ADVANCES IN FOOD ANALYSIS

LC-GC

for MOSH and MOAH quantification and identification

Marco Beccaria, PhD

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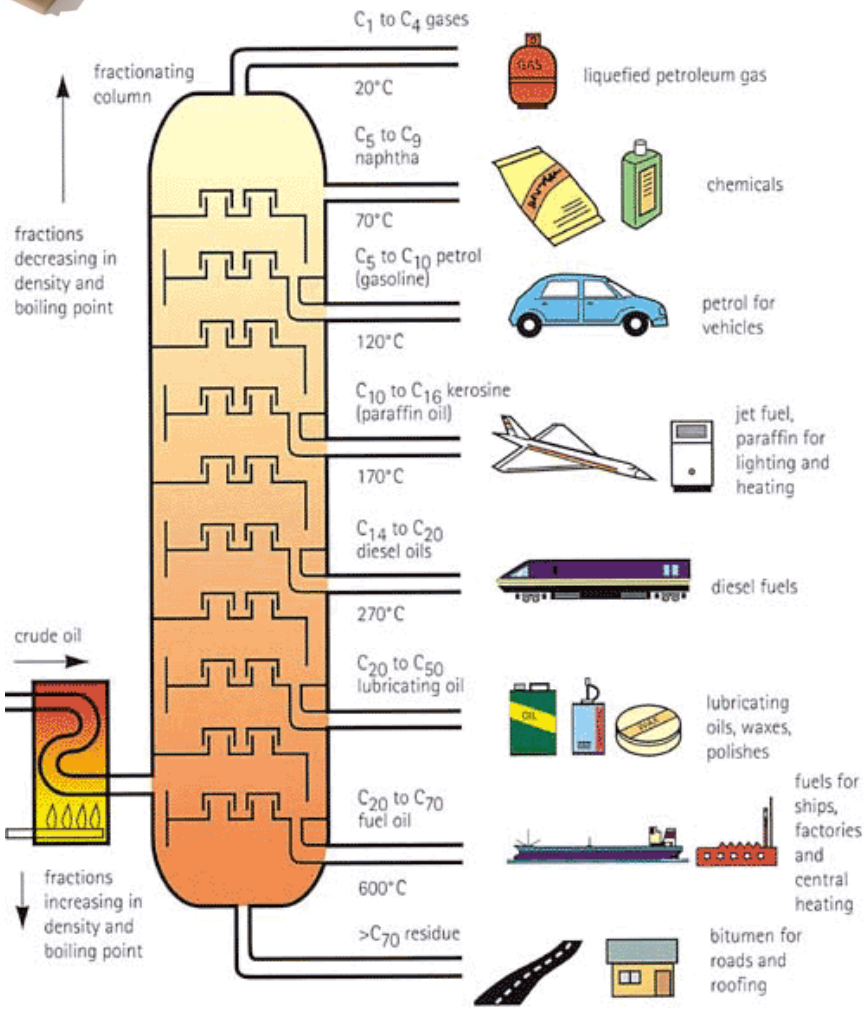
Mineral Oil Contamination

a wide range of products deriving from petroleum distillation fractions



Containing mainly:

-n-alkane
- isoalkane
- cycloalkane

MOSH

Mineral oil saturated hydrocarbons

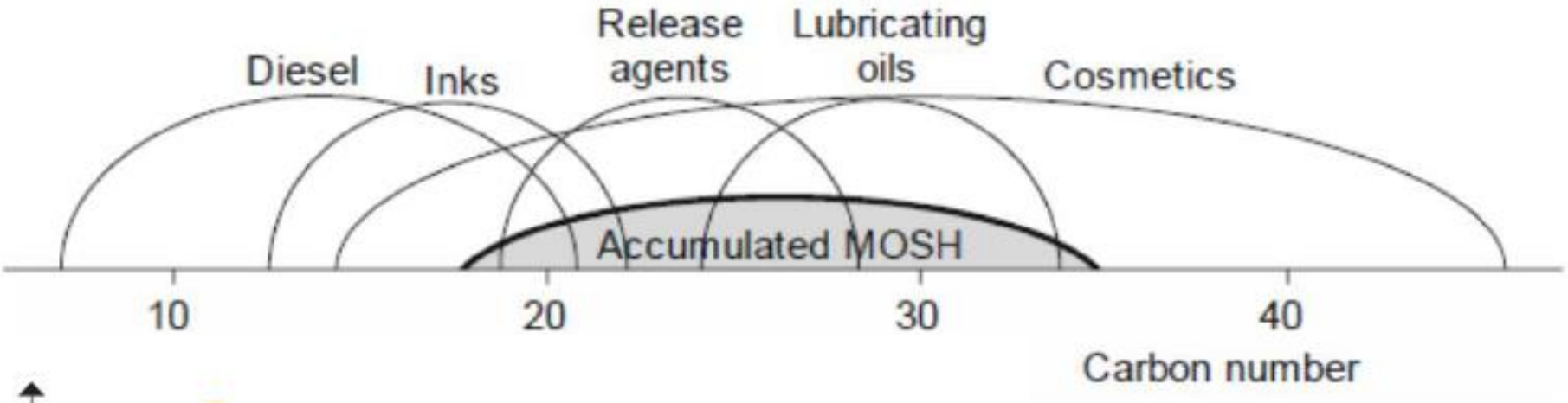
May contains also:

-Aromatic hydrocarbons, mainly alkylated

MOAH

Mineral oil aromatic hydrocarbons

MOH



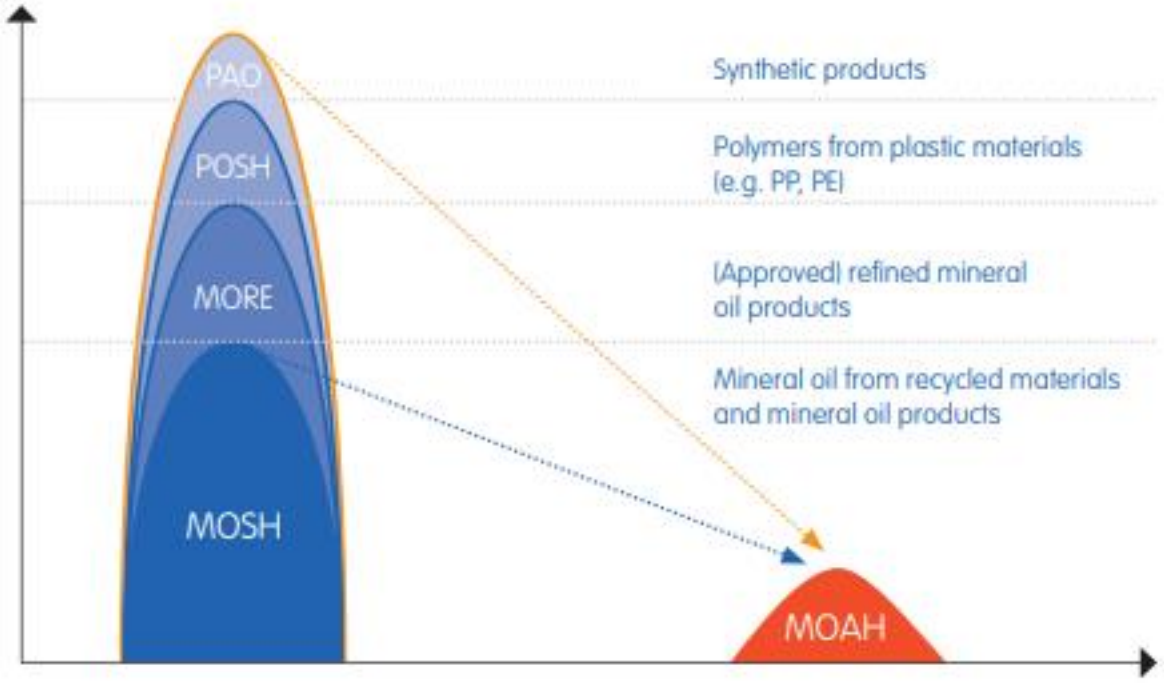


Figure 2: Shifting of the MOSH:MOAH ratio commonly found in mineral oil by MORE, POSH and PAO as MOSH analogues *[according to 14 and 15] (for abbreviations see definitions and text)*

Mineral Oil: Toxicology

MOAH

(Mineral Oil Aromatic Hydrocarbon)

→ Genotoxic, mutagenic, and carcinogenic, although a full toxicological evaluation of MOAH is lacking

→ Depends on the number of rings

MOSH

(Mineral Oil Saturated Hydrocarbon)

→ Effect still unclear BUT → Selectively accumulate in human body!

NEED

- ✓ More studies on exposure!
- ✓ Full characterization within the MOSH and MOAH fraction!

Mineral Oil: Occurrence in food

Packaging & FCM

Food additives: (food grade oil)

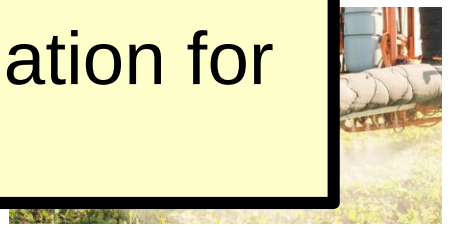
- mould release agents
- coating agents for confectionery
- anti-dust agents
- components of cheese rinds

Lubricants, cleaning products and engine oils

NEED:

Understand the source of contamination for preventing it!

ticides



veterinary medicinal products

Contamination (accidental or intentional) e.g. diesel, kerosene, motor oil, etc.

Transport and environment

Brief overview on the mineral oil analysis

Mineral oil

LC-GC

Brief overview on the mineral oil analysis

Mineral oil

LC-GC

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)

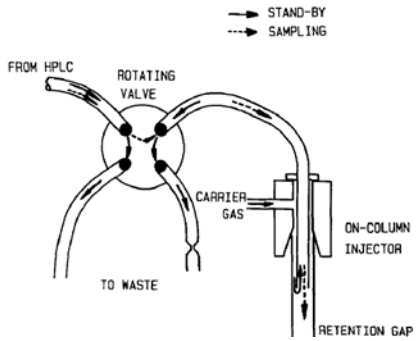
J Chromatogr. **1984** 295:55-61

1989

Partially Concurrent Eluent Evaporation with an Early Vapor Exit; Detection of Food Irradiation through Coupled LC-GC Analysis of the Fat

Maurus Biedermann, Konrad Grob*, and Werner Meier
Kantonales Labor, P. O. Box, CH-8030 Zürich, Switzerland

J High Resol Chromatogr. **1989** 12:591–598.



