SRA INSTRUMENTS
ANALYTICAL SOLUTIONS

SISSG
SOCIETÀ ITALIANA PER LO STUDIO DELLE SOSTANZE GRASSE

Perugia, June 15th -17th 2022

Advancing MOSH/MOAH analysis towards speciation and contaminants identification

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Hydrocarbon contamination in foodstuff

- Contamination of Mineral Oil Hydrocarbons (MOH) in various food products.
- Classification in aliphatic (MOSH) and aromatic (MOAH).
- Potential impact on consumers' health.
- In particular the presence of MOAH (especially with 3+ rings and low alkylation) raises concerns for increased risks in terms of toxicity.
- Different sources of contamination at different points in the production chain:
  - Raw material
  - Harvesting
  - Processing
  - Packaging
- Need for reliable, individual quantification of MOSH and MOAH.

efsa
European Food Safety Authority
EFSA Journal 2012;10(6):2704

SCIENTIFIC OPINION

Scientific Opinion on Mineral Oil Hydrocarbons in Food[1]

EFSA Panel on Contaminants in the Food Chain (CONTAM)[2, 3]

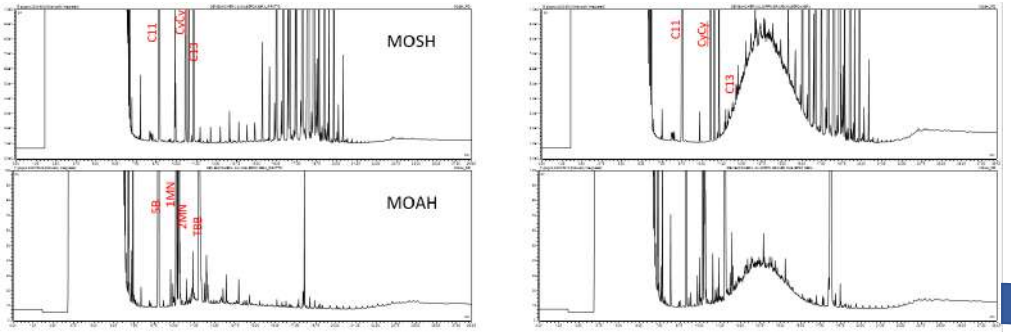
European Food Safety Authority (EFSA), Parma, Italy

This scientific output, published on 28 August 2013, replaces the earlier version published on 6 June 2012*.

MOSH/MOAH analysis

LC-GC-FID platform:

- Separation of aliphatic and aromatic fractions by LC.
- Individual quantification by GC-FID.
- High matrix complexity, limited chromatographic resolution.



More **detailed characterization** would be highly desirable to:

- Detect of interferences.
- Determine chemical (sub-)classes and confirm proper fraction separation.
- Obtain info on composition (e.g. # of aromatic rings in MOAH) for toxicity assessment.

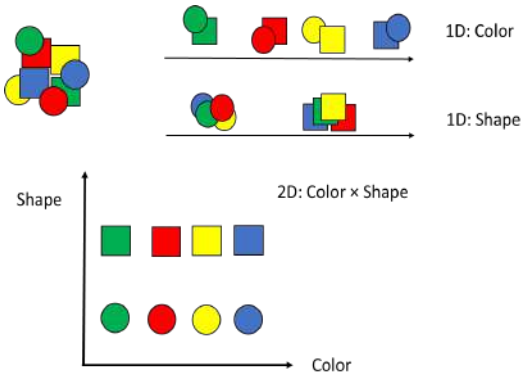
Goal → analytical methodology for more insightful speciation of LC-separated fractions.

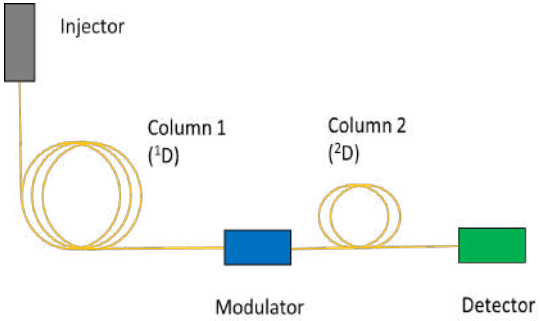
Objectives

- HIGHLY INFORMATIVE, SPECIATION OF CHEMICAL CLASSES.
- CONFIRMATORY TOOL FOR SAMPLES FOUND POSITIVE TO CONTAMINATION.
- FINGERPRINTING OF CONTAMINANTS TO IDENTIFY SOURCE.

Comprehensive two-dimensional GC (GC×GC)

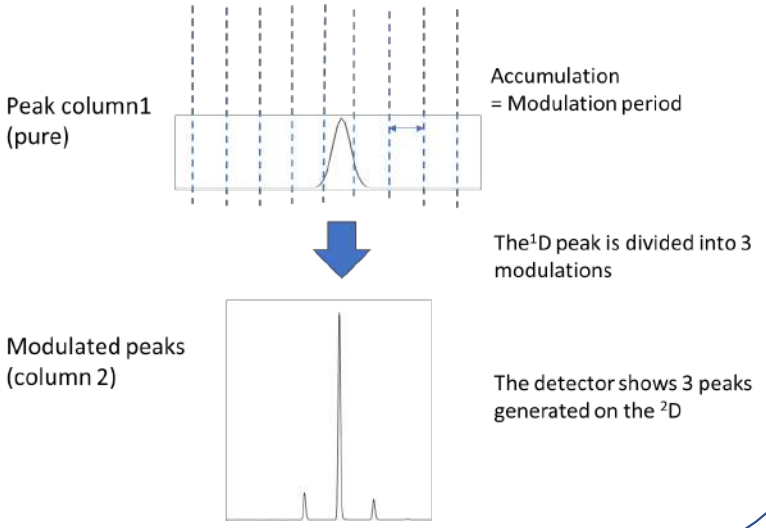
- **Two analytical columns** in a single analysis.
- An interface – the ***modulator*** – allows simultaneous, independent exploitation of both columns.
- Every compound undergoes **two** different separation **mechanisms**.
- Peaks distributed across a **2D space** reducing co-elutions and improving **separation power**.



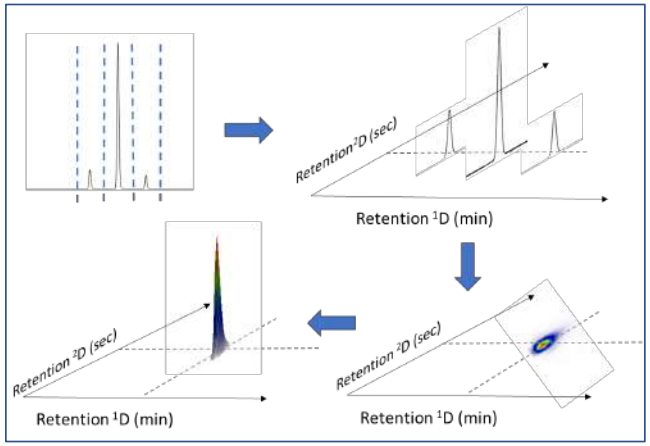


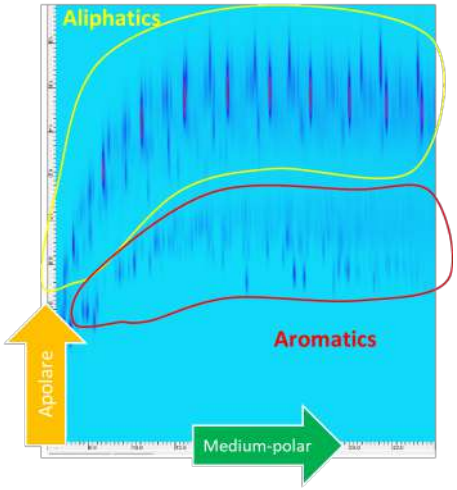
Modulator: periodically fractionates the eluate from column 1 switching between 2 phases:

- **ACCUMULATION** (few seconds): trapping of the fractions eluting from the primary column.
- **RE-INJECTION** (milliseconds): quick and exhaustive transfer into the second dimension.

