Determination of mineral oil hydrocarbons (MOH) in different foodstuffs

A complex mixture, a complex problem

„Best of“ practical examples

Institute Kirchhoff Berlin GmbH

- service company
  - ✓ 1983 founding of the institute, Bundesallee 19-20
  - ✓ 1986 acquisition of laboratory Dr. Hess, Albestraße 4
  - ✓ 2001 extension and combination, Albestraße 3-4
  - ✓ 1986 – 2015 at the site in Berlin Friedenau, Albestraße 3-4
  - ✓ Since 2015 with 120 qualified employees and over 4.500 m² space for laboratories appliances and offices at the site

Over 100 years food analytics in Berlin

- Since 1902 Dr. Lohmann, Dr. Hess, Fr. Dr. Hess, Dr. Kirchhoff -

Services

- Range of examinations according to DIN EN ISO 17025
  - ✓ chemical, microbiological, biochemical, physical-chemical analytics of:
    - food
    - Baby-Food
    - Pet-Food
    - Water (drinking-water, basin-water)
    - Food supplements
    - Pharmaceutical products
    - Cosmetics
    - Food allergens
    - Food and articles of daily needs

Background

Mineral oil residues in food

Many foods are contaminated with mineral oil components.

First findings mainly in dry foods like pasta or cereals.

Advent calendar alert in late 2012: Stiftung Warentest found mineral oil residues in chocolate.

Mineral oil can enter from various sources:

- recycling paper (printing inks)
- lubricating oils
- release agents
- dust binding agents
- packaging materials (e.g. jute bags)
- environmental pollution

Relevance

Mineral oil residues in food – tests of the NGOs

2010
Stiwa Rice

2010
Stiwa potato dumpling

2015
Foodwatch Dry Food

2011
ökotest Babytea

2015
Stiwa Gourmet oils

2011
ökotest Babytea

2015
Stiwa cosmetics

2014
Stiwa chocolate

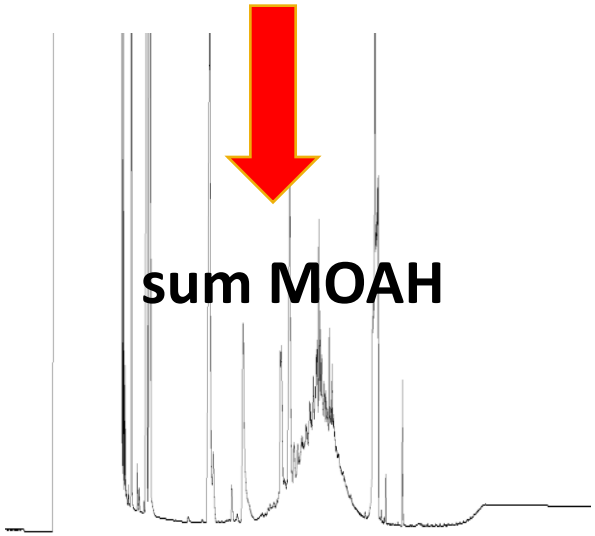
2012
Stiwa Advent calendar

2013
ökotest oat flakes

Analytical strategy

What is the „hump“?

online LC-GC-FID

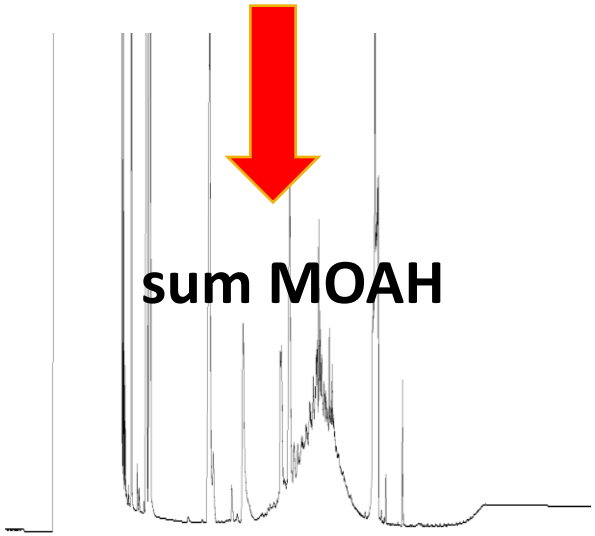


- ✓ 1D GC
- ✓ unspecific detector
- ✓ response of all substances nearly the same
- ✓ quantitative result
- ✓ sum of MOAH
- ✓ no information about type of substances

Analytical strategie

What is the „hump“?

online LC-GC-FID



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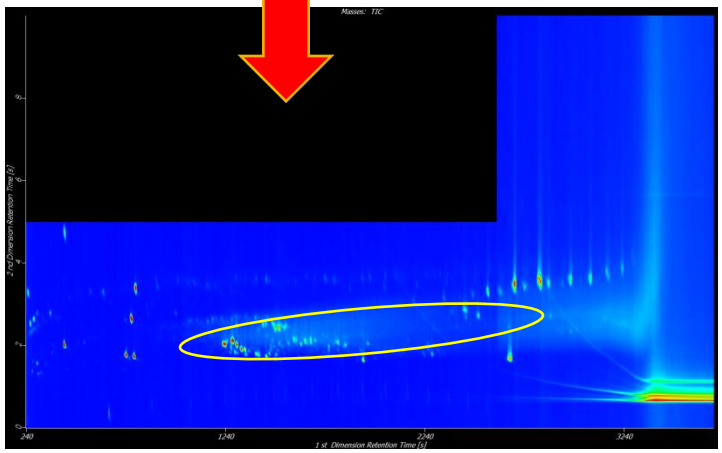
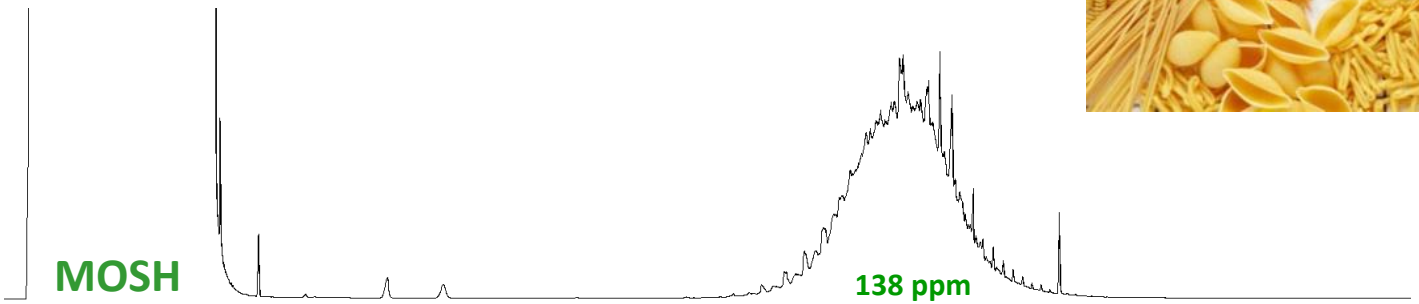
GCxGC-TOF(MS)

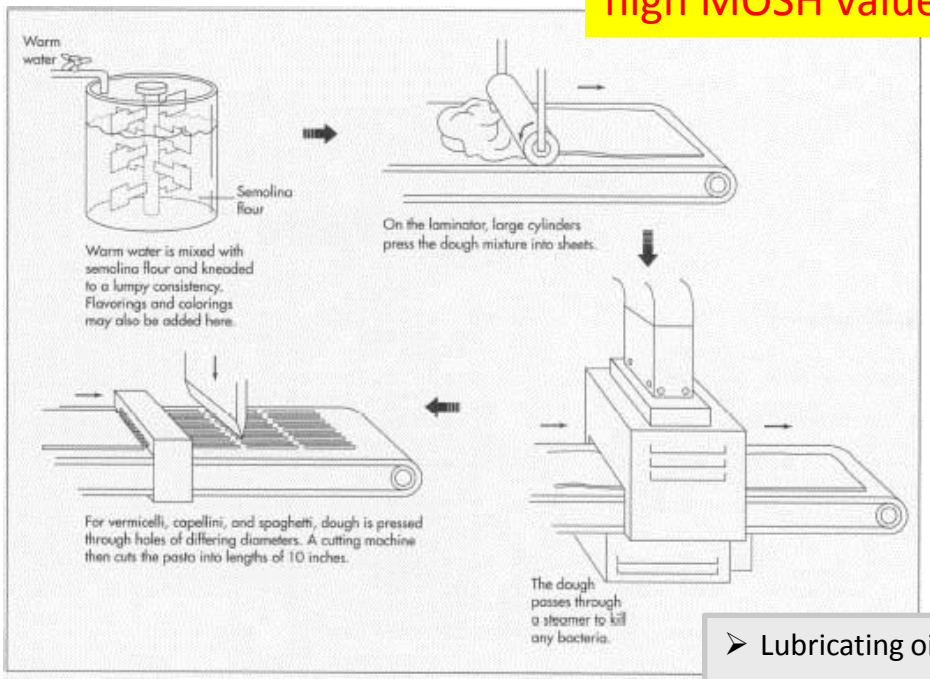


- ✓ 2D GCxGC
- ✓ mass selective detector
- ✓ qualitative result
- ✓ differentation according to substances classes possible