Brief overview on the mineral oil analysis

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As well as detection of pristane and phytane

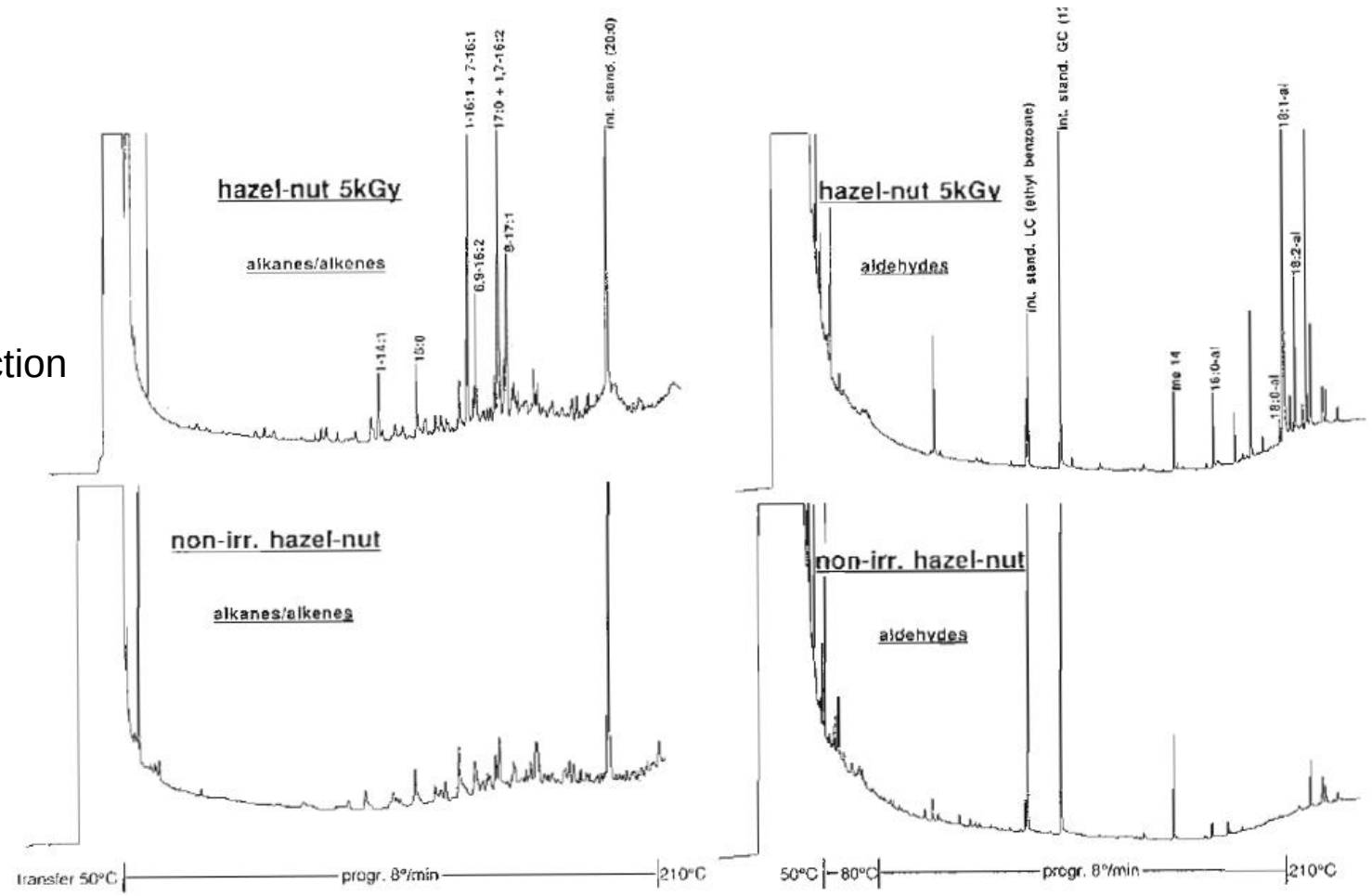


Figure 6

Alkane/alkene and aldehyde fractions of irradiated and non-irradiated hazelnuts. The poorly resolved alkanes in the matrix of the alkane/alkene fraction probably indicate a contamination of the nuts with mineral oil.

Brief overview on the mineral oil analysis

Partially Concurrent Eluent Evaporation with an Early Vapor Exit; Detection of Food Irradiation through Coupled LC-GC Analysis of the Fat

J High Resol Chromatogr. 1989 12:591–598.

Maurus Biedermann, Konrad Grob*, and **Werner Meier**
Kantonales Labor, P.O. Box, CH-8030 Zürich, Switzerland

MOH characteristic hump

As well as detection of pristane and phytane

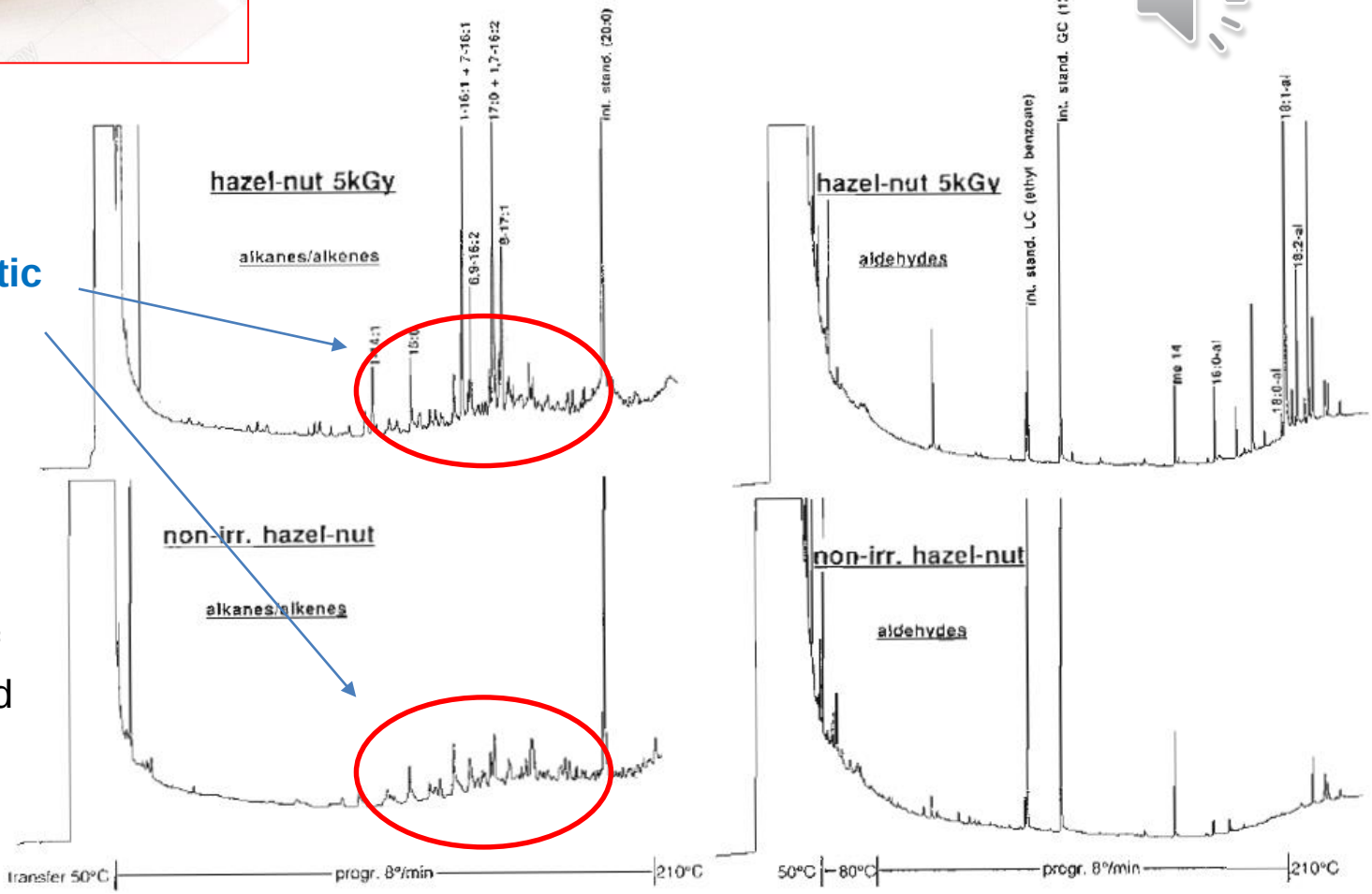


Figure 6

Alkane/alkene and aldehyde fractions of irradiated and non-irradiated hazelnuts. The poorly resolved alkanes in the matrix of the alkane/alkene fraction probably indicate a contamination of the nuts with mineral oil.

Brief overview on the mineral oil analysis

FOOD ADDITIVES AND CONTAMINANTS, 1991, VOL. 8, NO. 4, 437–446

Food contamination by hydrocarbons from lubricating oils and release agents: determination by coupled LC–GC

KONRAD GROB, ANNA ARTHO, MAURUS BIEDERMANN and JNES EGLI
Kantonales Labor, PO Box, CH-8030 Zürich, Switzerland

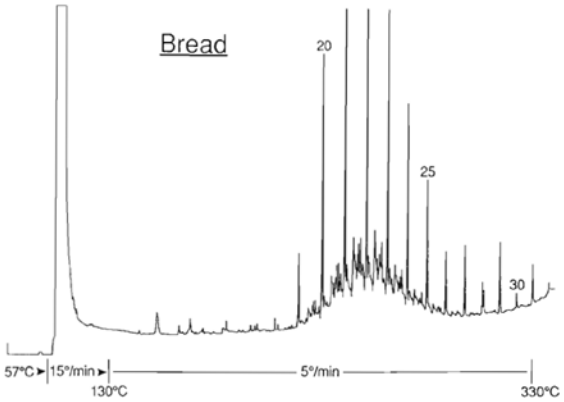


Figure 4. Hydrocarbons from the bottom crust of bread (330 mg/kg in a 10 mm crust), presumably used as release agent to prevent sticking during the baking process.

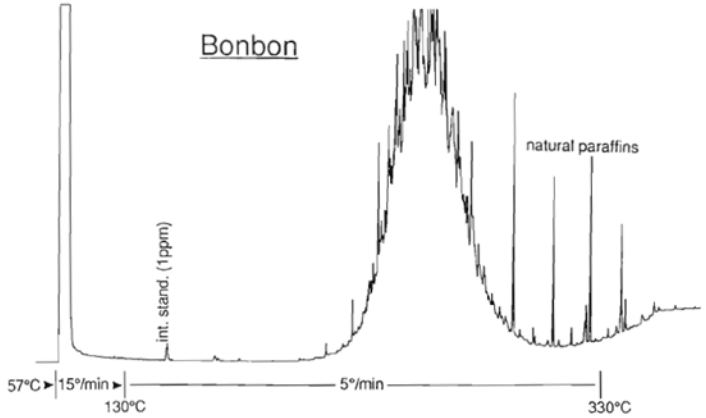


Figure 5. Mineral oil material C_{20}–C_{27} extracted from a hard, transparent bonbon, representing a 1000 mg/kg concentration. Internal standard (int. stand., n-C_{13}, 1 mg/kg).

