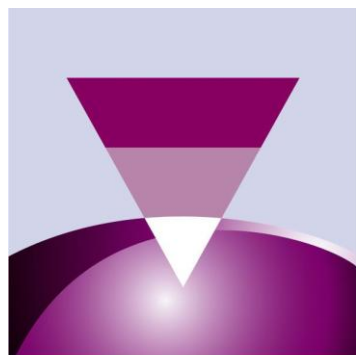


GC-Based hyphenated techniques for detailed characterization of complex samples



analytica 2026
24.–27. MÄRZ | MÜNCHEN

Giorgia Purcaro , Damien Eggermont, Aleksandra Gorska

Gembloux Agro Bio-Tech, University of Liège, Belgium

gpurcaro@uliege.be

Journal of Chromatography, 626 (1992) 25–32
Elsevier Science Publishers B.V., Amsterdam

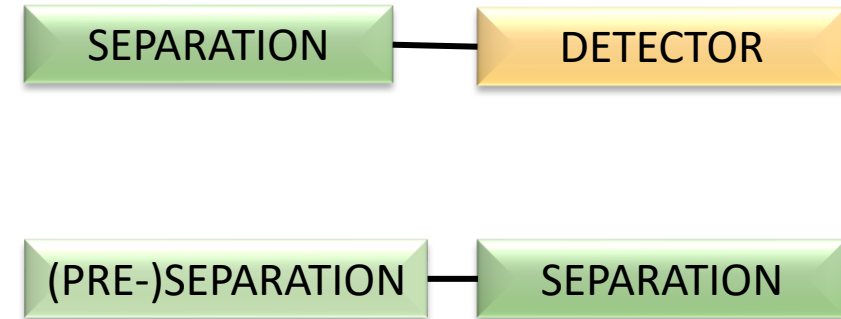
CHROM. 24 407

Review

Hyphenated high-performance liquid chromatography–capillary gas chromatography

Konrad Grob

Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland)



“Hyphenation of techniques may occur at the front or at the rear end of the main chromatographic separation step.

At the rear end (outlet of the main chromatograph), it involves sophisticated detectors, whereas the purpose of hyphenation **at the front end** is usually sample preparation or prepreparation -two totally different methods.”

Journal of Chromatography, 626 (1992) 25–32
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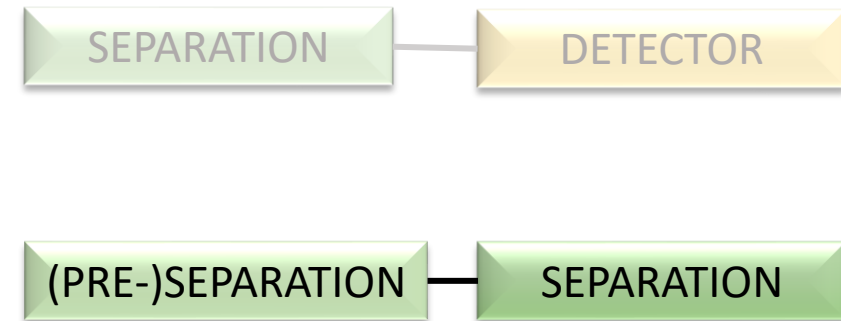
CHROM. 24 407

Review

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“reductionist
approach”

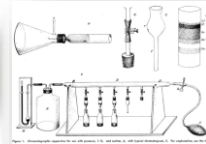
“interactionism” and -omics
sciences”

1800s **Wet chemistry era**
main components



1900s **Instrumental era**
minor and trace components

1906



1934 Introduction of the “Acidimeter” (automatic pHmeter)

1941 **LC**

1951 **GC**

1958 **Capillary column**

1959 **GC-MS**

1980 **LC-GC**

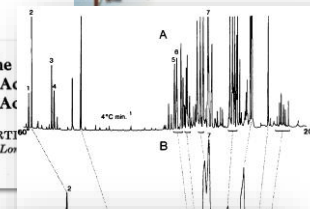
1991 **GC×GC**

2000 **LC×GC**

2005 **LC-GC×GC**

151. A NEW FORM OF CHROMATOGRAM
EMPLOYING TWO LIQUID PHASES
1. A THEORY OF CHROMATOGRAPHY
2. APPLICATION TO
OF THE HIGHER
By A. J. P. J.

Gas-liquid Partition Chromatography: the
Micro-estimation of Volatile Fatty Acids
Formic Acid to Dodecanoic Acid
By A. T. JAMES AND A. J. P. MARTIN
National Institute for Medical Research, Mill Hill, London
(Received 5 June 1951)



Time-of-Flight Mass Spectrometry and
Gas-Liquid Partition Chromatography
R. S. GOMES
Spectroscopy

Journal of Chromatographic Science, Vol. 18, October 1980

Multidimensional High Performance
Liquid Chromatography*
R. S. GOMES
Journal of Chromatographic Science, Vol. 29, June 1991

Comprehensive Two-Dimensional Gas Chromatography
using an On-Column Thermal Modulator Interface
Zaiyou Liu and John B. Phillips*
Department of Chemistry & Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

Comprehensive LC × GC for Enhanced Headspace Analysis

Wes W. C. Quigley
Department of Chemistry,
University of



Comprehensive multi-dimensional chromatographic studies on the
separation of saturated hydrocarbon ring structures
in petrochemical samples

R. Edam^a, J. Blomberg^{b,*}, H.-G. Janssen^c, P.J. Schoenmakers^a

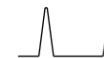
^a University of Amsterdam, Van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands
^b Shell Global Solutions, Shell Research & Technology Centre Amsterdam, Amsterdam, The Netherlands
^c Unilever Research and Development, Central Analytical Science, Delft, The Netherlands

Chromatography:

➤ Maximize separation resolution

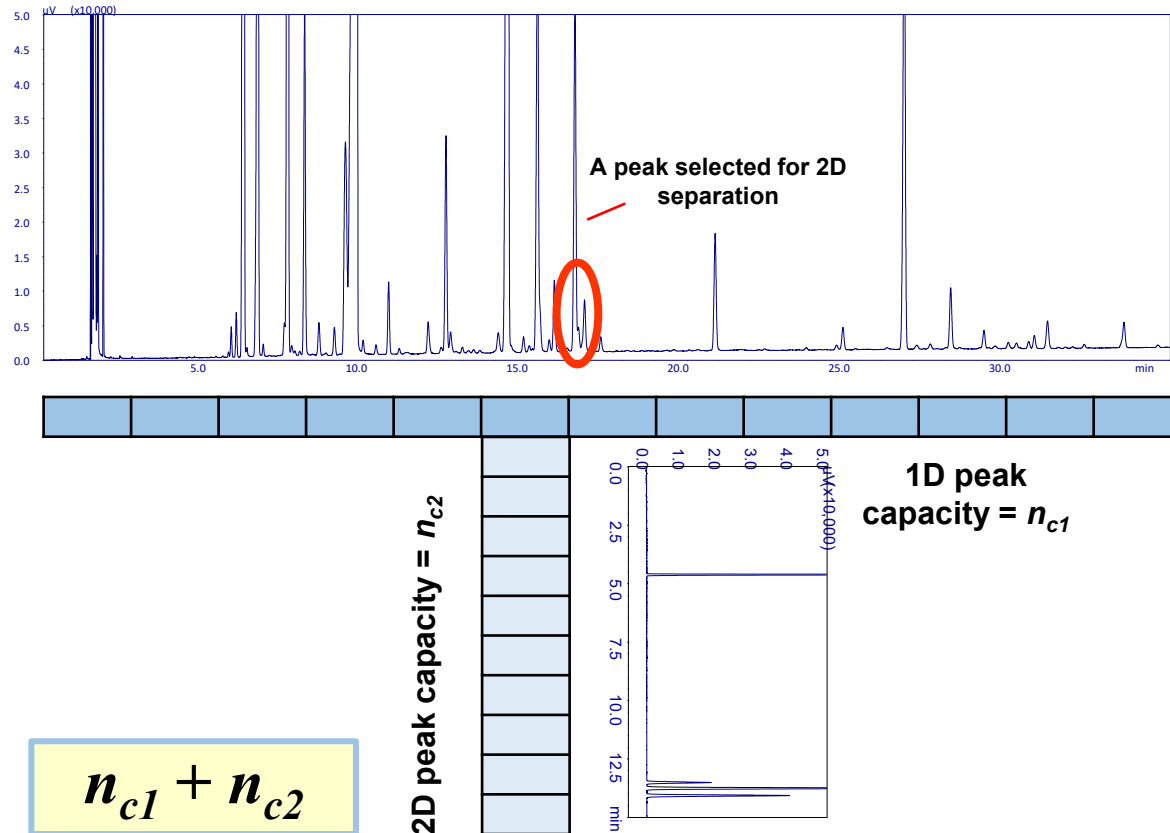


Multidimensional Chromatography



LC-GC

Heart-cutting mode



Journal of Chromatography, 295 (1984) 55–61
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,706

COUPLING OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY WITH CAPILLARY GAS CHROMATOGRAPHY

K. GROB, Jr.*, D. FRÖHLICH, B. SCHILLING, H. P. NEUKOM and P. NÄGELI
Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland)
(Received March 6th, 1984)

Journal of Chromatographic Science, Vol. 29, June 1991

Comprehensive Two-Dimensional Gas Chromatography using an On-Column Thermal Modulator Interface

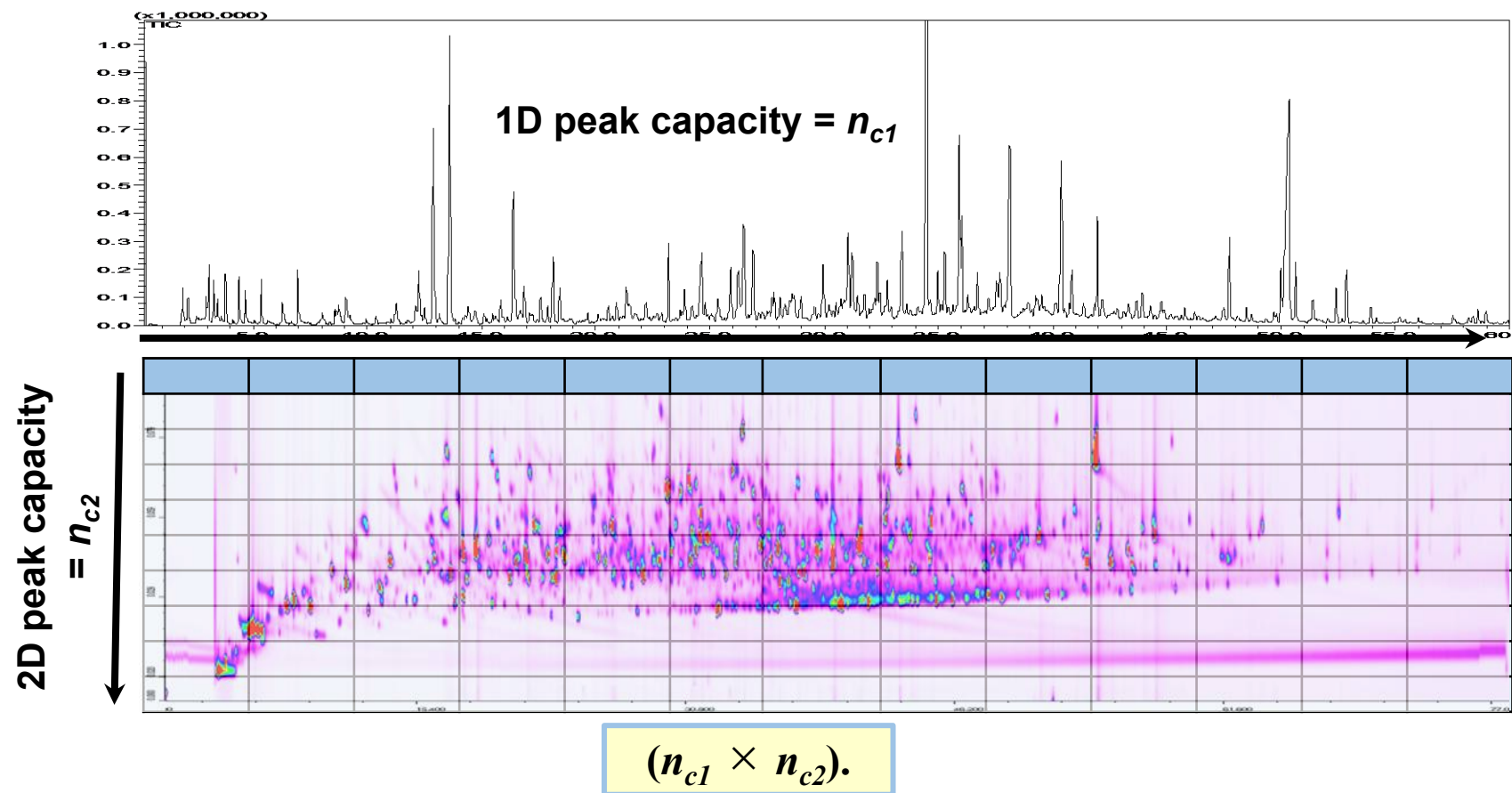
Zaiyou Liu and John B. Phillips*

Department of Chemistry & Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

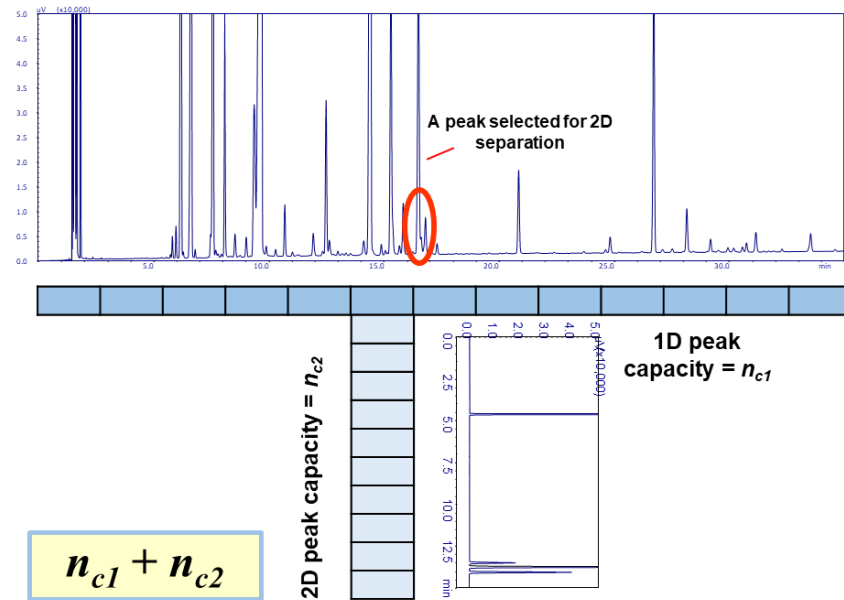
1991 GC×GC

GC×GC

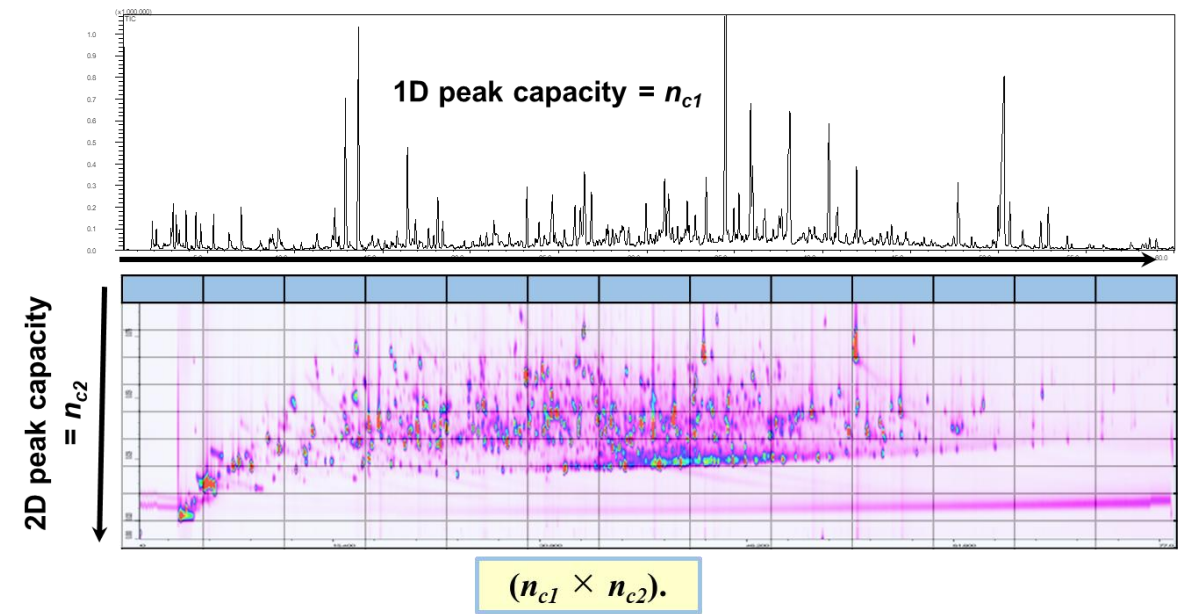
Comprehensive mode



Heart-cutting mode



Comprehensive mode



Ally of Sample Prep



Unveil and explored sample multidimensionality



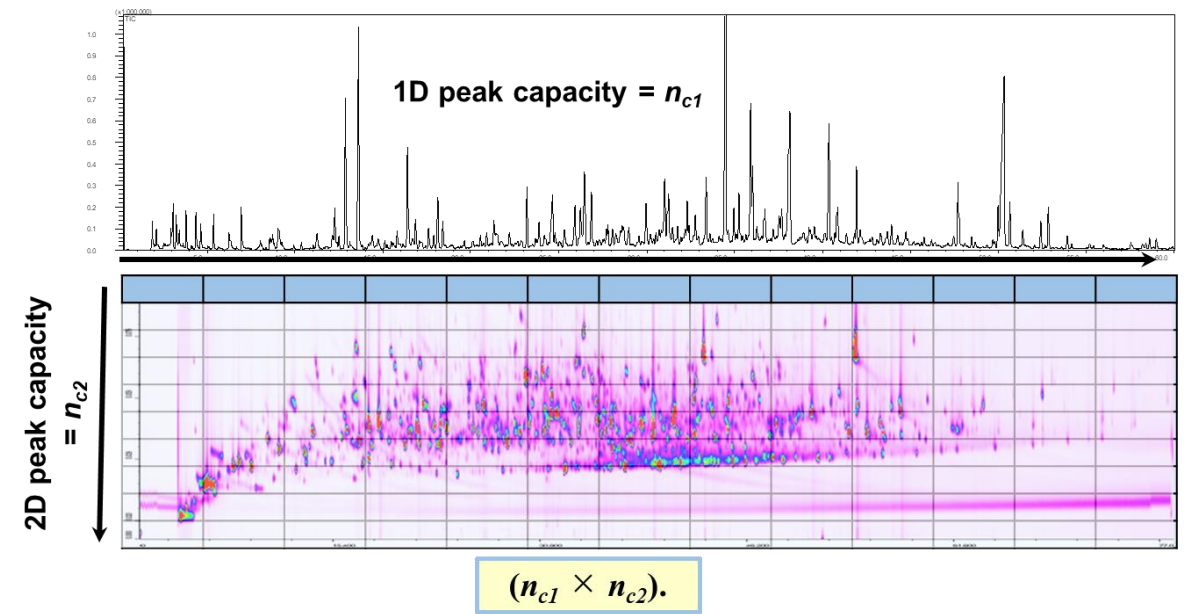
Heart-cutting mode



Ally of Sample Prep



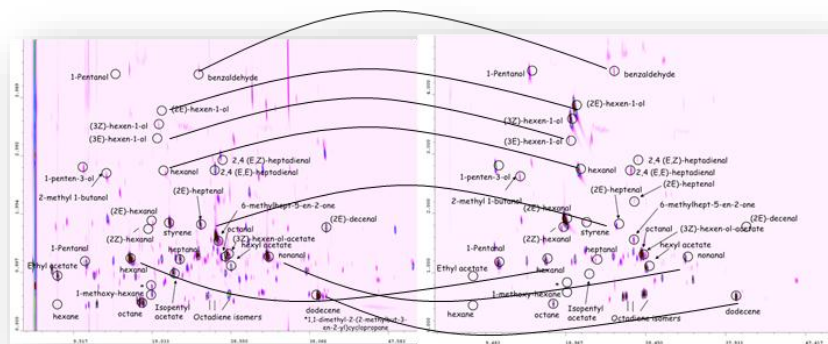
Comprehensive mode



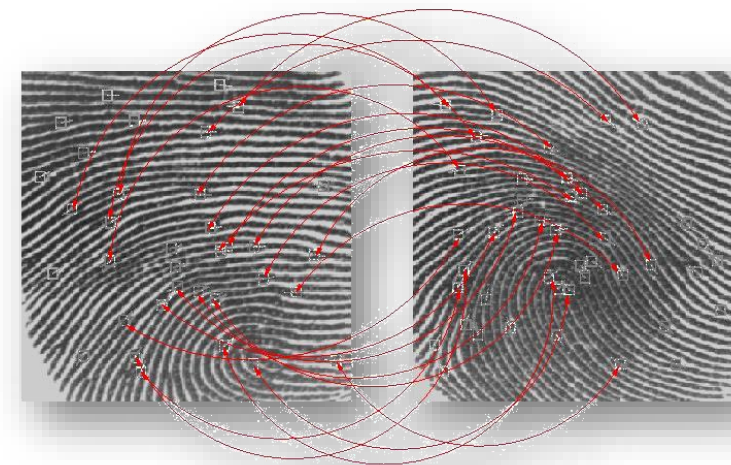
Unveil and explored sample multidimensionality



GC×GC



Chromatographic fingerprints



provide a unique situation where the data generated can be processed either following fingerprinting or profiling methodologies, providing multi-level information



Profiling:

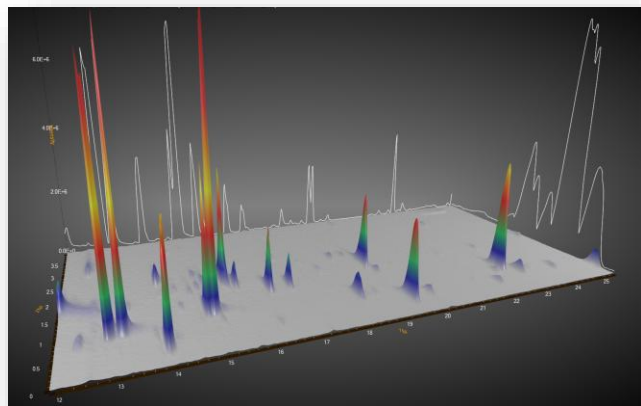
detailed analysis (either targeted or untargeted) to obtain quali and quantitative information on the compounds present in a sample