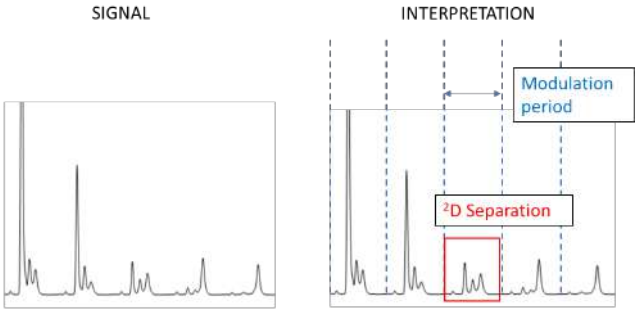


Comprehensive two-dimensional GC (GC×GC)

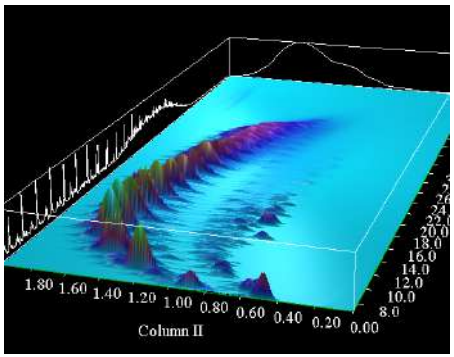


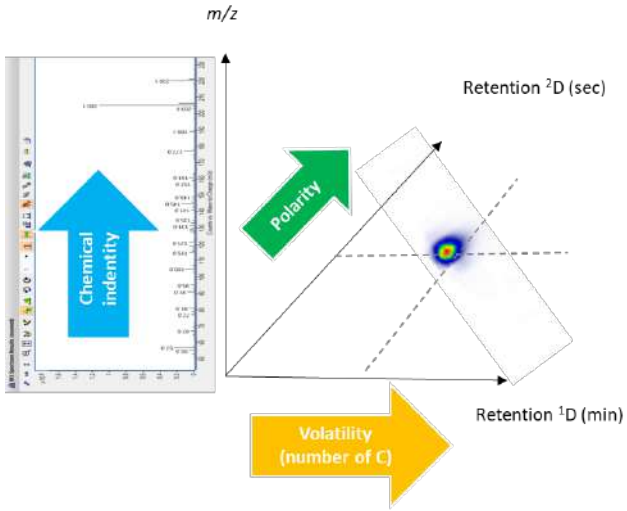


- 2D chromatograms: **highly organized** by chemical logic.
- **Position** in the 2D: info about **chemical/physical properties**.
- Mass Spectrometry (MS): a 3rd dimension essential for identification.
- Spectral quality benefits from reduced co-elutions.
- GC×GC-MS: excellent platform with unique characterization capability.



Signal = continuous series od fast separations performed by the secondary column.

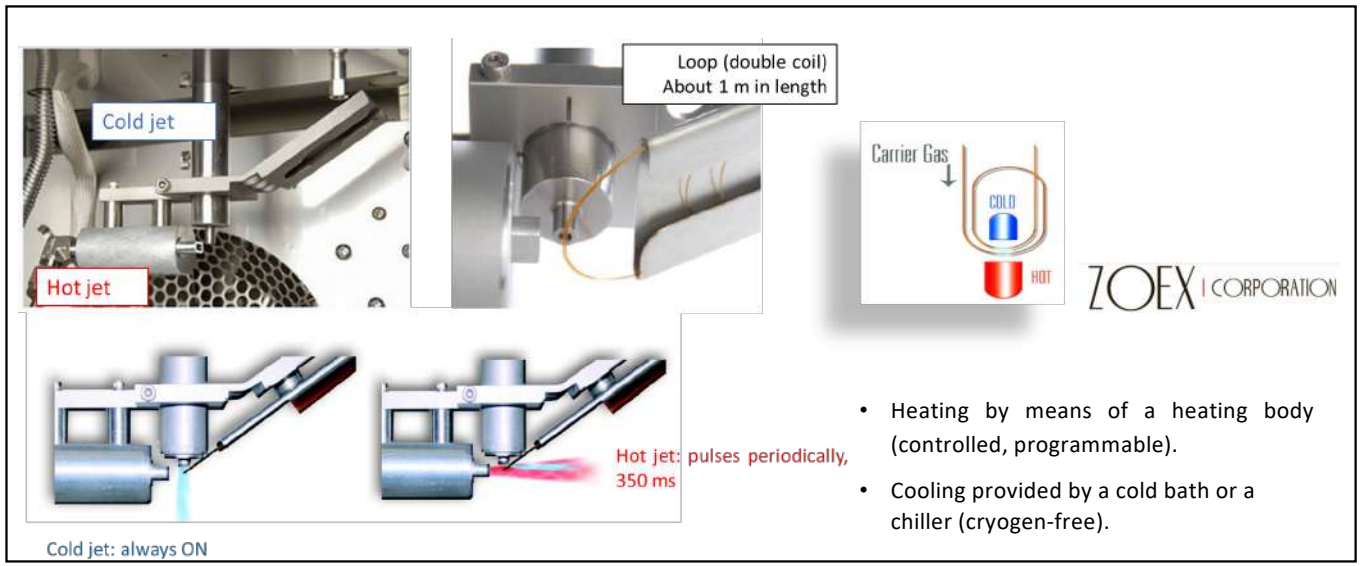




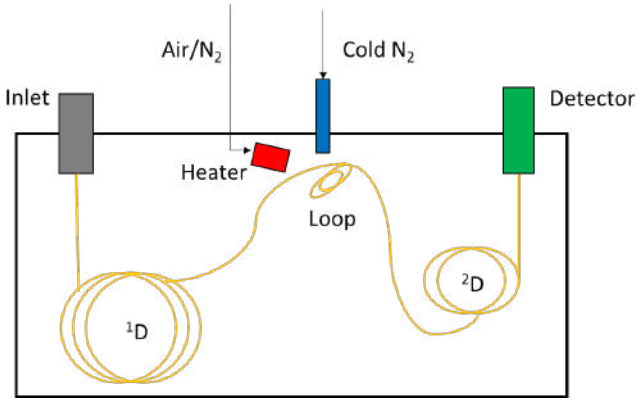
Comprehensive two-dimensional GC (GC×GC)

Thermal modulation

- Cooling and heating by streams of gas (***jets***) directed on the column:
  - **Cold** jet to create a cold spot and **trap** the molecules.
  - **Hot** jet for rapid **remobilization** of the molecules.
- This is repeated twice (*dual-stage*) to maximize the refocusing power.



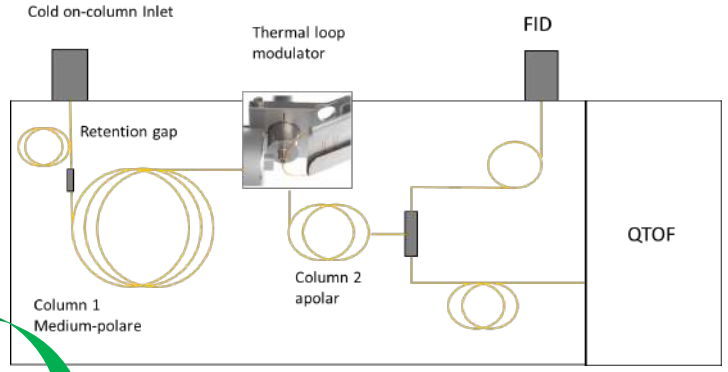
- Heating by means of a heating body (controlled, programmable).
- Cooling provided by a cold bath or a chiller (cryogen-free).