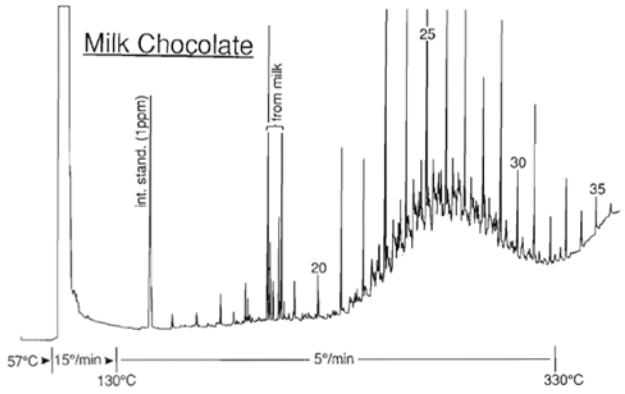


Figure 6. Hydrocarbons from a chocolate: 'hump' with dominating n-alkanes suggesting contamination with a lubricant, probably a vaseline. Some n-alkanes are labelled by the number of carbon atoms.

only MOSH was considered

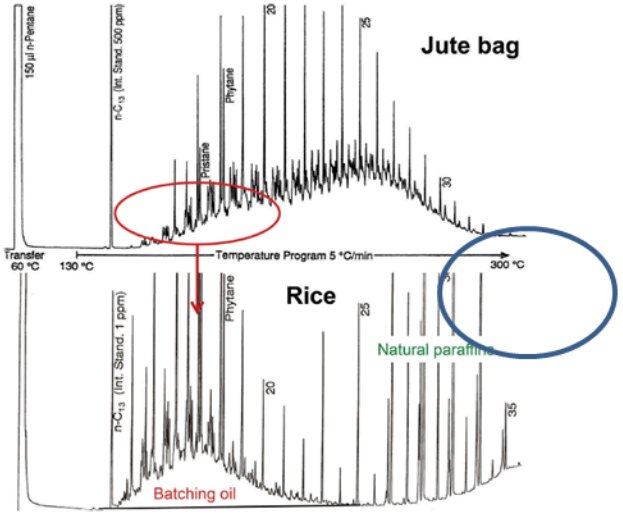
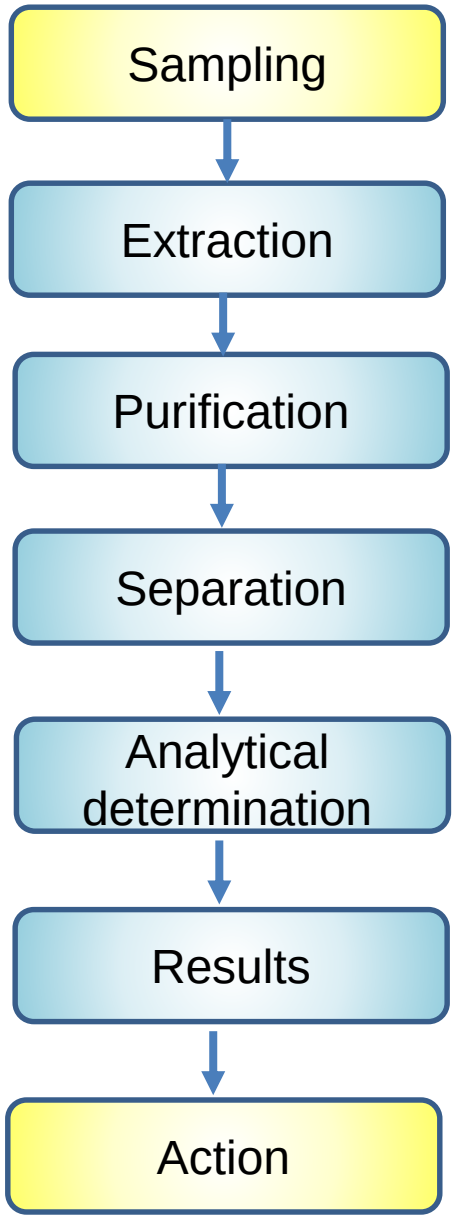


Figure 1. On-line HPLC–GC–FID of extracts from a jute bag and the rice that had been packed in the bag (adapted from Grob et al. 1991a).

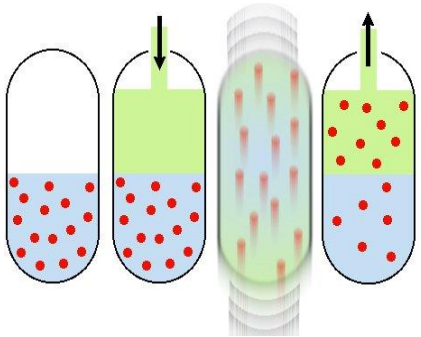
MOSH/MOAH Determination



MOSH/MOAH Determination

Extraction → Depends on the sample

LLE/SLE

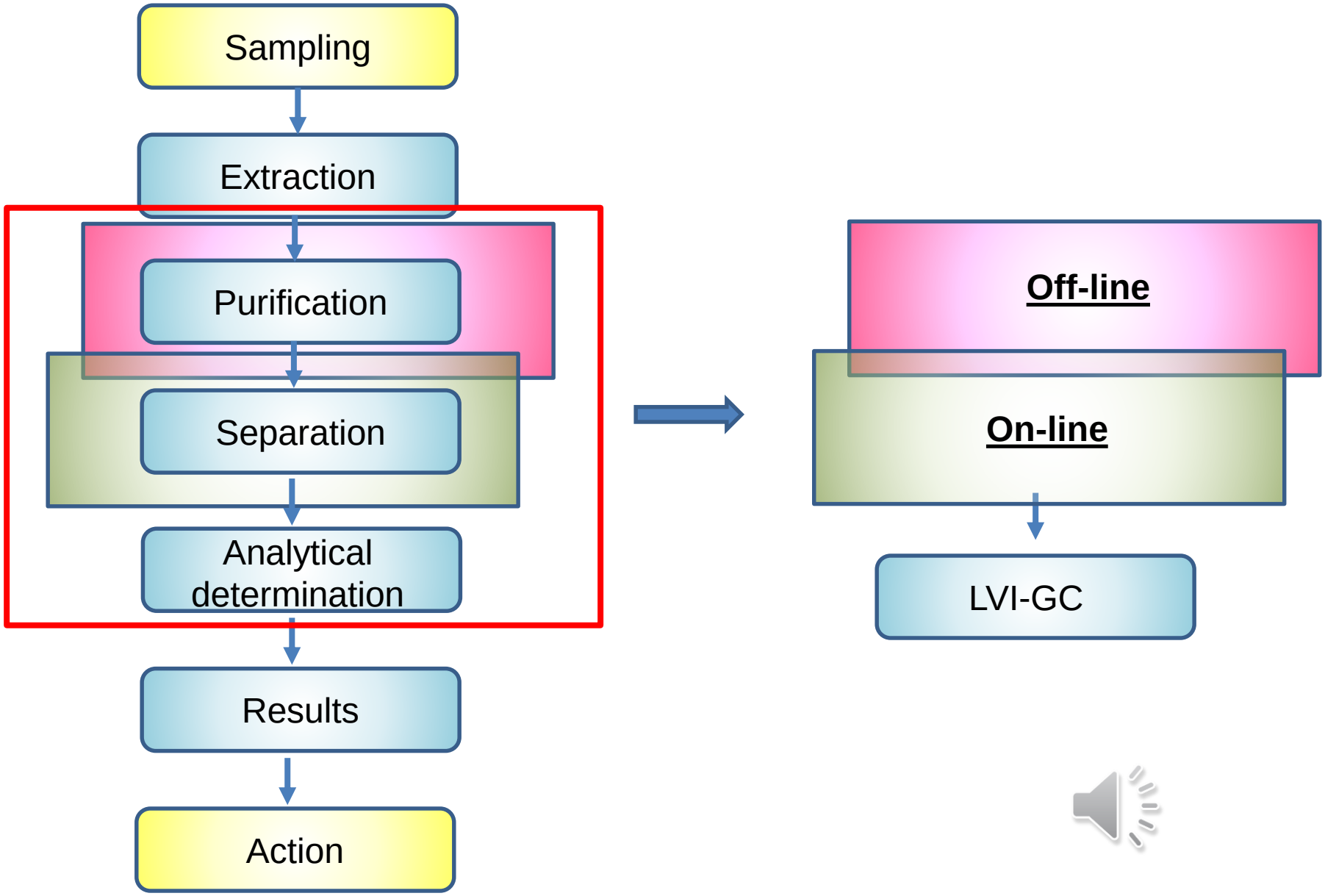


MAE/MAS

PLE

SPE

MOSH/MOAH Determination



On-line Analysis

LC-GC

LC-GC

- High efficiency in pre-separation → efficient sample clean-up
- On-line detection for accurate determination of the LC elution windows
- The entire fraction of sample material is transferred to GC → low detection limit
- Close system → rules out sample contamination during preparation
- HPLC enables reuse of the same column for many analyses
- Automation → high throughput (e.g. MOSH/MOAH analysis: 35 injections/day)

LC-GC Interface

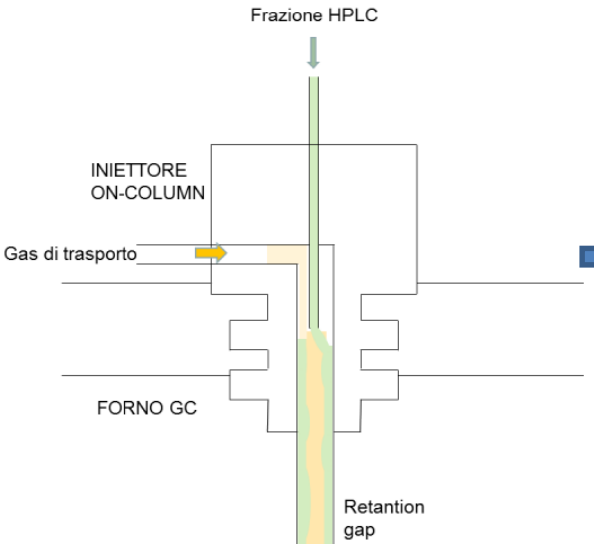
Mineral oil

LC-GC

On-column type transfer device

"**partially concurrent eluent evaporation**"

LC-GC Interface



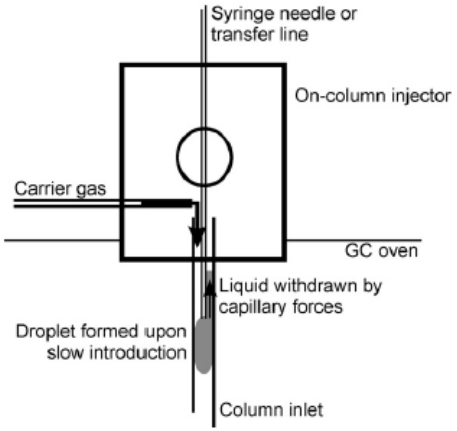


Fig. 2. Sample liquid pulled backwards between the needle or transfer line and the wall of the column inlet upon slow injection or sample transfer.

Memory effect in the **0.5-3%** range

Journal of Chromatography A, 1216 (2009) 8652–8658

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Memory effects with the on-column interface for on-line coupled high performance liquid chromatography-gas chromatography: The Y-interface

Maurus Biedermann, Koni Grob*

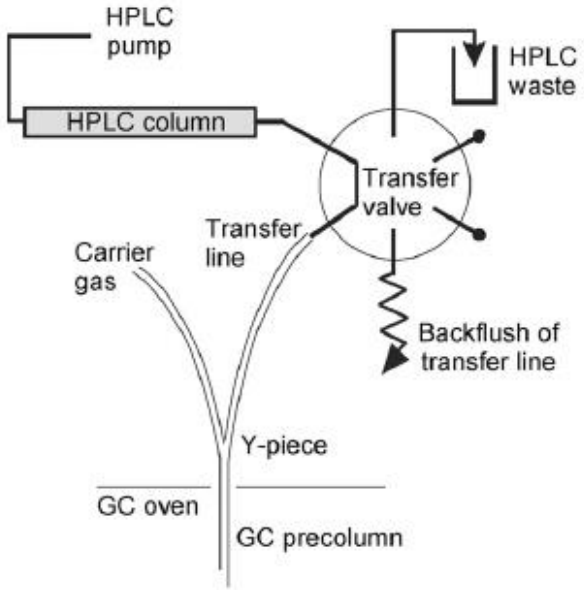


Fig. 9. The Y-interface.