Fingerprinting:

High throughput method capable of capturing relevant information but not necessarily achieving quantitative information





➤ Intensity data from the whole (or selected zone) chromatogram

FINGERPRINT

Unspecific information

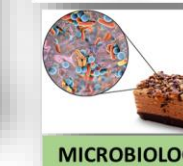


➤ Measurement of peaks areas

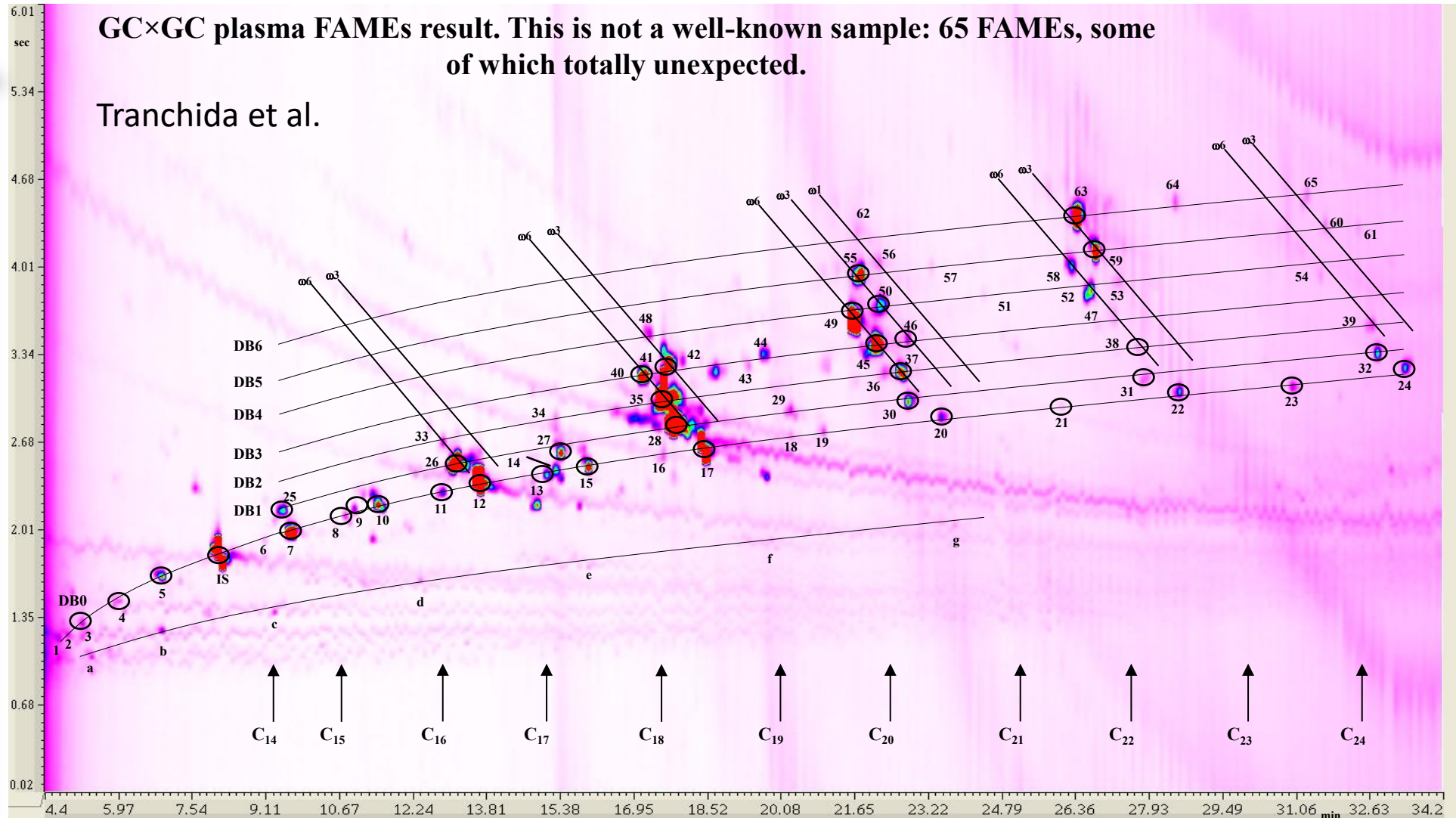
**Component
PROFILE**

➤ Determination of individual compounds

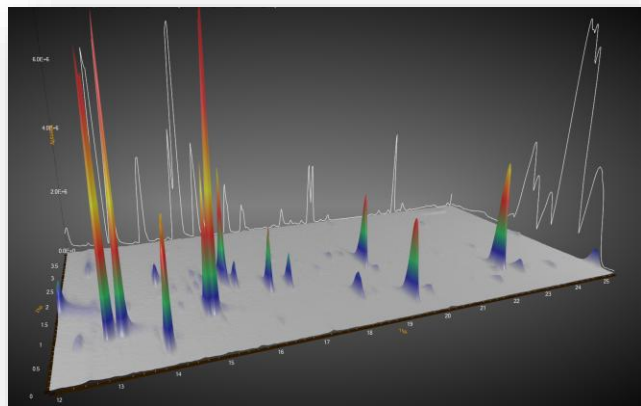
**Peak
PROFILE**



POLARITY



VOLATILITY



➤ Intensity data from the whole (or selected zone) chromatogram

FINGERPRINT

Unspecific information

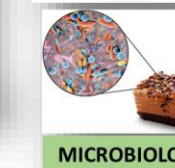
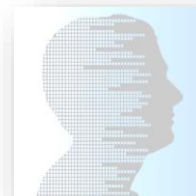


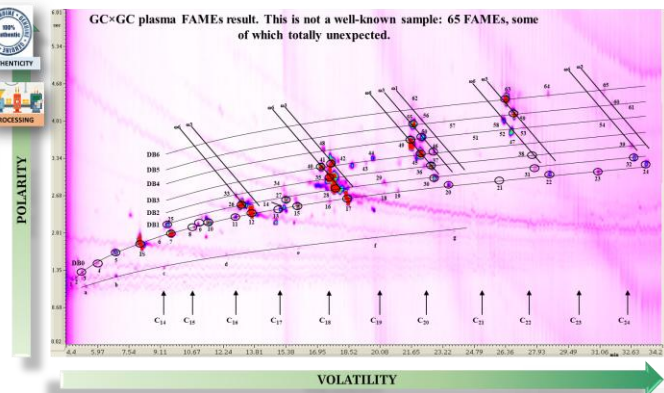
➤ Measurement of peaks areas

Component
PROFILE

➤ Determination of individual compounds

Peak
PROFILE





Selectivity of different fibers

Journal of Chromatography A, 1251 (2012) 208–218



Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

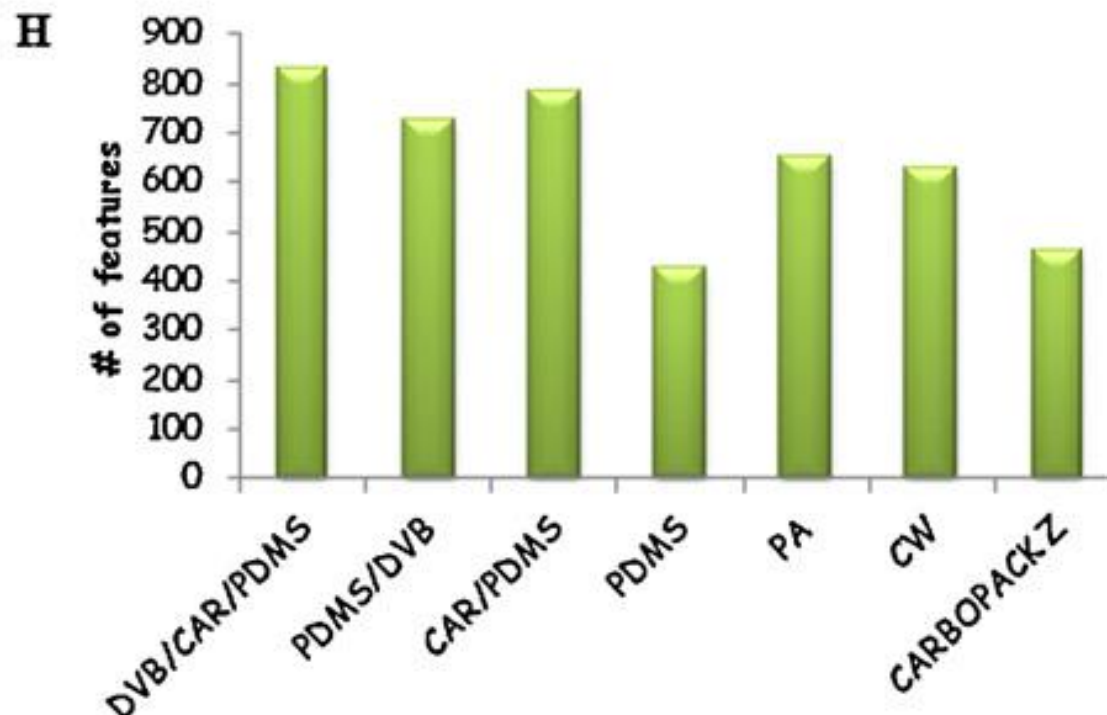


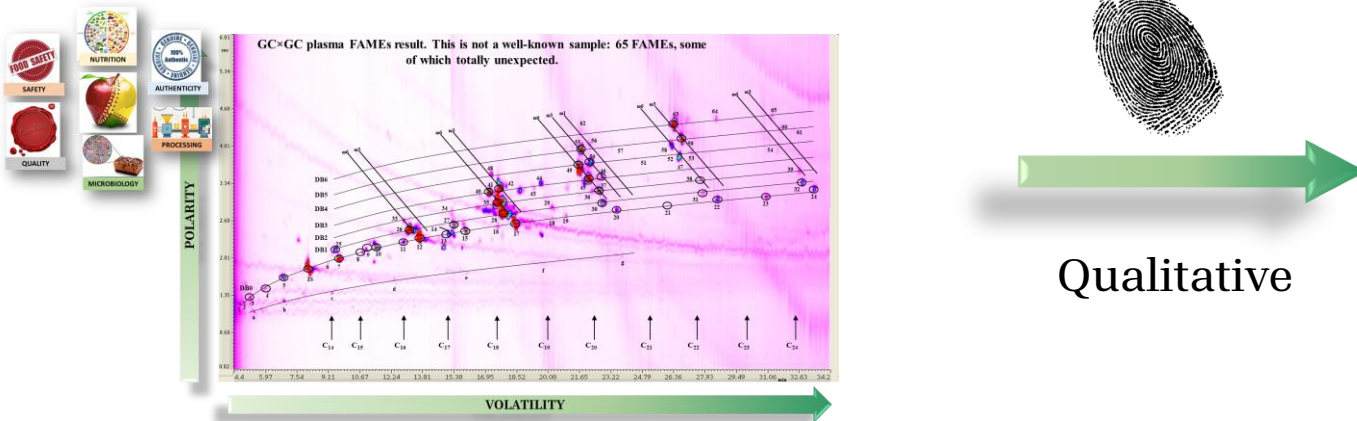
Solid phase microextraction coupled with comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry for high-resolution metabolite profiling in apples: Implementation of structured separations for optimization of sample preparation procedure in complex samples[☆]

Sanja Risticvic^a, Jennifer R. DeEl^b, Janusz Pawliszyn^{a,*}

^a Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

^b Agriculture Development Branch, Ontario Ministry of Agriculture, Food and Rural Affairs, Simcoe, Ontario, Canada





Selectivity of different fibers

Journal of Chromatography A, 1251 (2012) 208–218



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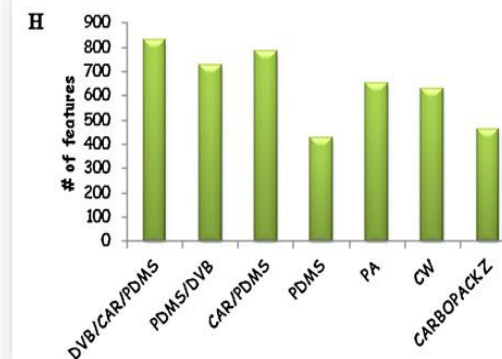
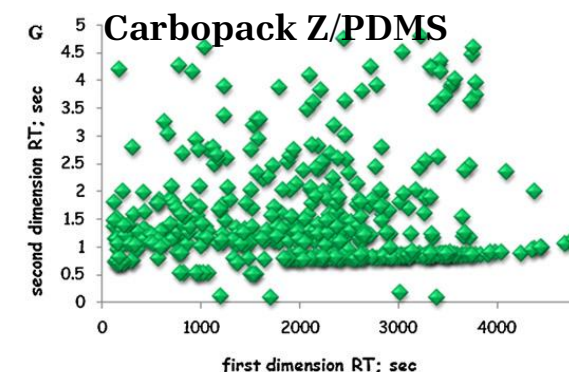
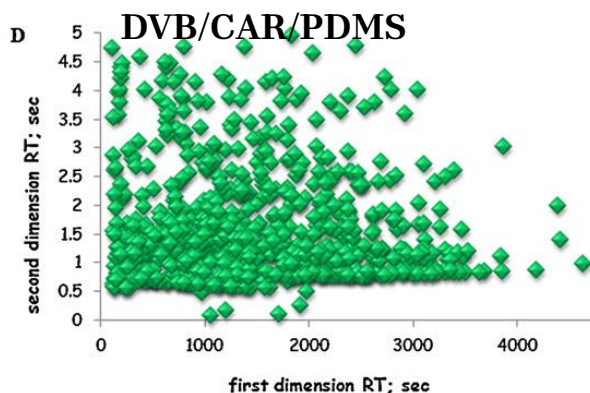
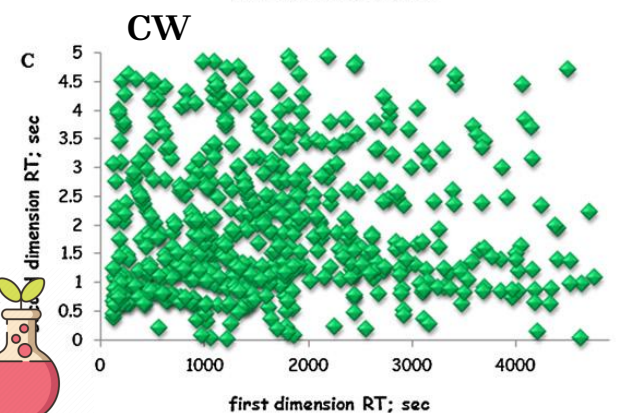
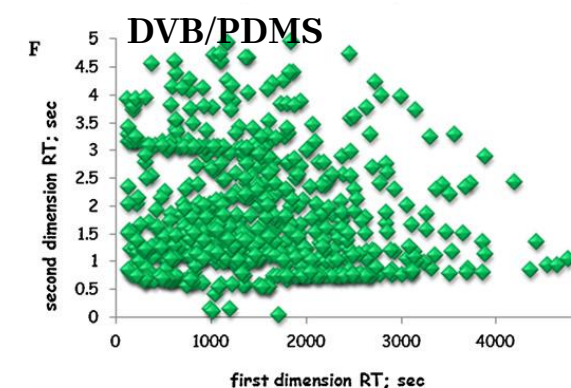
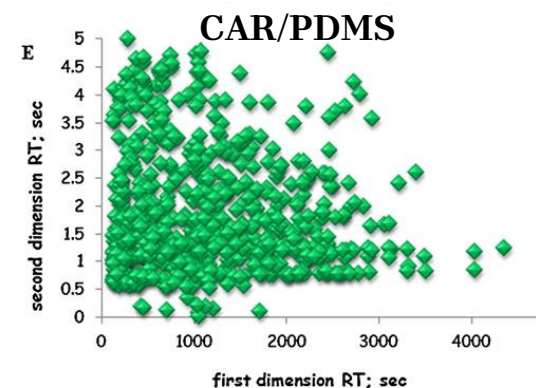
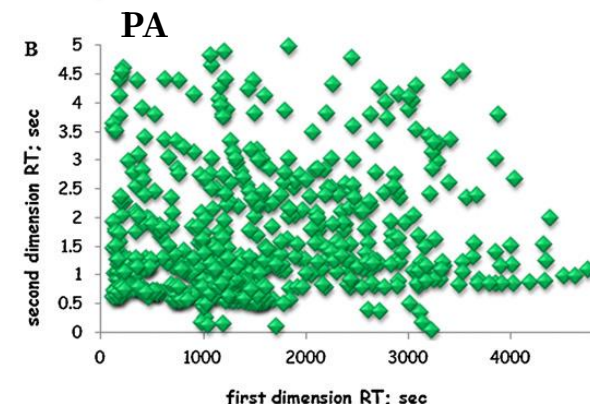
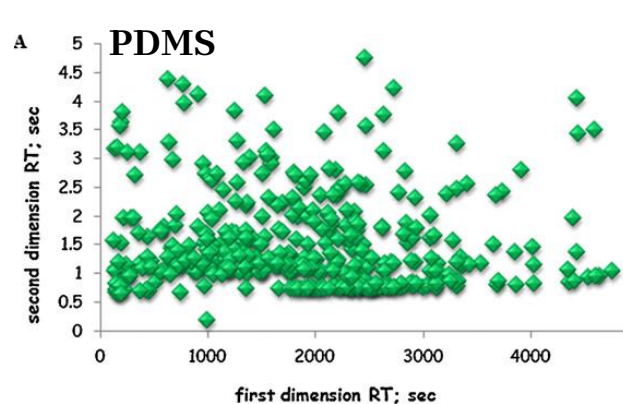
Journal of Chromatography A

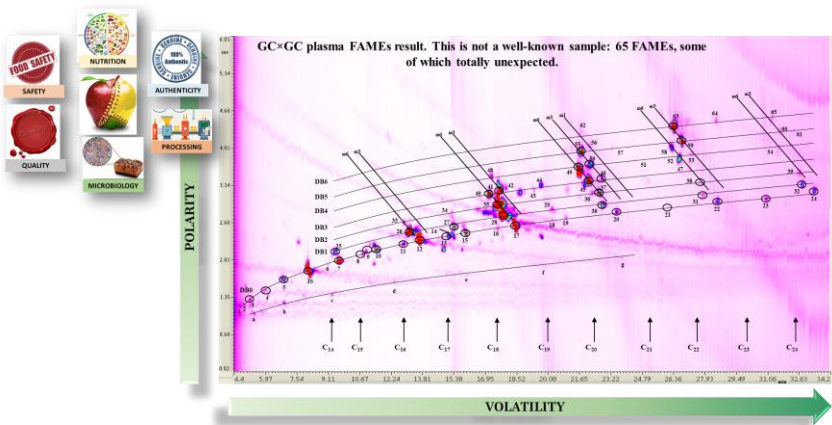
journal homepage: www.elsevier.com/locate/chroma



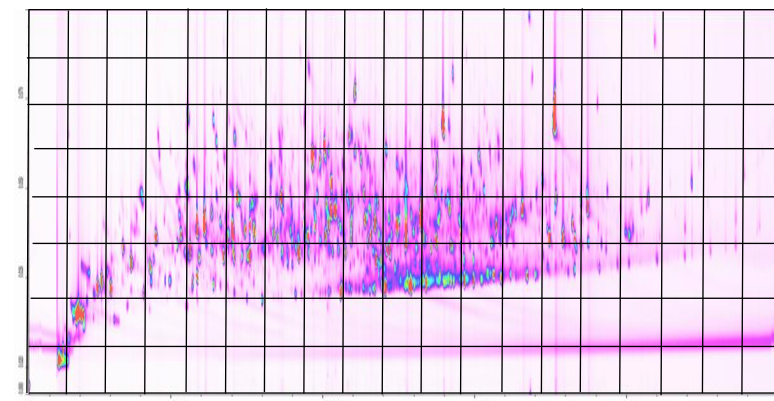
Solid phase microextraction coupled with comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry for high-resolution metabolite profiling in apples: Implementation of structured separations for optimization of sample preparation procedure in complex samples[☆]

Sanja Risticovic^a, Jennifer R. DeEll^b, Janusz Pawliszyn^{a,*}





Qualitative &
Quantitative



TIME PROFILE

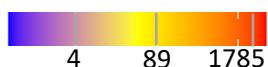
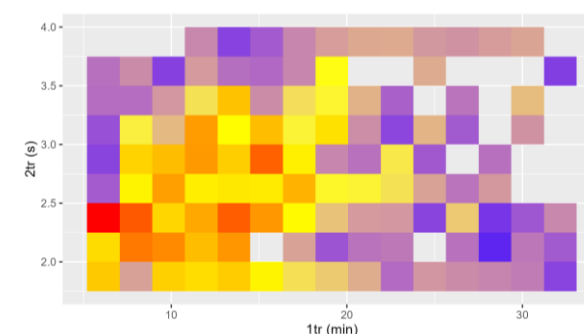
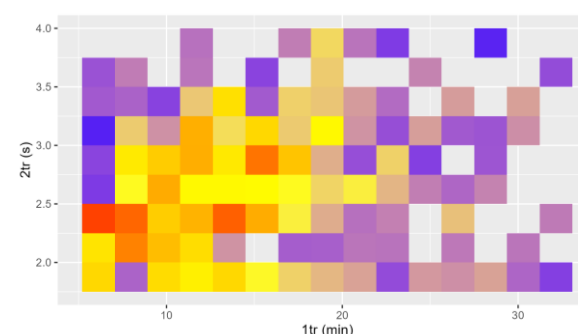
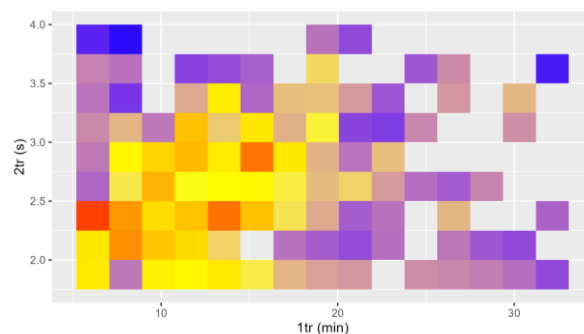
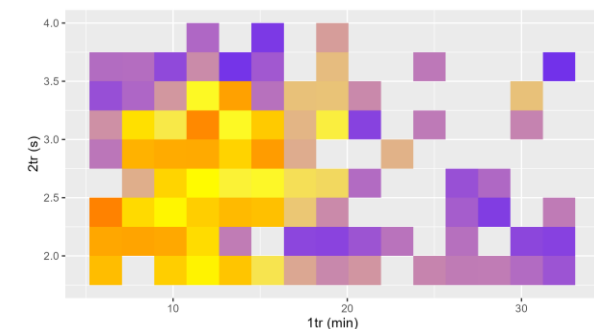
Area