Noodles

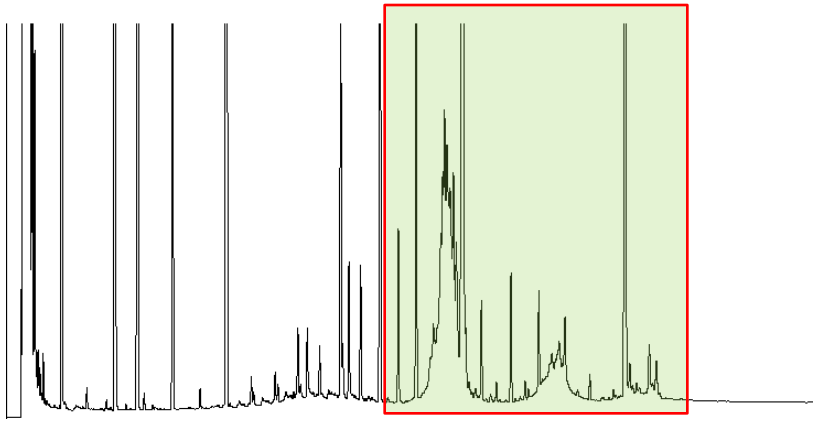


high MOSH value, free of MOAH

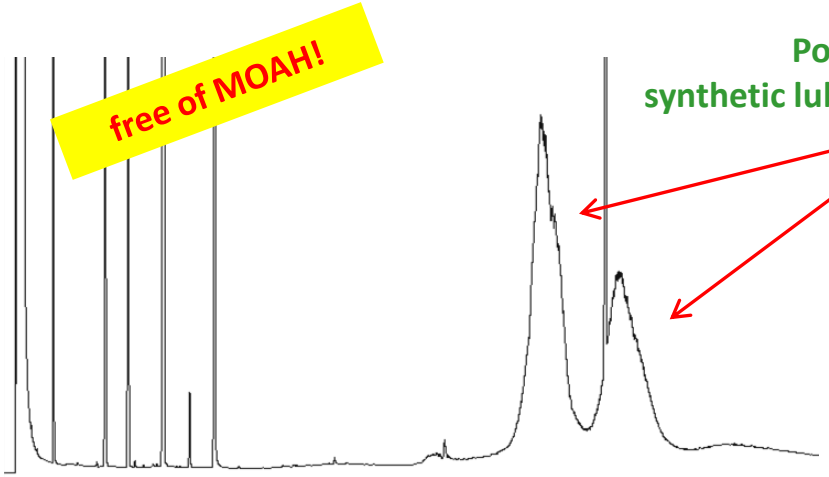


- Lubricating oil for the industrial installations, machinery
- Processing aid: release agent

Chocolate

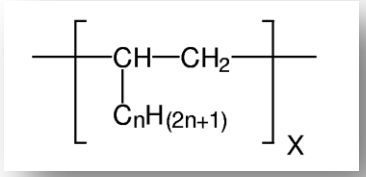


molding machine



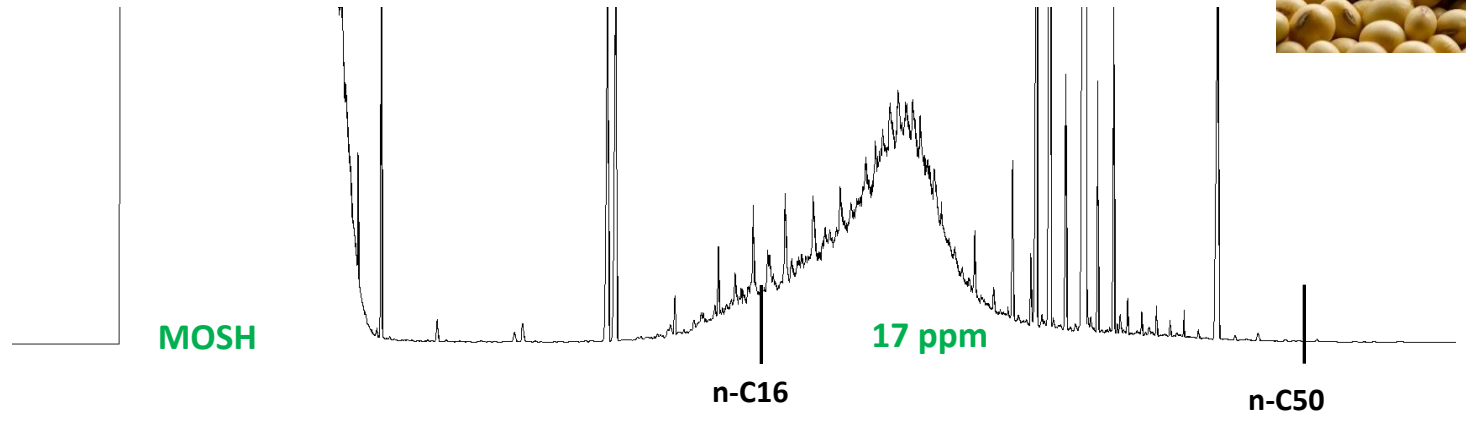
Poly-alpha-Olefin
synthetic lubricating oil (Production)

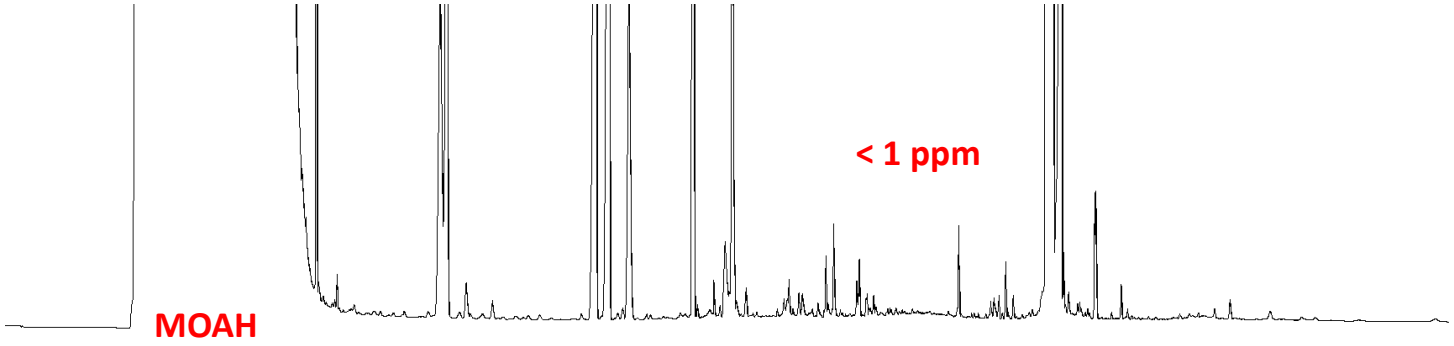
Oligomeres
from Hexen



Soybeans

Online-HPLC-GC/FID





Soybeans

Online-HPLC-GC/FID

[Code of Federal Regulations]
[Title 21, Volume 3]
[Revised as of April 1, 2015]
[CITE: 21CFR172.878]

TITLE 21--FOOD AND DRUGS
CHAPTER I--FOOD AND DRUG ADMINISTRATION
DEPARTMENT OF HEALTH AND HUMAN SERVICES
SUBCHAPTER B--FOOD FOR HUMAN CONSUMPTION (CONTINUED)

PART 172 -- FOOD ADDITIVES PERMITTED FOR DIRECT ADDITION TO FOOD FOR HUMAN CONSUMPTION

Subpart I--Multipurpose Additives

Sec. 172.878 White mineral oil.