Biedermann M, Grob K, J Chromatogr A 1216 (2009) 8652

LC-GC for MOSH and MOAH determination

J. Agric. Food Chem. 2009, 57, 8711–8721

Aromatic Hydrocarbons of Mineral Oil Origin in Foods: Method for Determining the Total Concentration and First Results

Maurus Biedermann, Katell Fiselier, and Kon[illegible] Gros

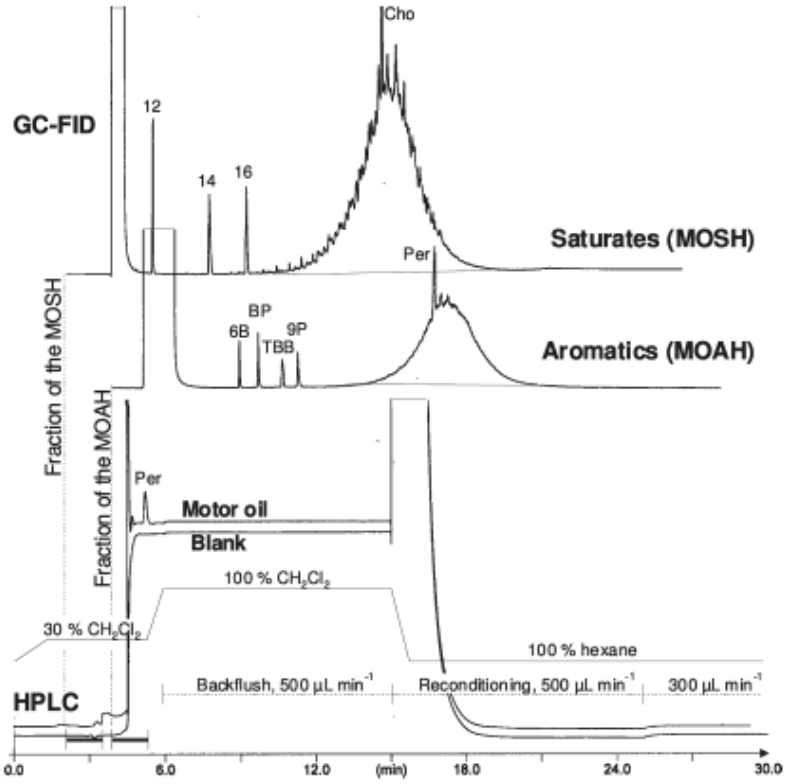
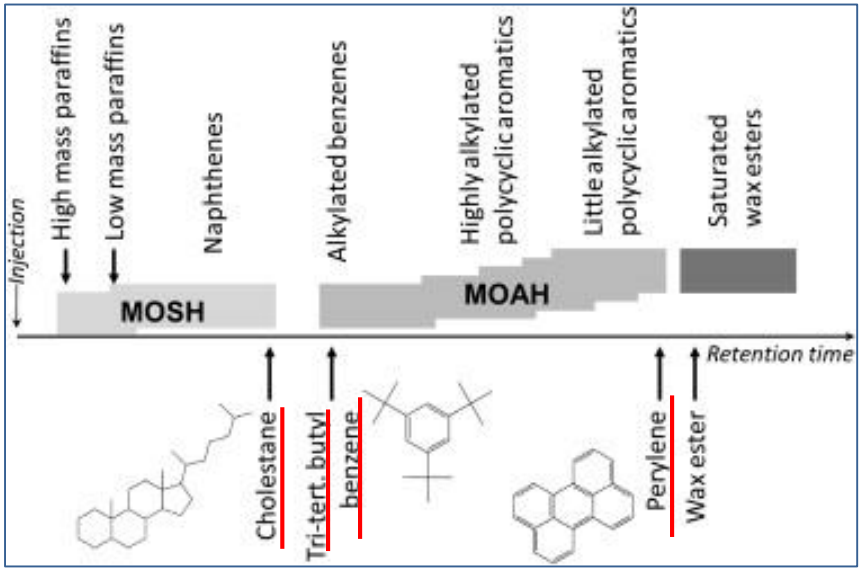


Figure 1. Analytical procedure visualized by the chromatograms of a motor (lubricating) oil. Labeled peaks indicate internal standards for determining concentrations and verification of the performance.