10 min

25 min

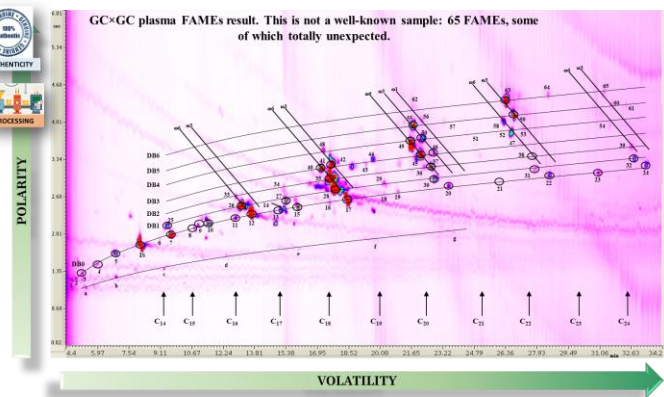
35 min

50 min

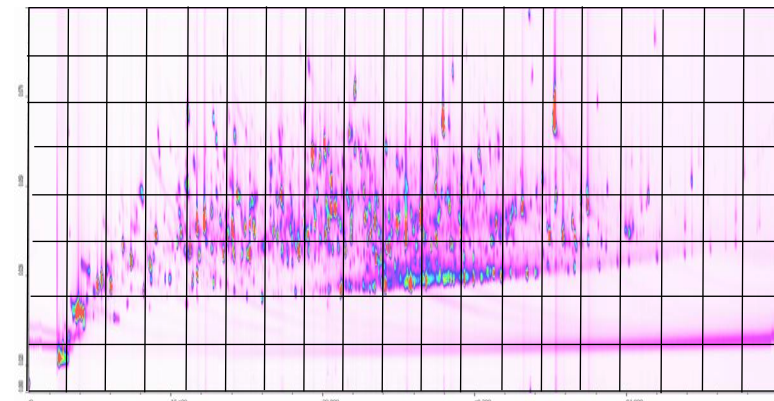


Chocolate aroma profile

Cozzolino R., Eggermont D., Malorni L., Purcaro G., ACA 2026 1385 345015

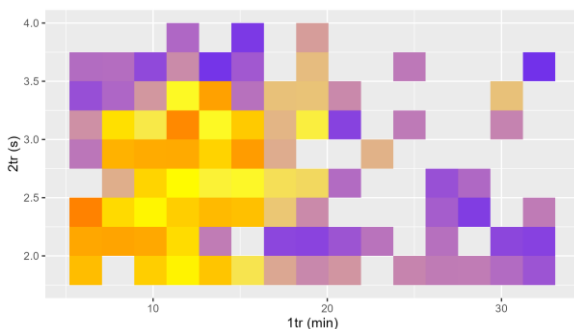


Qualitative &
Quantitative

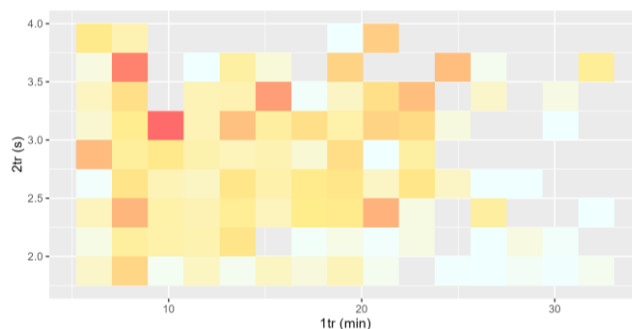


TIME PROFILE

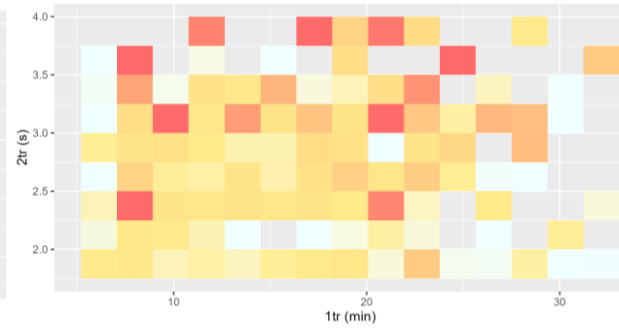
Area
10 min



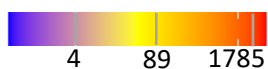
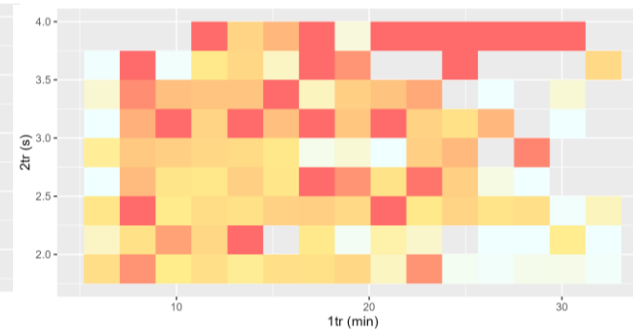
25 min



35 min



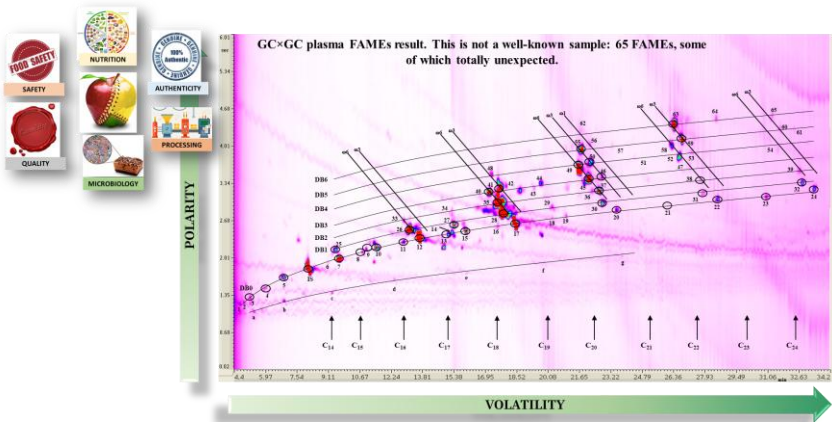
50 min



Chocolate aroma profile



“improvement plots”



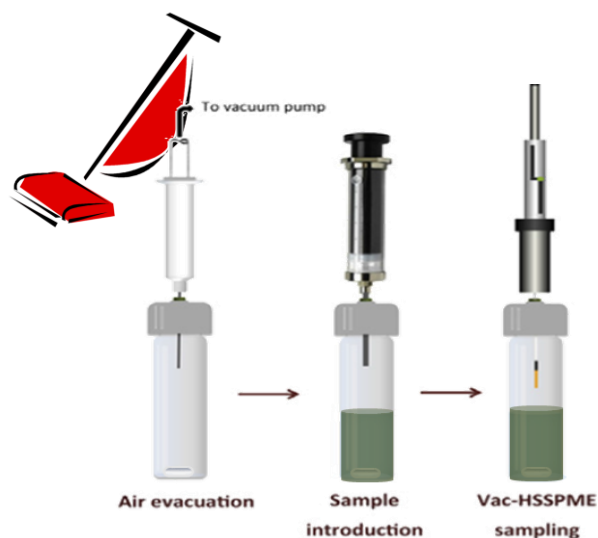
HS-SPME

1cm fiber 100 μ m :
0.6 μ L



Selectivity of different techniques

Vac-HS-SPME

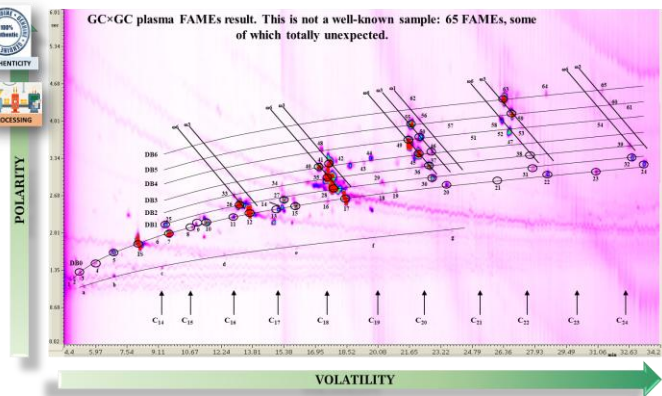


HiSorb®



~10.5mm x 0.8 mm:
~ 63 μ L





Selectivity of different techniques

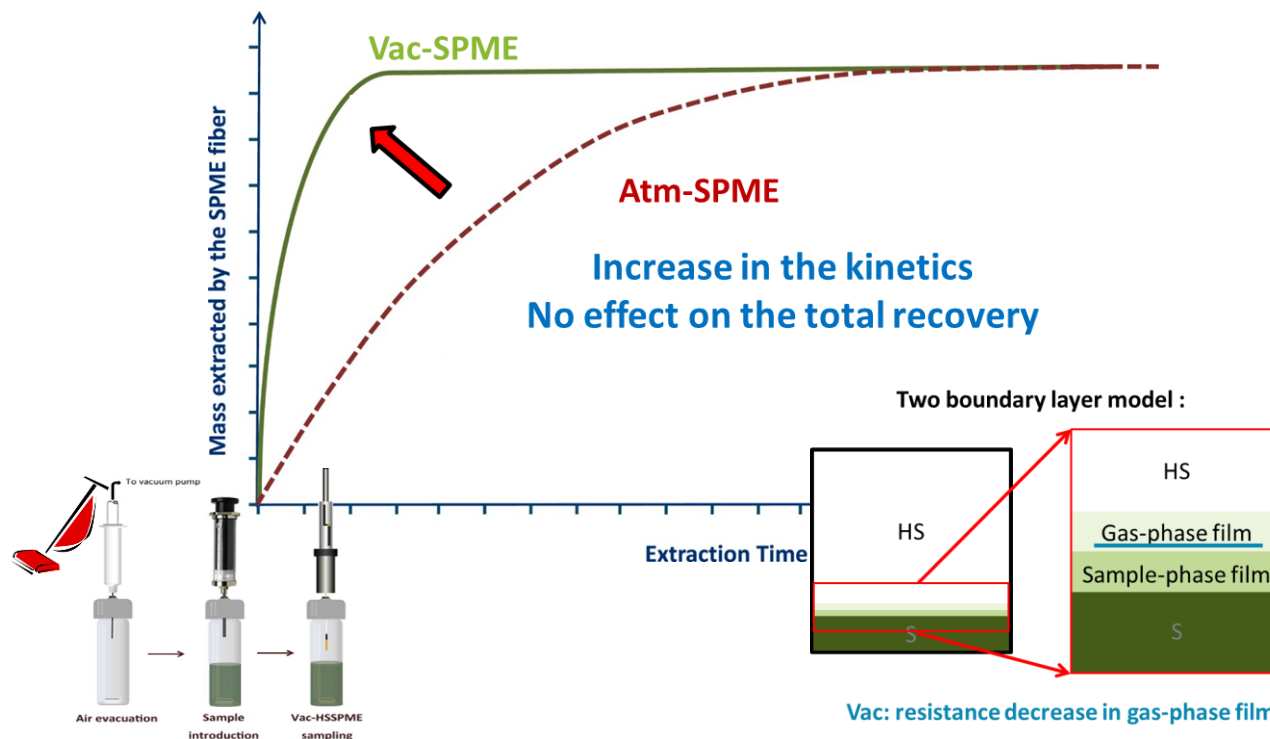
HS-SPME



1cm fiber 100μm :
0.6 μL



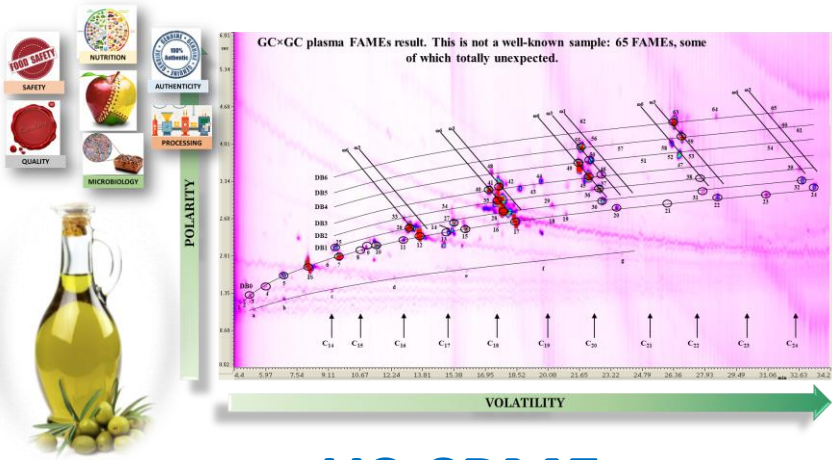
Vac-HS-SPME



HiSorb®



~10.5mm x 0.8 mm:
~ 63 μL



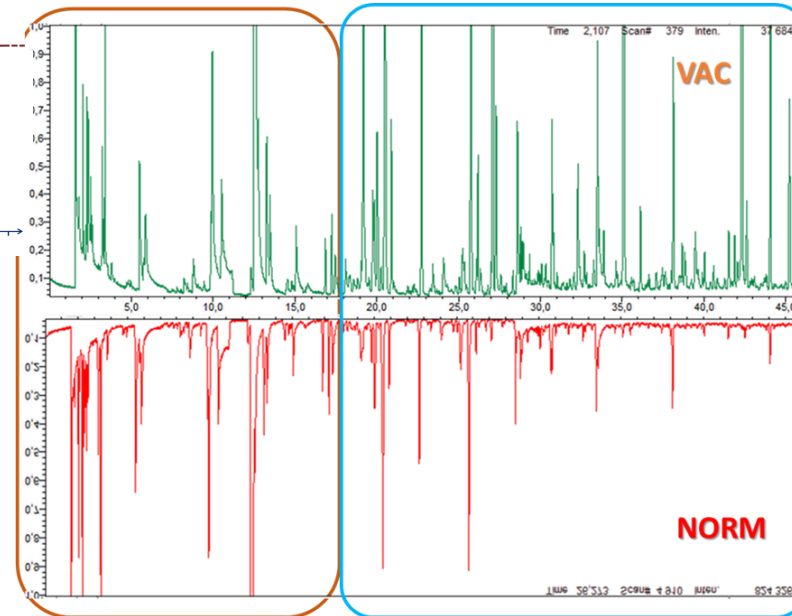
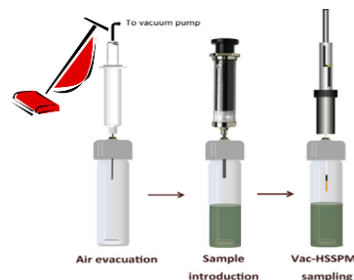
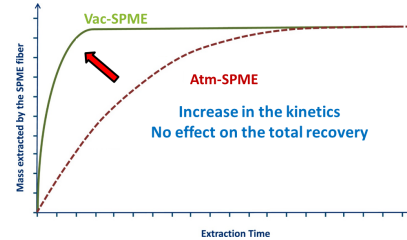
Selectivity of different techniques

HS-SPME

Vac-HS-SPME

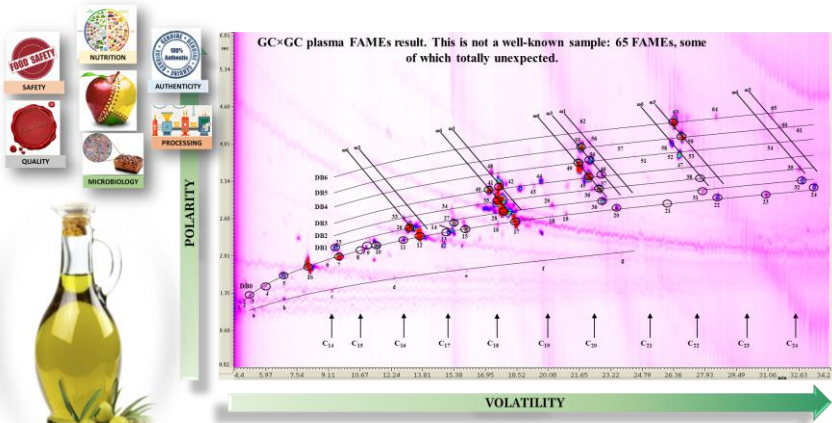
HiSorb®

1cm fiber 100μm :
0.6 μL



~10.5mm x 0.8 mm:
~ 63 μL





HS-SPME



Selectivity of different techniques

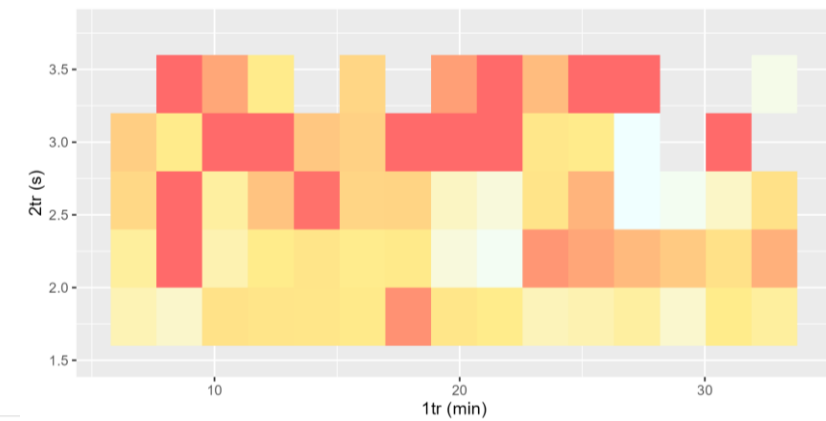
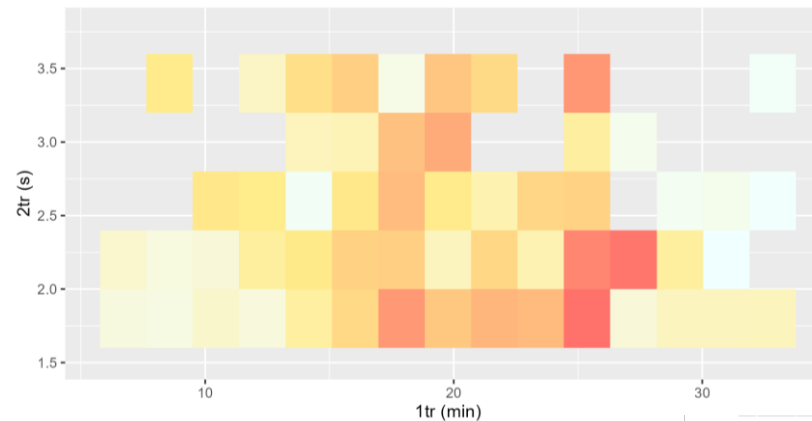
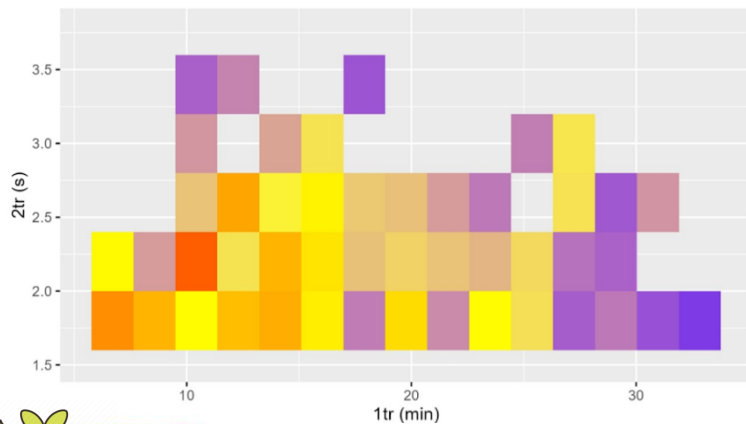
Vac-HS-SPME

HiSorb®

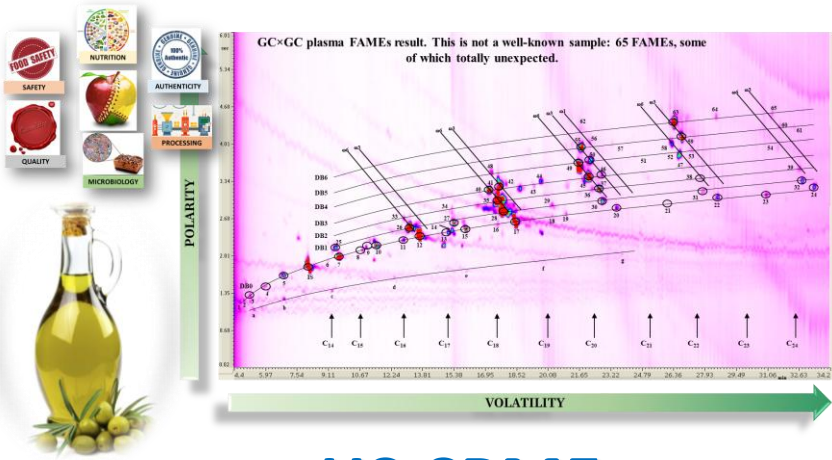
Vac-HS-SPME/HS-SPME

HiSorb/HS-SPME

R-HS-SPME



“improvement plots”



