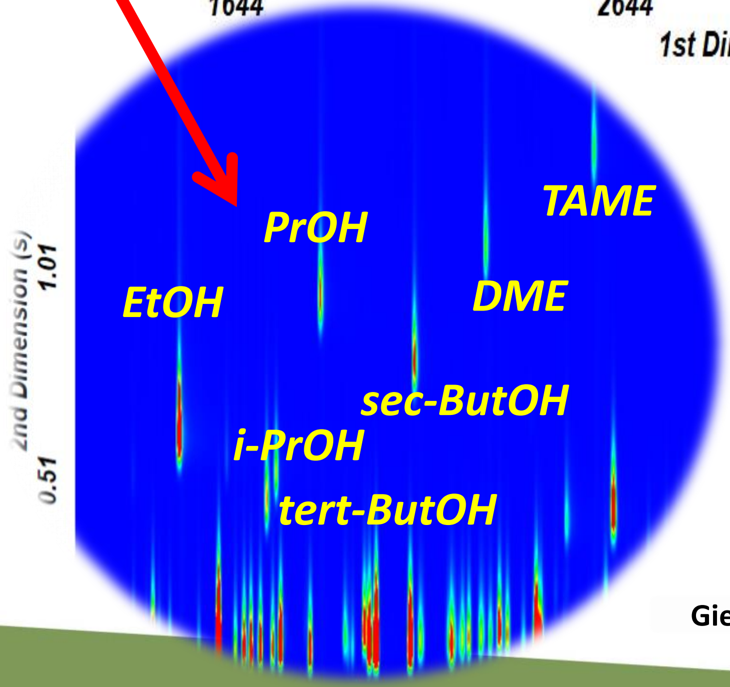




Case Study #1: Blending (Oxygenates in Gasoline)



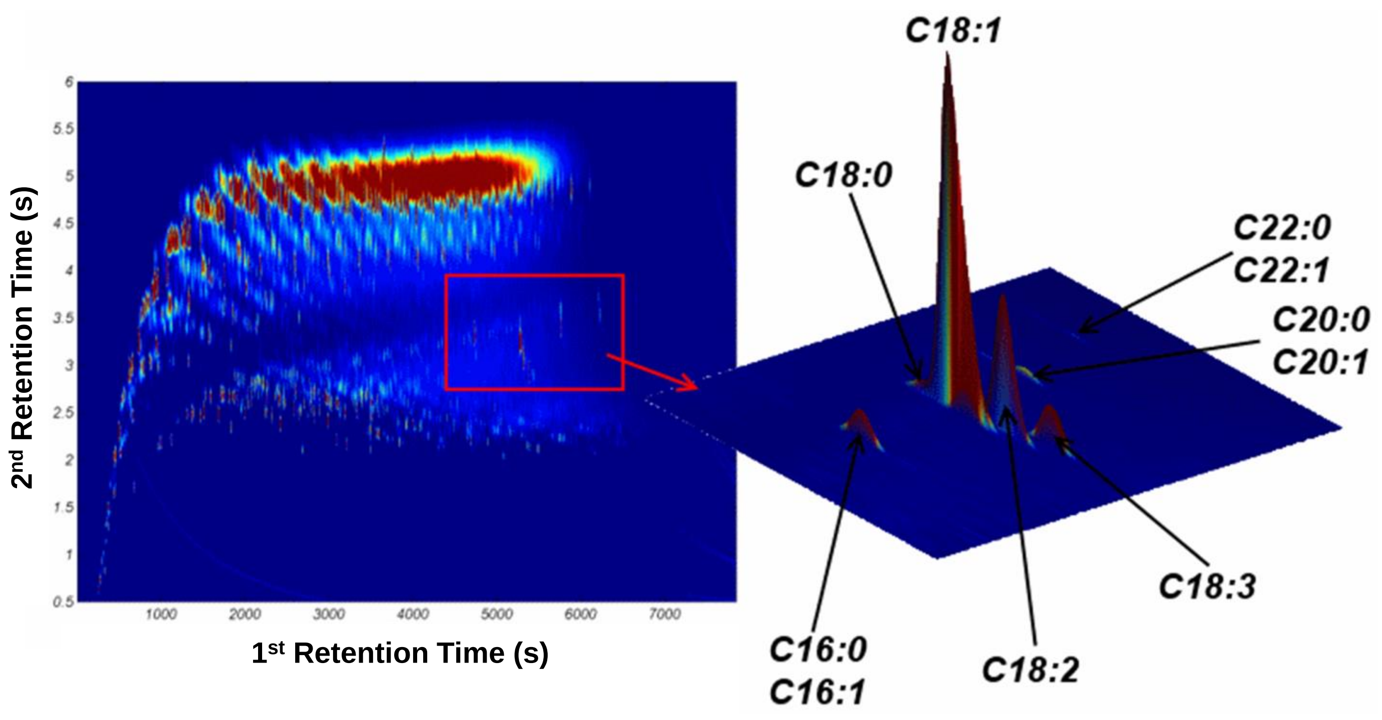
1st column:
HP1 (100m × 250µ × 0.5µ)
2nd column:
DB-Wax (0.8m × 100µ × 0.2µ)