+ 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**

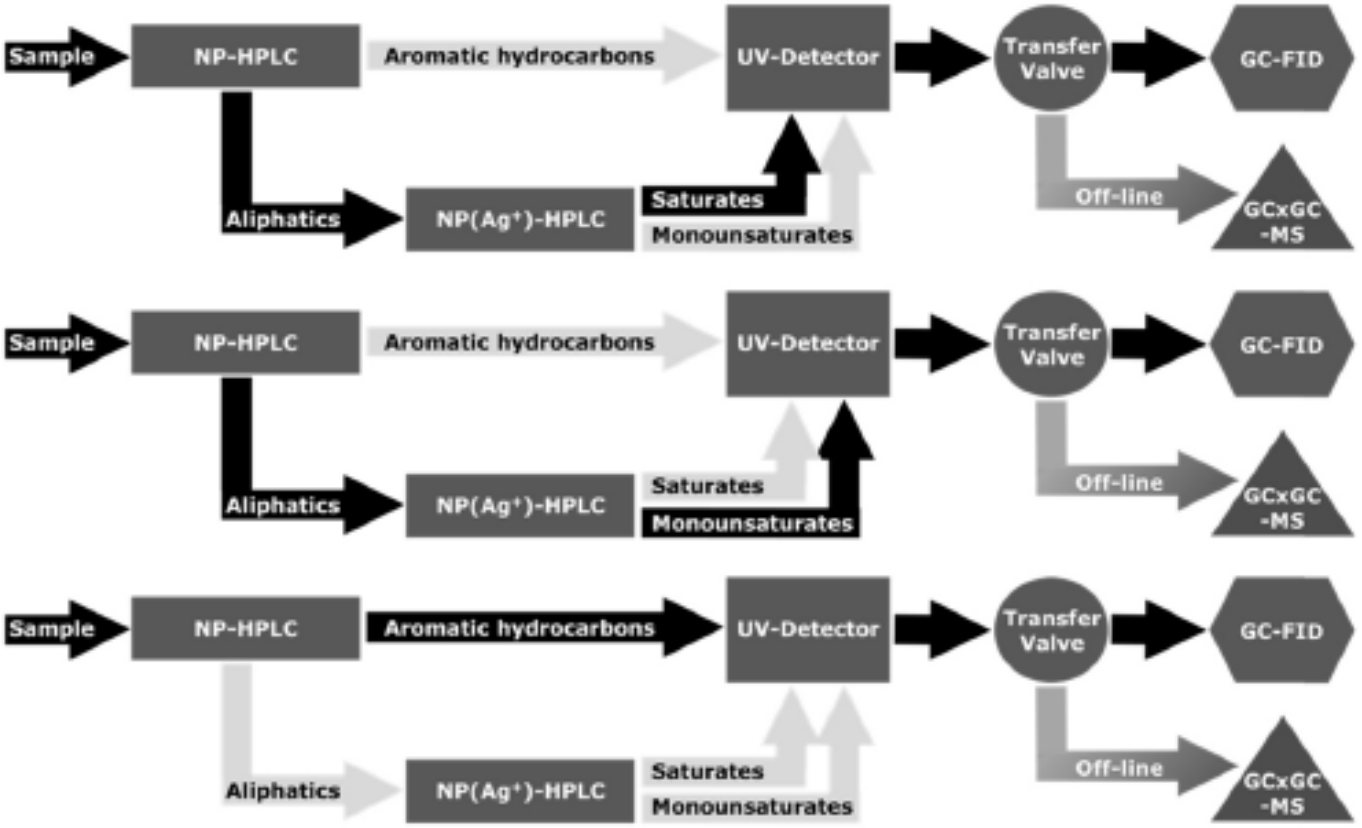
MOSH interferences

Polyolefin Oligomeric Hydrocarbond (POH) : POSH

POMH

On-line removal

LC-LC-GC-FID



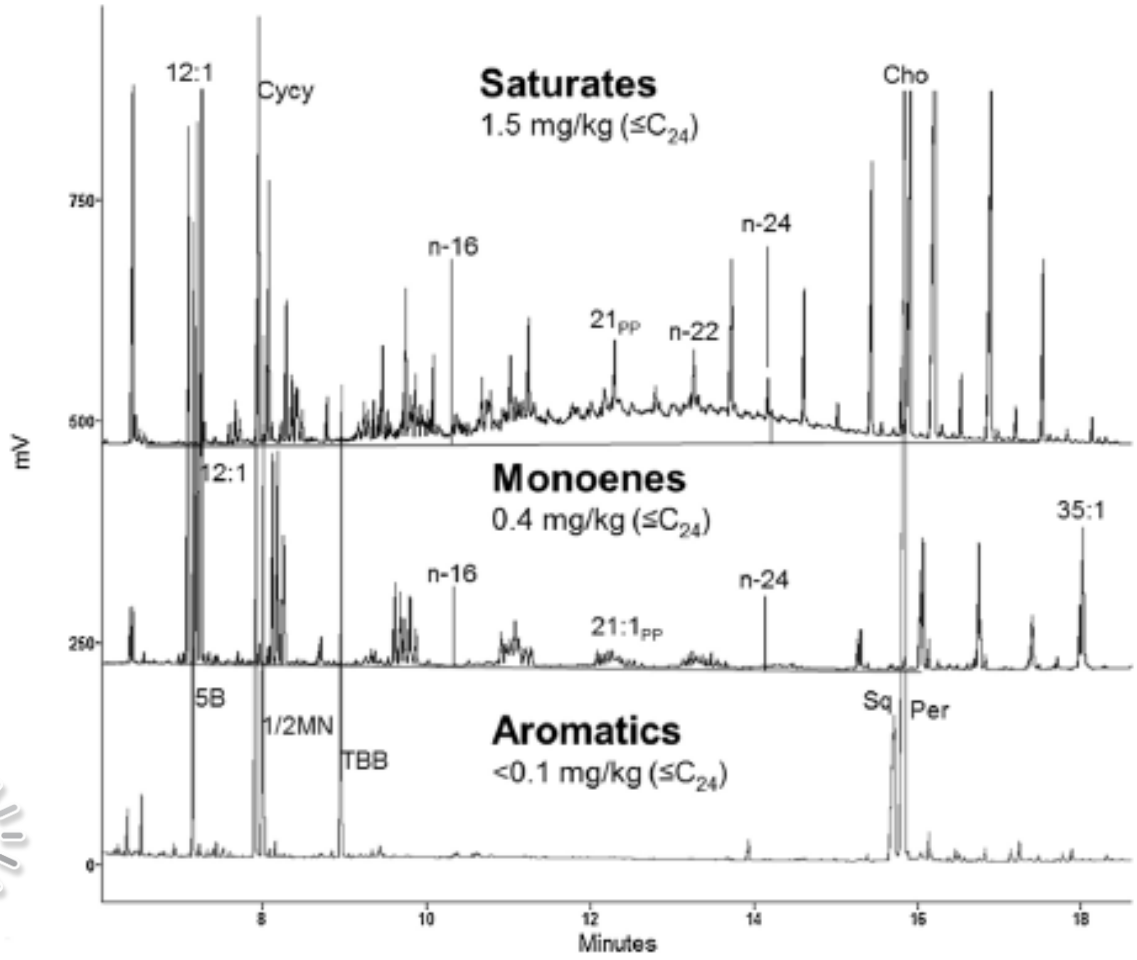
J. Chromatogr. A 1402 (2015) 94–101

MOSH interferences

Polyolefin

On-line removal

LC-LC-GC-FID

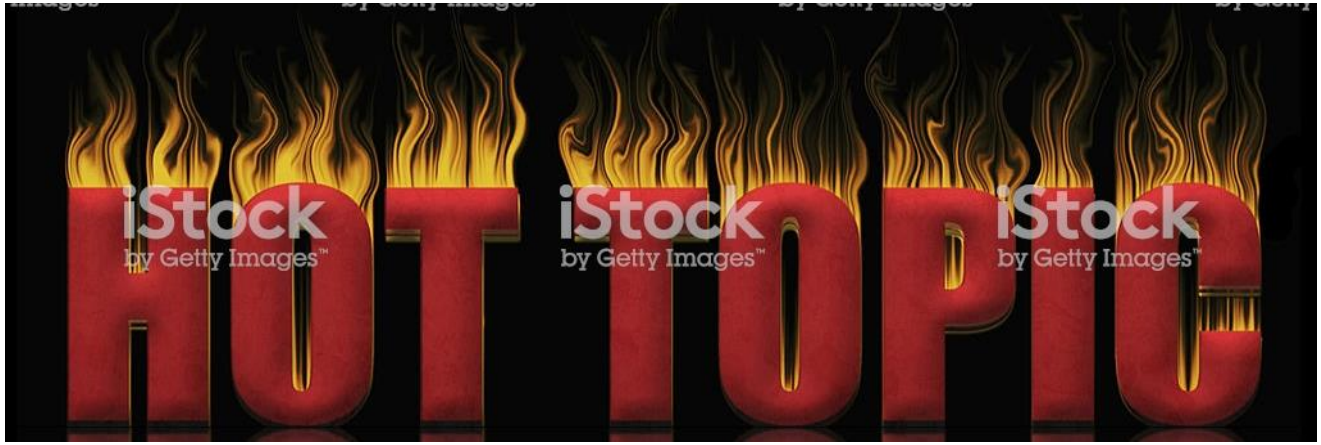


MOSH and POSH

POMH

MOAH

THE HOTTEST ISSUE



CONFIRMED

CONFIRMATORY METHOD

COMMISSION DECISION

of 12 August 2002

implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results

(notified under document number C(2002) 3044)

(Text with EEA relevance)

(2002/657/EC)

2.3. CONFIRMATORY METHODS FOR ORGANIC RESIDUES AND CONTAMINANTS

Confirmatory methods for organic residues or contaminants shall provide information on the chemical structure of the analyte. Consequently methods based only on chromatographic analysis without the use of spectrometric detection are not suitable on their own for use as confirmatory methods. However, if a single technique lacks sufficient specificity, the desired specificity shall be achieved by analytical procedures consisting of suitable combinations of clean-up, chromatographic separation(s) and spectrometric detection.

The following methods or method combinations are considered suitable for the identification of organic residues or contaminants for the substance groups indicated:

FID or MS?

FID

- Not a selective detector
- Response is proportional to the amount of hydrocarbon not to the type of hydrocarbon

Since it is **not** a **selective** detector sample preparation must guarantee that only MOSH and MOAH enter the detector

MS

- Selective detector
- Response may be very different for two different hydrocarbon compounds with the same number of carbons, such as n-C6 and aromatic-C6 (benzene)

Difficult selection of **proper standard** (often not available)

Suitable for (bio)**markers**, such as hopanes and specific PAHs

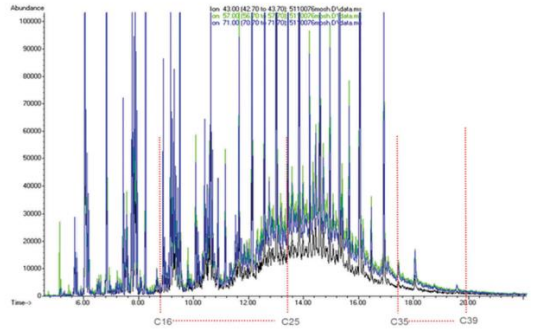
FOOD ADDITIVES & CONTAMINANTS: PART A, 2017
VOL. 34, NO. 6, 1052–1071
https://doi.org/10.1080/19440049.2017.1306655

FID or MS?

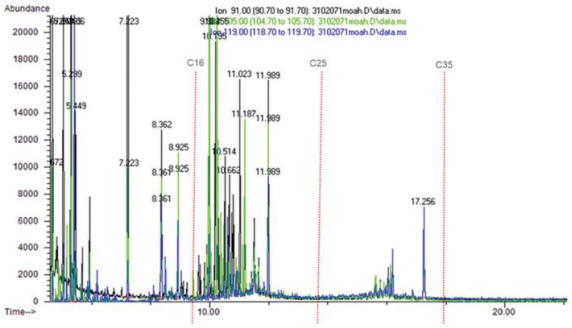
Understanding the contamination of food with mineral oil: the need for a confirmatory analytical and procedural approach

Lionel W. Spack[a], Gabriela Leszczyk[b], Jesus Varela[c], Hervé Simian[c], Thomas Gude[d] and Richard H. Stadler[c]

m/z 43, 57, 71, 85 → **MOSH** BUT = **Hydrocarbon of natural and/or synthetic origin**, like terpenes, natural waxes, oligomeric polyolefin **(POSH)**



m/z 91,105,119,133 → **MOAH** BUT = **Terpenes, terpenoids, carotenoids,etc**



European Food Safety Authority

EFSA Journal 2012;10(6):2704

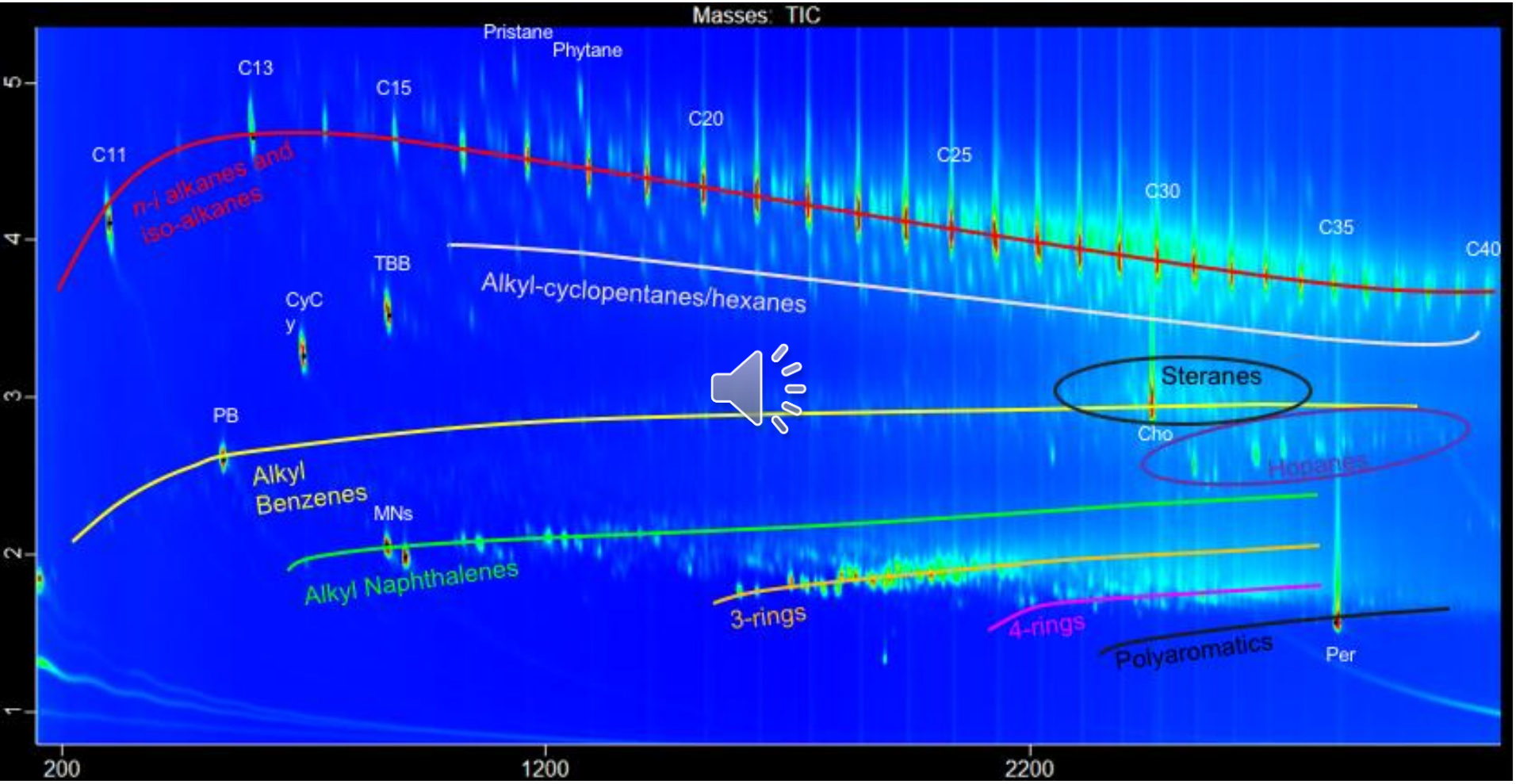
SCIENTIFIC OPINION

Scientific Opinion on Mineral Oil Hydrocarbons in Food[1]

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

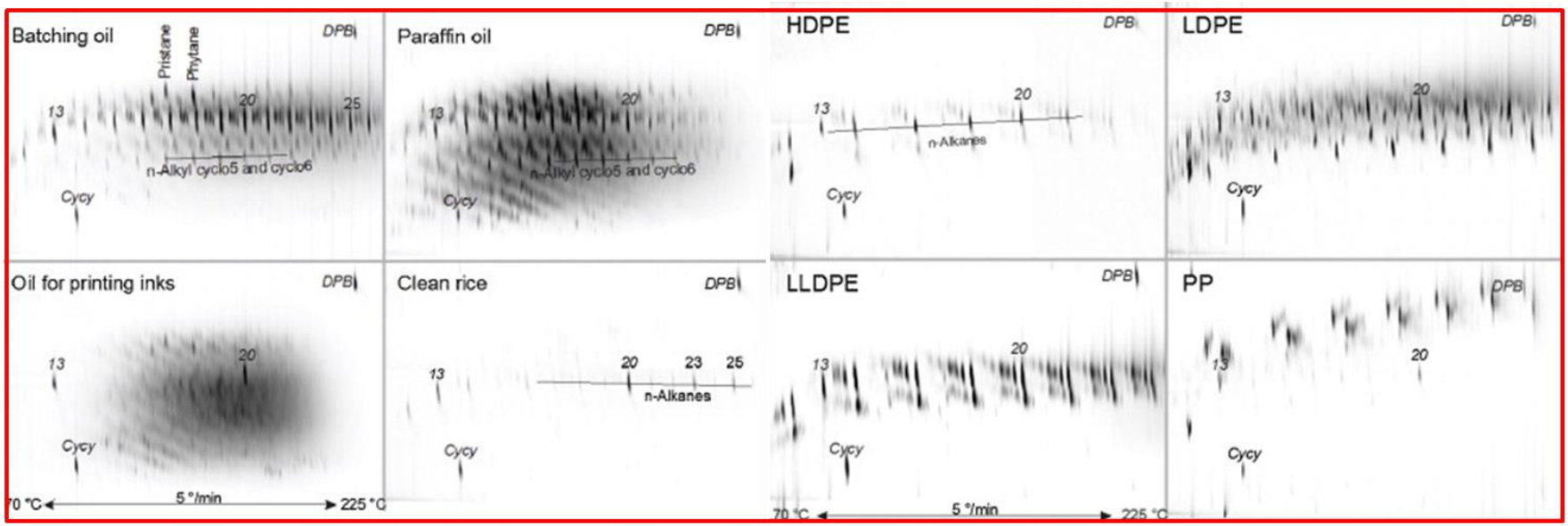
Currently, the most efficient methods for analysis of MOSH and MOAH in food and feed comprise extraction followed by pre-separation by **high performance liquid chromatography (HPLC) on-line coupled to GC with flame ionisation detection (FID)**. Detection limits depend on the mass distribution, the sample matrix and any prior enrichment, and can be as low as 0.1 mg/kg. **Comprehensive GCxGC-FID** enables a rough separation and quantification of paraffins and naphthenes in the MOSH fraction, but it is of limited practicality for routine analysis. Contamination with polyolefin oligomeric saturated hydrocarbons (POSH), e.g. from plastic bags, heat sealable layers or adhesives, may interfere with MOSH analysis. Analytical capacity to distinguish the different MOAH subclasses in food is limited. For this purpose, **GCxGC appears to be the most effective method**. Due to the complexity and the variable composition of MOH mixtures, it is not possible to define certified standards of general applicability.