HS-SPME



Selectivity of different techniques

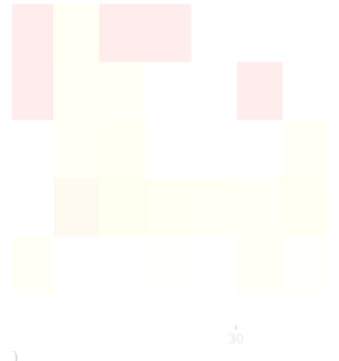
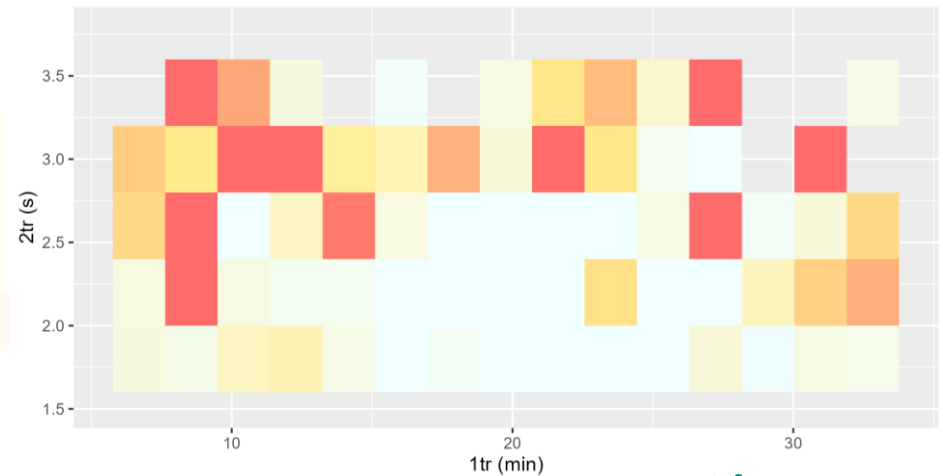
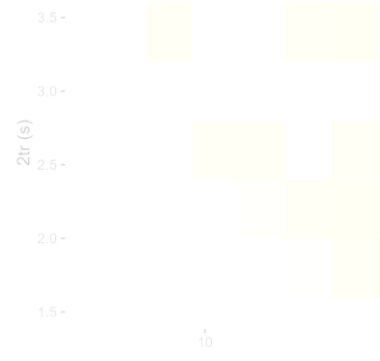
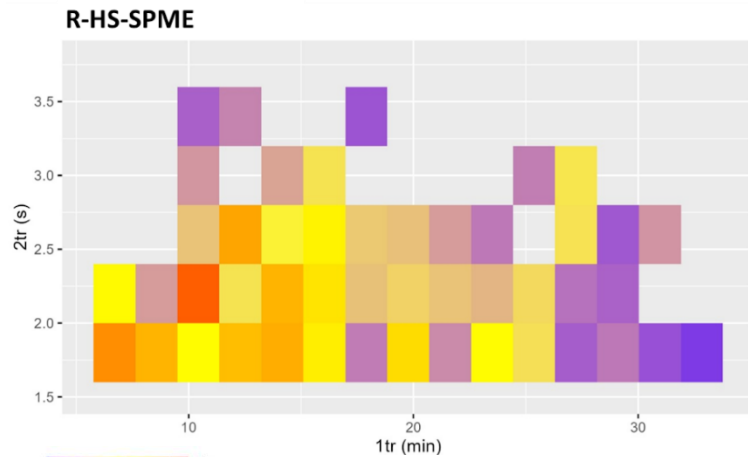
Vac-HS-SPME

HiSorb®

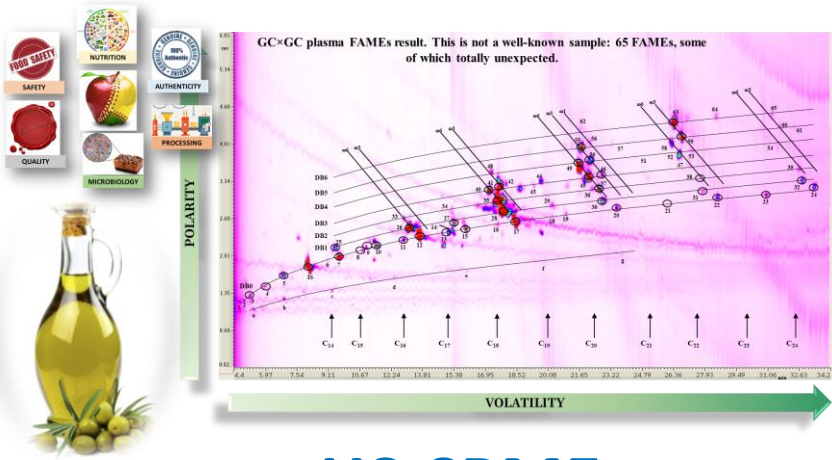
Vac-HS-SPME/HS-SPME

HiSorb/Vac-HS-SPME

HiSorb/HS-SPME



“improvement plots”

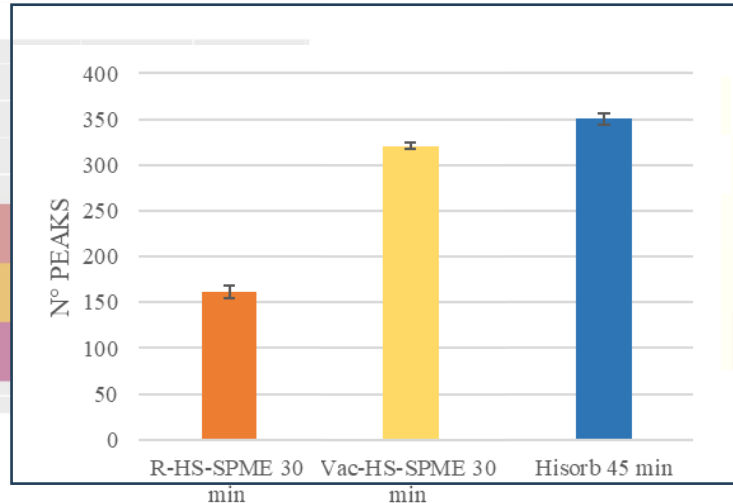
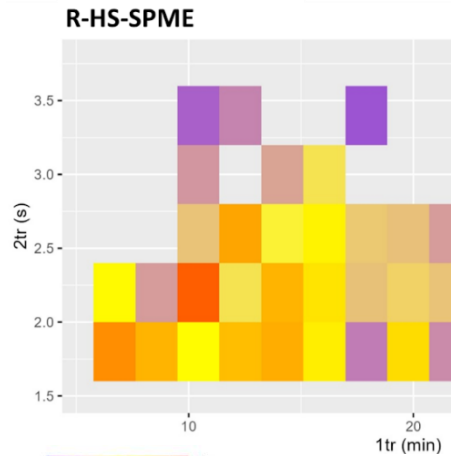


Selectivity of different techniques

HS-SPME

Vac-HS-SPME

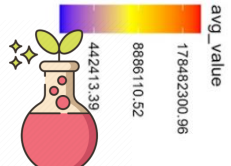
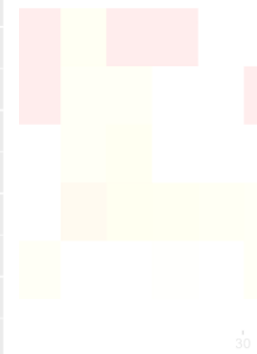
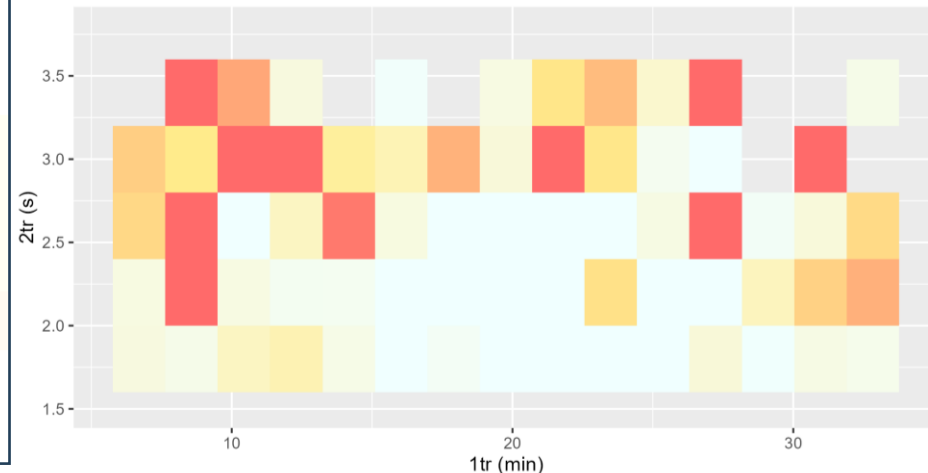
HiSorb®



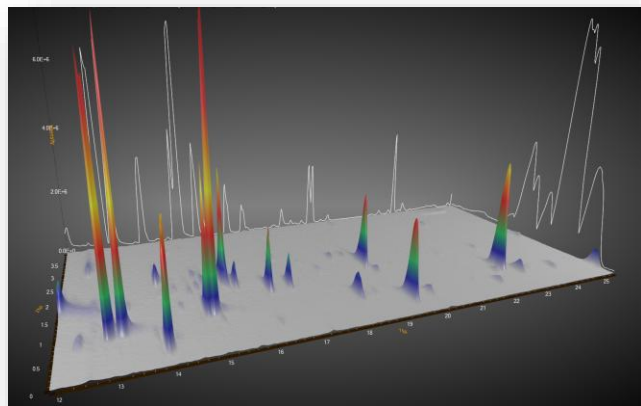
Vac-HS-SPME/HS-SPME

HiSorb/Vac-HS-SPME

HiSorb/HS-SPME



“improvement plots”



➤ Intensity data from the whole (or selected zone) chromatogram

FINGERPRINT

Unspecific information



➤ Measurement of peaks areas

**Component
PROFILE**

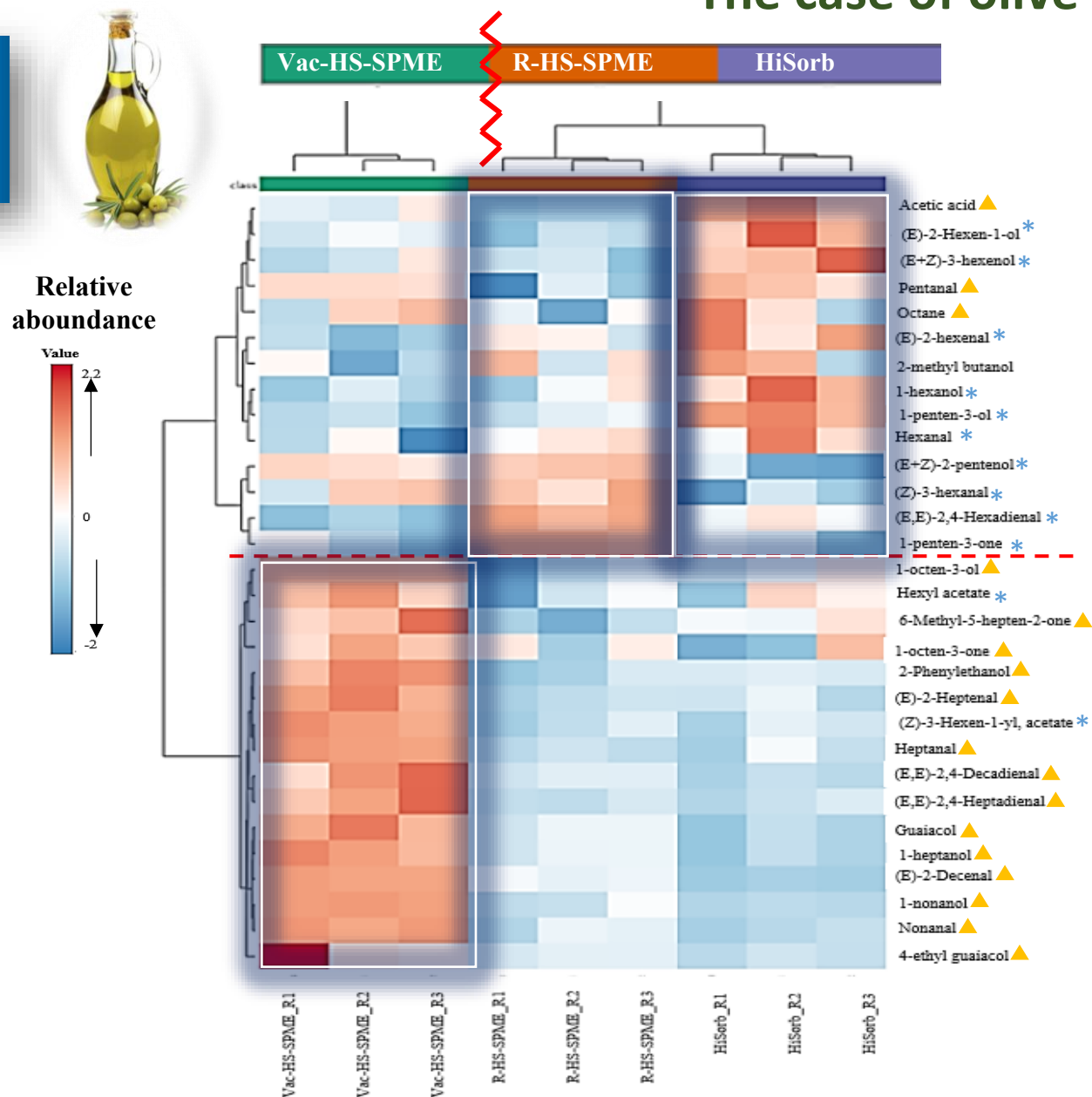
➤ Determination of individual compounds

**Peak
PROFILE**



The case of olive oil

Selectivity of different techniques



Higher
volatility



Lower
volatility



Lipoxygenase (LOX) Pathway *

Series of biochemical reactions that lead to the formation of C5–C6 aldehydes, alcohols, and their corresponding esters, which are responsible for green and fruity aroma notes.

C7-C12 VOCs ▲

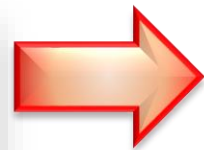
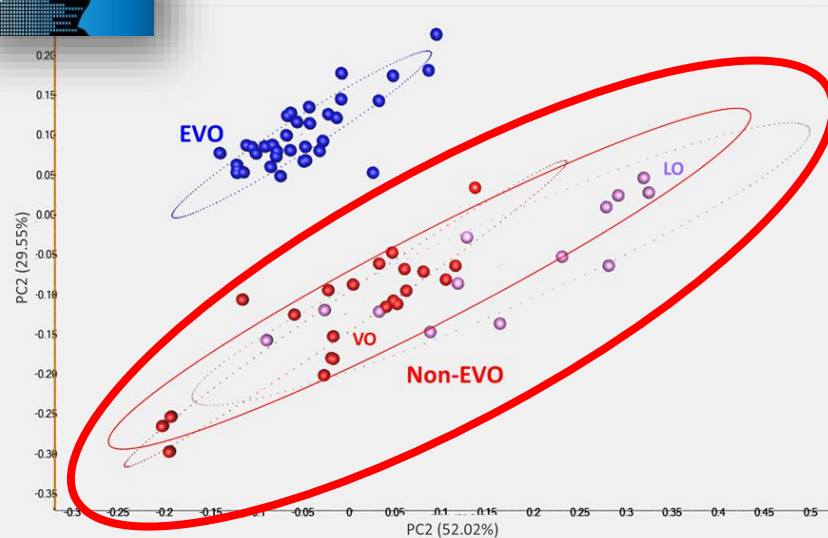
Compounds typically associated with oxidative and microbiological defects, often linked to poor quality or improper preservation of the raw material and inadequate storage conditions.

The case of olive oil

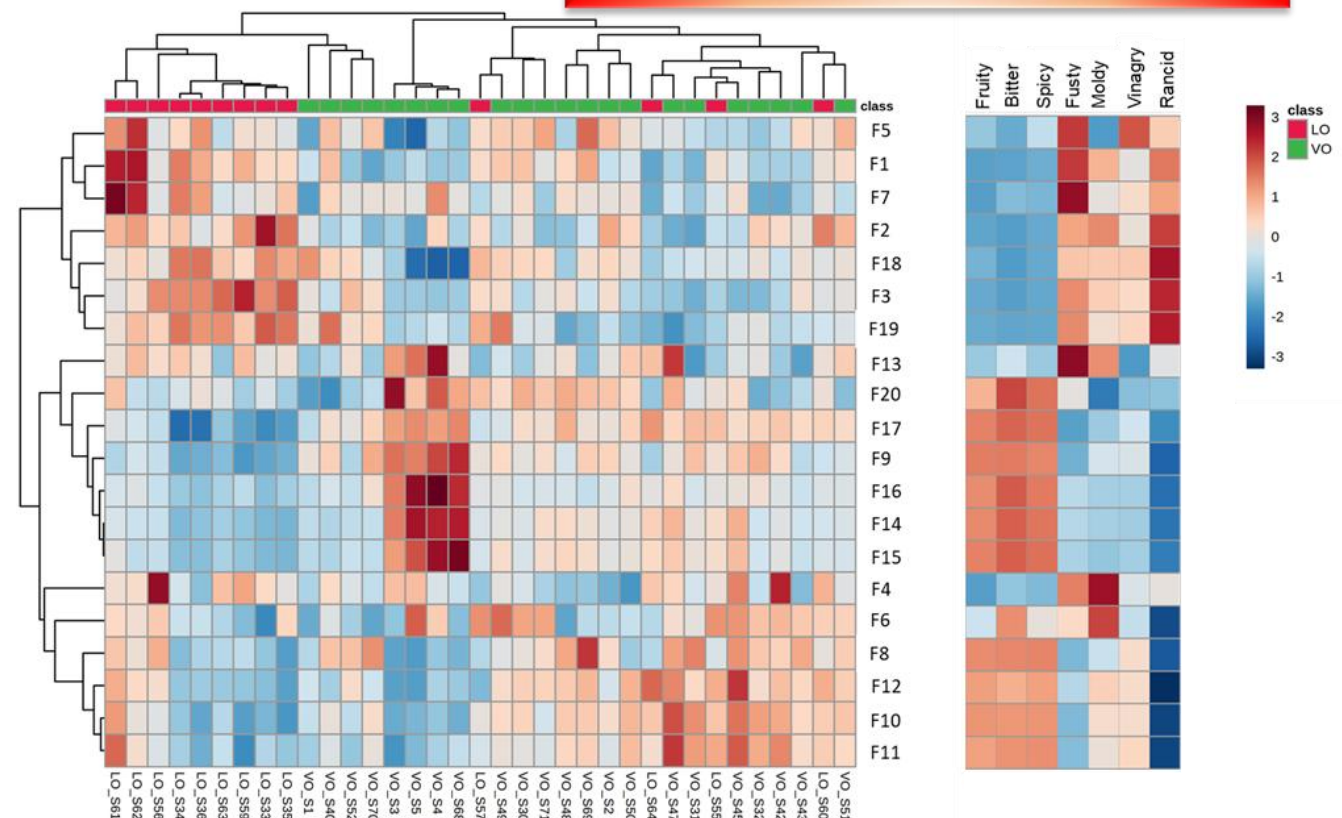


69 Samples:

34 EVO, 22 VO, and 13 LO



VO vs LO

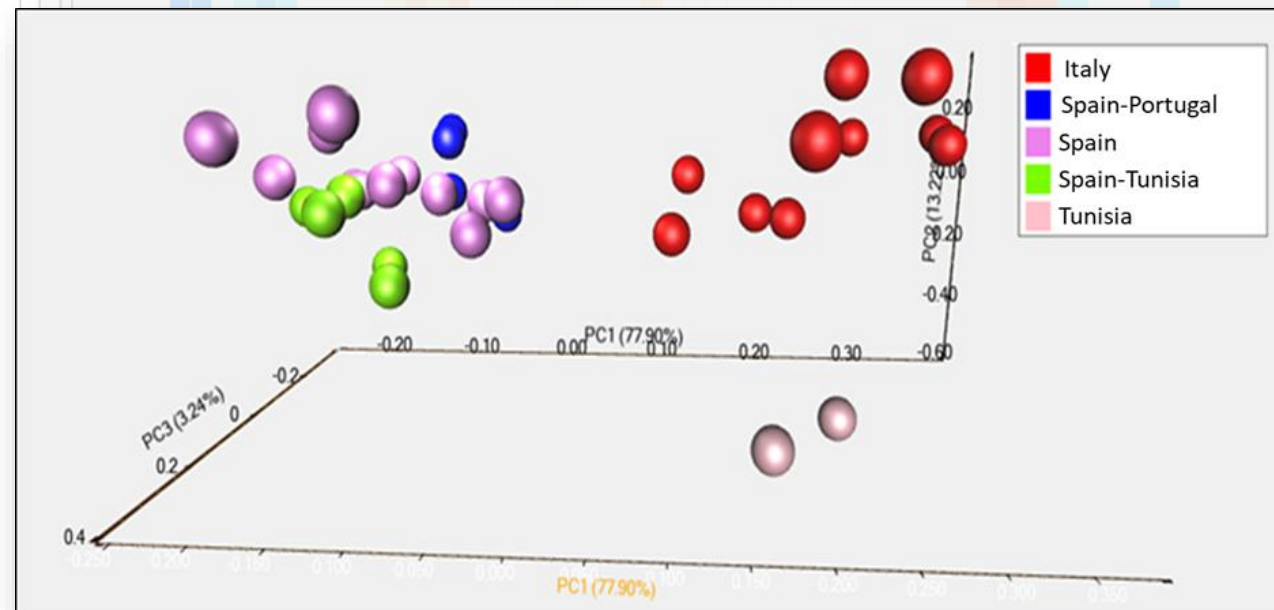
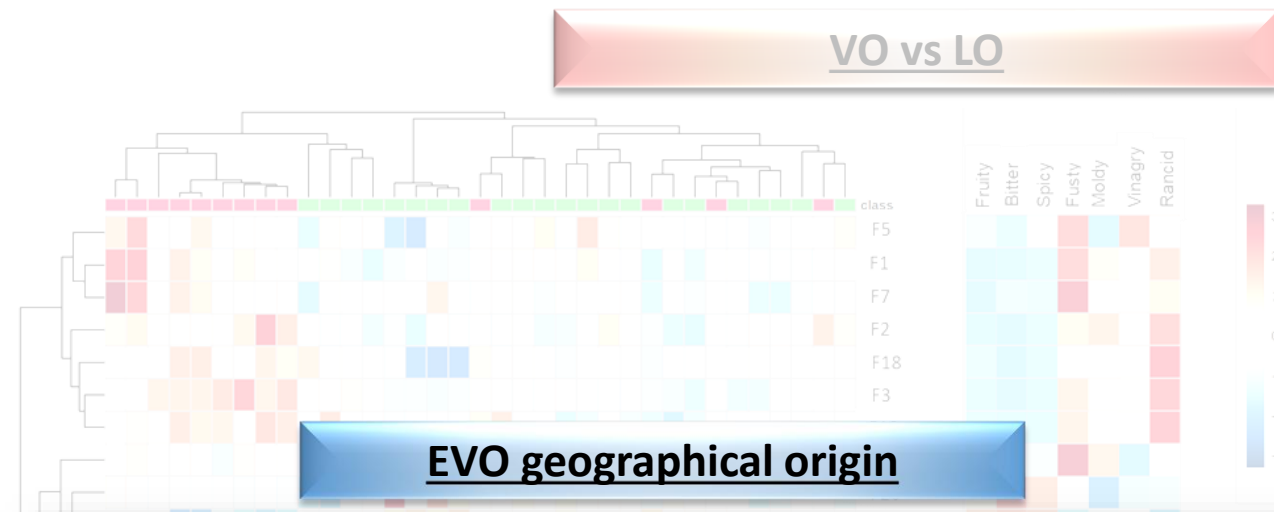
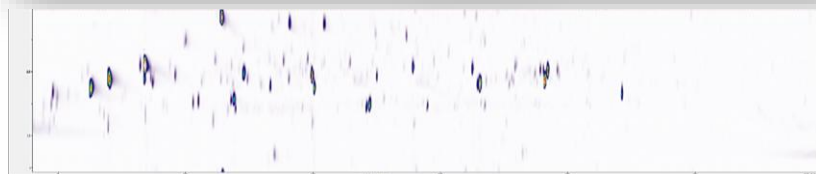
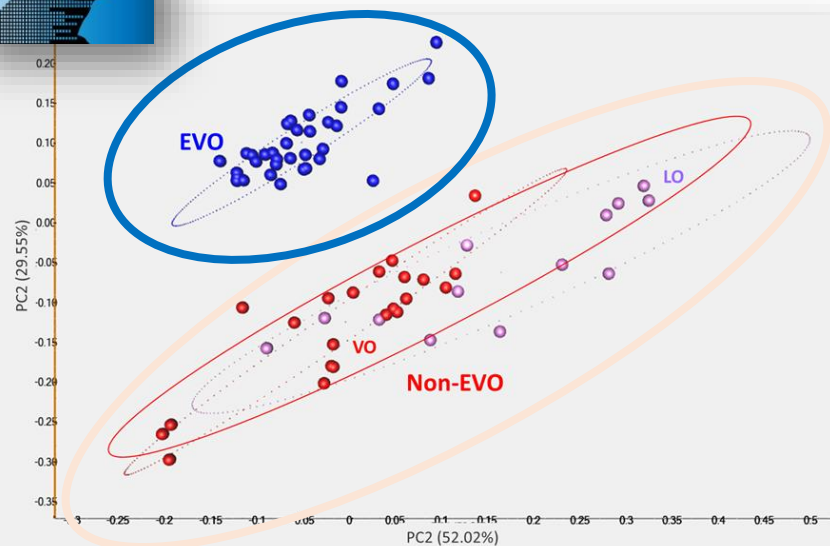