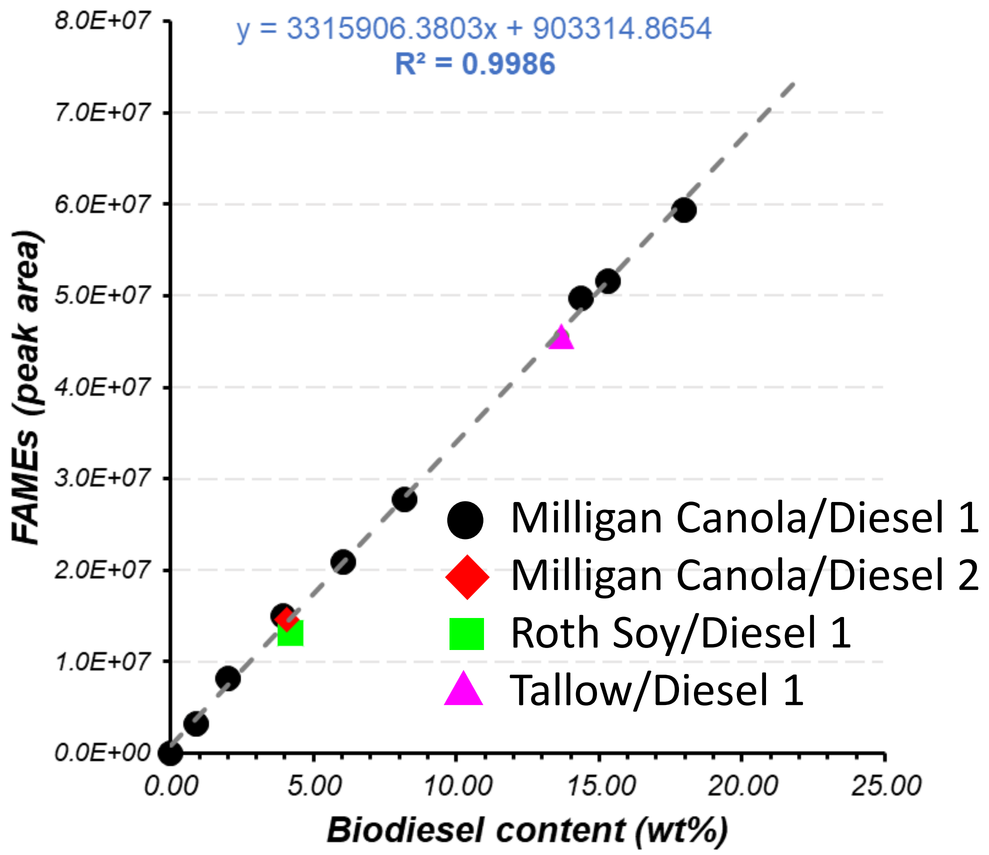
- **Oxygenates** are well separated in two dimensions, allowing for more accurate quantification
- **Ethanol peak,** if tailing - does not interfere with the quantification of other hydrocarbons

Gieleciak, R., Sobotowski, R. Natural Resources Canada, CanmetENERGY-CDEV-2013-2173-CP

Case Study #2: Blending (Diesel/Biodiesel)



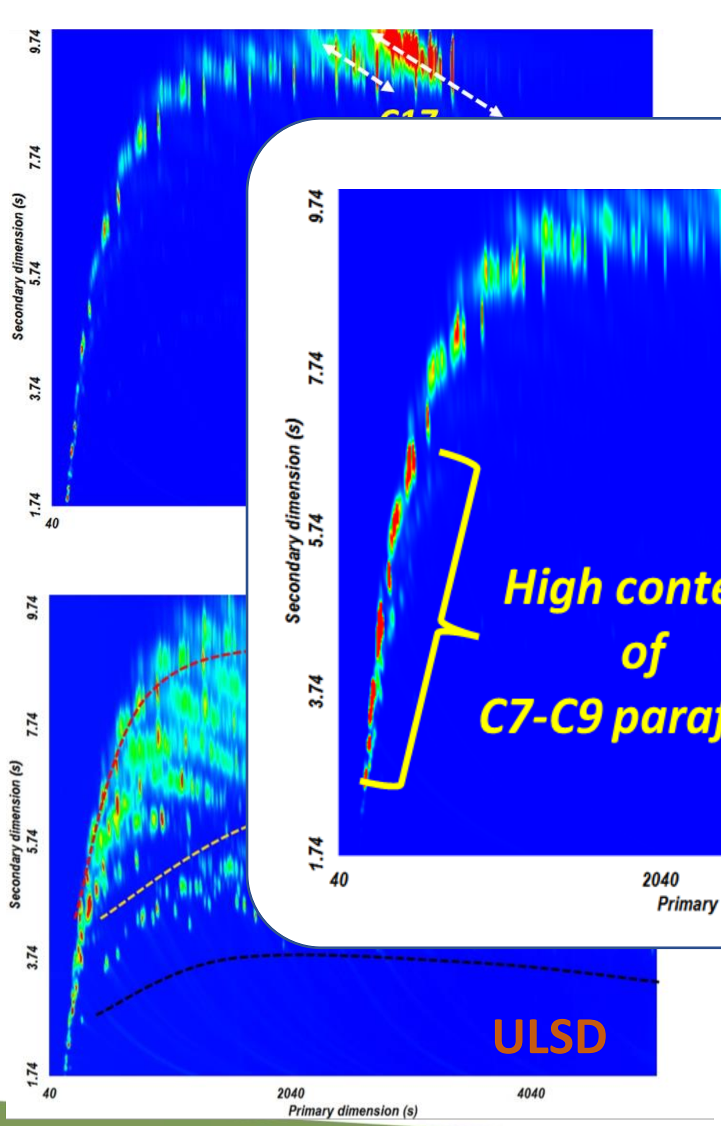
2 vol% of Milligan Canola biodiesel in diesel