White mineral oil may be safely used in food in accordance with the following conditions:

(a) White mineral oil is a mixture of liquid hydrocarbons, essentially paraffinic and naphthenic in nature obtained from petroleum. It is refined to meet the following specifications:

(1) It meets the test requirements of the United States Pharmacopeia XX (1980) for readily carbonizable substances (page 532).

(2) It meets the test requirements of U.S.P. XVII for sulfur compounds (page 400).

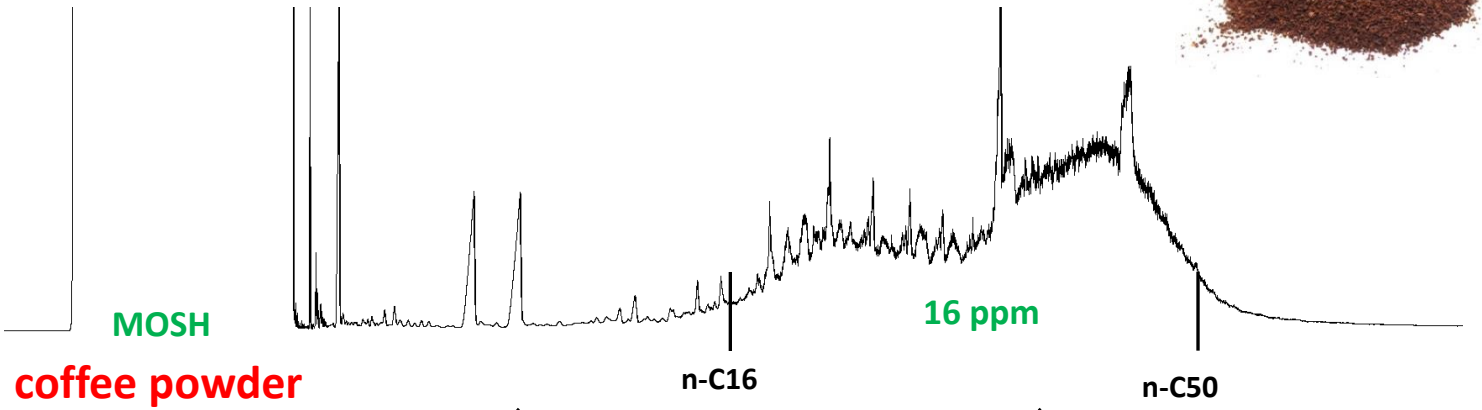
(3) It meets the specifications prescribed in the "Journal of the Association of Official Analytical Chemists," Volume 45, page 66 (1962), which is incorporated by reference, after correction of the ultraviolet absorbance for any absorbance due to added antioxidants. Copies of the material incorporated by reference are available from the Center for Food Safety and Applied Nutrition (HFS-200), Food and Drug Administration, 5100 Paint Branch Pkwy., College Park, MD 20740, or available for inspection at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to: *http://www.archives.gov/federal_register/code_of_federal_regulations/ibr_locations.html*.

(b) White mineral oil may contain any antioxidant permitted in food by regulations issued in accordance with section 409 of the Act, in an amount not greater than that required to produce its intended effect.

(c) White mineral oil is used or intended for use as follows:

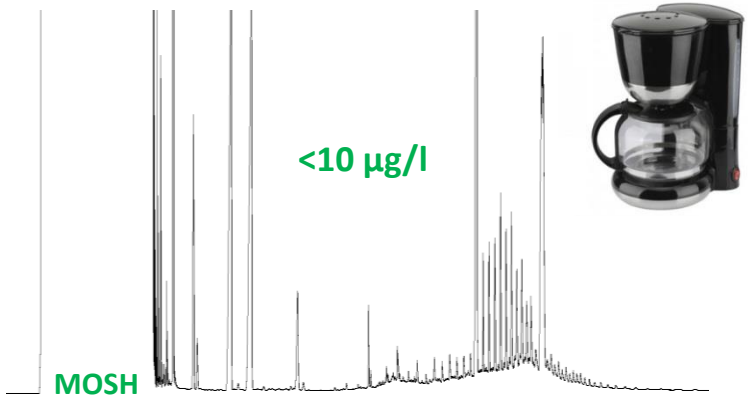
Use	Limitation (inclusive of all petroleum hydrocarbons that may be used in combination with white mineral oil)
15. As a dust control agent for wheat, corn, soybean, barley, rice, rye, oats, and sorghum	Applied at a level of no more than 0.02 percent by weight of grain.