GC×GC

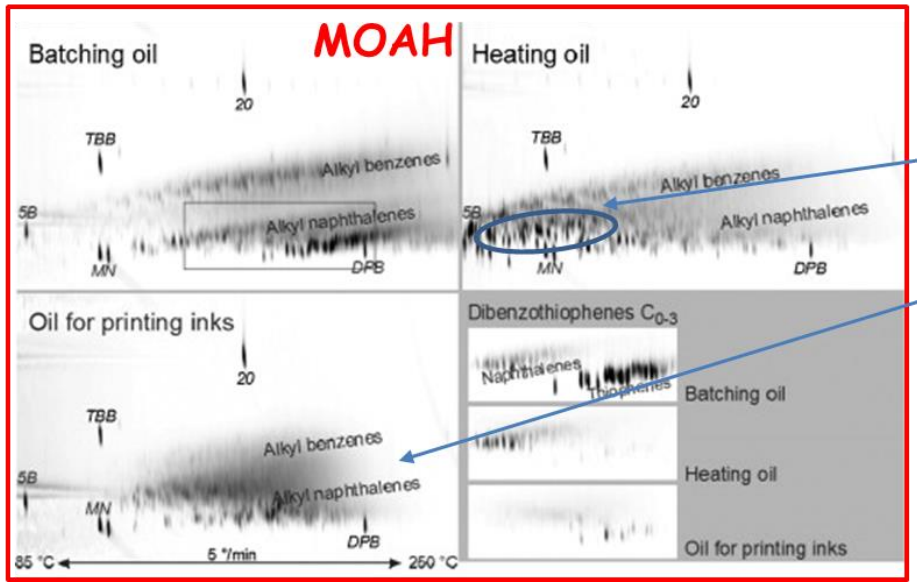

Masses: TIC
Pristane
Phytane
C13
C15
C20
C25
C30
C35
C40
C11
n-/ alkanes and iso-alkanes
TBB
CyC y
Alkyl-cyclopentanes/hexanes
PB
Steranes
Cho
Hopanes
Alkyl Benzenes
MNs
Alkyl Naphthalenes
3-rings
4-rings
Polyaromatics
Per
5
4
3
2
1
200
1200
2200

GC×GC

MOSH



MOAH

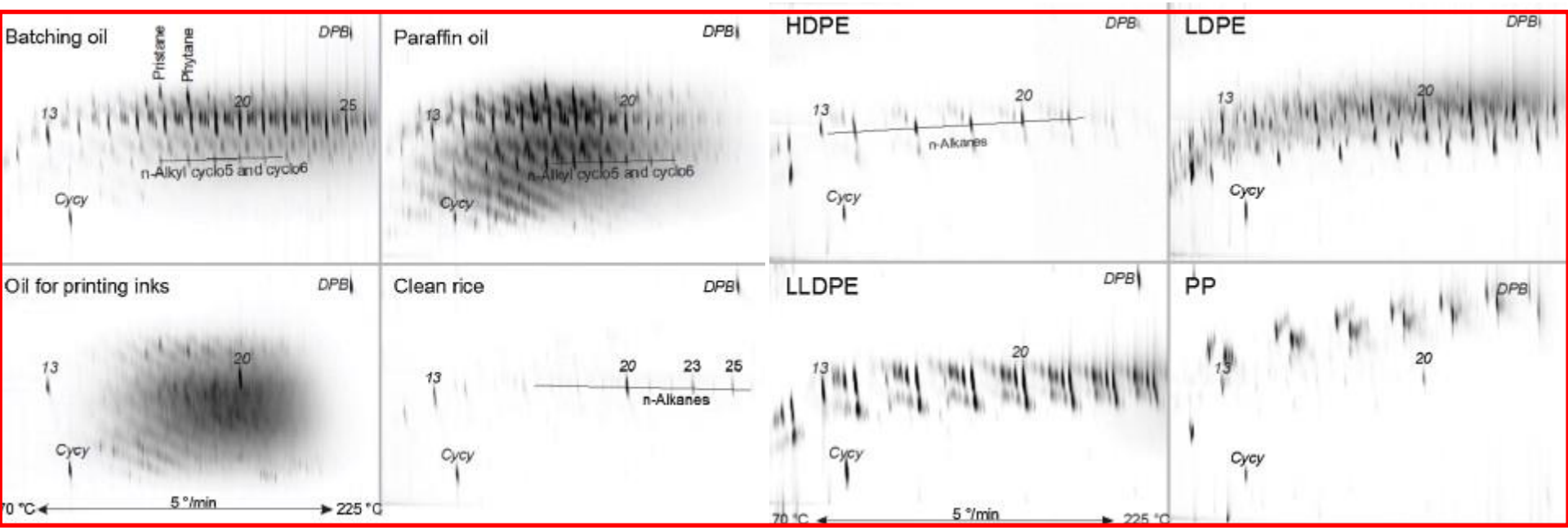


Product formed during raffination

When strongly treated (hydrogenation) the alkyl benzene and naphthalenes no distinguishable

GC×GC

MOSH



MOAH

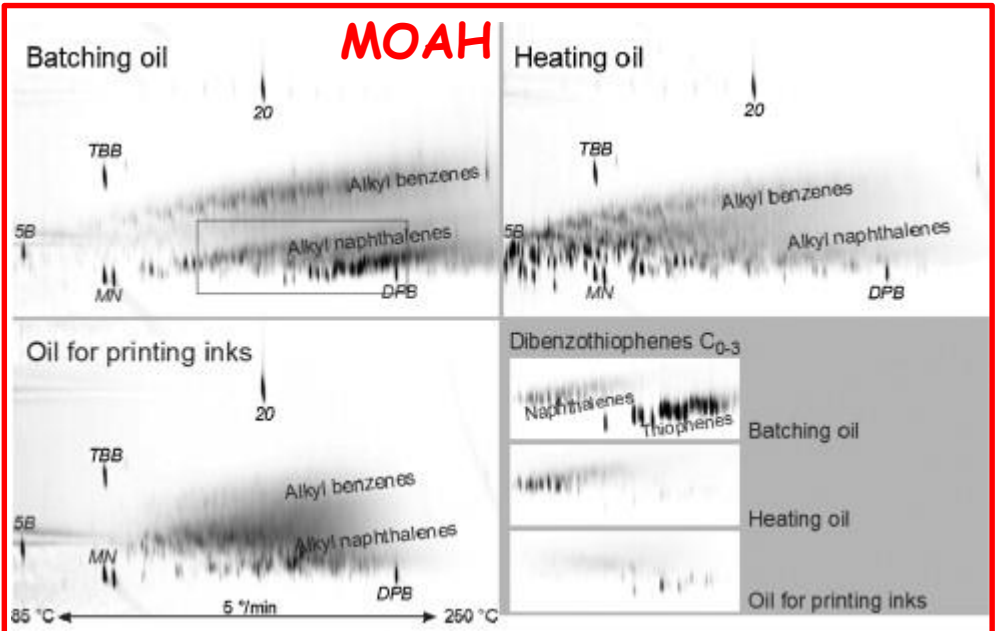
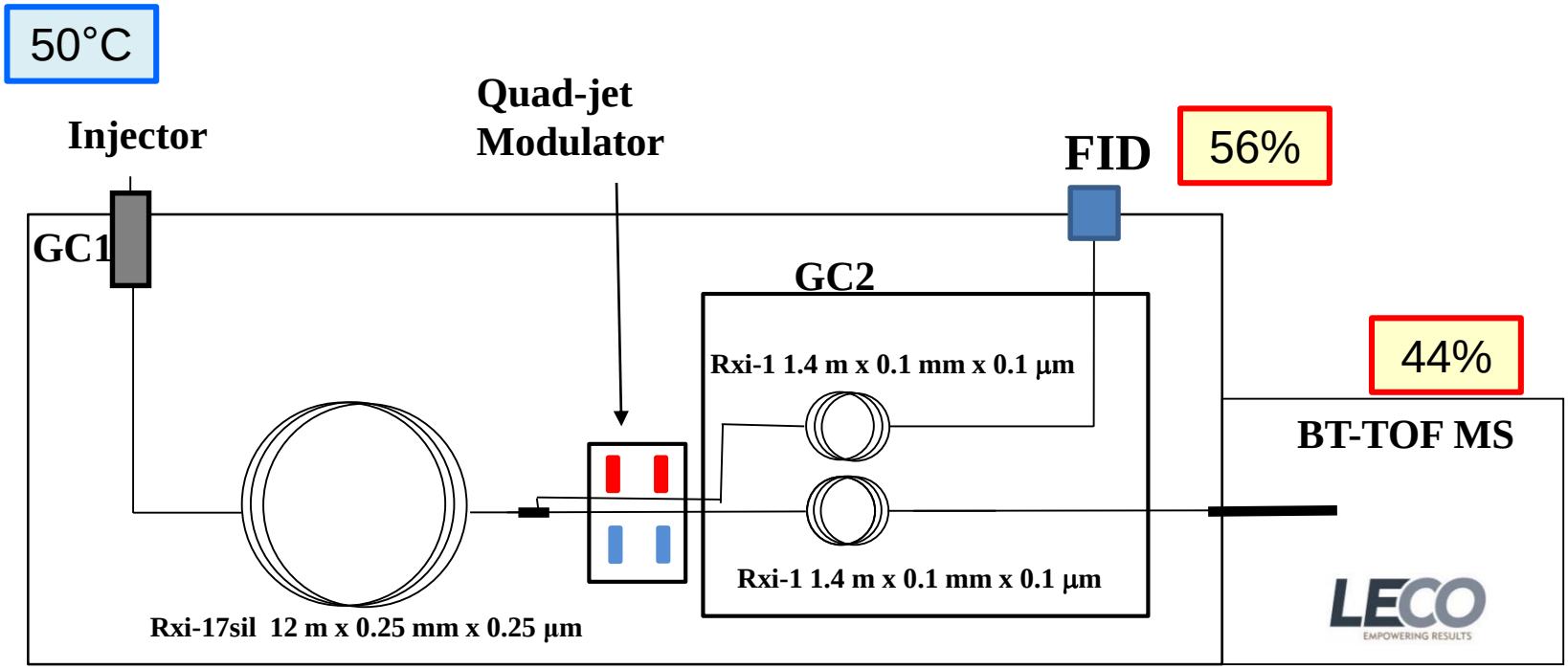