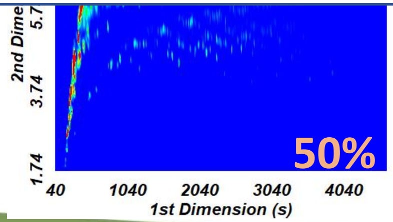


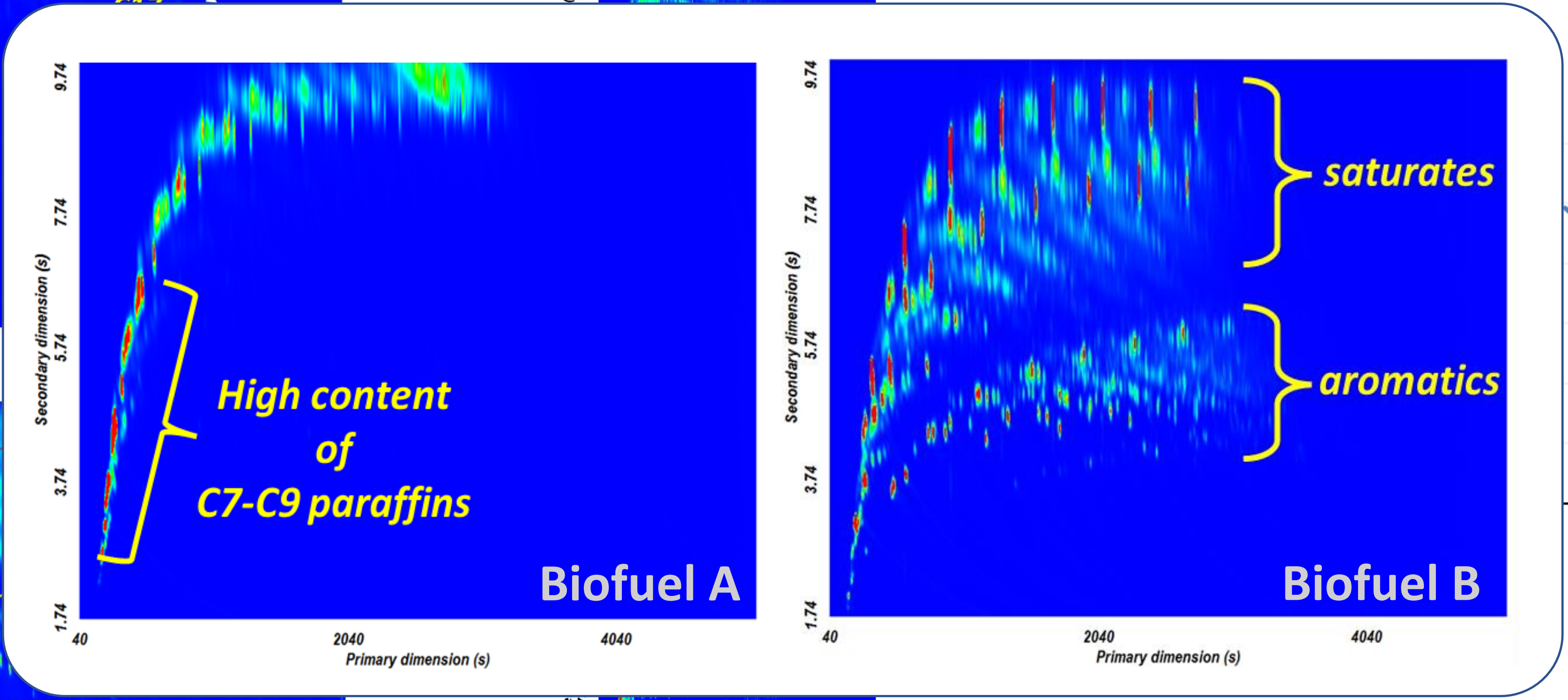
The total peak areas (C16-C20 of FAMES) plotted as a function of biodiesel concentration

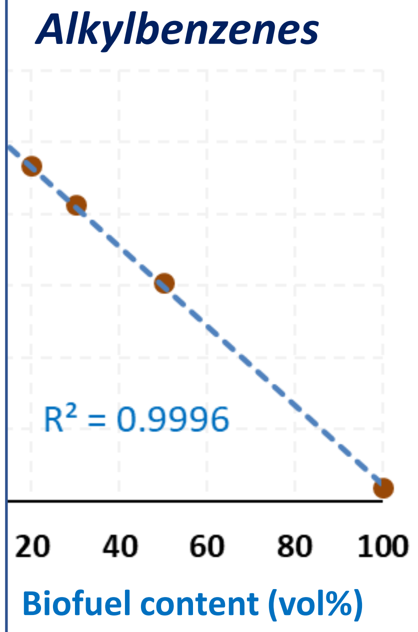
Gieleciak, R., Fairbridge, C., Hager, D. Transportation Technologies and Fuels Forum 2013, Ottawa, Ontario, Canada

Case Study #3: Blending (Renewable/Diesel)









Petrucci, T.; Michaelian, K.; Gieleciak, R. et al Energy & Fuels 2017, 31, 13775

Case Study #4: Co-processing (Canola Oil/HVGO)