The case of olive oil

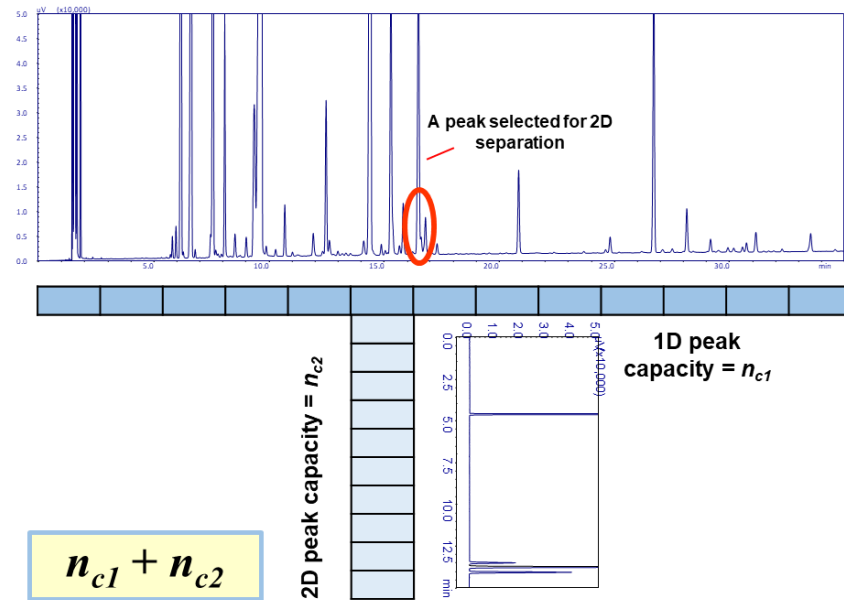


69 Samples:

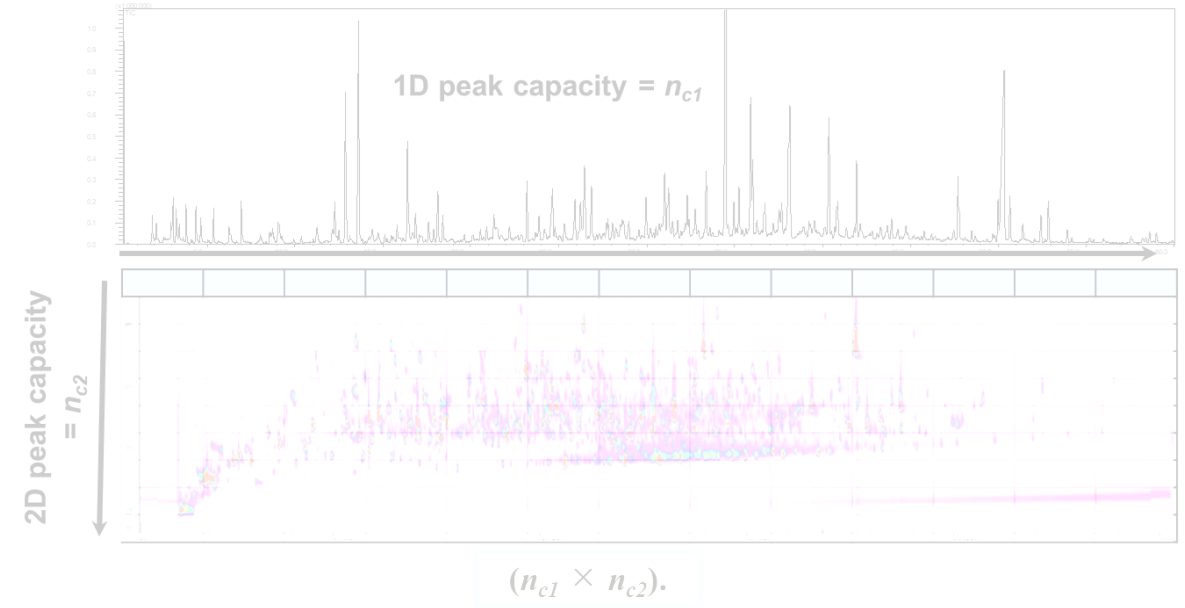
34 EVO, 22 VO, and 13 LO



Heart-cutting mode



Comprehensive mode



Ally of Sample Prep

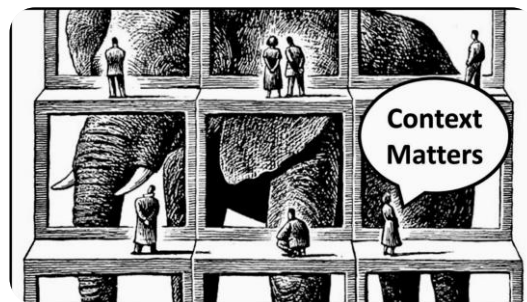


Unveil and explored sample multidimensionality



MINERAL OIL HYDROCARBONS (MOH): DEFINITION

a wide range of products deriving from petroleum distillation fractions



MOSH Mineral oil saturated hydrocarbons	MOAH Mineral oil aromatic hydrocarbons
n-alkanes branched alkanes mono-naphthenes di-naphthenes tri-naphthenes	mono ring aromatics, partly hydrogenated (right side) 2 ring aromatics, partly hydrogenated (right side) 3 ring aromatics, partly hydrogenated (right side)

-n-alkane
- isoalkane
- cycloalkane

Aromatic hydrocarbons, mainly
alkylated

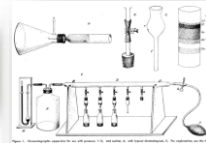
“reductionist
approach”

“interactionism” and -omics
sciences”

1800s **Wet chemistry era**
main components

1900s **Instrumental era**
minor and trace components

1906



1934 Introduction of the “Acidimeter” (automatic pHmeter)

1941 **LC**

1951 **GC**

1958 **Capillary column**

1959 **GC-MS**

1980 **LC-GC**

1991 **GC×GC**

2000 **LC×GC**

2005 **LC-GC×GC**



151. A NEW FORM OF CHROMATOGRAM
EMPLOYING TWO LIQUID PHASES
1. A THEORY OF CHROMATOGRAPHY
2. APPLICATION TO THE HIGHER
OF THE HIGHER

By A. J. P. J.

From the Wool Industries Research Institute

Gas-liquid Partition Chromatography: the
Micro-estimation of Volatile Fatty Acids
Formic Acid to Dodecanoic Acid

By A. T. JAMES AND A. J. P. MARTIN
National Institute for Medical Research, Mill Hill, London

(Received 5 June 1951)

Time-of-Flight Mass Spectrometry and
Gas-Liquid Partition Chromatography

R. S. GOMES
Spectroscopy

Multidimensional High Performance
Liquid Chromatography*

Journal of Chromatographic Science, Vol. 29, June 1991

Comprehensive Two-Dimensional Gas Chromatography
using an On-Column Thermal Modulator Interface

Zaiyou Liu and John B. Phillips*
Department of Chemistry & Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

Comprehensive LC × GC for Enhanced Headspace Analysis

Wes W. C. Quigley
Department of Chemistry,
University of



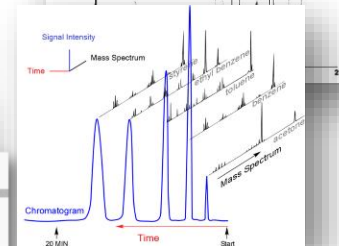
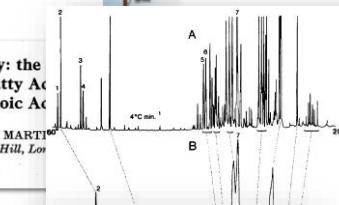
Comprehensive multi-dimensional chromatographic studies on the
separation of saturated hydrocarbon ring structures
in petrochemical samples

R. Edam^a, J. Blomberg^{b,c}, H.-G. Janssen^c, P.J. Schoenmakers^a

^a University of Amsterdam, Van 't Hoff Institute for Molecular Sciences, Amsterdam, The Netherlands

^b Shell Global Solutions, Shell Research & Technology Centre Amsterdam, Amsterdam, The Netherlands

^c Unilever Research and Development, Central Analytical Science, Vlaardingen, The Netherlands



Chromatography:

➤ Maximize separation resolution

Journal of Chromatography, 295 (1984) 55-61

Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,706

1984

COUPLING OF HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY
WITH CAPILLARY GAS CHROMATOGRAPHY

K. GROB, Jr.*, D. FRÖHLICH, B. SCHILLING, H. P. NEUKOM and P. NÄGELI

Kantonales Labor, P.O. Box, CH-8030 Zürich (Switzerland)

(Received March 6th, 1984)



Mineral oil



LC-GC

Received: 19 August 2020 | Revised: 4 October 2020 | Accepted: 26 October 2020

DOI: 10.1002/jssc.202000901

REVIEW ARTICLE

Journal of
SEPARATION SCIENCE

Evolution of hyphenated techniques for mineral
oil analysis in food

Nicola Sdrigotti^{1,2} | Maurine Collard¹ | Giorgia Purcaro¹

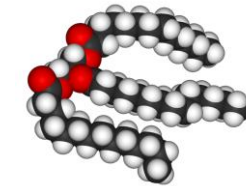
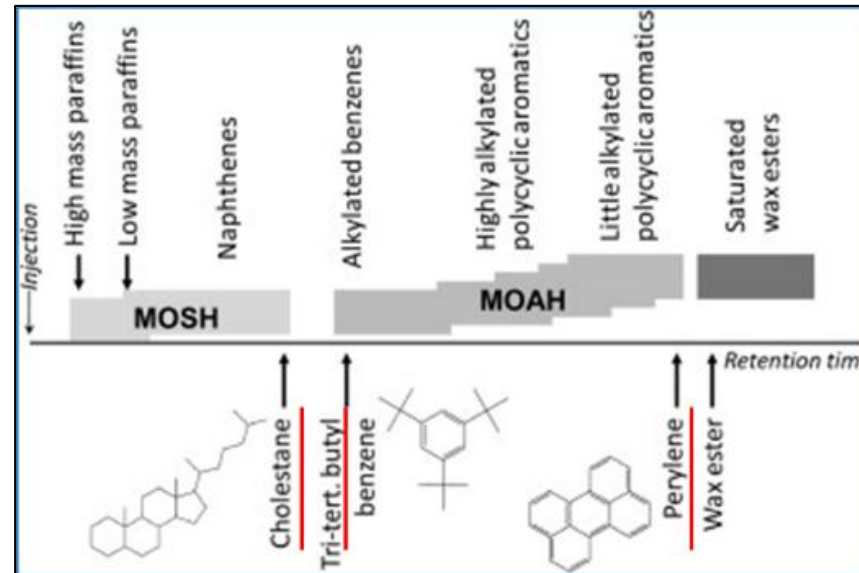
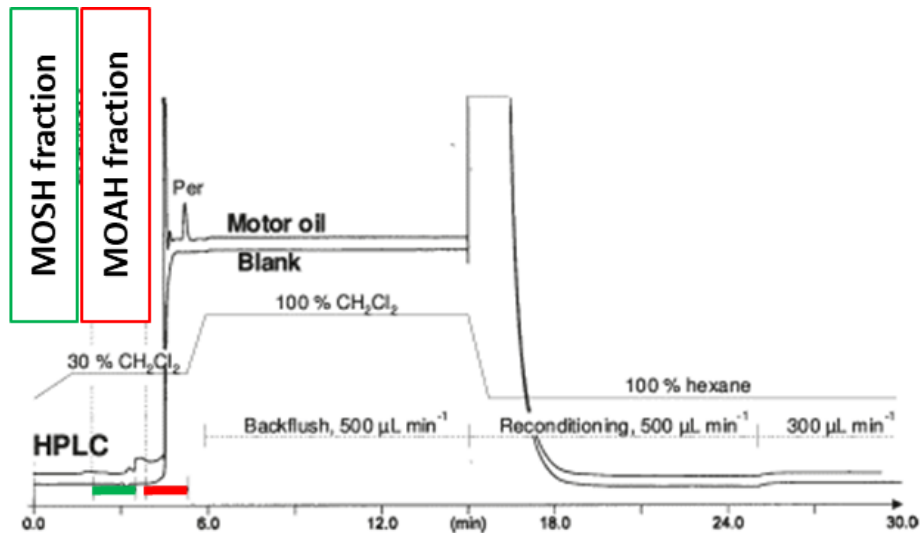
The case of Mineral Oil Hydrocarbons (MOSH/MOAH)



LC

Sample preparation step

- ✓ Purification from TAGs
- ✓ Pre-fractionation



TAGs and more polar compounds retained in the LC silica column

+ C11, C13 and CyCy (cyclohexylcyclohexane)

C11/CyCy

loss of volatiles

C13/CyCy

possible coelution

CyCy

quantification

+ 5B (pentyl benzene), 1MN (1-Me Na) and 2MN (2-Me Na)

5B

loss of volatiles

1MN=2MN

possible coelution/

quantification

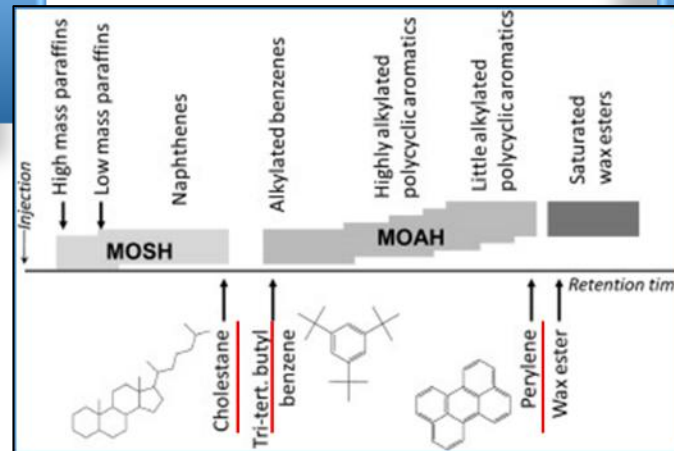
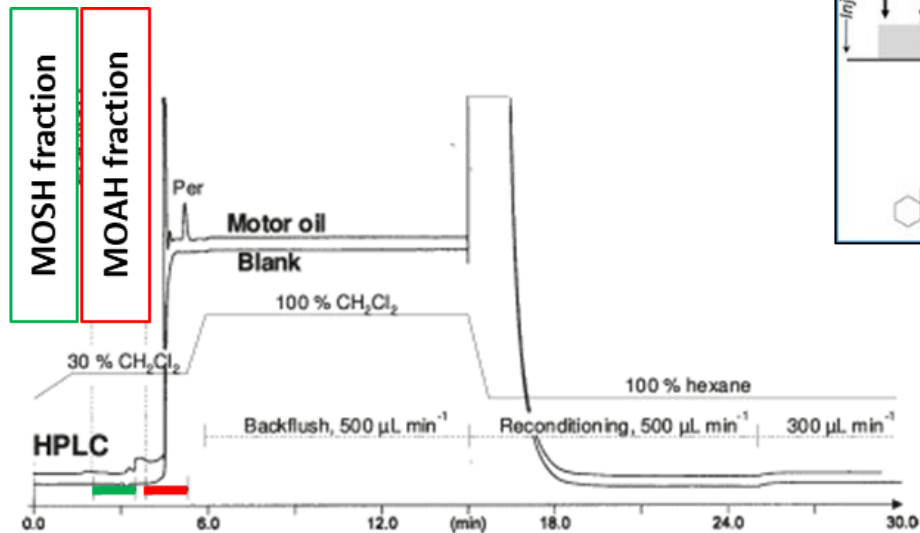
The case of Mineral Oil Hydrocarbons (MOSH/MOAH)



LC

Sample preparation step

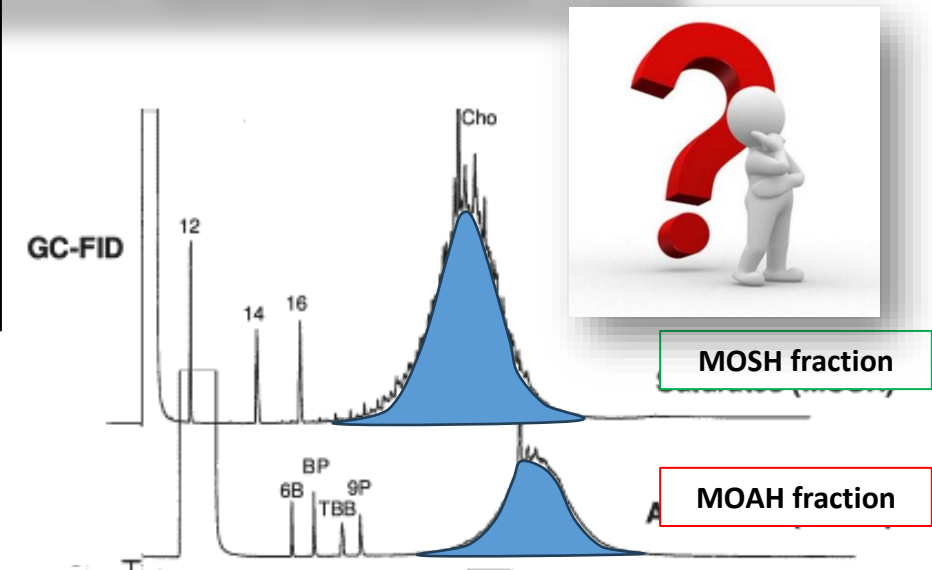
- ✓ Purification from TAGs
- ✓ Pre-fractionation

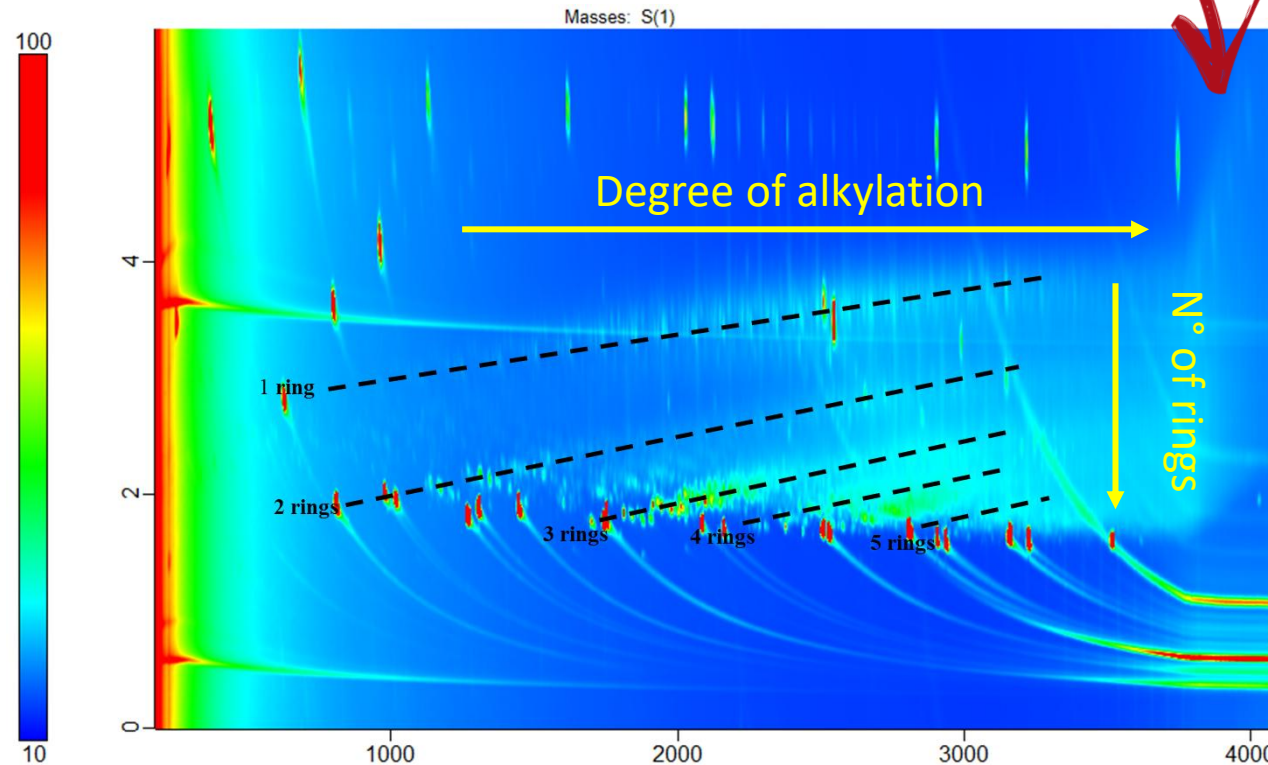
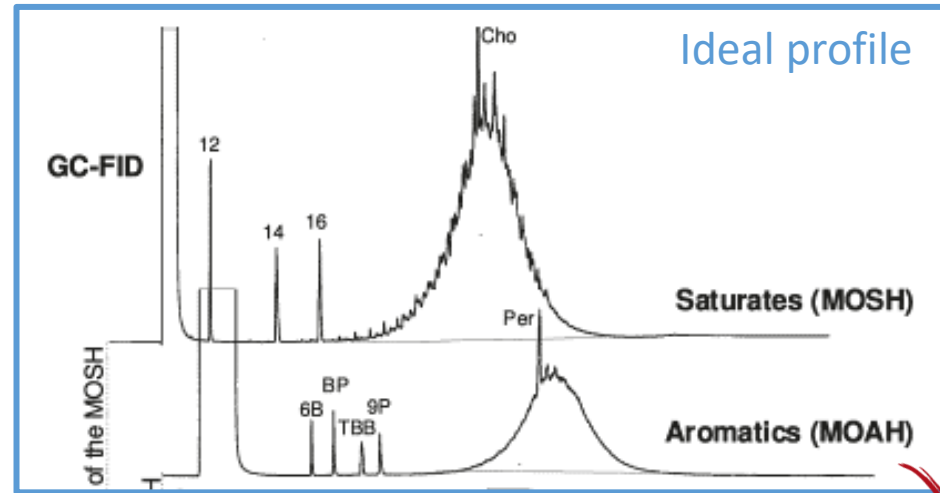