Online-HPLC-GC/FID

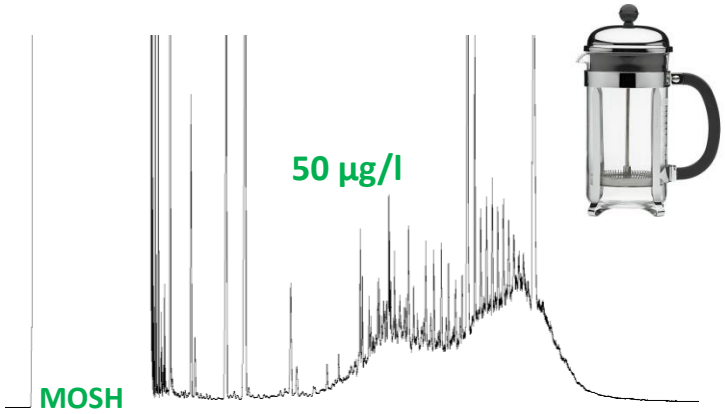


coffee powder

coffee infusion



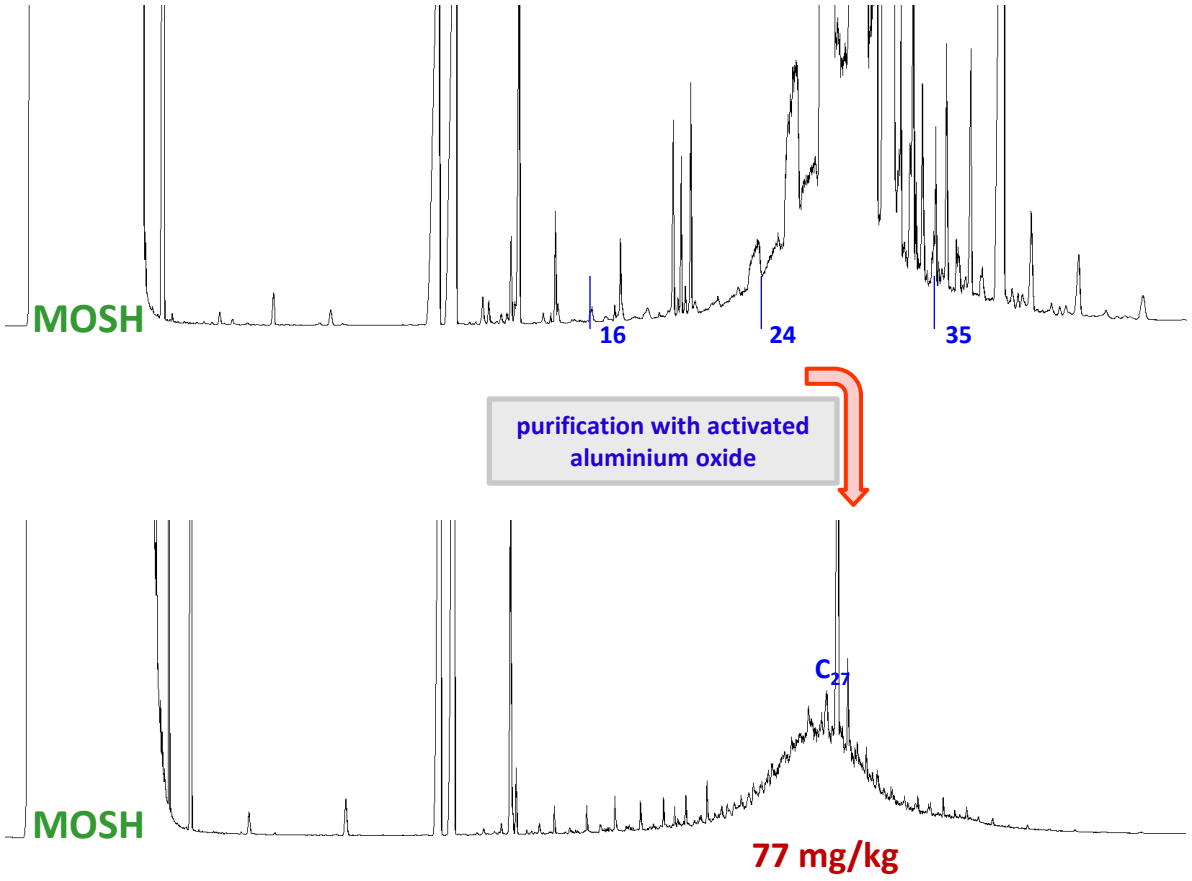
filter-machine



French Press

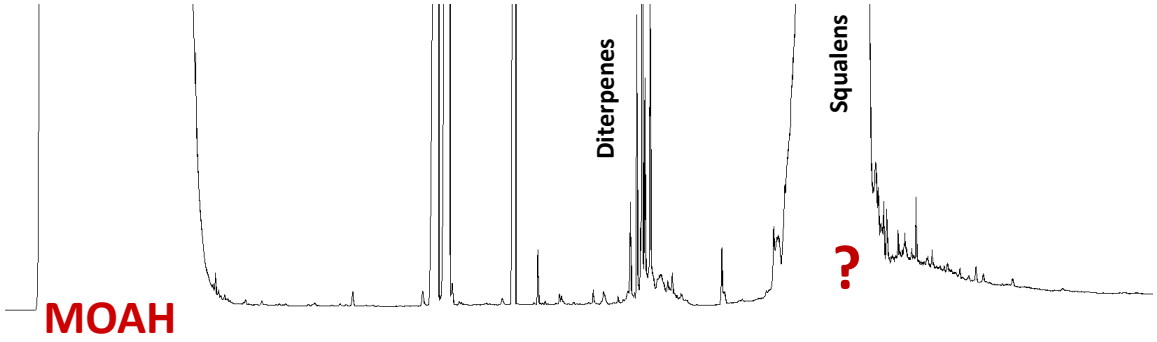
Sunflower oil

strong interferences

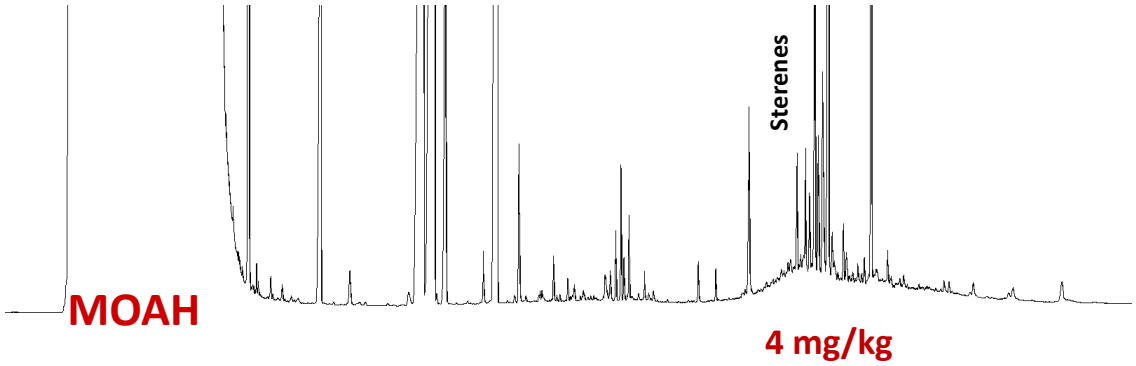


-> no significant retention for longchain iso-alkanes
-> no significant retention for n-alkanes until C20
-> high increasing retention for longchain n-alkanes

Peanut Oil

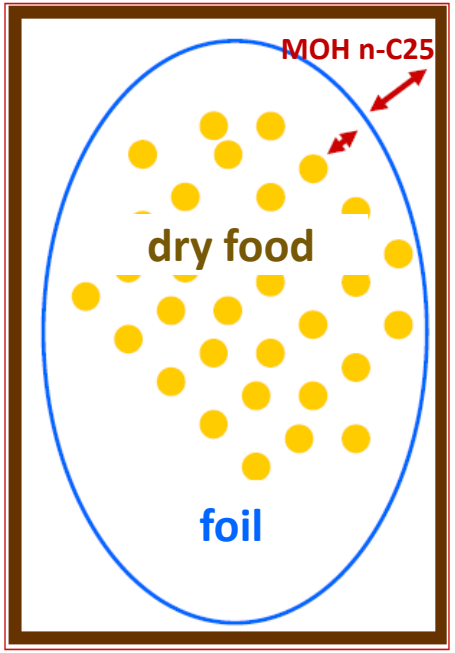


Epoxydidation



Migration from the packaging

into dry food

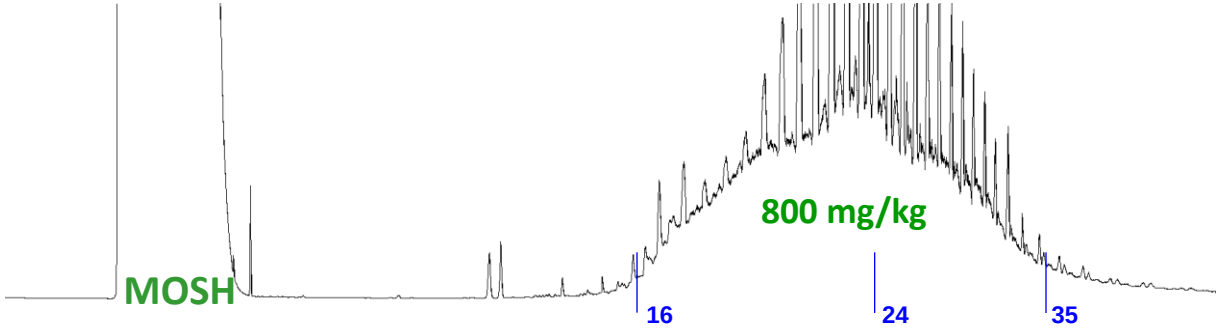


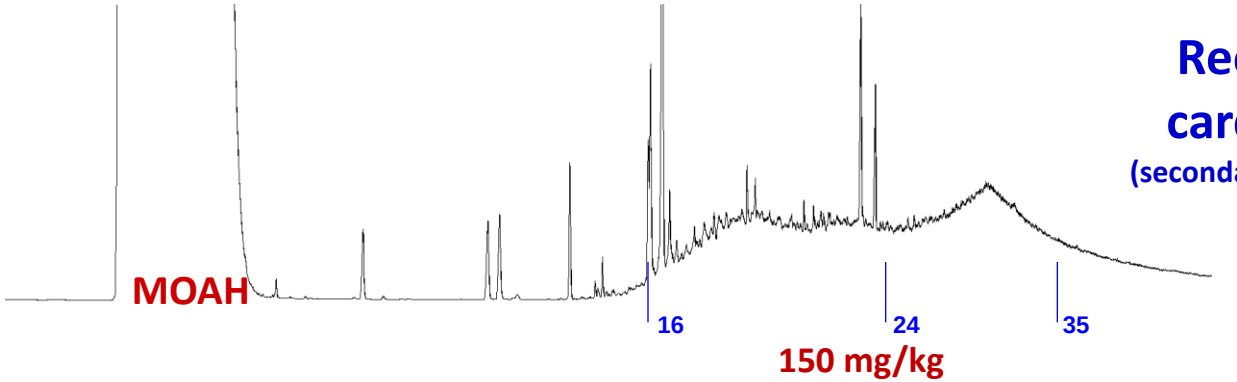
FCM

Mineral oil constituents which are released from food contact materials (FCM) enter food either by direct contact between the package and the solid food or through the gas phase (evaporation and recondensation).