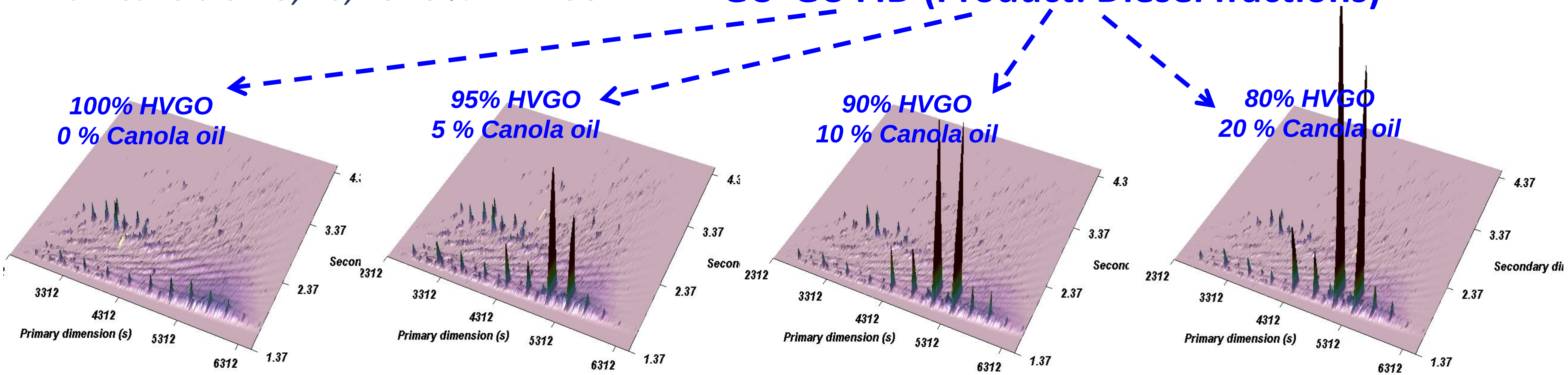
Feedstocks:

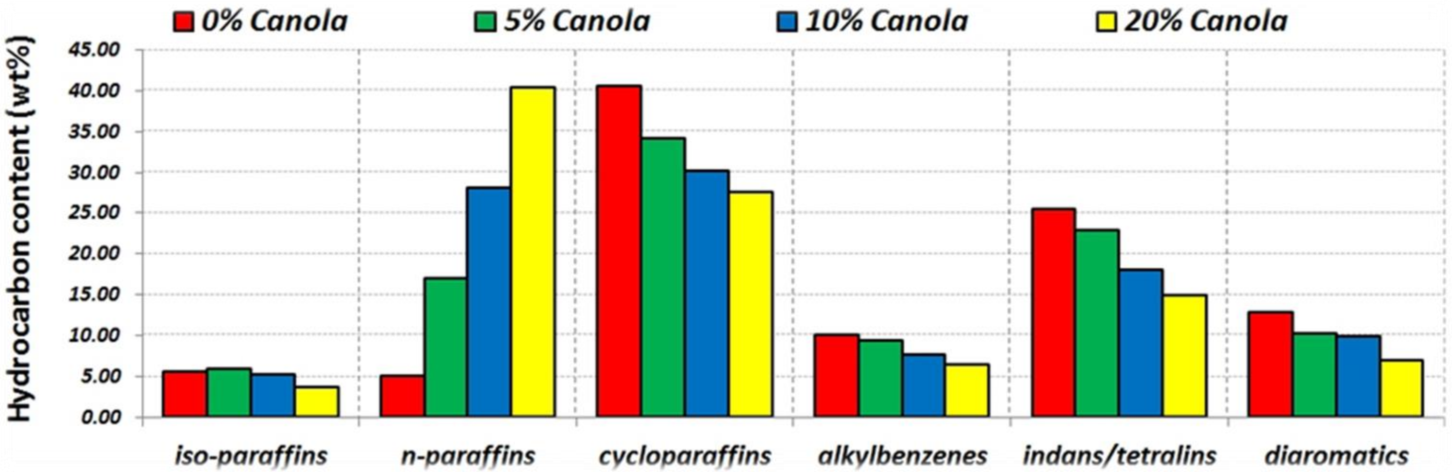
Heavy vacuum gas oil (HVGO)

Raw canola oil: 5, 10, 20 vol% in HVGO

Hydrotreating → Distillation

GC×GC-FID (Product: Diesel fractions)