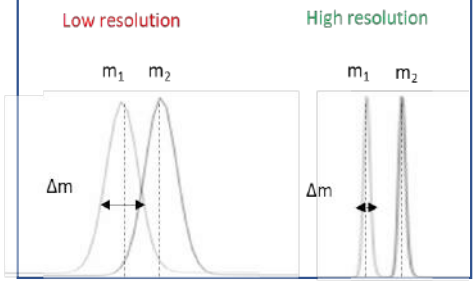
Platform configuration

AGILENT 8890GC - 7250 QTOF
ZOEX ZX2 THERMAL MODULATOR)
SRA OPTIMODE

- On-column, sample introduction up to 25 µL
- Parallel detection: qualitative/quantitative output.
- High Resolution Mass Spectrometry: added value for heteroatoms (e.g. oxygen).

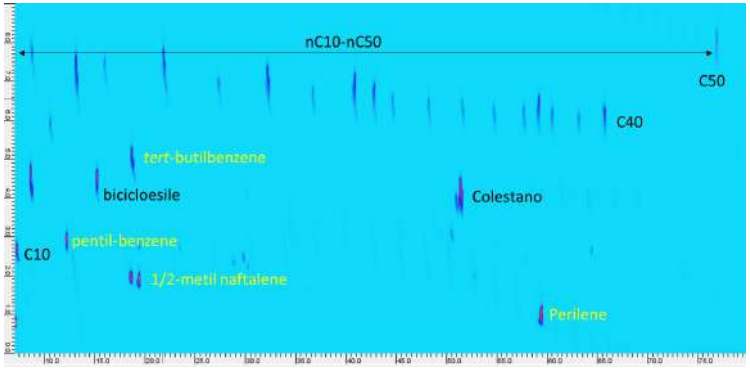


$$Resolution = \frac{m}{\Delta m}$$

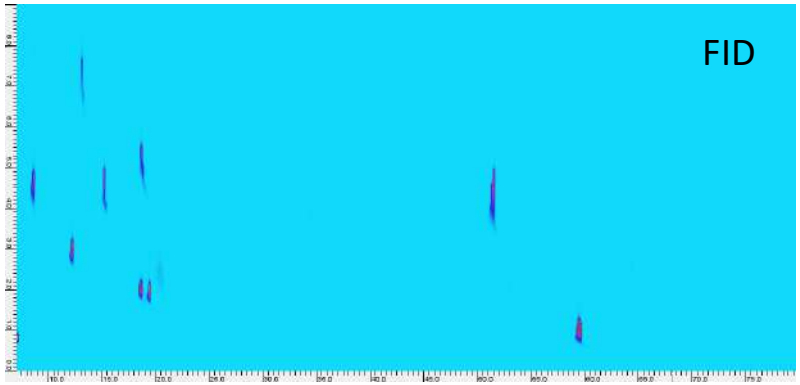


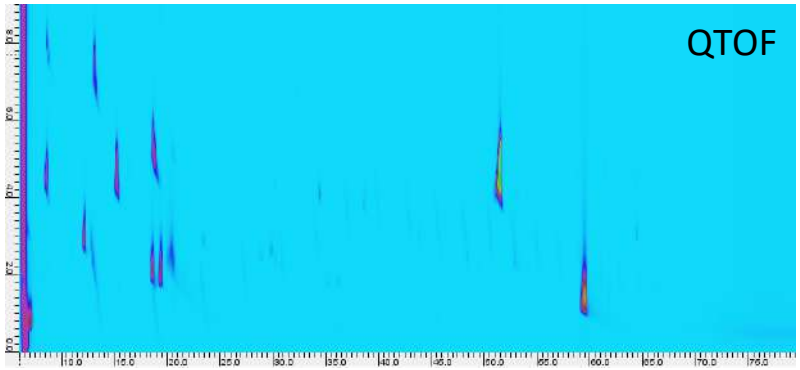
FEATURE	BENEFIT
High Resolution (> 25,000 FWHM)	• Selectivity • Sensitivity (S/N, noise reduction)
Accurate mass (< 2 ppm)	• Formula generation • Identity confirmation (targets) • Unknowns' identification.
MS/MS mode	• Structural elucidation
Variable ionization energy (12-16 eV)	• Confirm molecular ion • Selectivity

Performance assessment

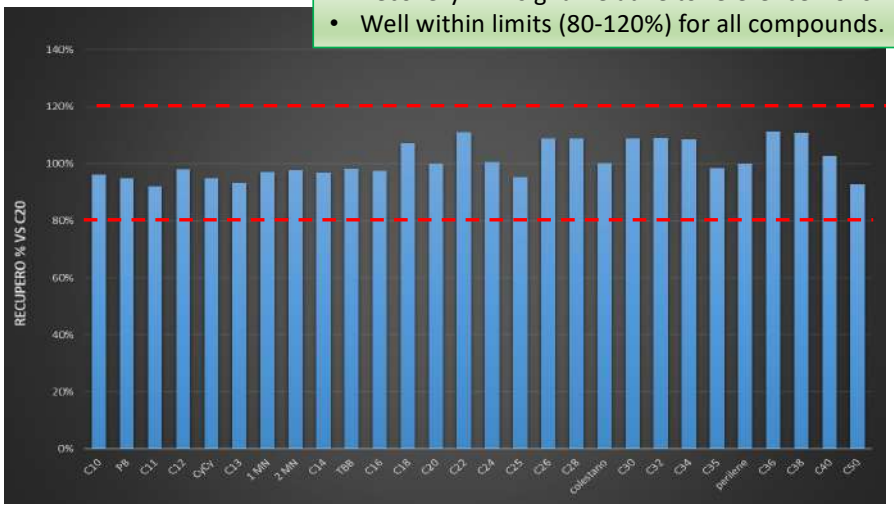


Extended mix:
- Mix nC10-40
- Mix nC10-C50
- IS markers (also aromatics)





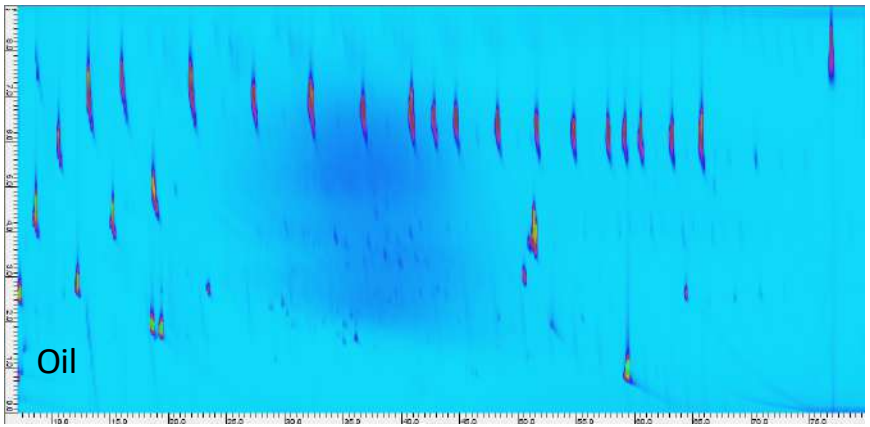
- Recovery: FID signal relative to reference - C20.
- Well within limits (80-120%) for all compounds.

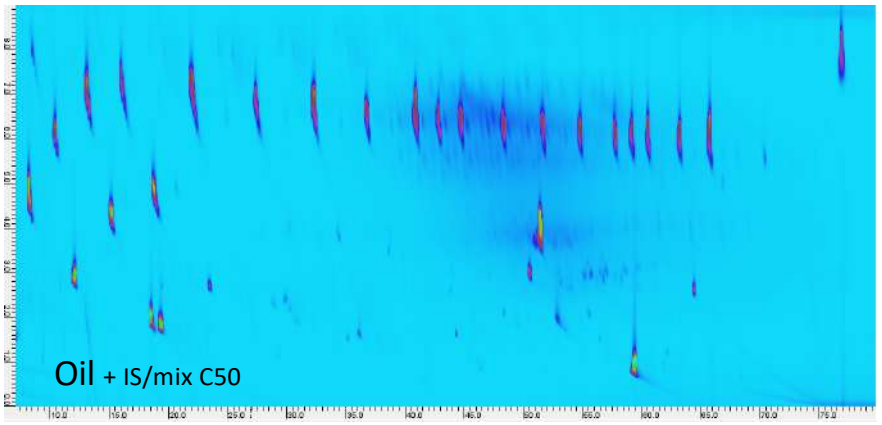


- Consistent 2D chromatographic profiles.
- Not necessary to perform laborious, troublesome alignment.
- Intuitive and flexible use of smart templates between the 2 channels.