GC

Analytical Determination

- ✓ Analytical Separation
- ✓ Quantification





MOH

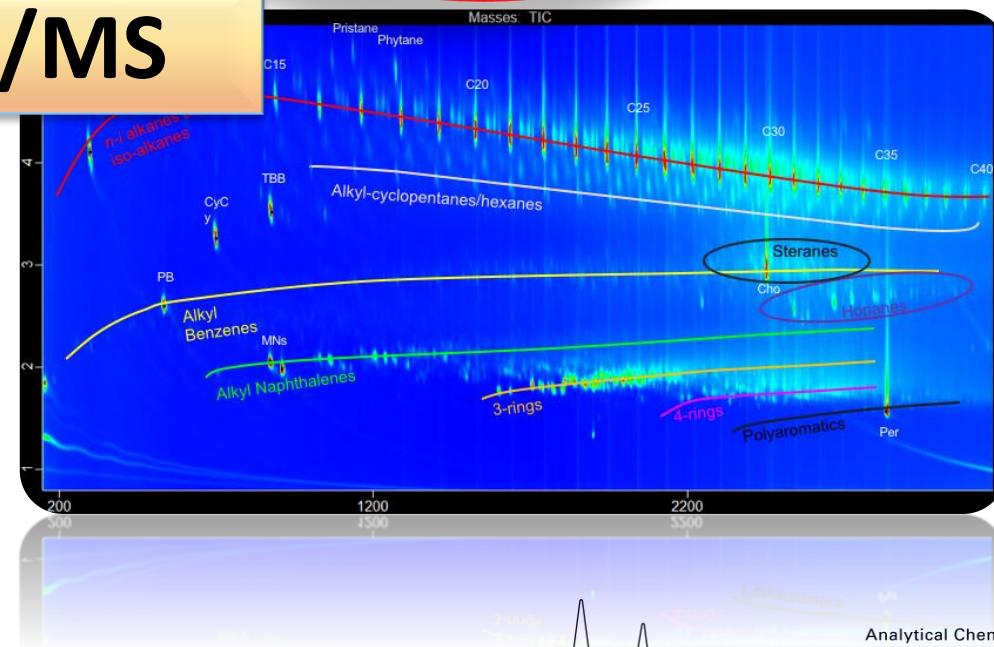
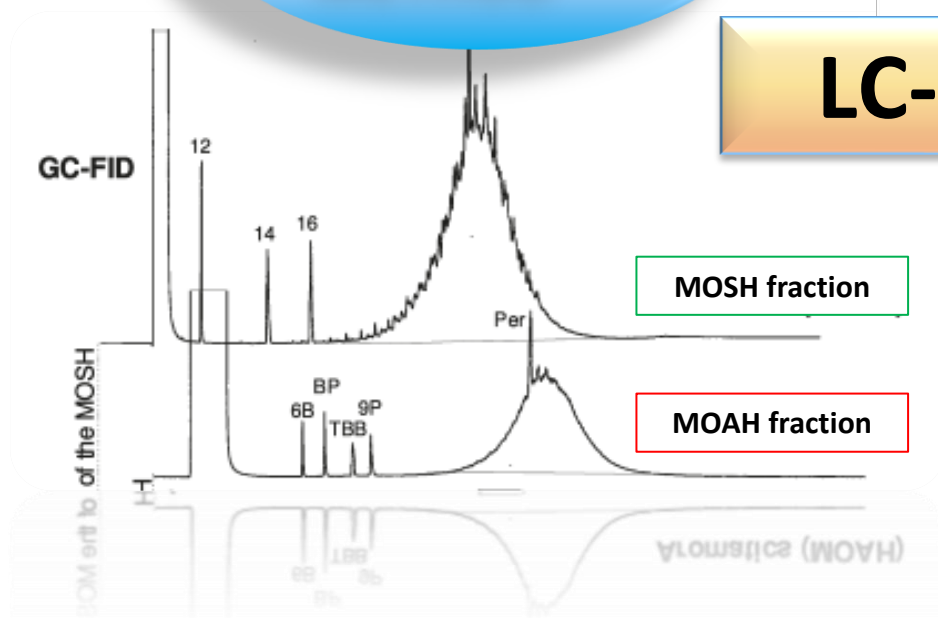
LC-GC

**ROUTINE
METHOD**

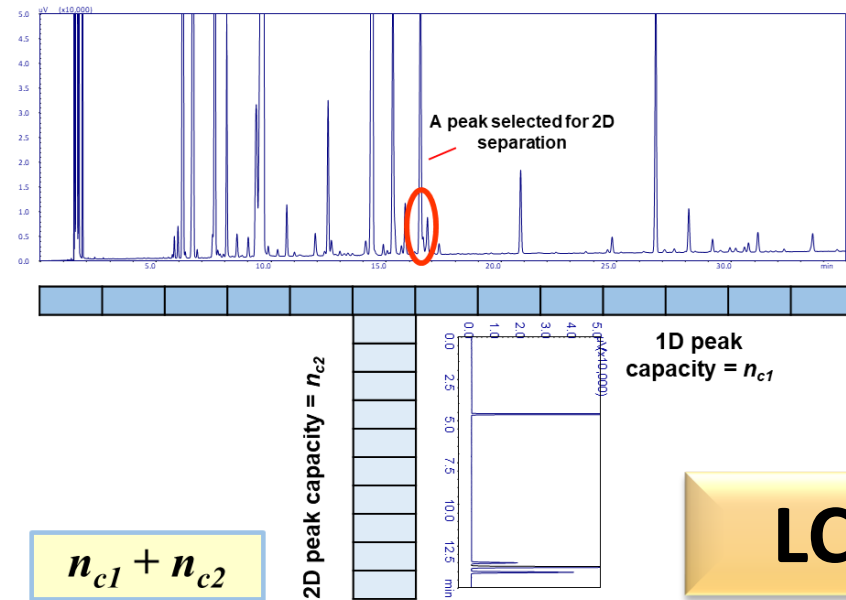
GC×GC

**CONFIRMATORY
METHOD**

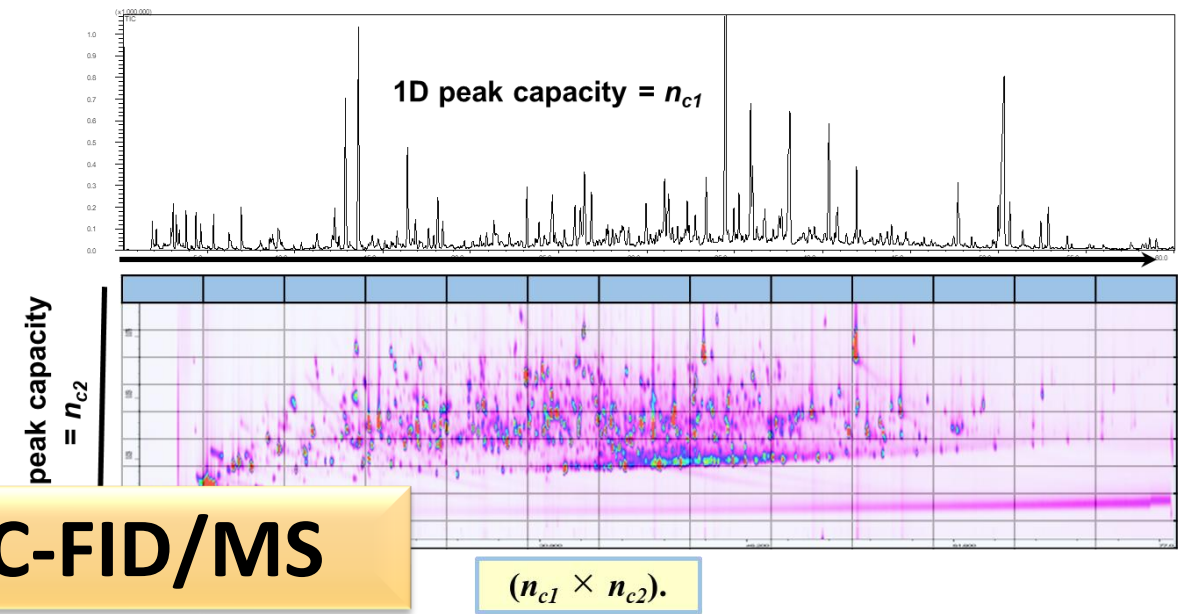
LC-GC×GC-FID/MS



Heart-cutting mode



Comprehensive mode



LC-GC×GC-FID/MS

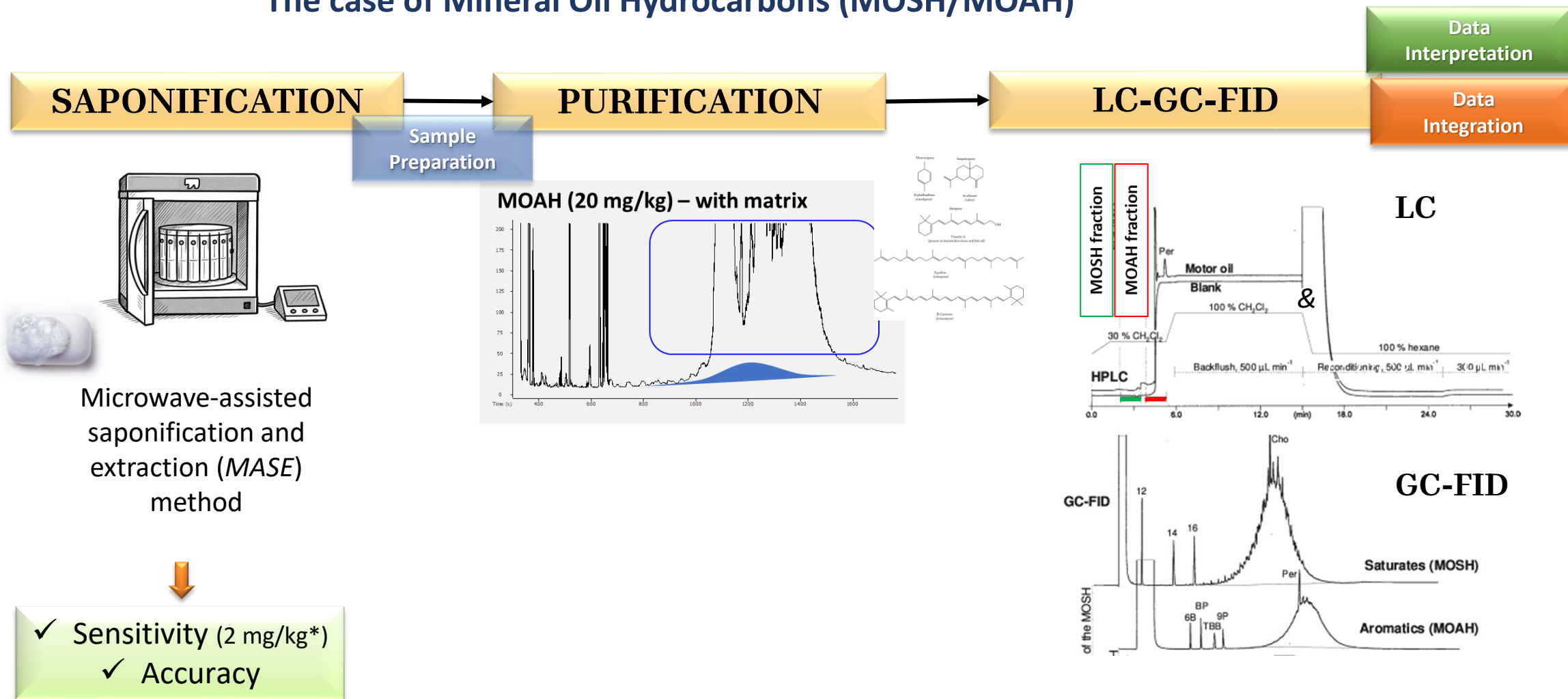
Ally of Sample Prep



Unveil and explored sample multidimensionality



The case of Mineral Oil Hydrocarbons (MOSH/MOAH)



The case of Mineral Oil Hydrocarbons (MOSH/MOAH)

SAPONIFICATION

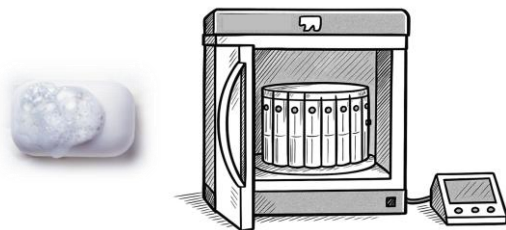
PURIFICATION

LC-GC-FID

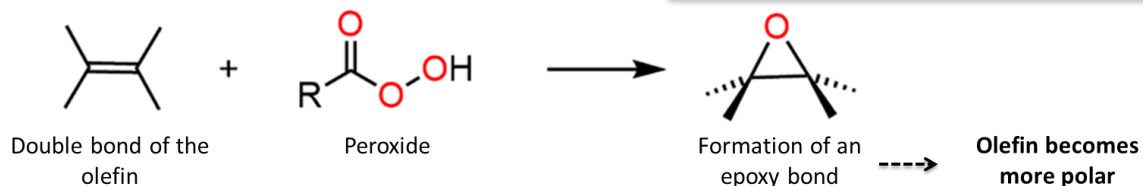
Data
Interpretation

Data
Integration

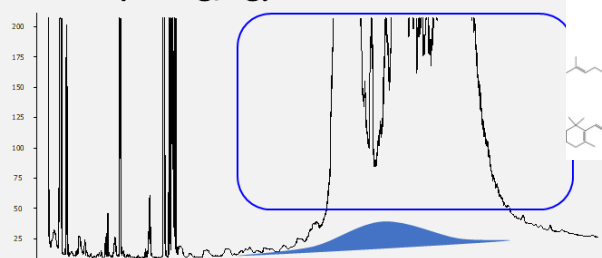
Sample
Preparation



Microwave-assisted saponification
and extraction (MASE) method

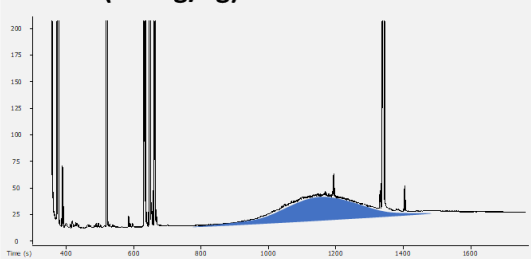


MOAH (20 mg/kg) – with matrix

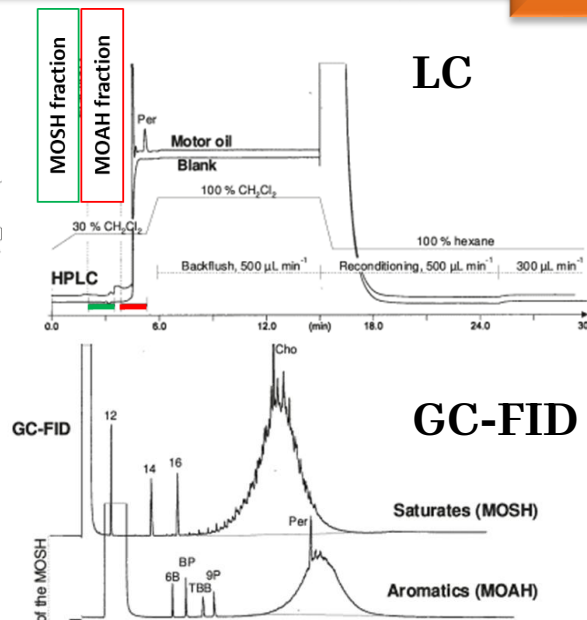


EPOXIDATION

MOAH (20 mg/kg) – without matrix



Works rather well but also **attacks**
MOAH due to their double bonds



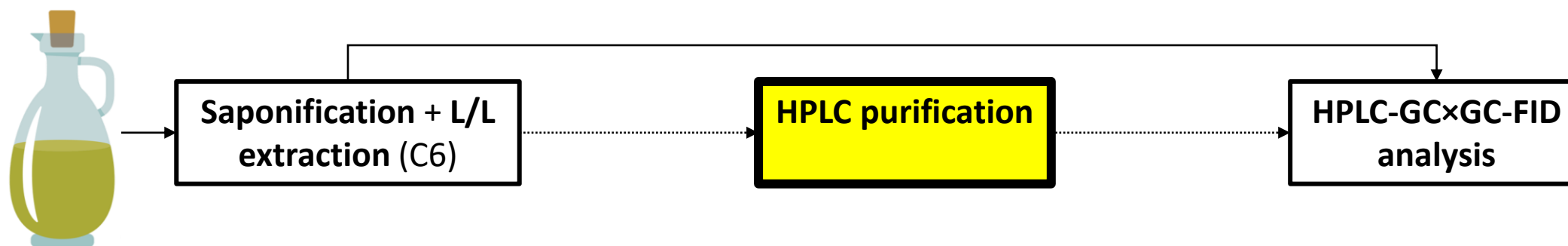
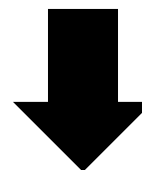
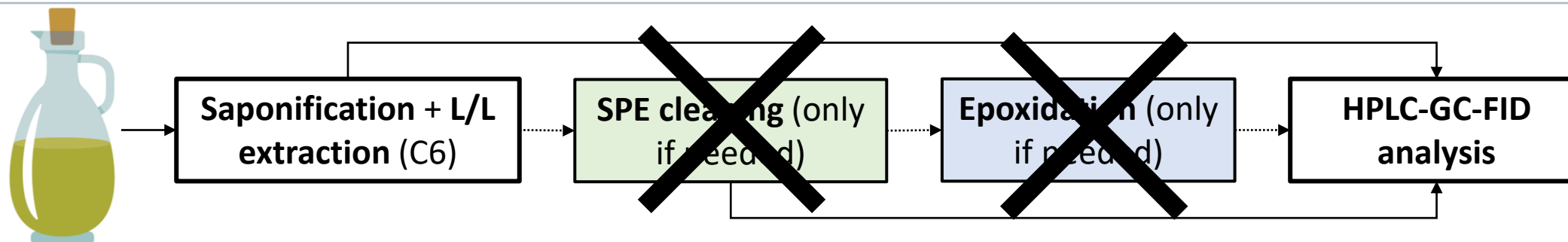
ISO 20122:2024

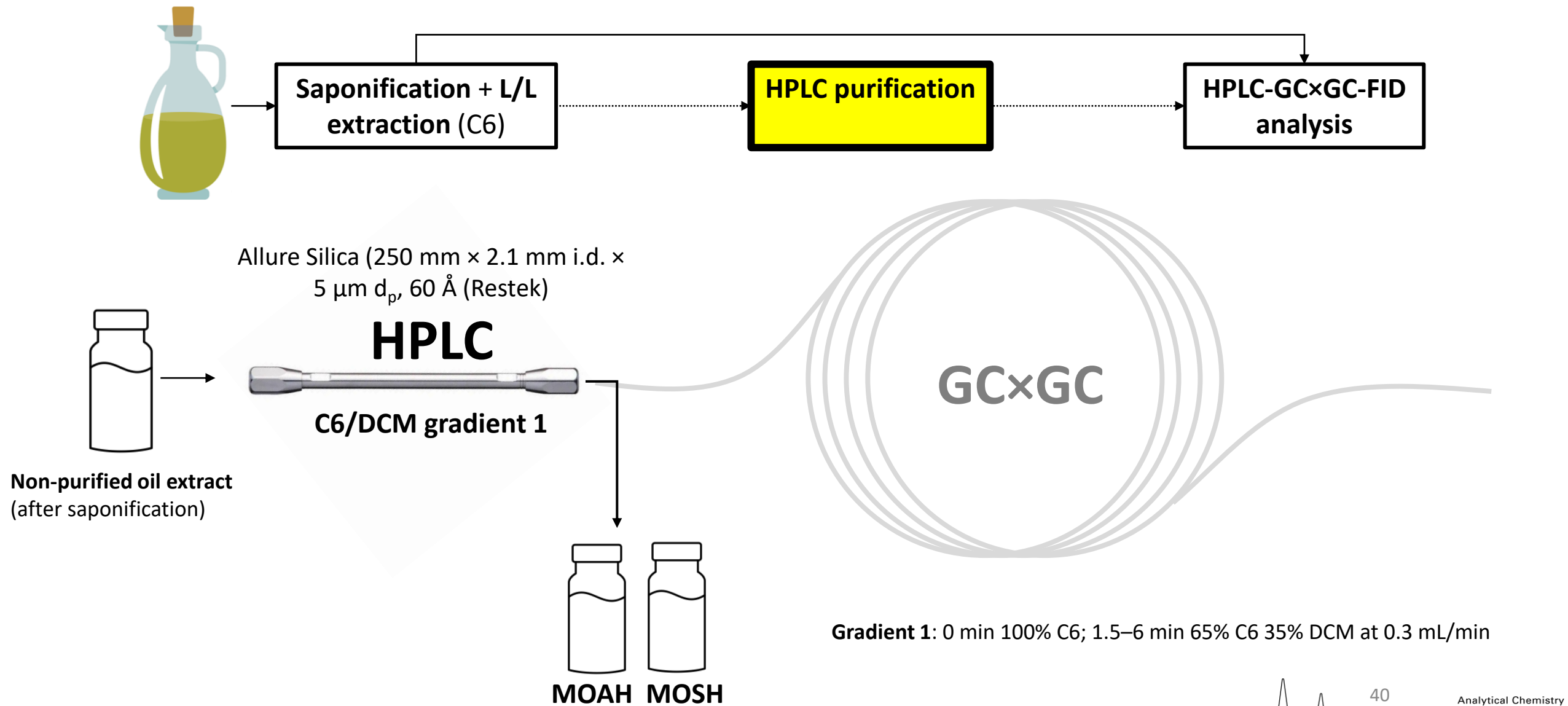
Vegetable oils — Determination of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) with online-coupled high performance liquid chromatography-gas chromatography-flame ionization detection (HPLC-GC-FID) analysis — Method for low limit of quantification