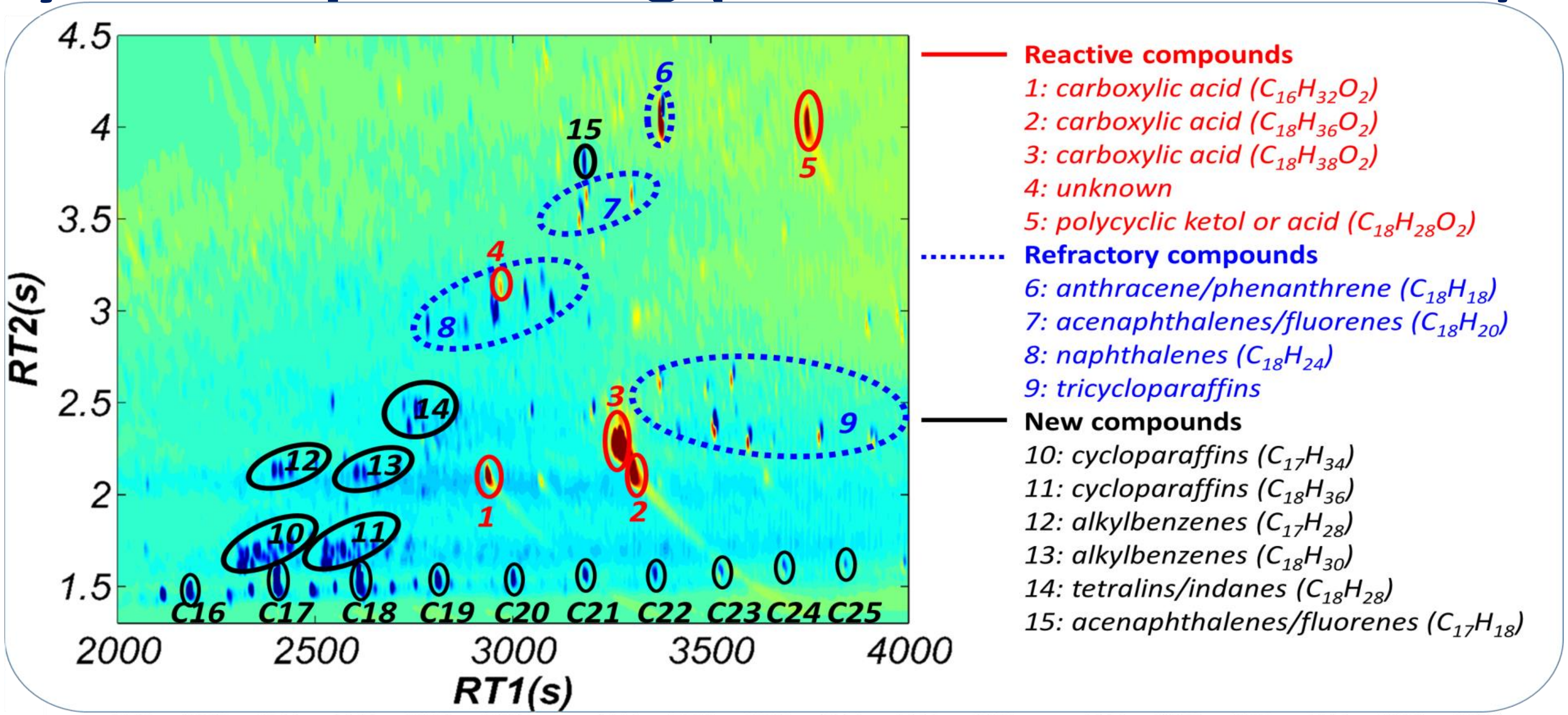
Gieleciak, R.; Ferooqi, H.; Chen, J. Energy & Fuels 2021, 35, 17721

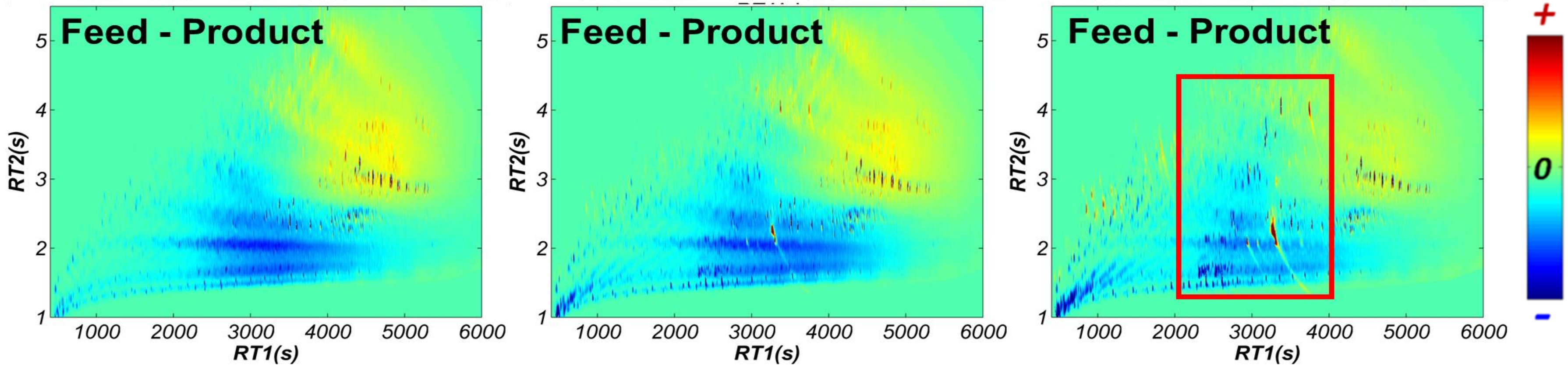
Case Study #5: Co-processing (HTL Biocrude and VGO)

Hydrotreating

Feedstocks:

Vacuum gas oil (VGO)
HTL biocrude distillate (IBP-525°C): 5, 10, 15 vol% in VGO





HTL
Hydrothermal liquefaction

Xing, T.; Alvarez-Majmutov, A.; Gieleciak, R.; Chen, J. Energy & Fuels 2019, 33, 11135

Case Study #6: Co-processing (HTL Biocrude and VGO)

Hydrotreating

Feedstocks:

Vacuum gas oil (VGO)
HTL biocrude distillate
*(IBP-525°C): **7.5% in VGO***

Hydrocracking

Feedstocks:

HT - VGO
HT – biocrude blend

Products

HC-VGO

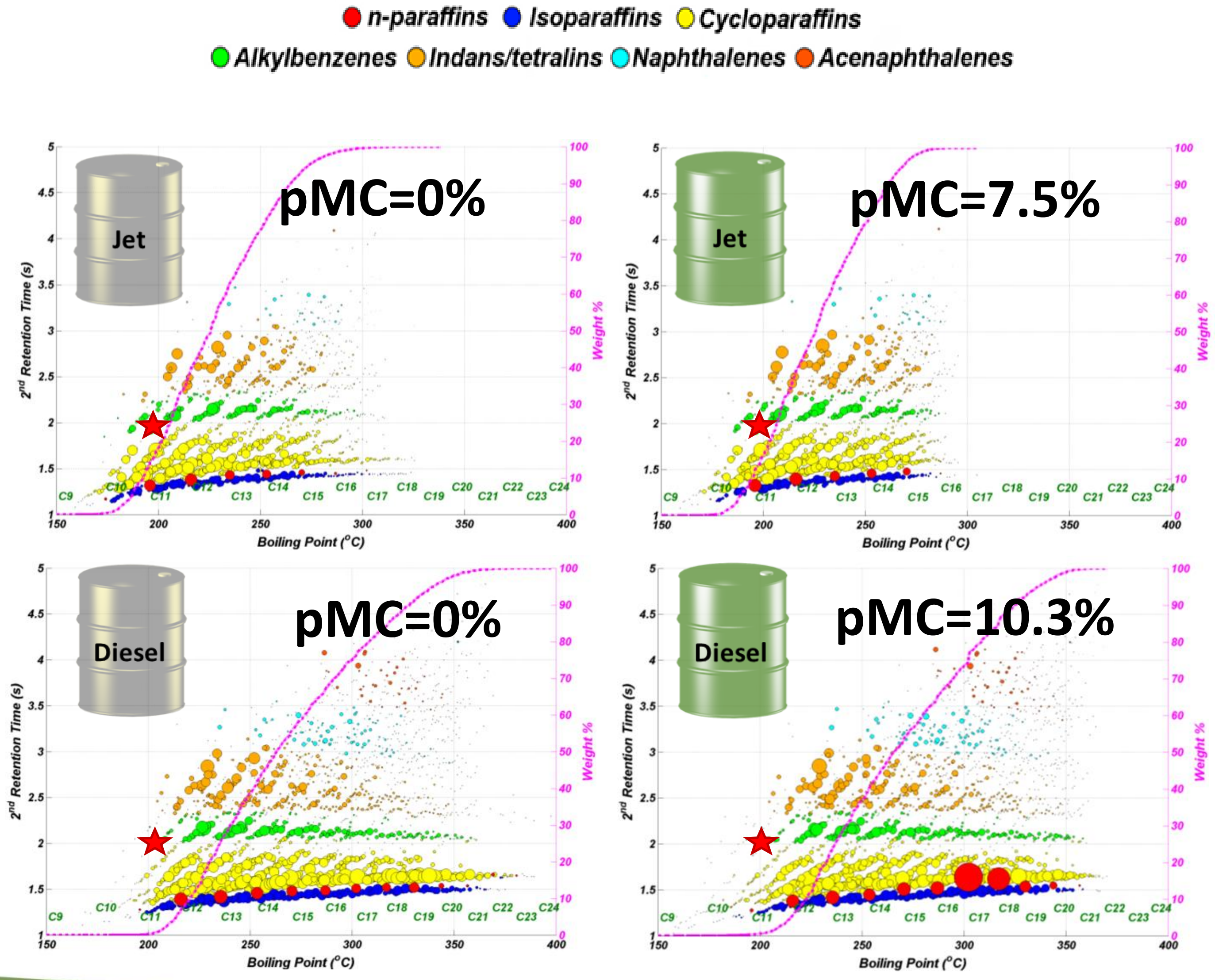
&

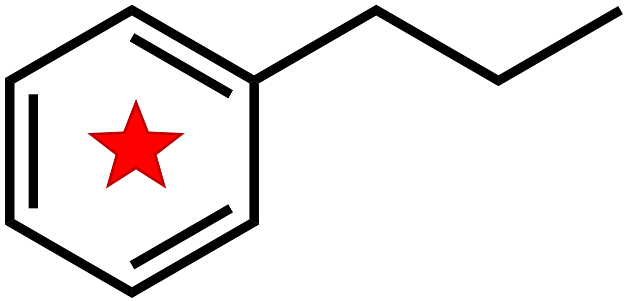
HC-biocrude blend

Distillation

Badoga, S.; Alvarez-Majmutov, A.; Xing, T.; Gieleciak, R.; Chen, J. Energy & Fuels 2020, 34, 7160

Case Study #6: Co-processing (HTL Biocrude and VGO)





When the materials are co-processed it is **virtually impossible** to distinguish between components produced from renewable feeds and those produced from fossil feeds

pMC - percent Modern Carbon

Badoga, S.; Alvarez-Majmutov, A.; Xing, T.; Gieleciak, R.; Chen, J. Energy & Fuels 2020, 34, 7160

Summary

- GC×GC method:
  - Very quick and reliable method to quantifying renewable content in simple blends (oxygenates in gasoline, biodiesel (FAMEs) in diesel, finished biofuels/petro fuels).
  - Excellent for resolving, identifying, and quantifying individual components in biocrudes, as well as end products.
  - Good method for tracking biogenic carbon species (for example, oxygenates) until they become hydrocarbons.
- When blended feedstocks are co-processed, it is virtually impossible to distinguish (by GC×GC) between components produced from renewable feeds and those produced from fossil feeds.