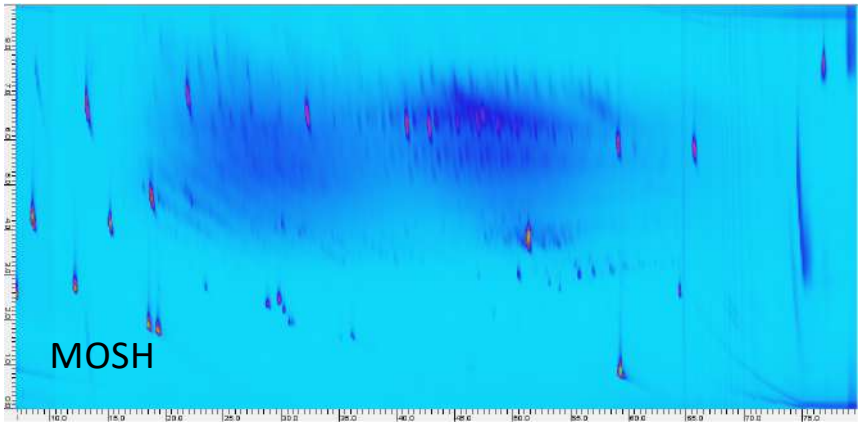
2D profiles

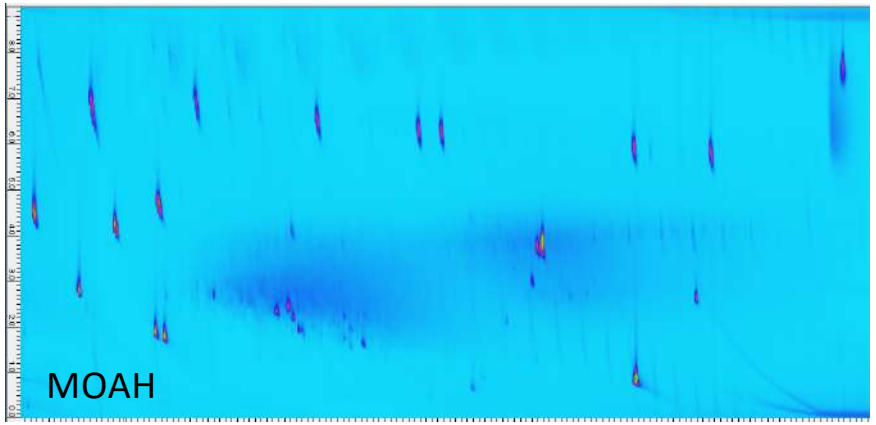
Neat lubricants
+ IS + alkanes





Mix of lubricants
Fractionated by LC
+ IS/RT mix



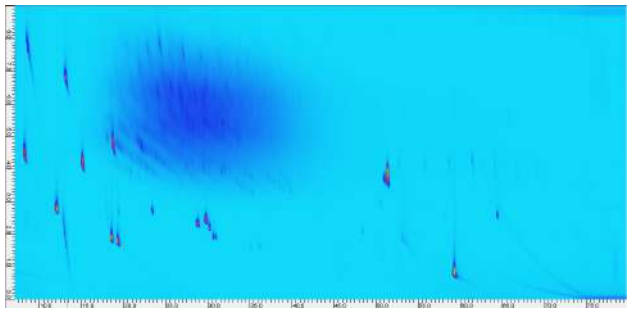


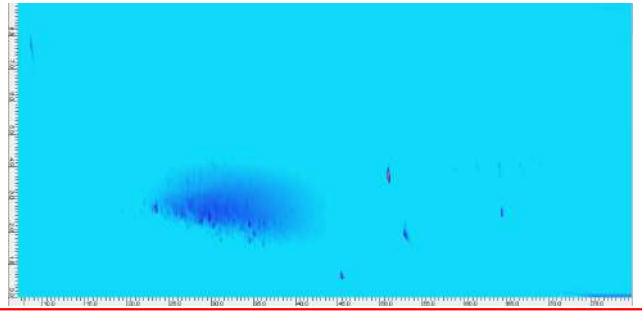
2D plots of LC fractions - FID

MOSH

MOAH

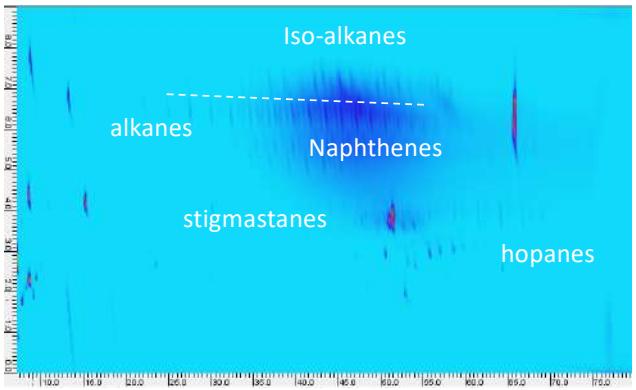
Oil 1

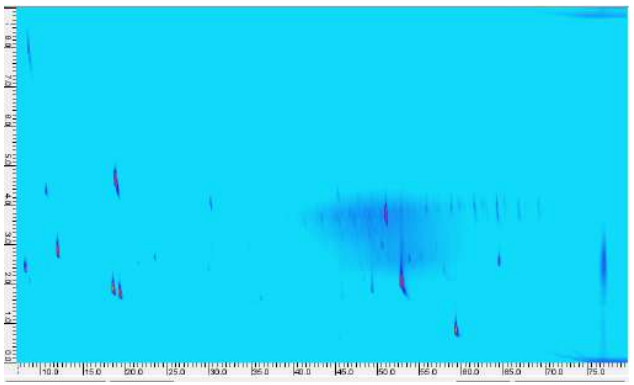




Quantitative info
MOSH:MOAH = 3 : 1
(graphic are signal)
Consistent with LC-GC-FID