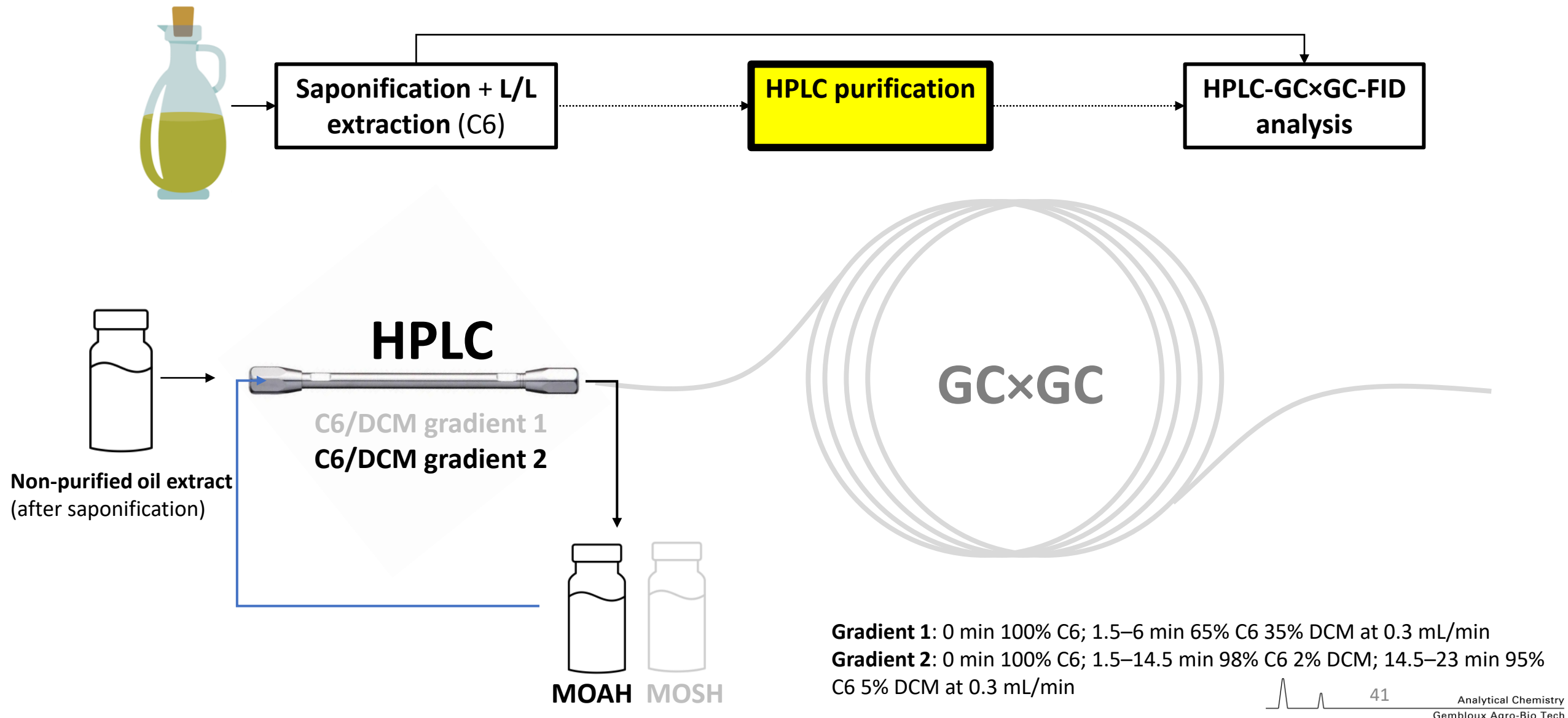


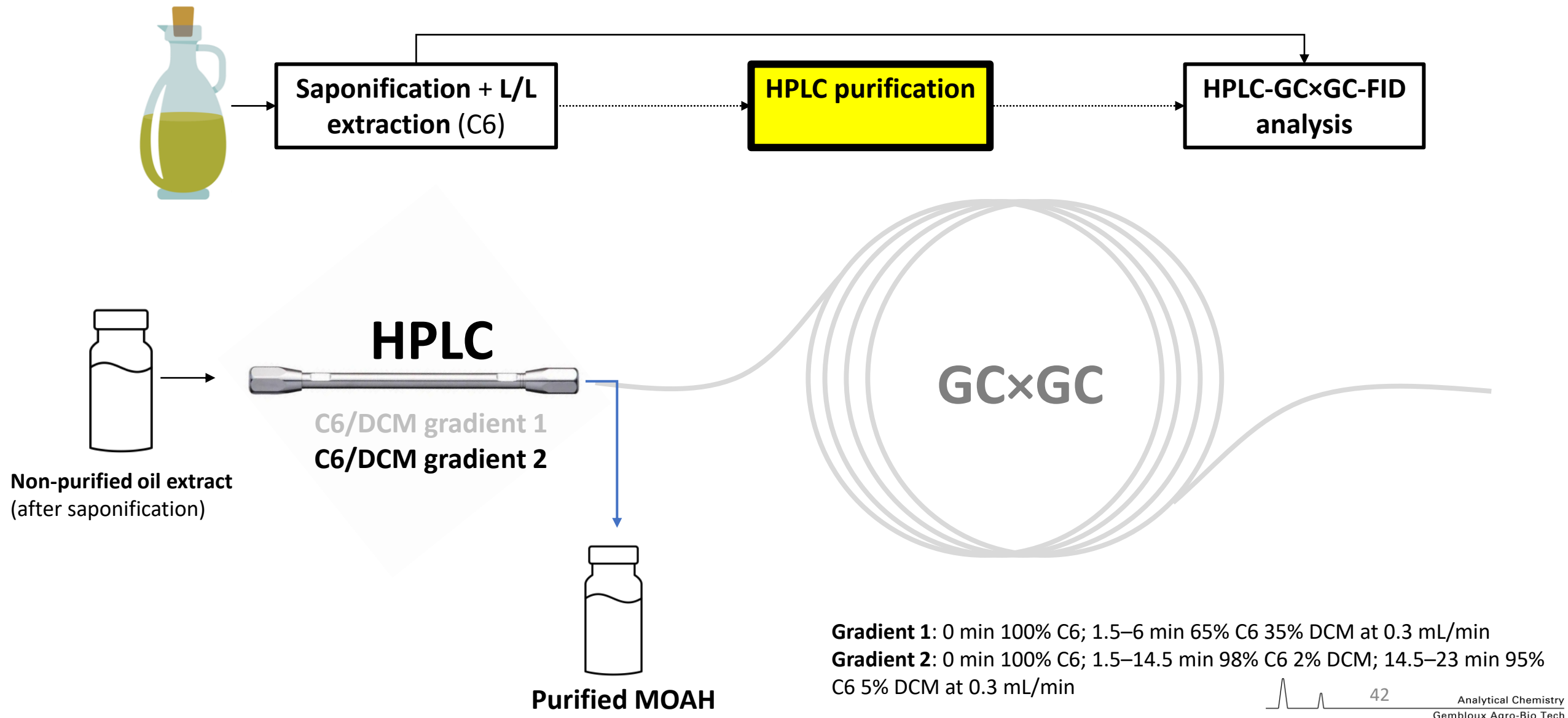
Analytical Chemistry
Gembloux Agro-Bio Tech

ISO 20122:2024 **Vegetable oils** — Determination of mineral oil saturated hydrocarbons (MOSH) and aromatic hydrocarbons (MOAH) with online coupled HPLC-GC-FID analysis — Method for low limit of quantification









2025

Journal of Chromatography A 1743 (2025) 465684

Contents lists available at ScienceDirect

Journal of Chromatography A

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



Purification of mineral oil aromatic hydrocarbons and separation based on the number of aromatic rings using a liquid chromatography silica column. An alternative to epoxidation

Aleksandra Gorska^{a,*,} Grégory Bauwens^{a,} Marco Beccaria^{b,} Giorgia Purcaro^{a,*}

LC-GC×GC-FID/MS



Very good removal of carotenoids and squalene

Other terpenoids are less well removed



Epoxidation

mCPBA

82% ± 10%

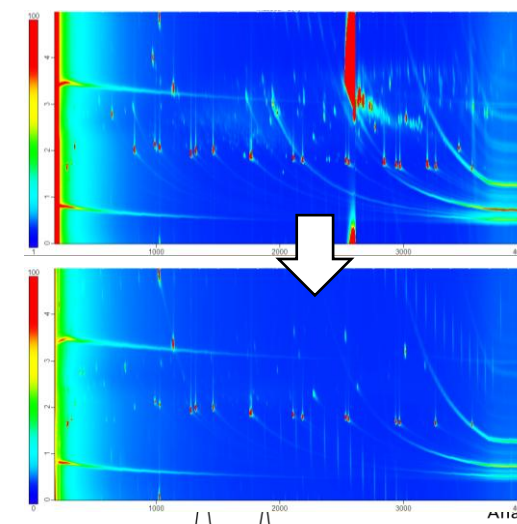
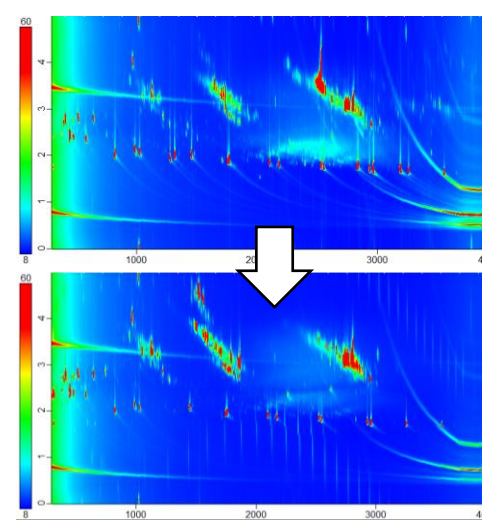
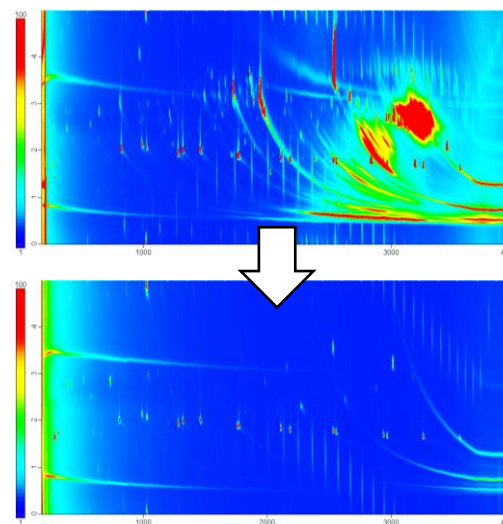
performic acid

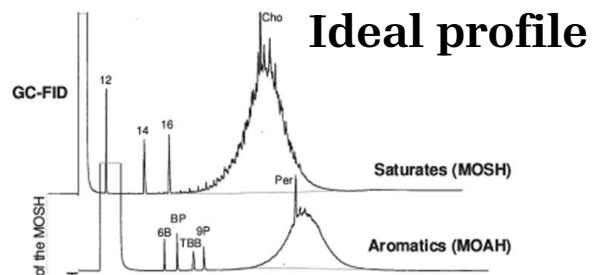
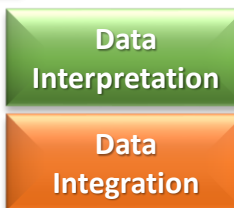
71 ± 16%



MOAH Recovery LC Purification:

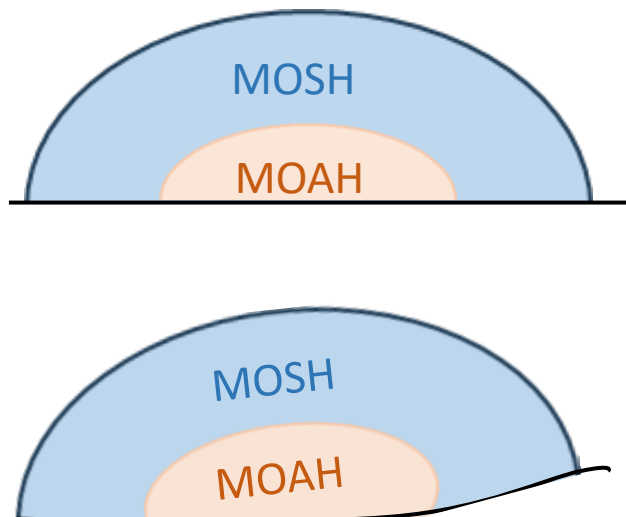
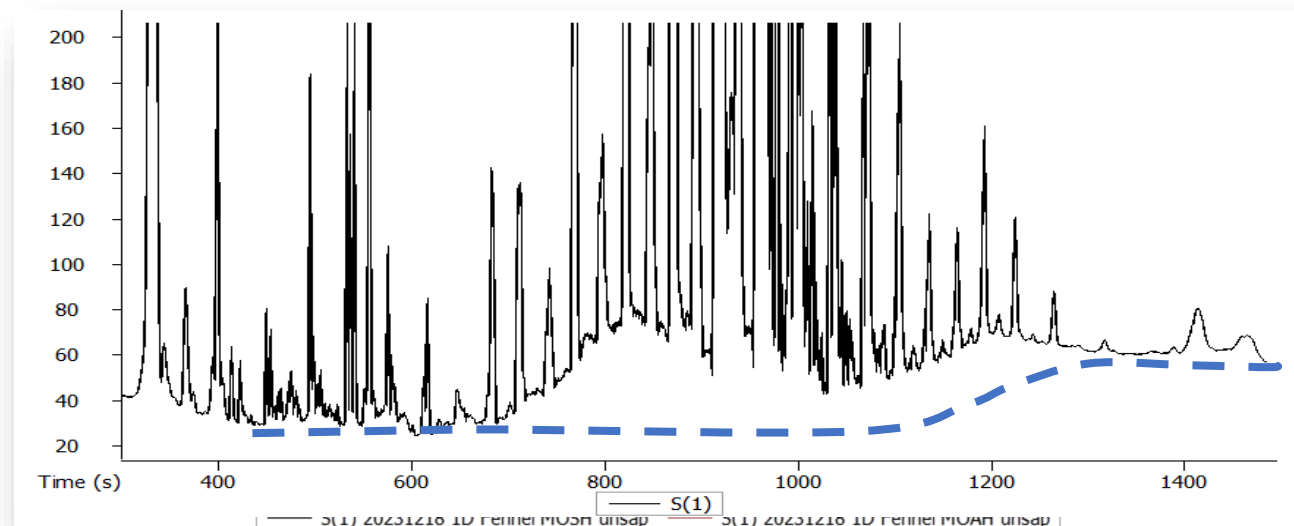
94% ± 2%





➤ **Baseline**

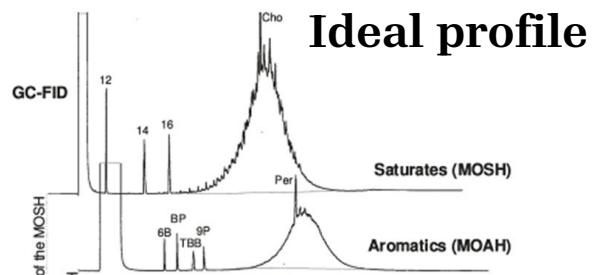
MOSH vs MOAH – No purification



EXTRACTION/SAPONIFICATION

PURIFICATION

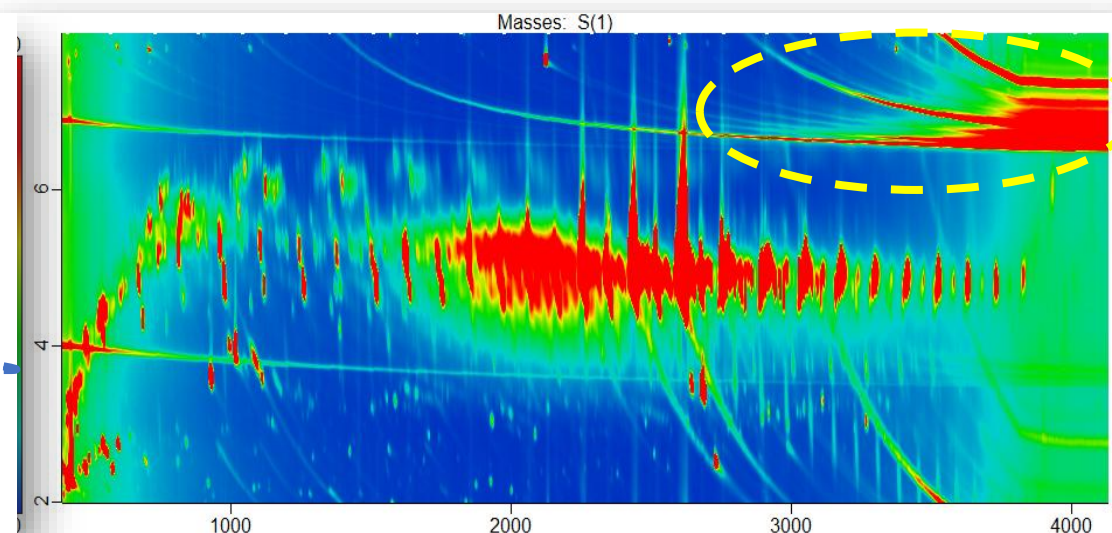
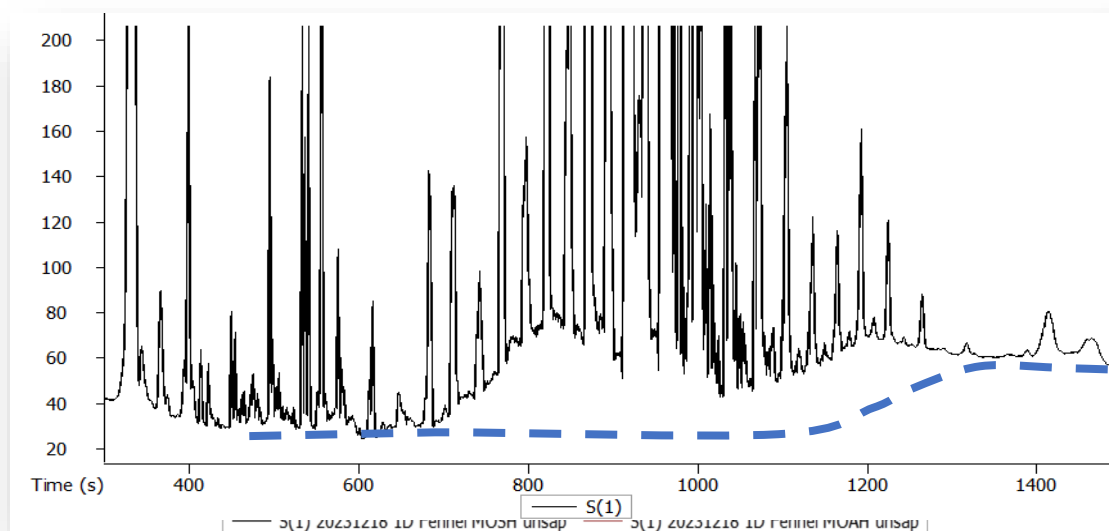
LC-GC×GC-FID/MS



How to support the interpretation?

GC×GC

More accurate quantification



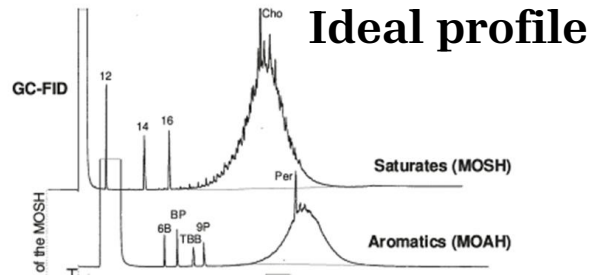
EXTRACTION/SAPONIFICATION

PURIFICATION

LC-GC-FID

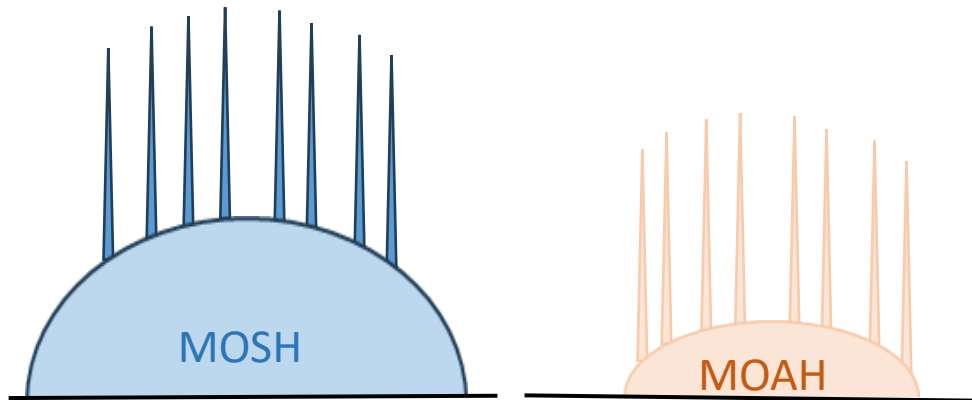
Data
Interpretation

Data
Integration



- Baseline
- Riding peaks

Trimming or not the riding peaks? And how?