Acknowledgments

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- Industrial collaborators and partners

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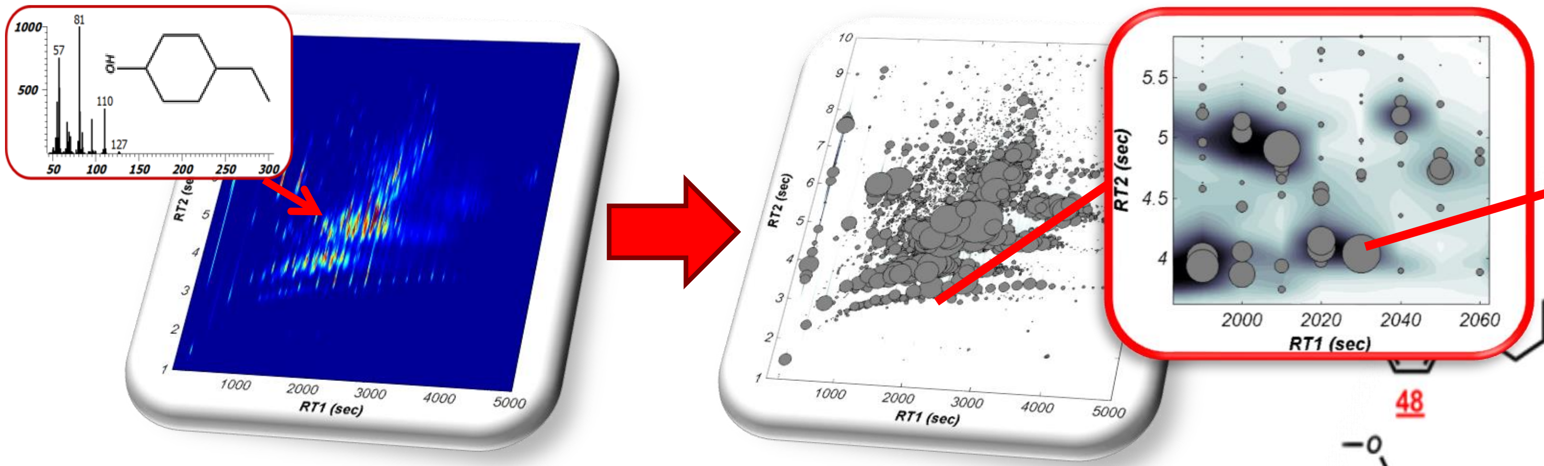
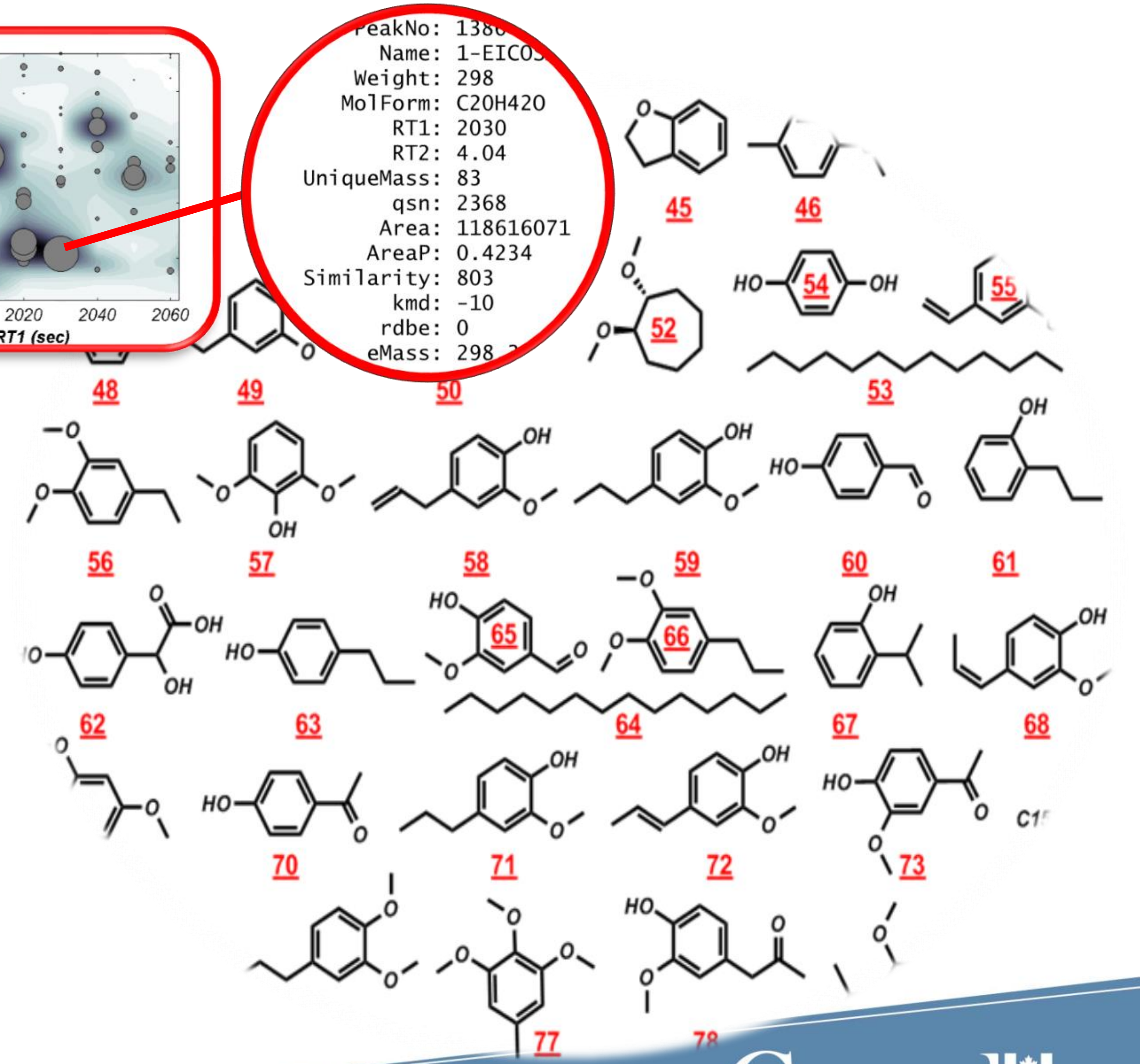
Backup slides