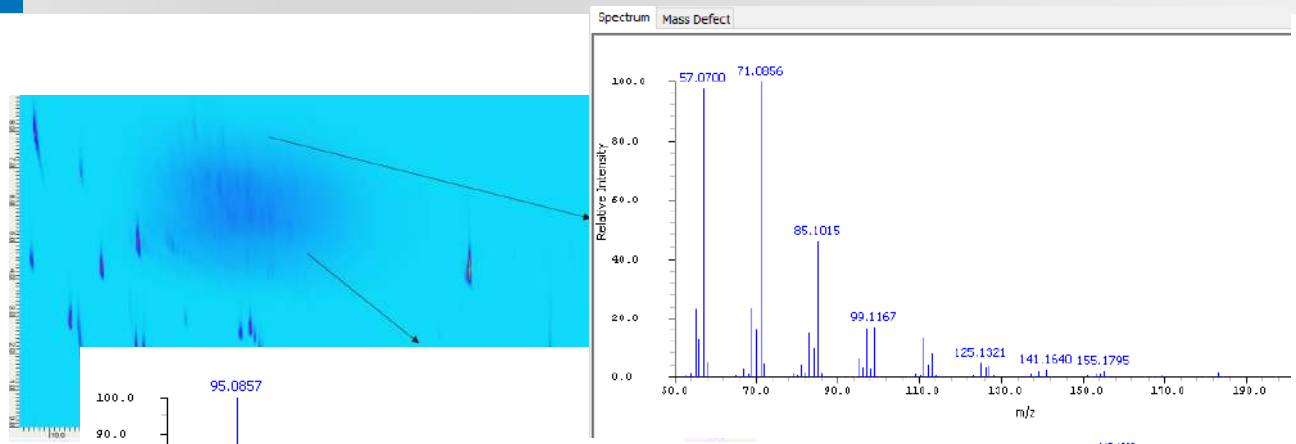
Oil 2

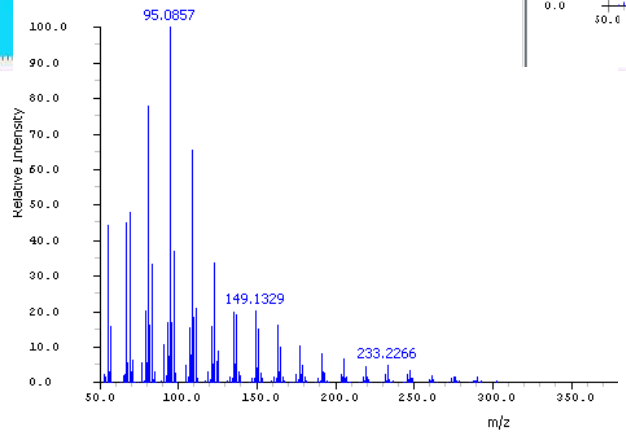


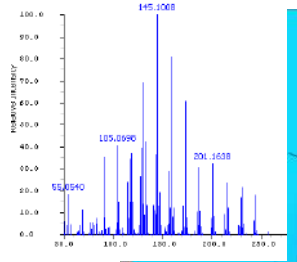


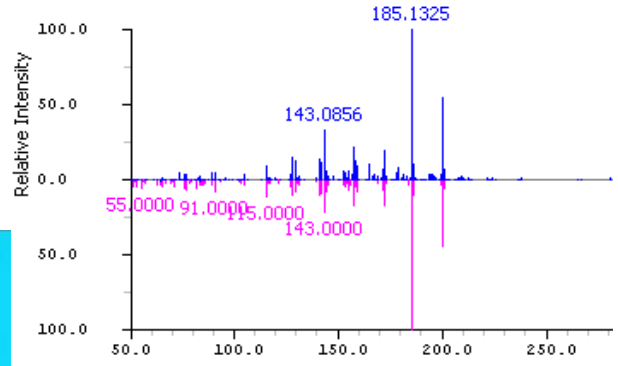
Qualtitative info
Class identification
Carbon number distribution