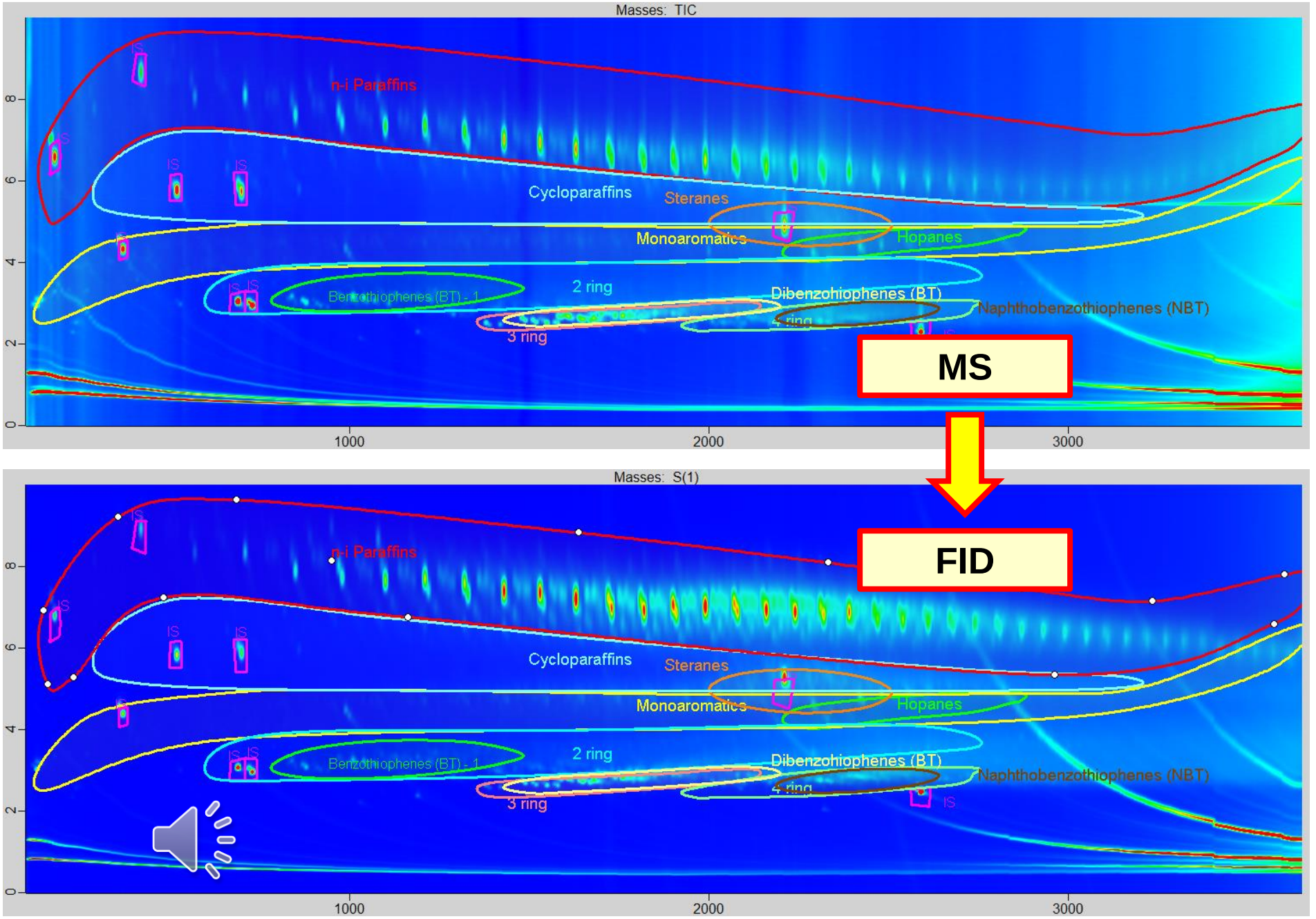
Table 1
Summary of the characteristics and their potential interpretation.

Characteristic	Indication
Repeat units of 1 C-atoms	MOSH
Pristane, phytane	MOSH
n-Alkyl cyclopentanes/hexanes	Mineral oil
Repeat units of 2 C-atoms	POSH from PE
Peak clusters clearly above n-alkanes	POSH from PP
MOSH and MOAH of same volatility range	Single contaminant
Diisopropyl naphthalenes (DIPN)	Recycled paperboard
Dibenzothiophenes	Little refined oil
Percentage of MOAH	Degree of raffination
Clearly separated band in MOAH	No hydrogenation
Perhydro pyrenes	Hydrogenated oil
“Gray cloud”, slanted bands of naphthenes	Hydrogenated oil
Upper limit of mass range	Migration conditions

GC × 2GC–MS/FID system

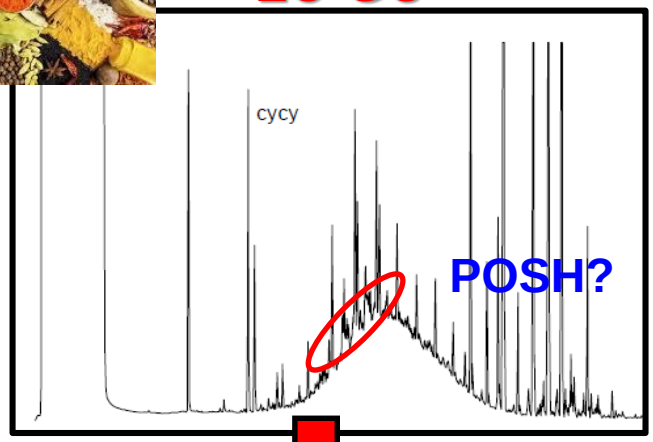


Classification “translation”



MOSH fraction

LC-GC

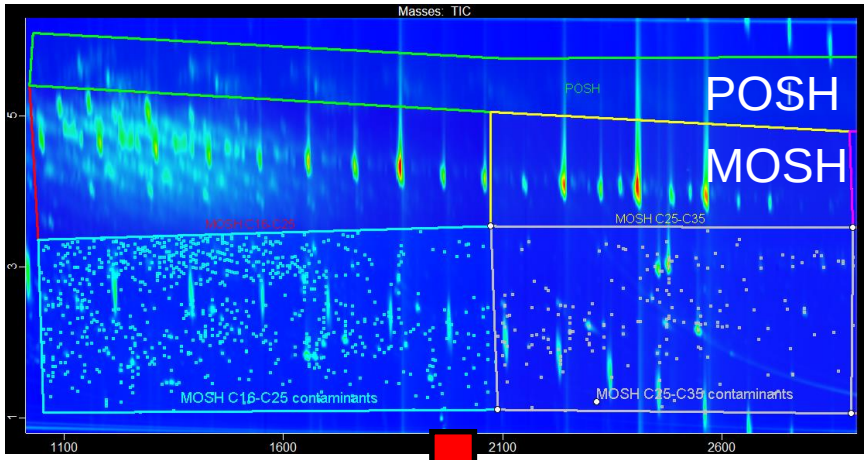


Routine strategy:

- ✓ Subtract the shaped peak from the top of the hump
- ✓ MOSH quantified with possible **POSH**
- ✓ Other purification strategies

Source of contamination: **plastic FCM**

GC×GC



Confirmatory strategy:

- ✓ Confirm presence of **POSH**

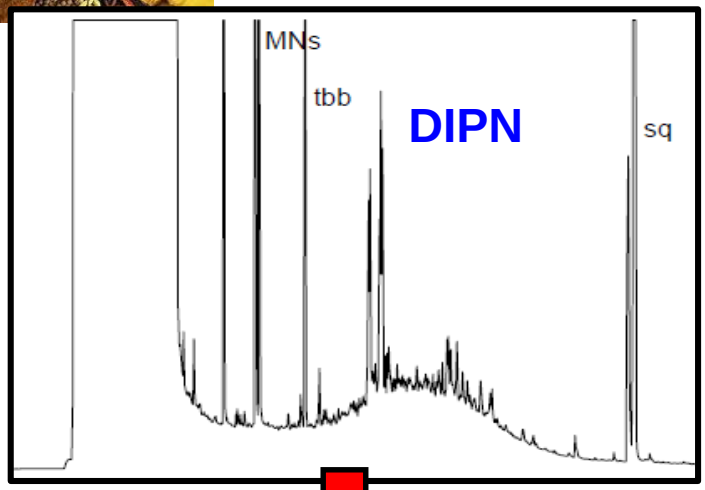
MOSH reliably quantified

Within class classification for toxicological evaluation

toxicological evaluation

Spice extract: MOAH fraction

LC-GC



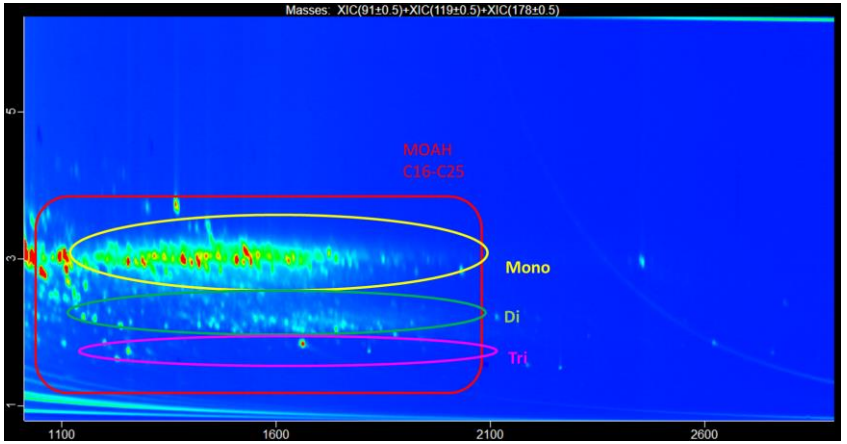
Routine strategy:

✓ Subtract the shaped peak from the top of the

✓ **DIPN** easily detected

Origin of contamination : **Recycled paperboard**

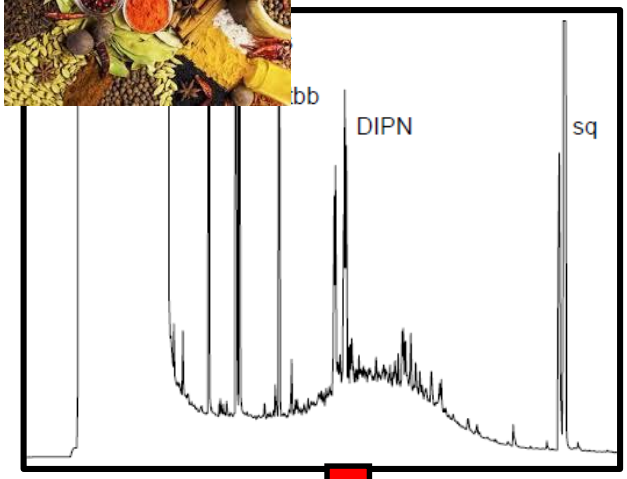
GC×GC



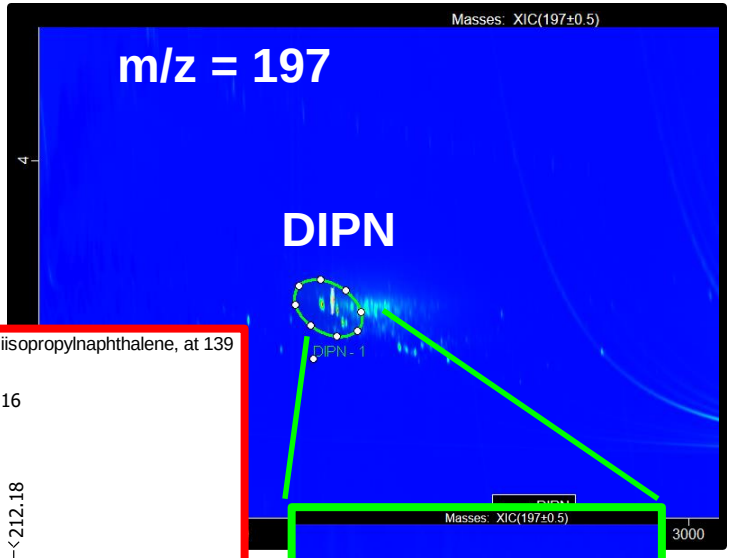
Within class classification (Mono-, di, and triaromatics)