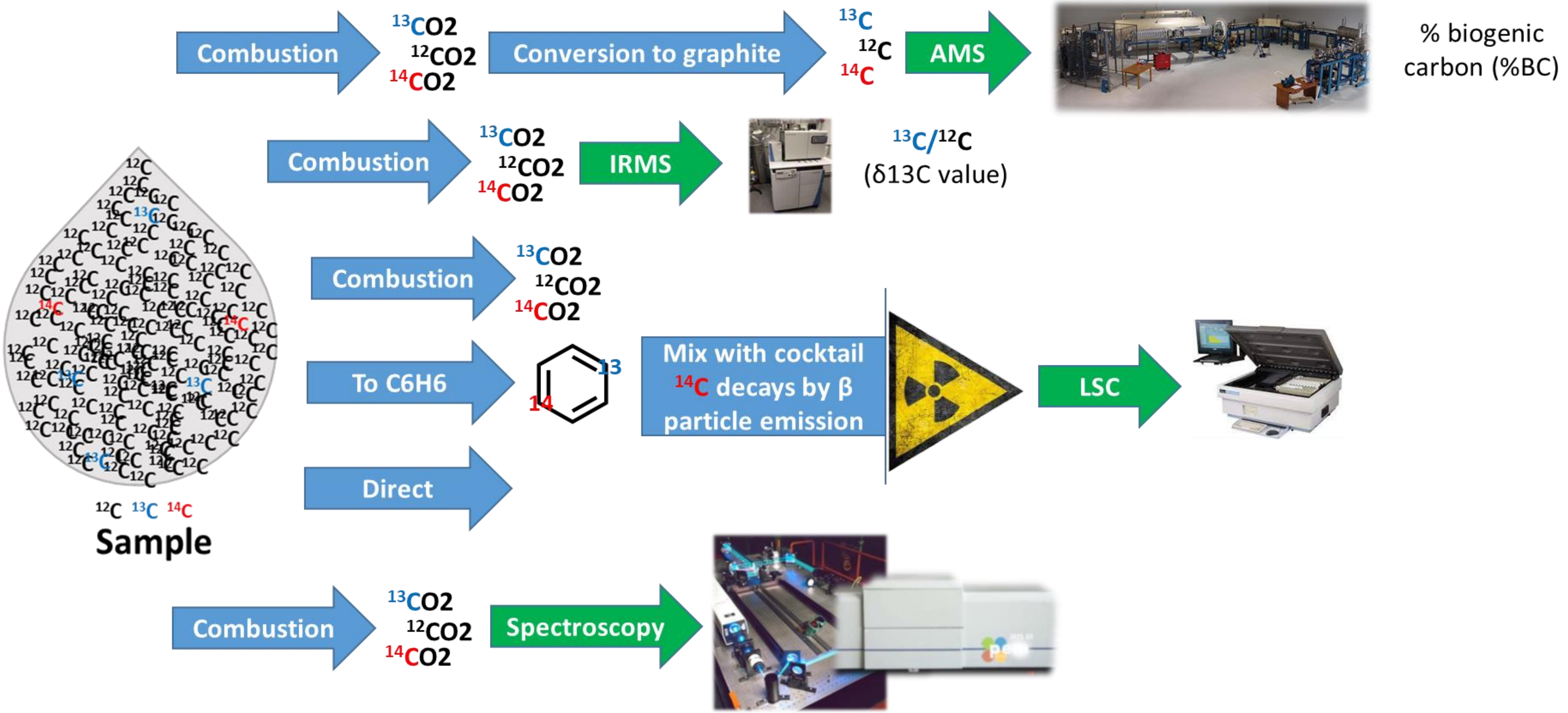
GC×GC-TOFMS for speciation of oxygenates





- For speciation of **oxygenate compounds** in biocrude, we need **GC×GC-TOFMS**
- Recently, we developed a suite of algorithms for visualization and quick translation of instrument data to peak table
- **Good method for tracking biogenic carbon species until they become hydrocarbons**

TOFMS: Time-of-Flight Mass Spectrometry



AMS – accelerator mass spectrometry, **LSC** – liquid scintillation counting, **IRMS** – isotope ratio mass spectrometry, **Spectroscopic** methods include cavity ringdown and intracavity optogalvanic spectroscopy