2D plots of LC fractions - QTOF







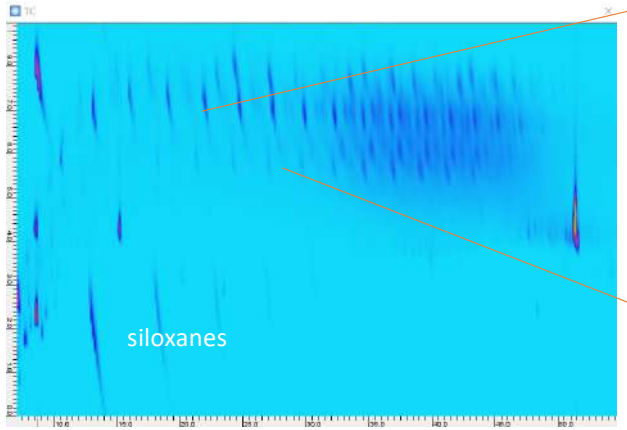


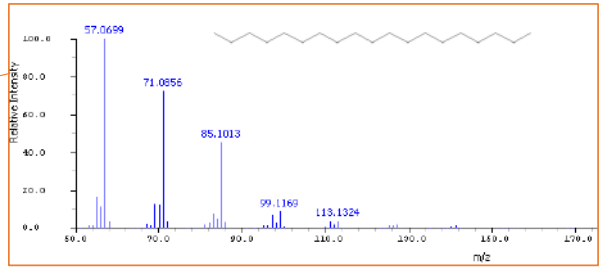
2D plots of LC fractions - QTOF

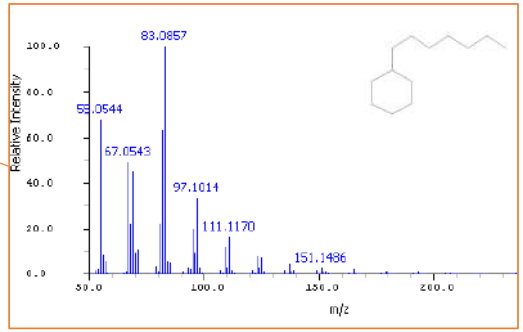
MOSH

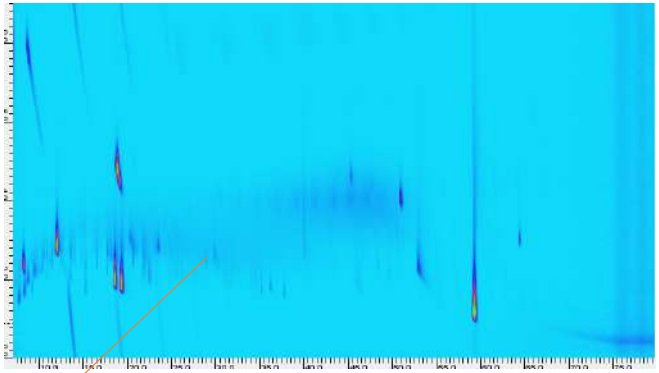
MOAH

Oil 1

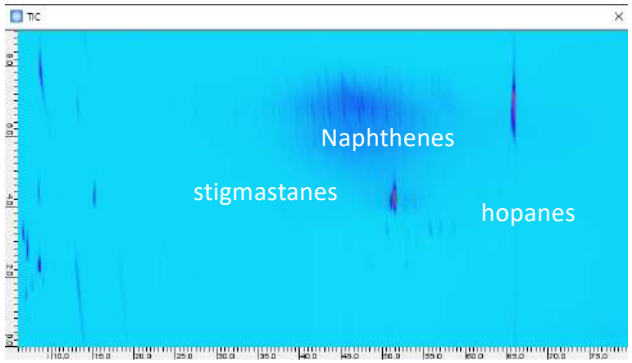


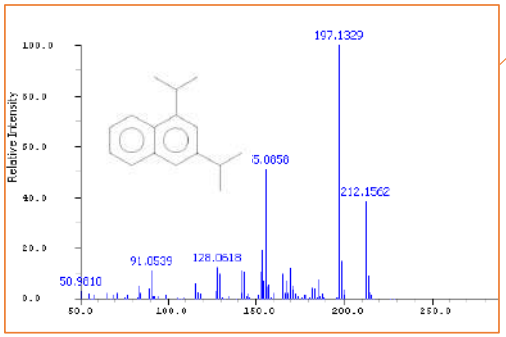


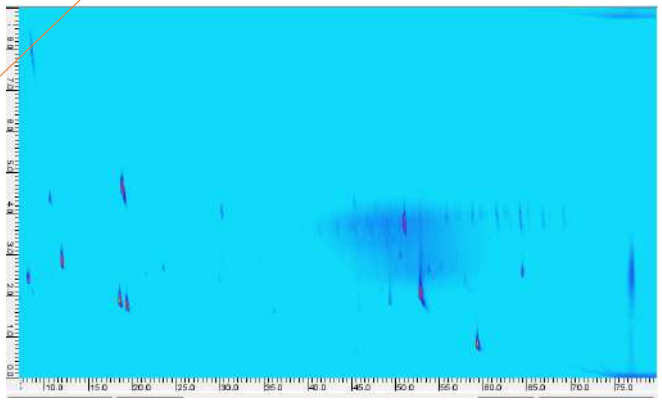




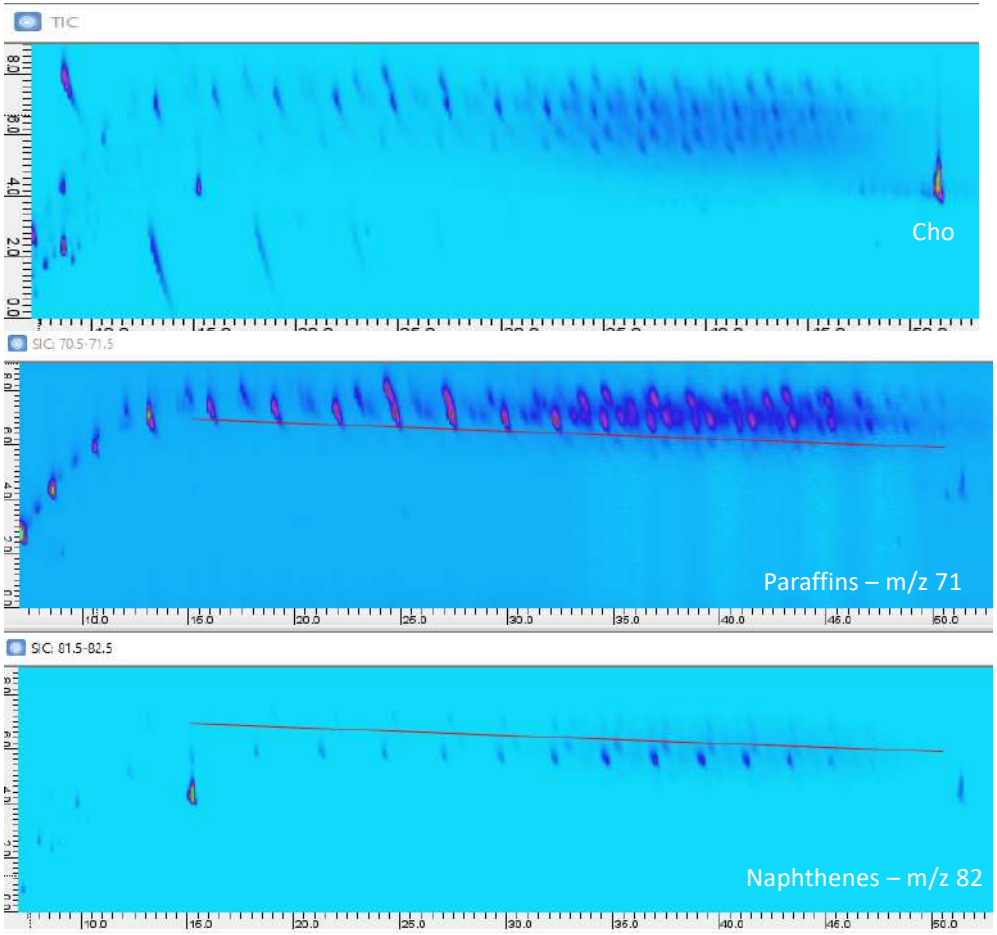
Oil 2

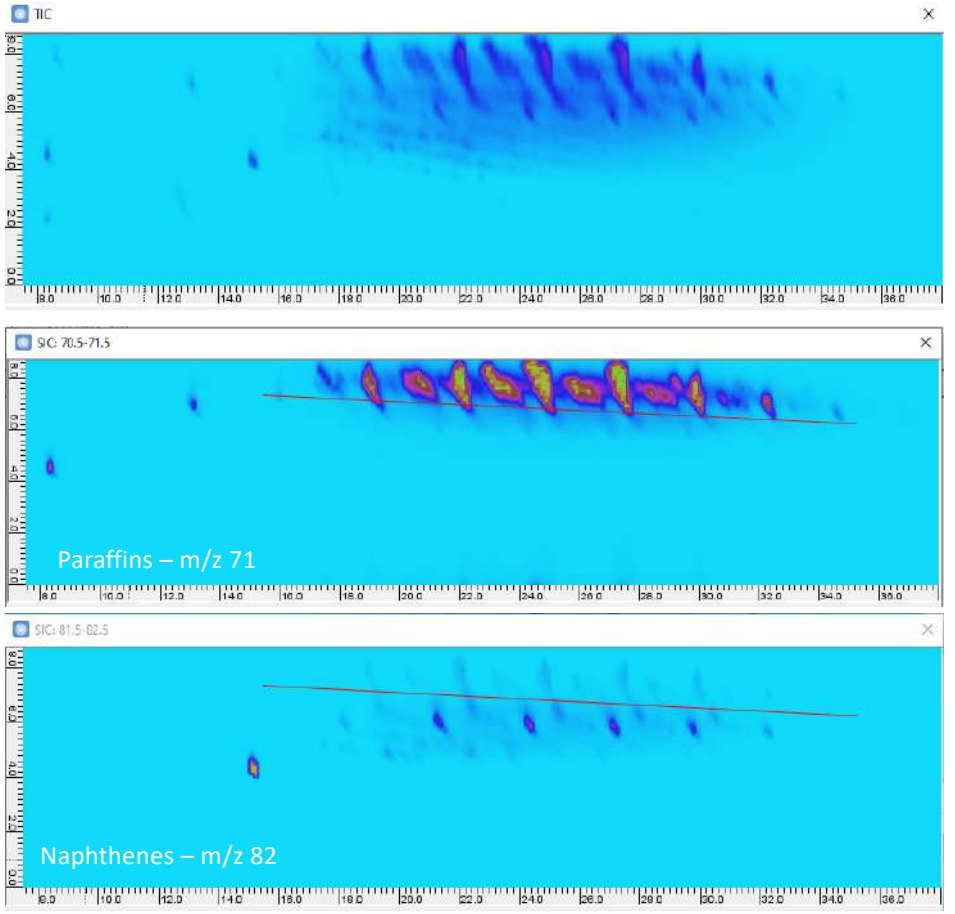




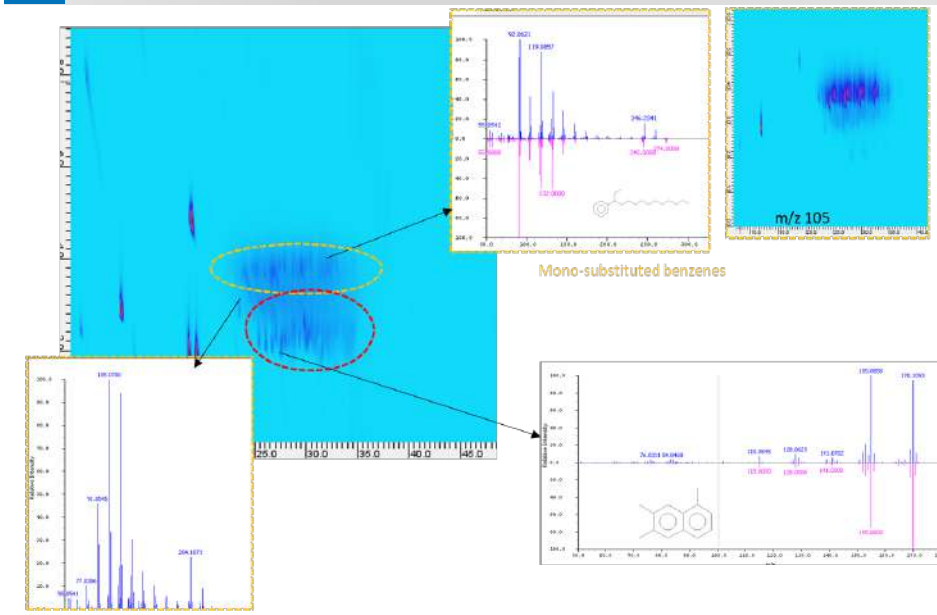


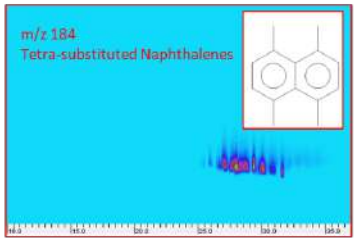