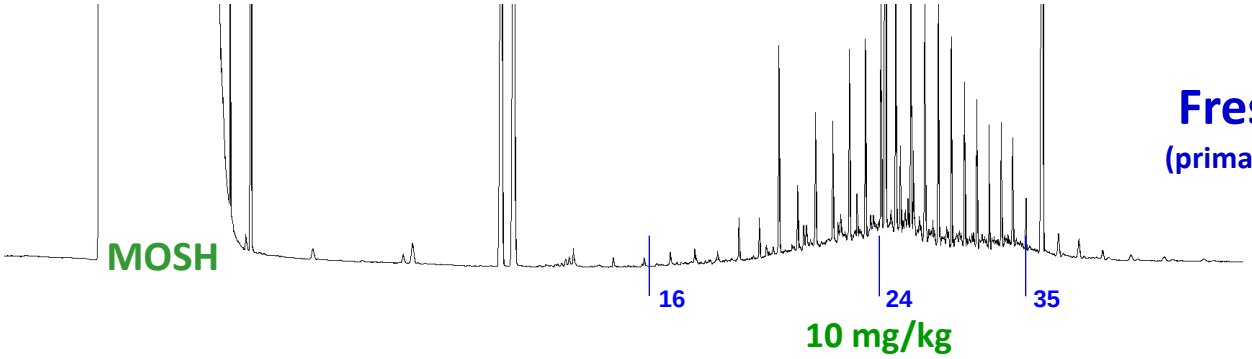
Penetration from outer packaging through inner pouches or bags represents another possible mechanism.

Carton board



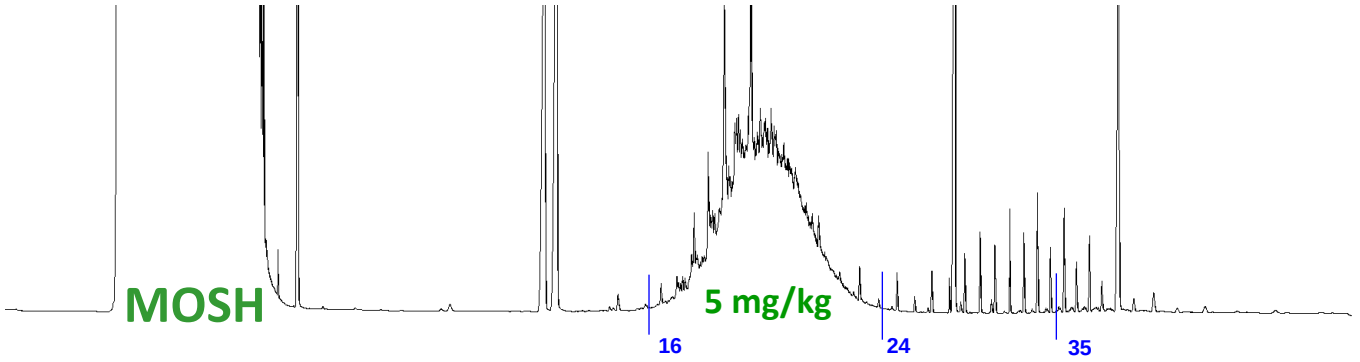


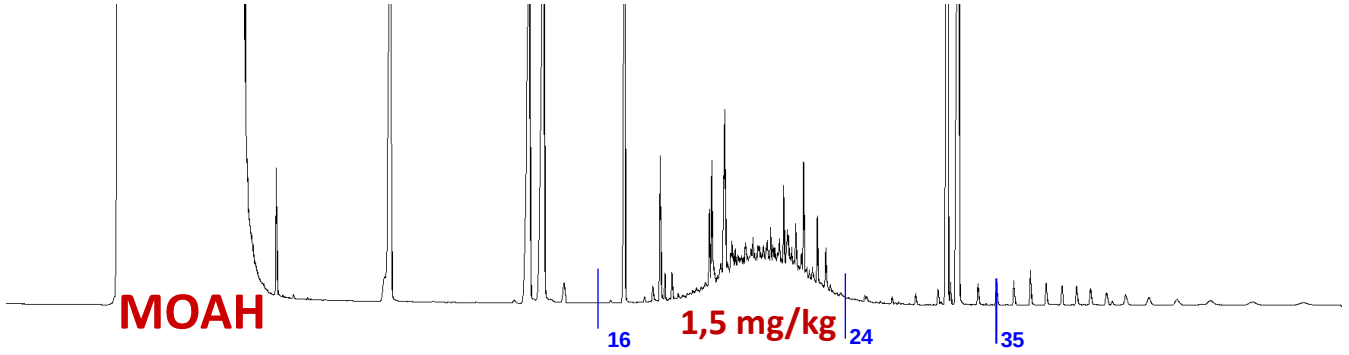
Recycling cardboard
(secondary cardboard)



Fresh fibre
(primarily cardboard)