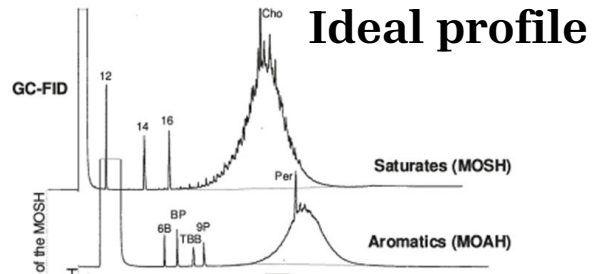
EXTRACTION/SAPONIFICATION

PURIFICATION

LC-GC-FID

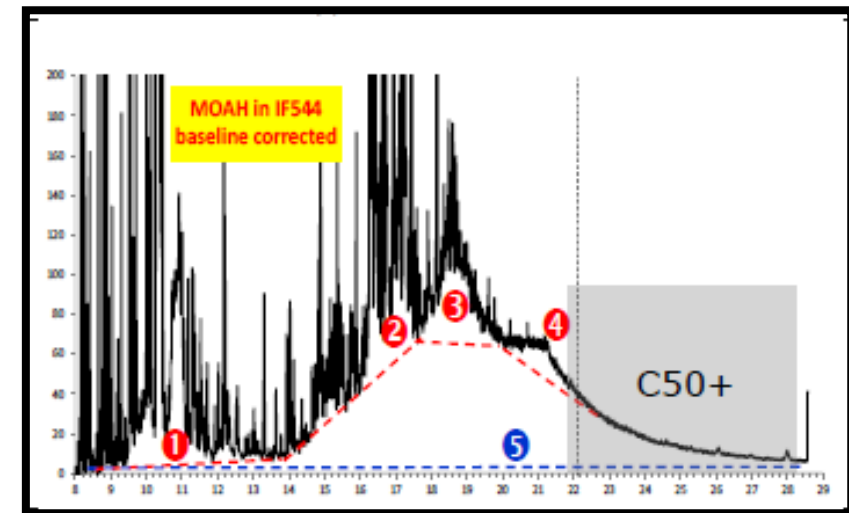
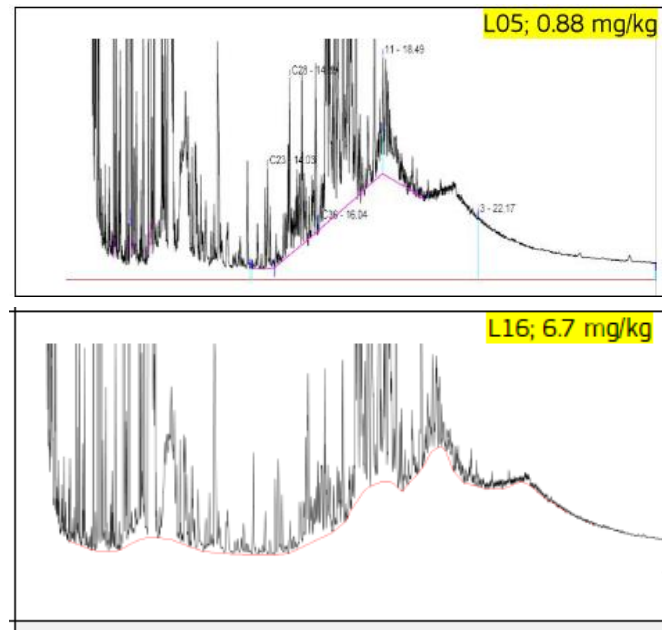
Data
Interpretation

Data
Integration



- Baseline
- Riding peaks

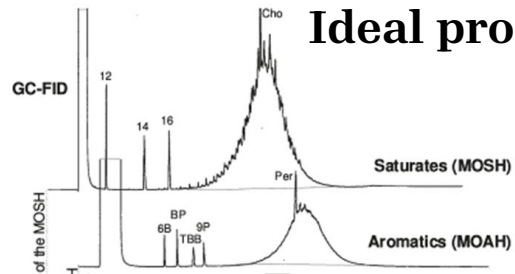
Trimming or not the riding peaks? And How?



EXTRACTION/SAPONIFICATION

PURIFICATION

LC-GC×GC-FID/MS

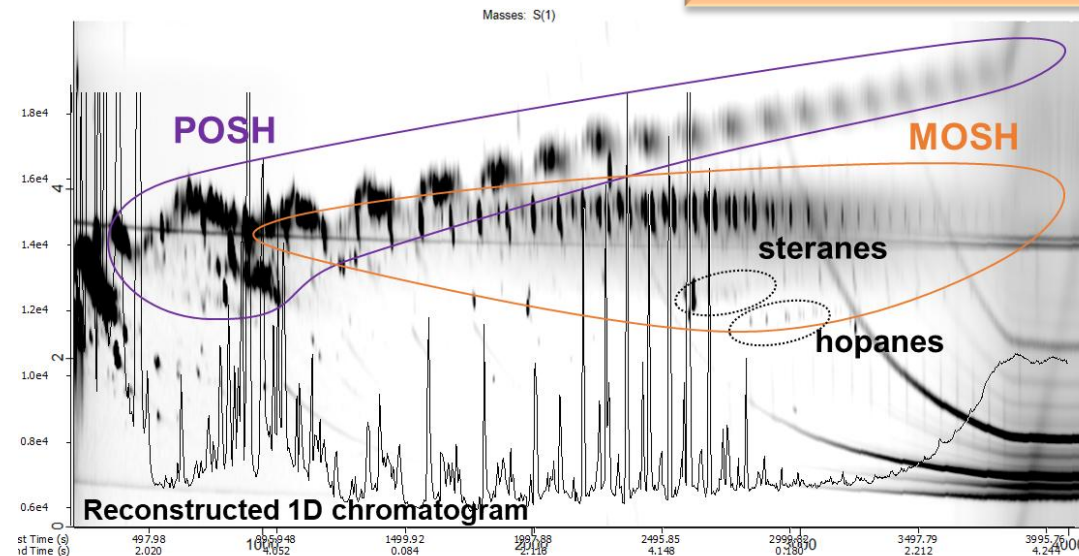


Ideal profile

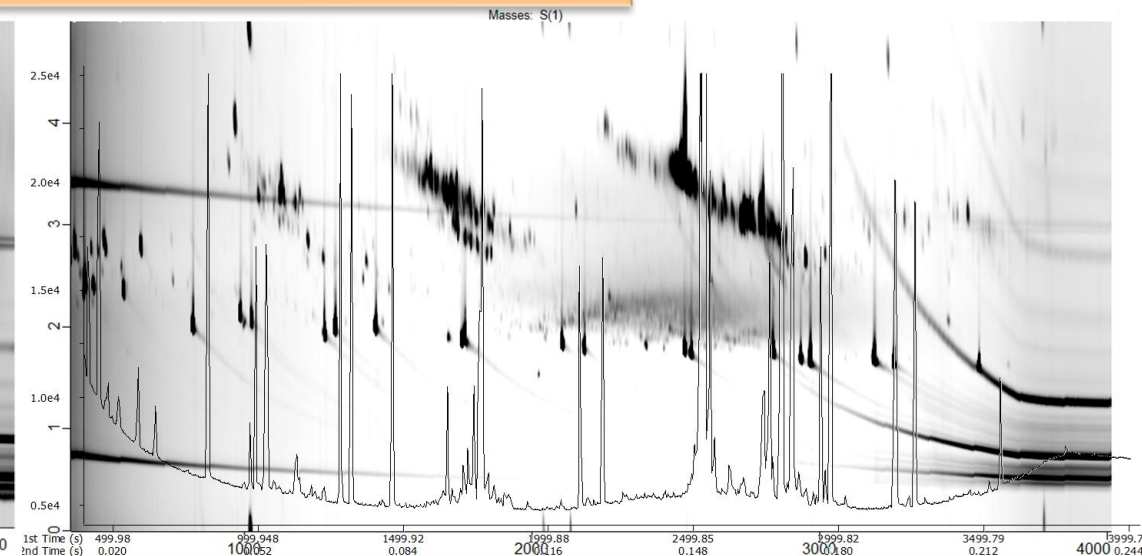
How to support the interpretation?

GC×GC

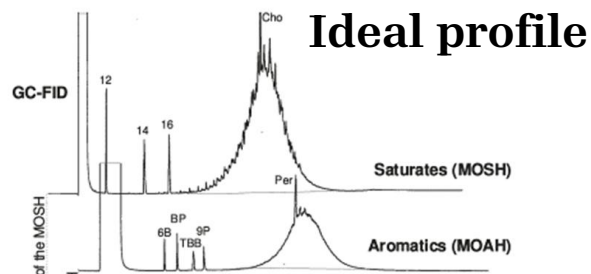
Easier interpretation



MOSH

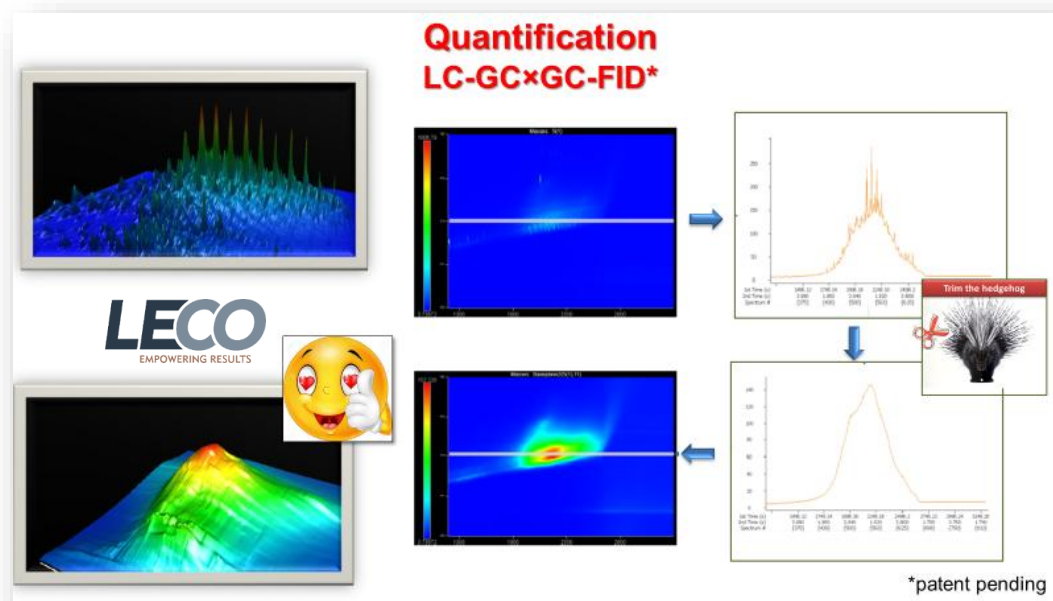


MOAH

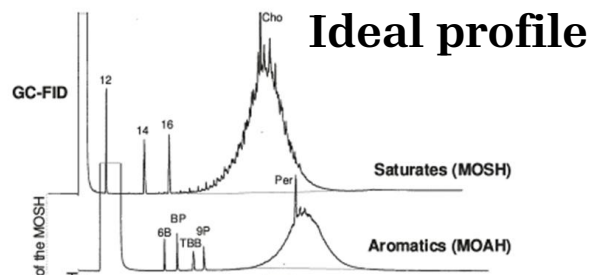


How to support the interpretation?

GC×GC

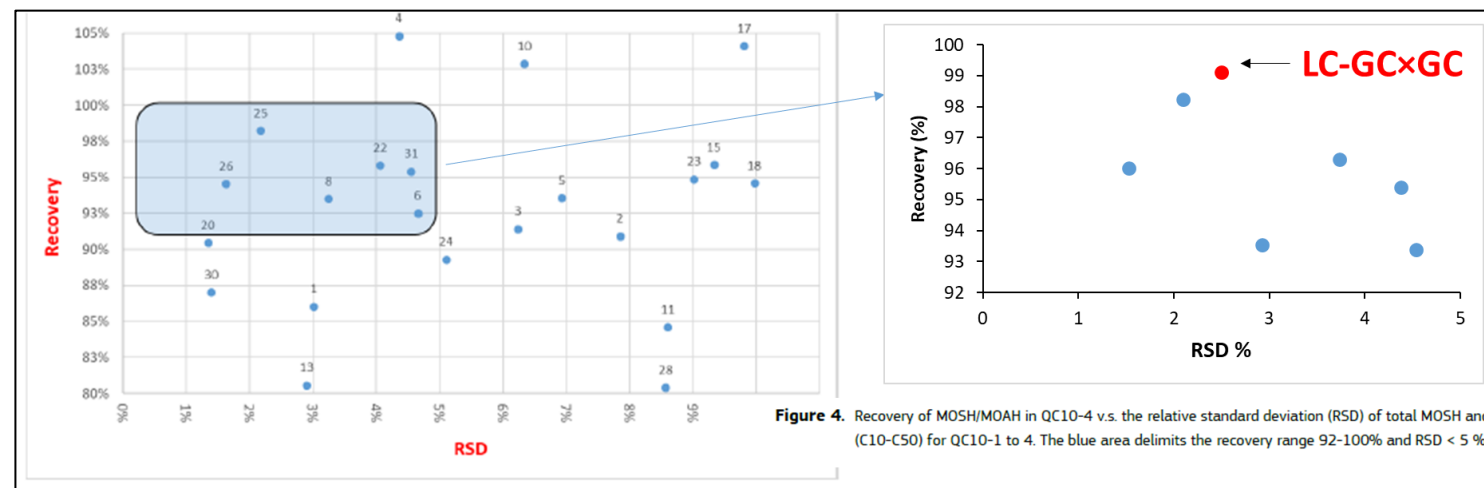


**MOSH & MOAH
& sub-classes
quantification in 2D**



How to support the interpretation?

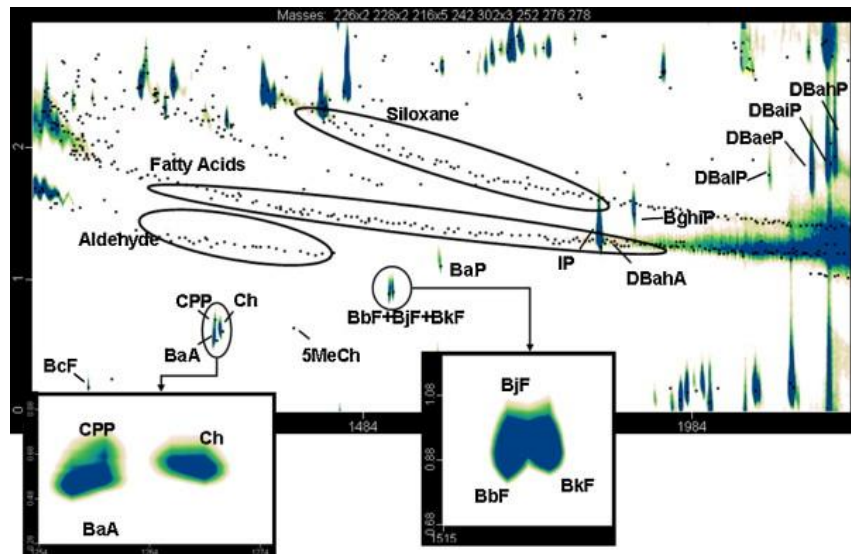
GC×GC



Analysis of PAHs

➤ Do you really need GC×GC separation to analyze PAHs?

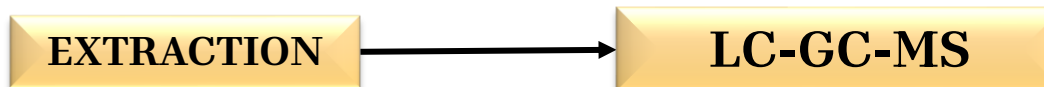
NOT for separation



Purcaro et al. JCA 2007 1-2 284-291

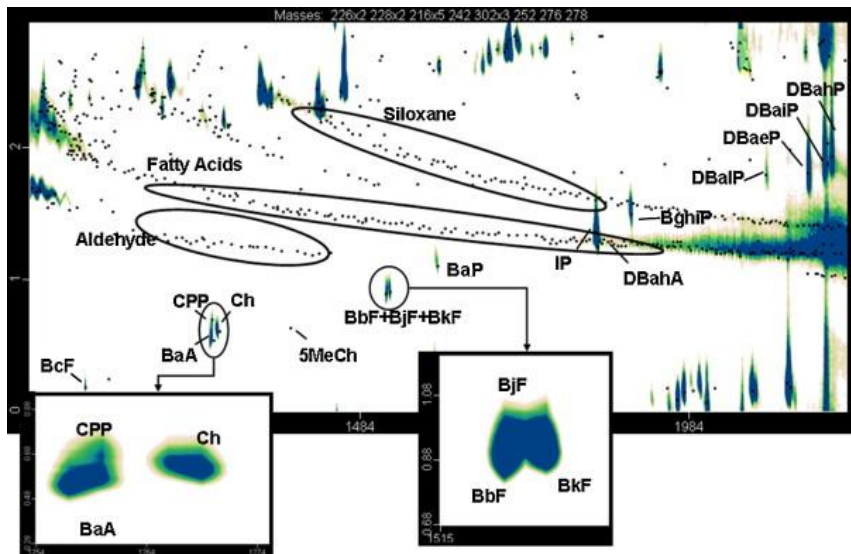
Analysis of PAHs

➤ Do you really need GC×GC separation to analyze PAHs?

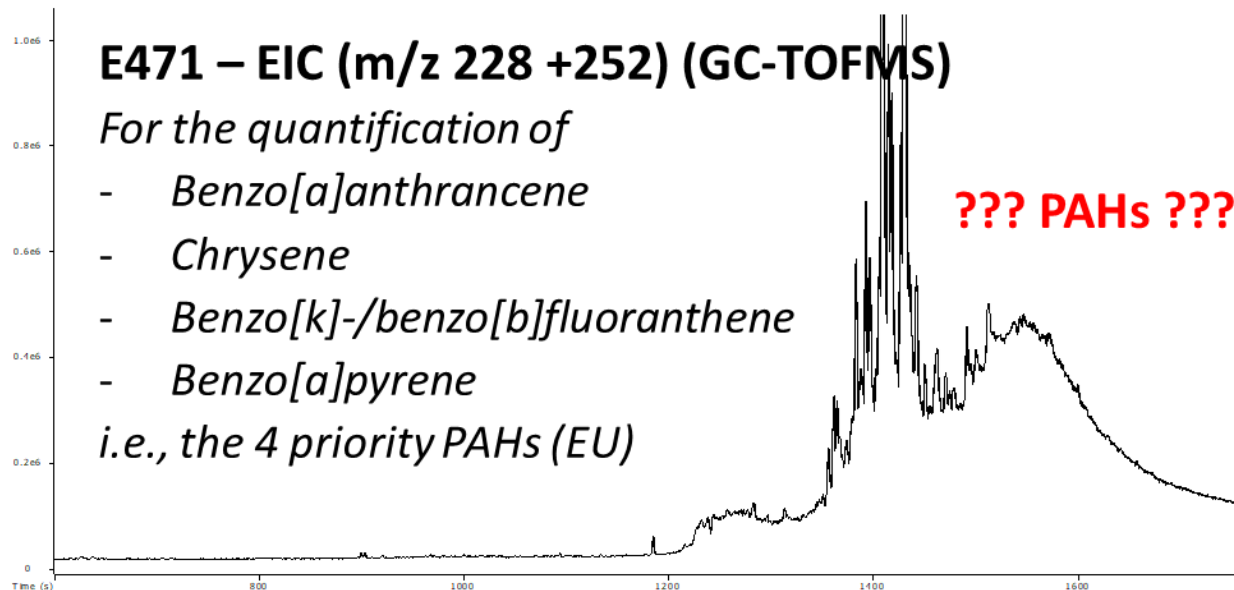


Analysis of PAHs in food additives

mono- and diglycerides of fatty acids (E471)



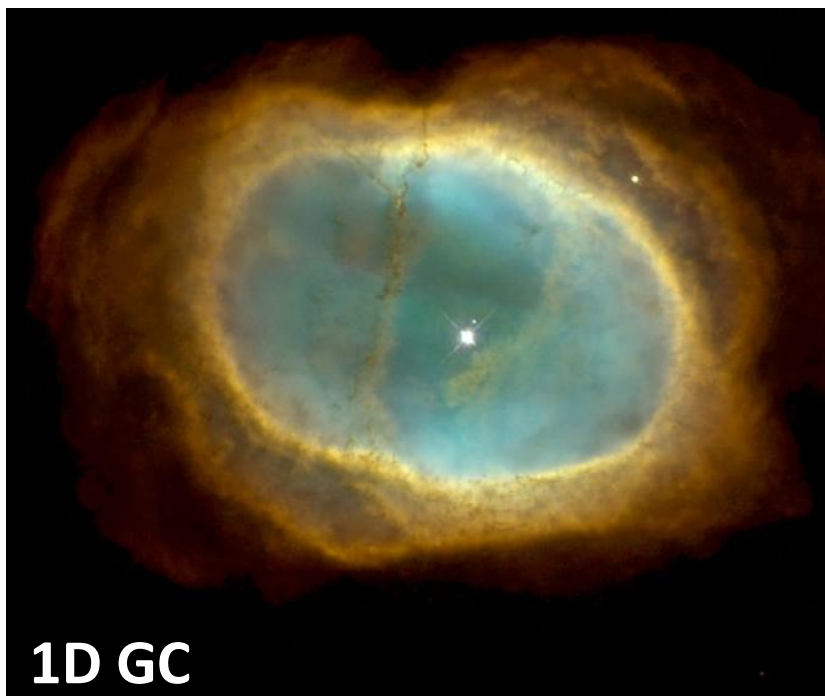
Purcaro et al. JCA 2007 1-2 284-291





Are hyphenated GC-based techniques worth the effort?

Southern Ring Nebula



1998 Hubble Telescope



Webb Space Telescope's view today



Support

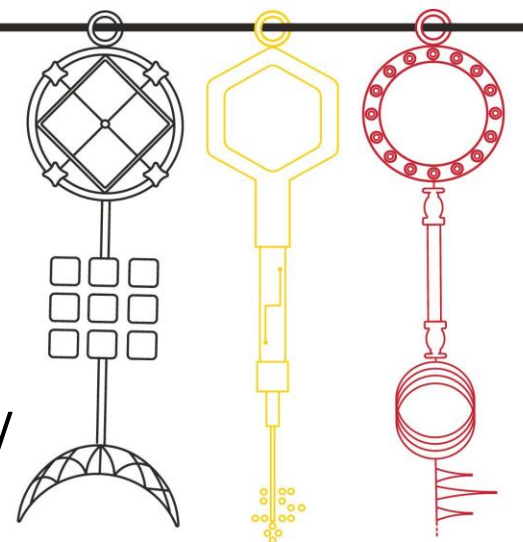
Simplify

JOIN

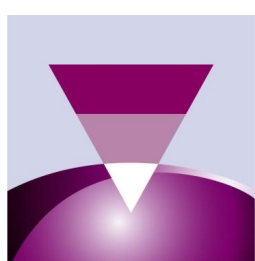
ExTech 2026

6-9 JULY 2026

GEMBLoux AGRO-BIO TECH



BECAUSE SCIENCE IS THE KEY



analytica 2026
24.-27. MÄRZ | MÜNCHEN



Thank you for the attention

Research team

Giorgia Purcaro

Sophie Vancraenenbroeck
Aleksandra Gorska
Damien Eggermont
Donatella Ferrara
Damien Pierret

Carlo Bellinghieri
Chaimae Chaibi
Nicola Ruin
Mattia Grego



LECO
EMPOWERING RESULTS

RESTEK
Pure Chromatography

SHIMADZU
Excellence in Science

SepSolve
Analytical



MARKES
international

MILESTONE
HELPING
CHEMISTS

TRAJAN

fnr
LA LIBERTÉ DE CHERCHER

GL Sciences