MOSH classification

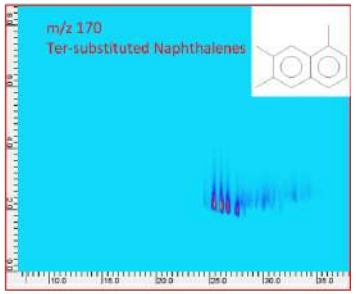


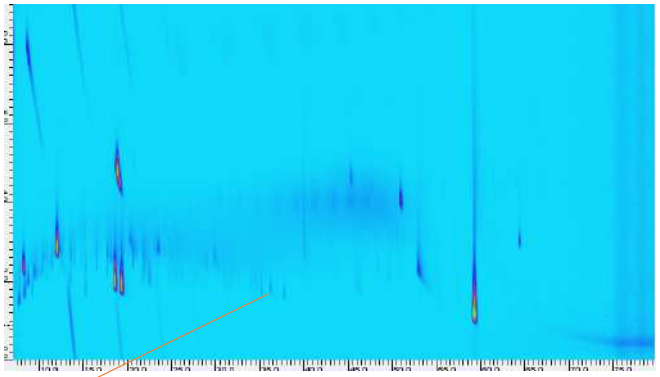


MOAH classification

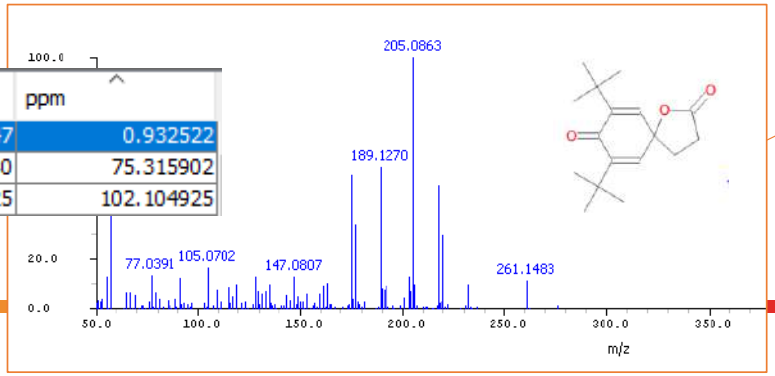




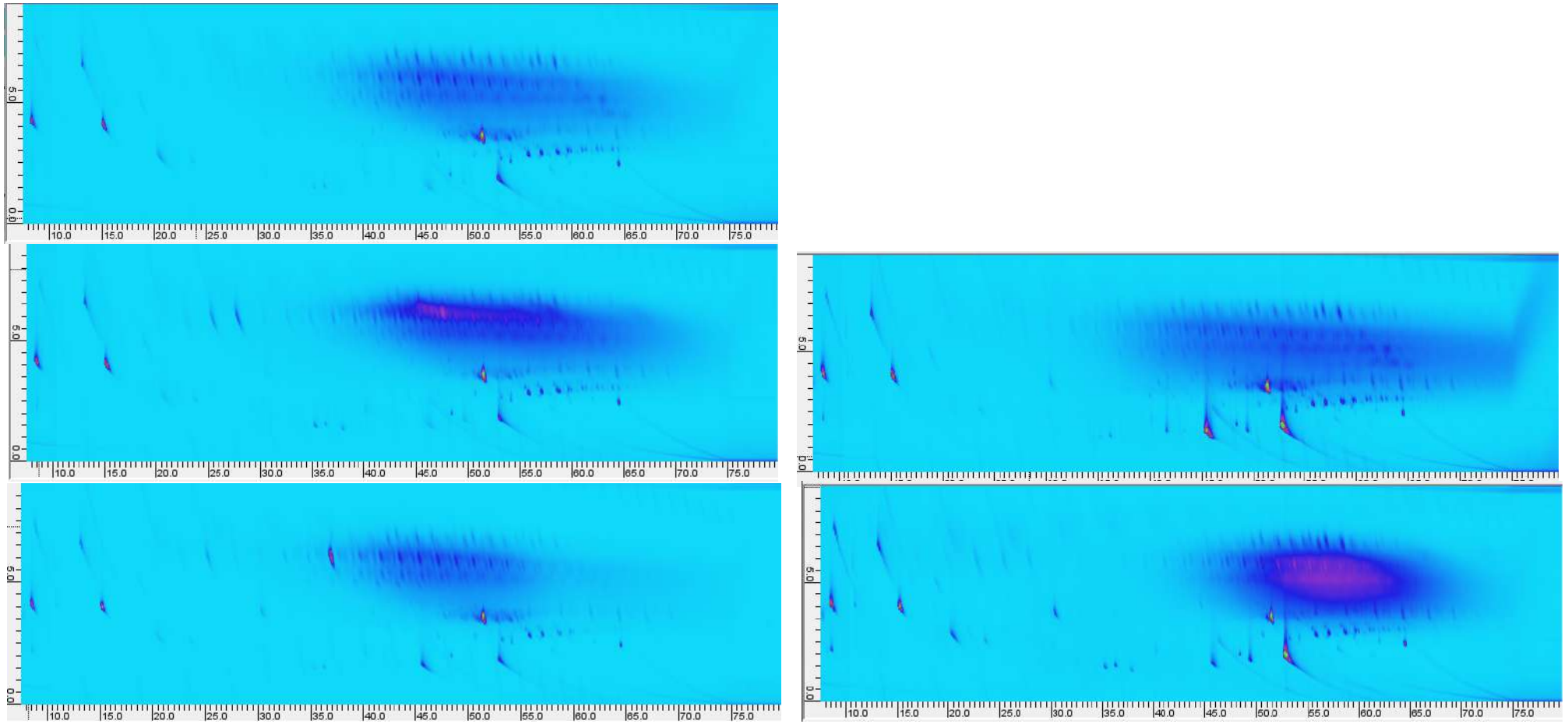




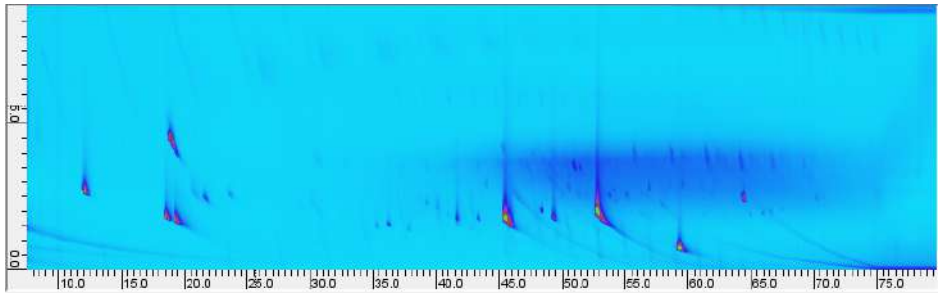
Formula	Mass	Difference (mmu)	ppm
C12H13O3+	205.085921	-0.191247	0.932522
C16H13+	205.101177	-15.447380	75.315902
C15H9O+	205.064791	20.938125	102.104925

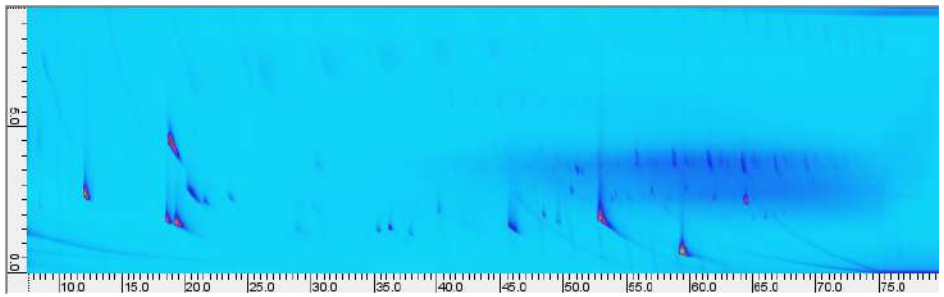


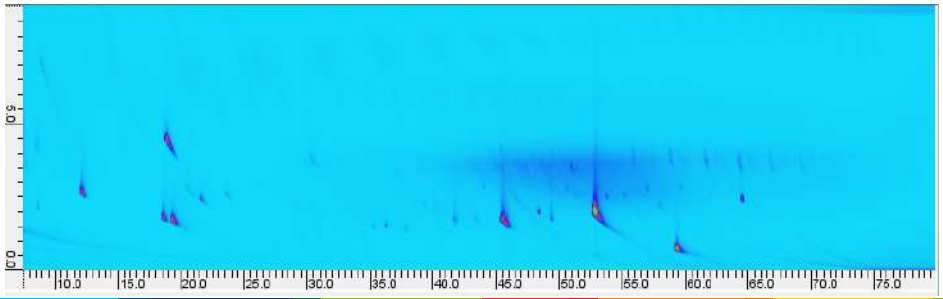
Fingerprinting – MOSH of various lubricants