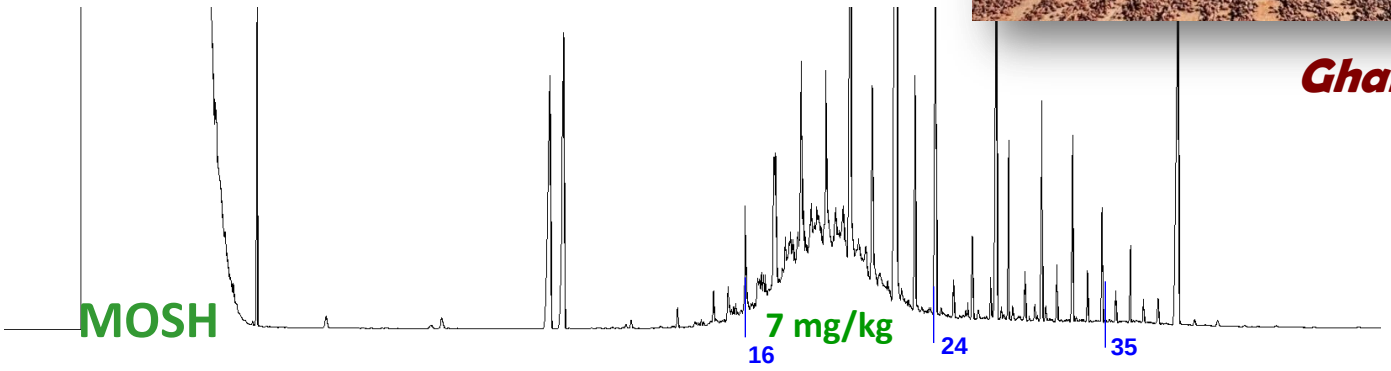
Cornflakes

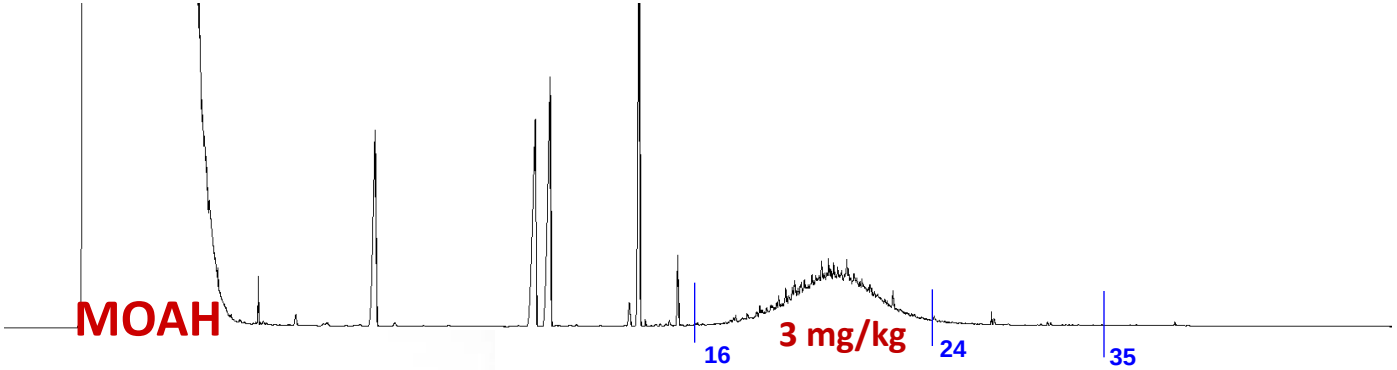




Cacao beans

Ghana



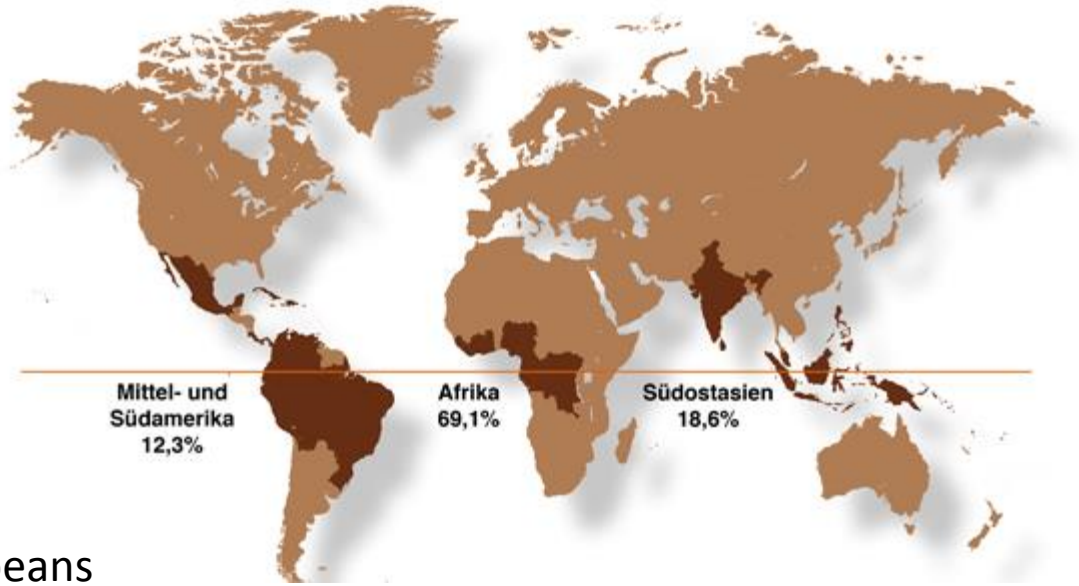


Origin: mineral batching oil used for spinning jute fibers contaminated the cacao beans packed in corresponding bags during transport.

Project LCI

- 14 jutebags from 7 different countries

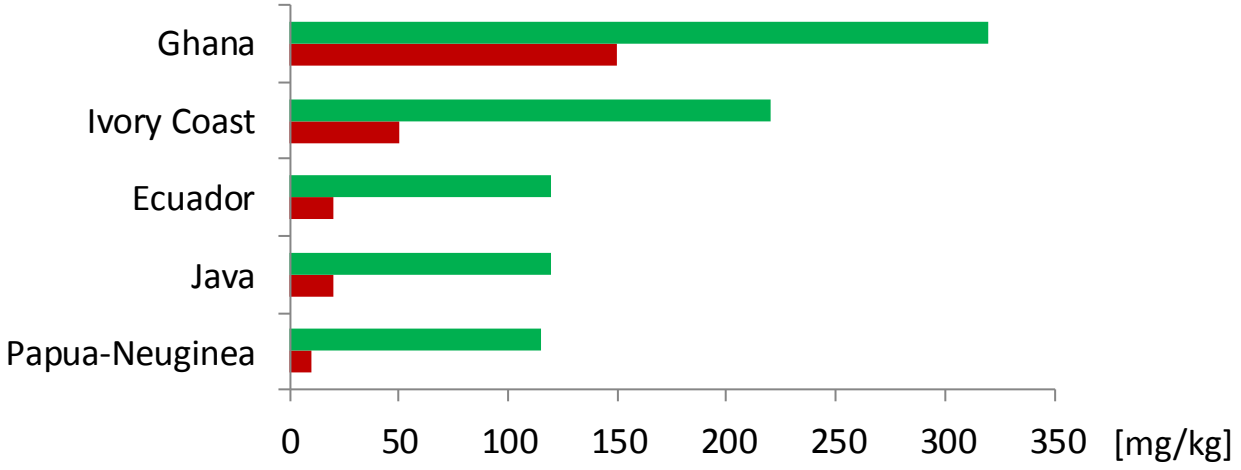
- Ivory coast (3)
- Ecuador (2)
- Ghana (2)
- Papua Neu Ginea
- Java
- India (4)
- Nigeria



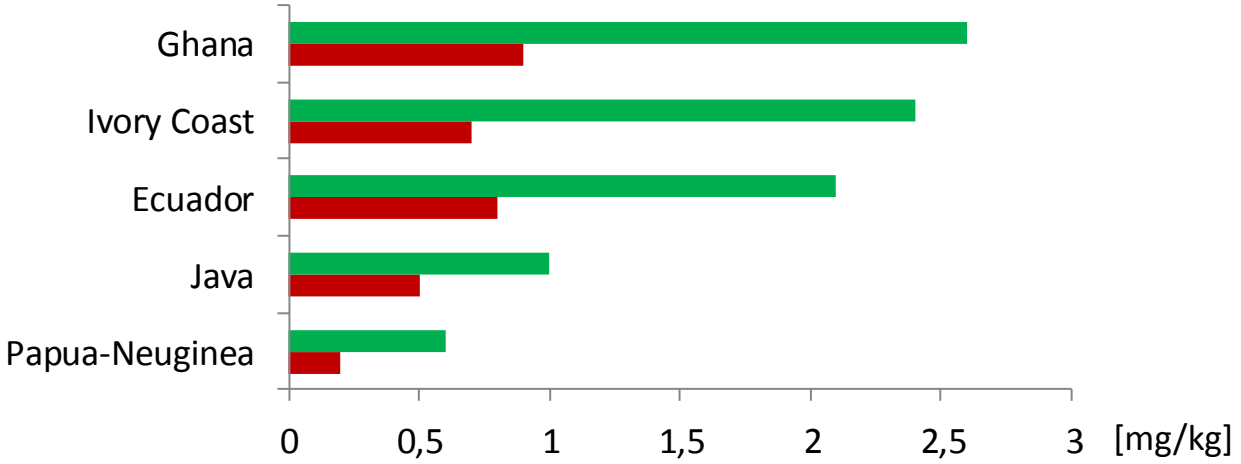
- 5 samples cacao beans
- 1 samples cacao shells