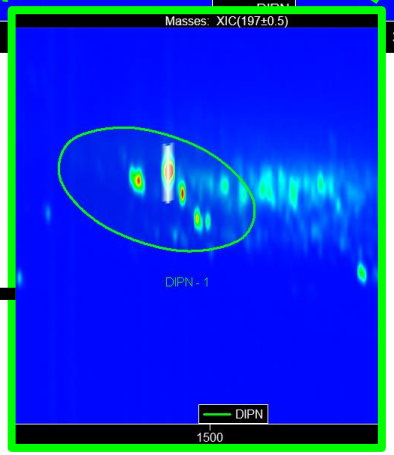
toxicological evaluation

Spice extract: MOAH fraction



DIPN



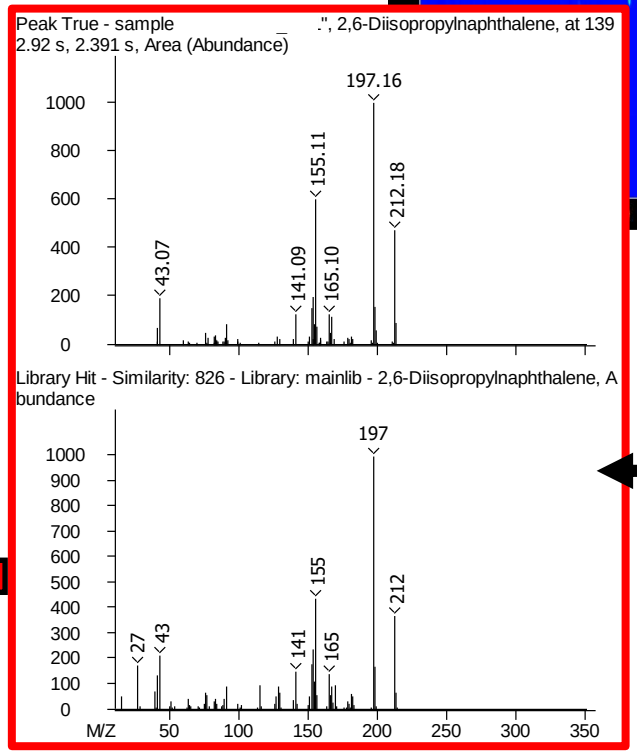


Routine strategy:

✓ Subtract the shaped peak from the top of the hump

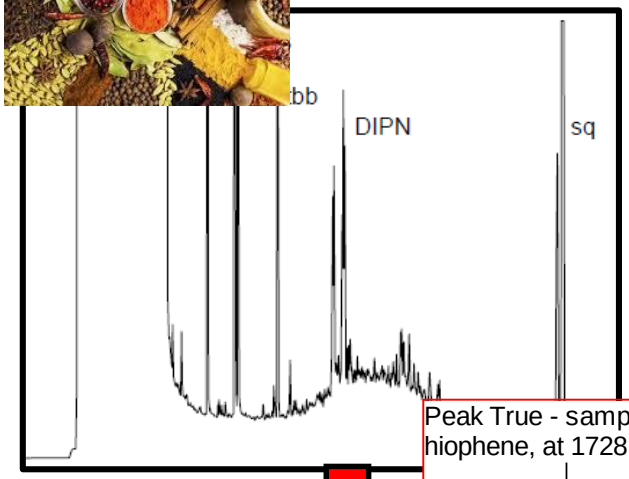
✓ **DIPN** easily detected

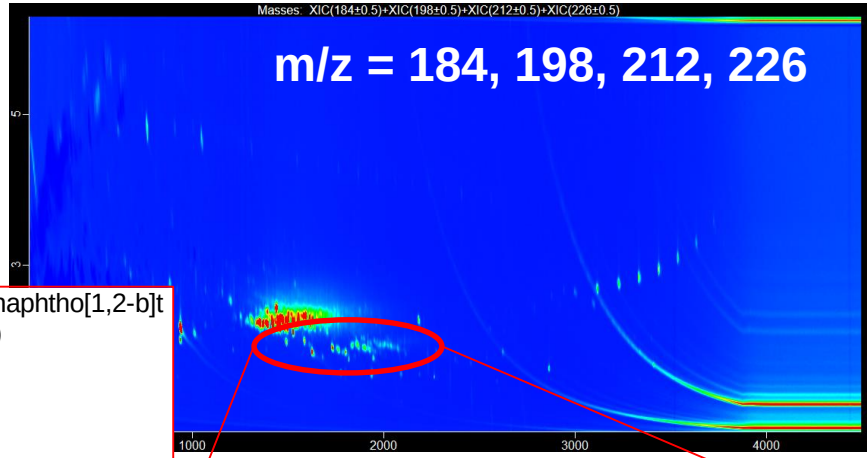
Origin of contamination : **Recycled paperboard**



Spice extract: MOAH fraction

-S-containing components



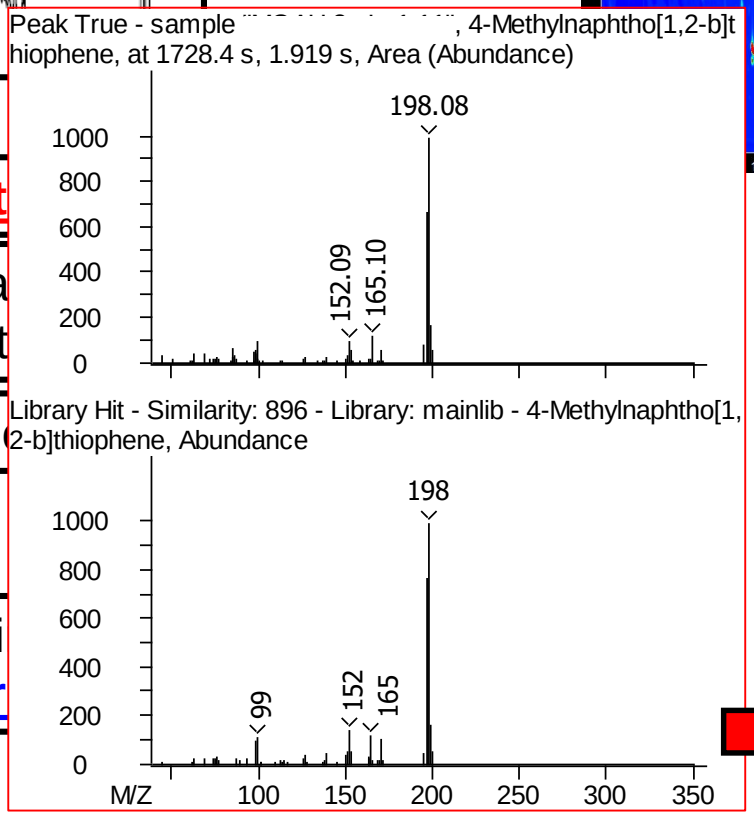


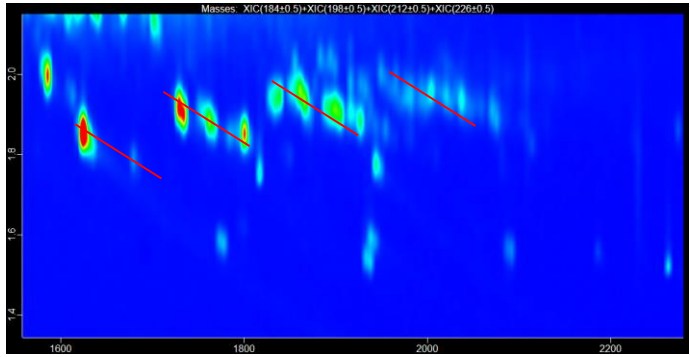
Routine strat

✓ Subtract the sha
from the top of t

✓ DIPN easily d

Origin of contami
Recycled paper





Jute bags

WHERE ARE WE GOING?

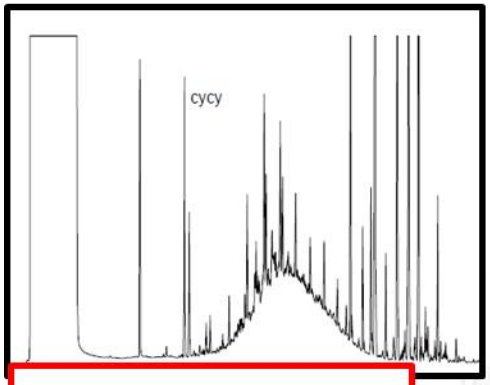
Toward a MULTIDIMENSIONAL REGULATORY METHOD

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

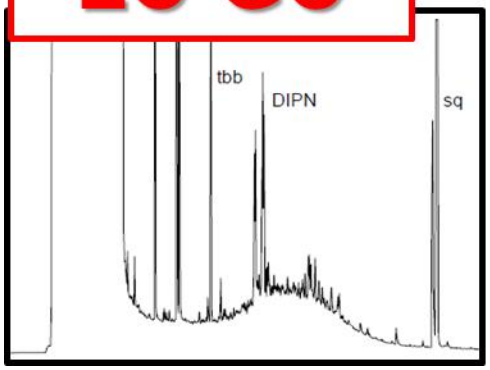
SCIENTIFIC OPINION

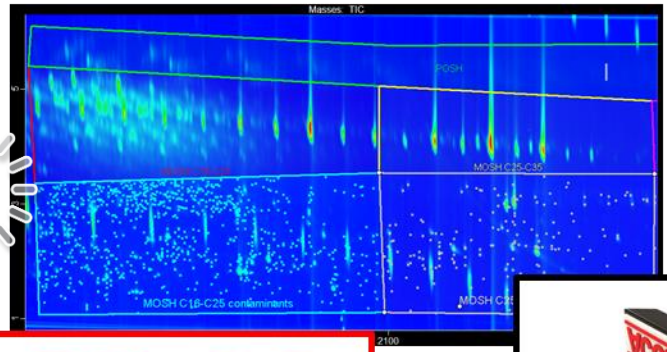
Scientific Opinion on Mineral Oil Hydrocarbons in Food[1]

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

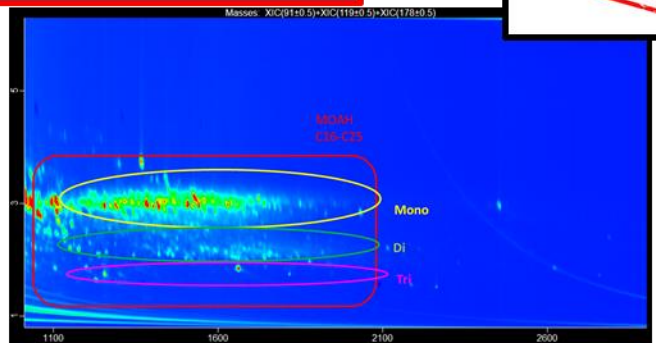


LC-GC





GC×GC



Goals

Routine method

LC-GC

Confirmatory method

GC×GC

WHERE ARE WE GOING?

Toward a MULTIDIMENSIONAL REGULATORY METHOD

NEXT STEP

LC-GC×GC-FID/ToFMS