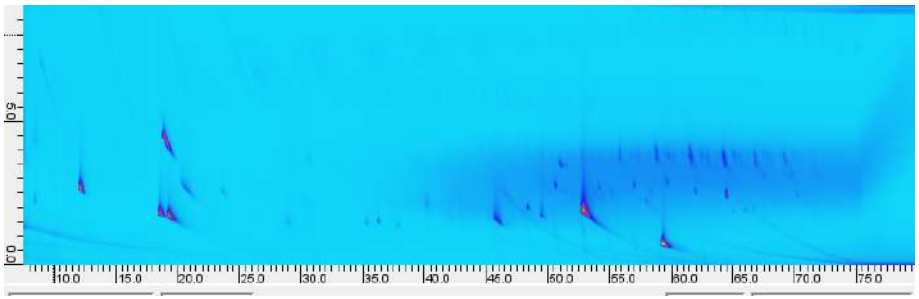


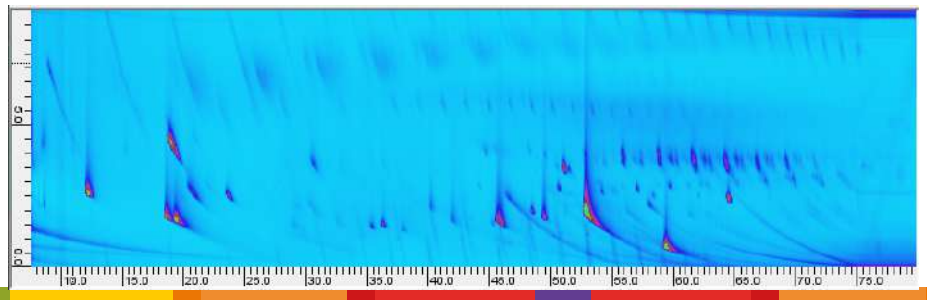
Fingerprinting - MOAH of various lubricants



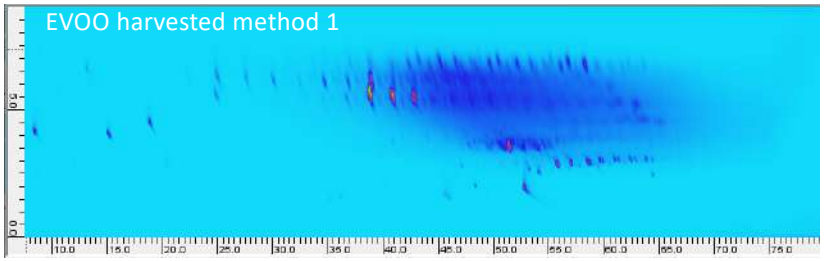


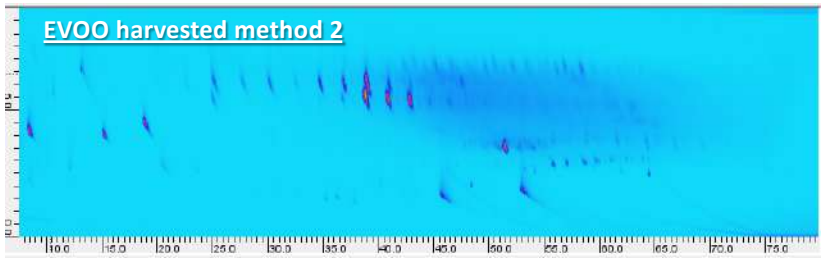


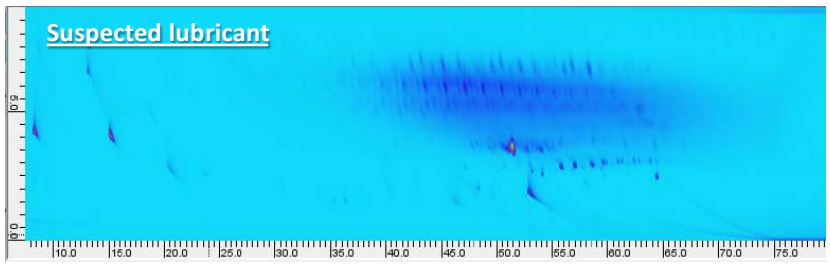


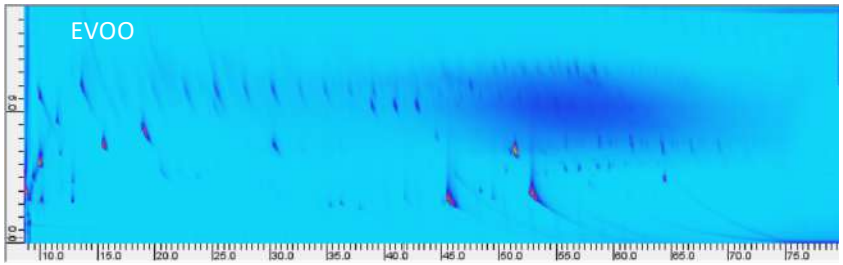


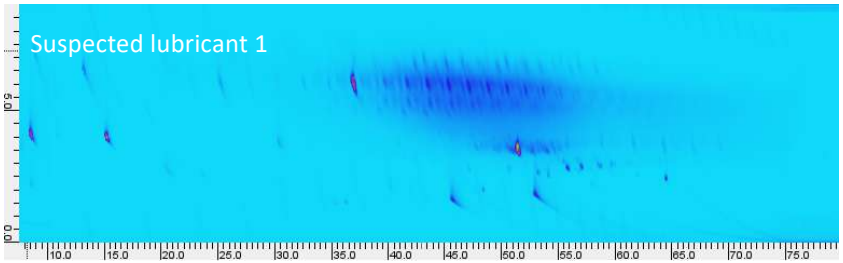
Fingerprinting – EVOO samples (MOSH)

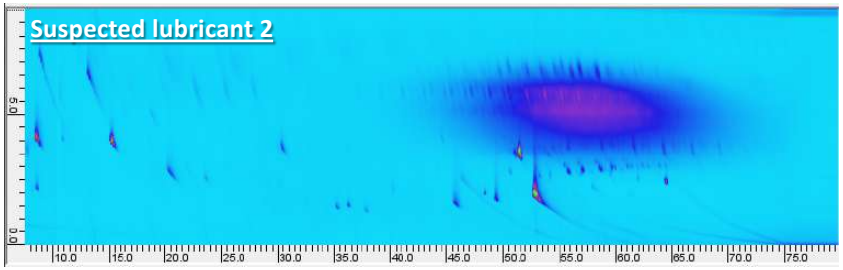












Conclusions

- Two-dimensional analytical platform based thermally modulated GC×GC with parallel FID/QTOF detection.
- This solution advances characterization capability and offers the possibility to perform more informative and accurate analysis of MOSH and MOAH fractions.
- Powerful additional tool, complementary to the reference methodology, for more insightful investigation of samples positive to contamination.
- Possibility to characterize more in details both fractions.
- Effective fingerprinting tool for determining with good confidence the source of contamination.

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