Project LCI

Jutebags

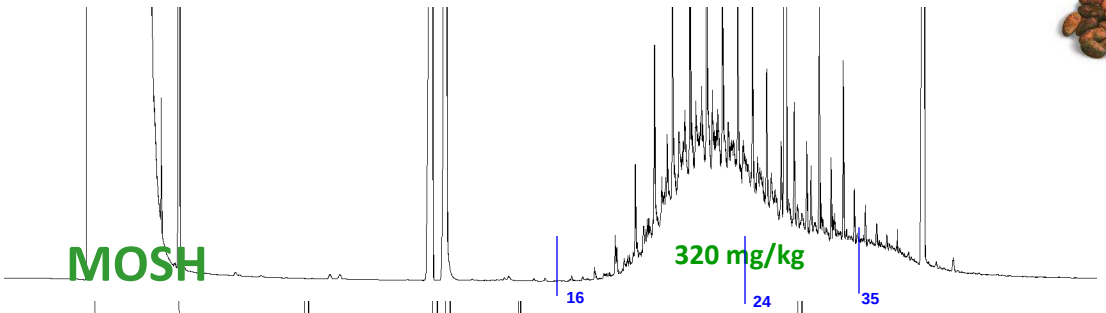


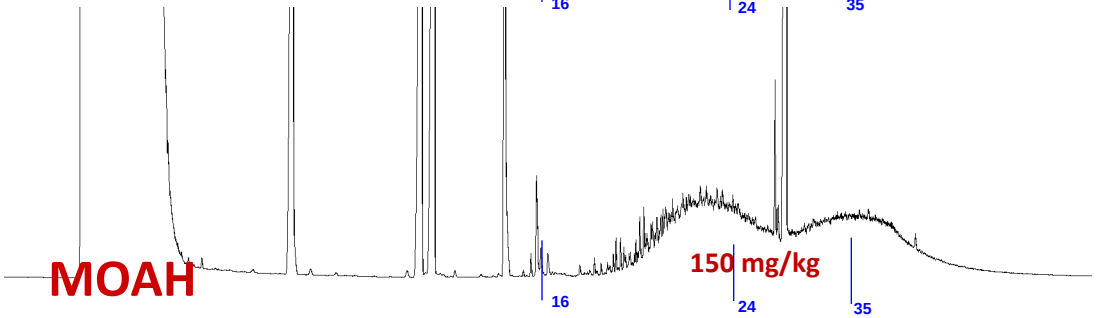
Cacao beans



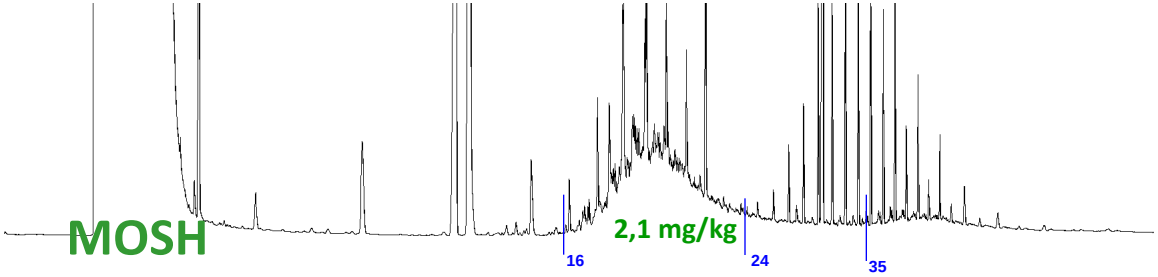
Cacaobeans + Jutebag

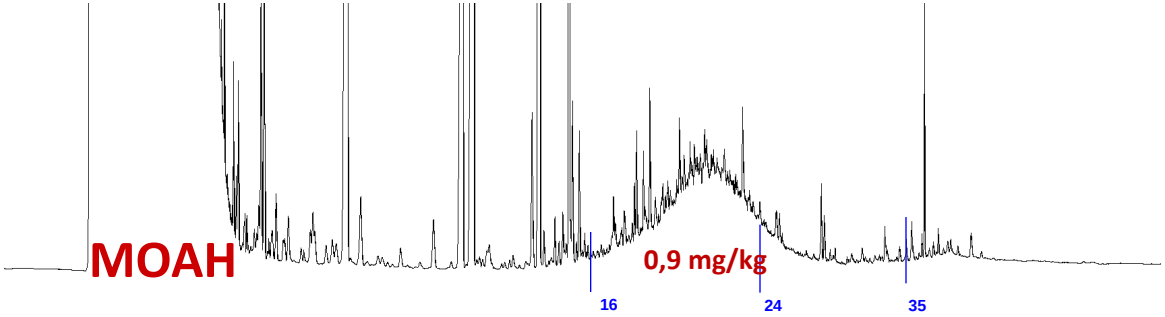
Online-HPLC-GC/FID





Jutebag



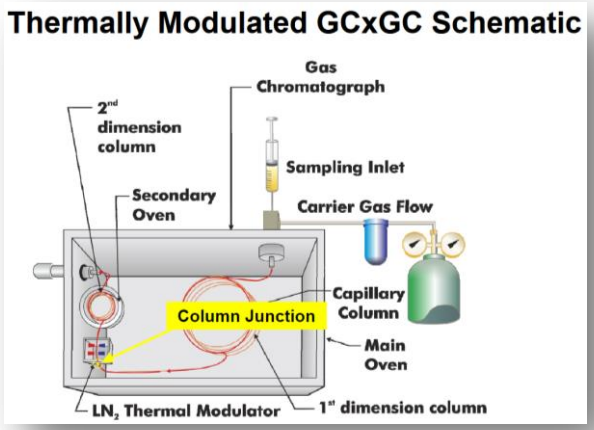


Cacao beans

Characterization of the aromatic hydrocarbon-fraction

GCxGC-TOF MS

In the determination of mineral oil hydrocarbons a single-component analysis is not possible because of the enormous number of compounds. The mixtures can be extensive characterized but by two-dimensional GC (GCxGC). With GCxGC-TOF MS the MOAHs can be grouped on the number of aromatic rings.
In the GCxGC two columns with orthogonal separation properties (polar / non-polar) are used instead of a GC separation column, thereby it is possible to enhance the chromatographic resolution, and thus the peak capacity significantly. There is a separation by boiling points and polarity. The eluate of the first column is divided into fixed set units, thermally focused, further separated on the second column, and finally detected. It is necessary to perform a very rapid chromatography on the second column to make the separation times of both columns compatible. This generates very narrow peak widths, which are mapped by a high-speed receiving detector system such as the TOF.



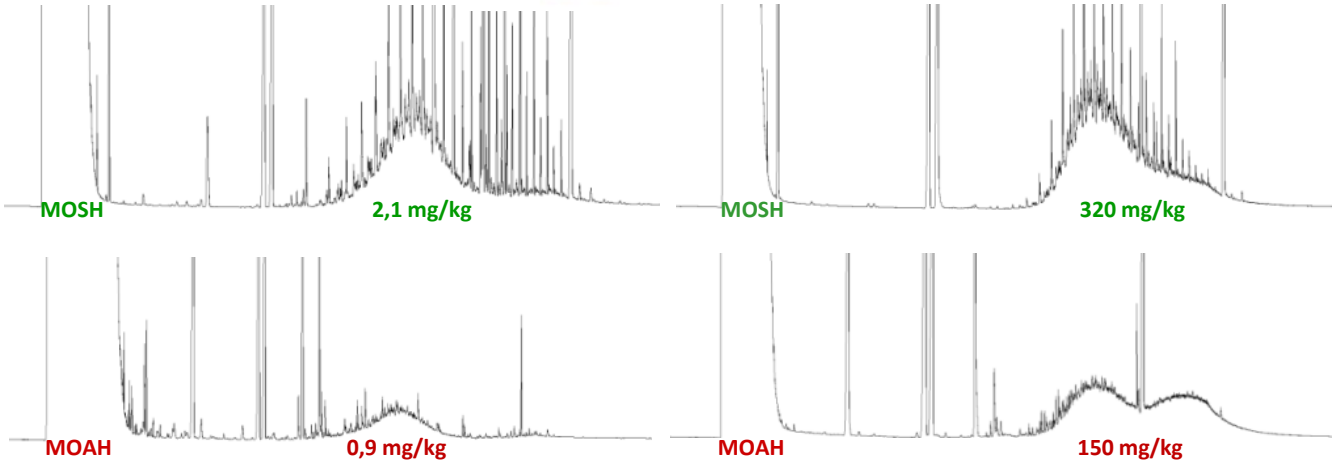
Cacaobeans + Jutebag

Online-HPLC-GC/FID and GCxGC/TOF MS

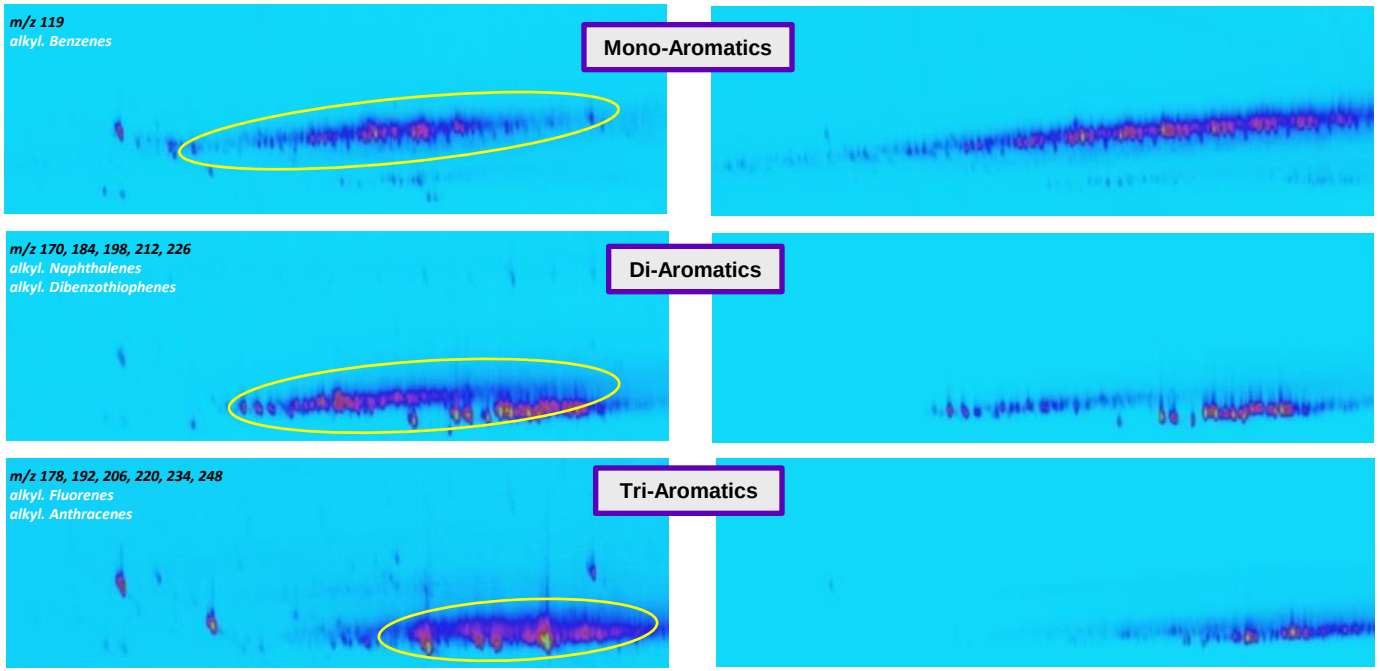
Cacaobeans

Jutebag

Online-HPLC-GC/FID



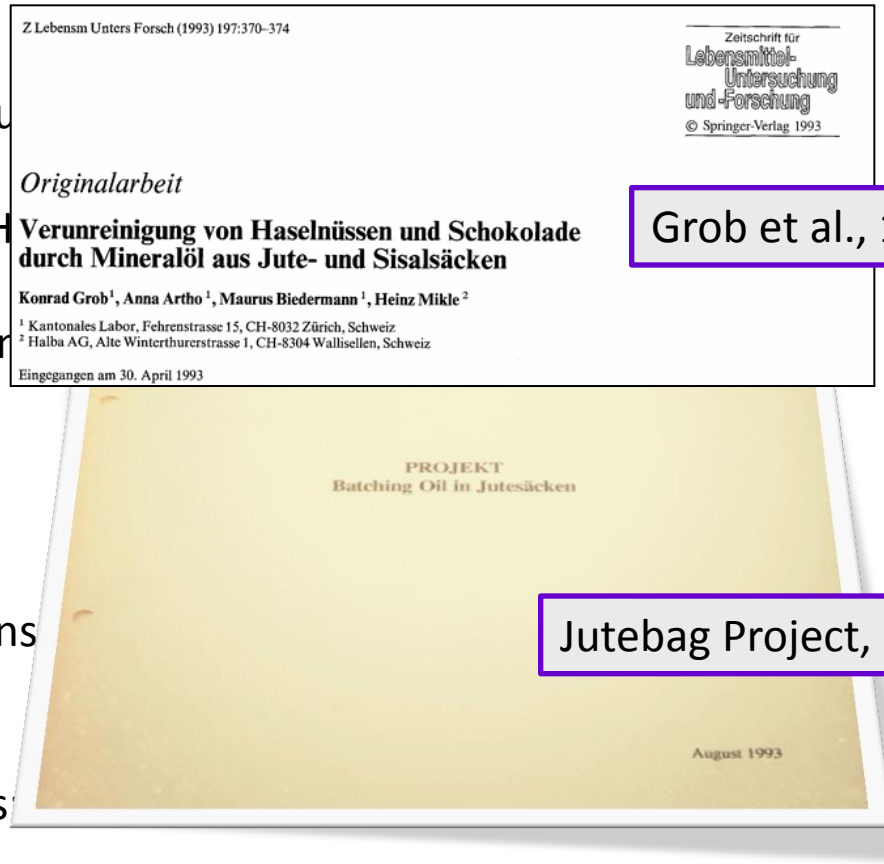
GCxGC/TOFMS



Project LCI

Results

- no of the ju
- next MOSH
- different ar
- Jutebags:
- Cacao Beans
- Hypothesis



Z Lebensm Unters Forsch (1993) 197:370–374

Zeitschrift für Lebensmittel-Untersuchung und -Forschung

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Originalarbeit

Verunreinigung von Haselnüssen und Schokolade durch Mineralöl aus Jute- und Sisalsäcken

Konrad Grob [1], Anna Artho [1], Maurus Biedermann [1], Heinz Mikle [2]

[1] Kantonales Labor, Fehrenstrasse 15, CH-8032 Zürich, Schweiz
[2] Halba AG, Alte Winterthurerstrasse 1, CH-8304 Wallisellen, Schweiz

Eingegangen am 30. April 1993

PROJEKT
Batching Oil in Jutesäcken

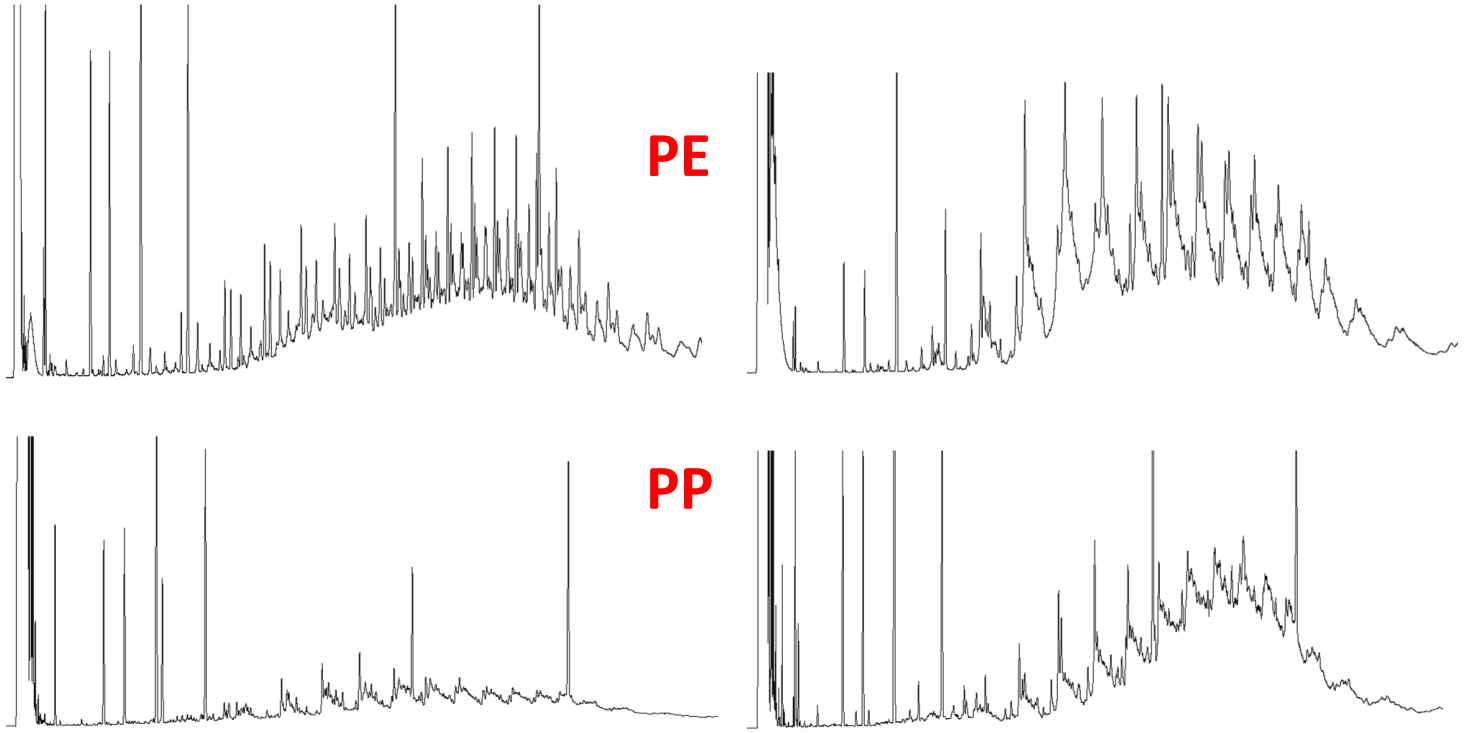
August 1993

Grob et al., 1993

Jutebag Project, IKB 1993

w

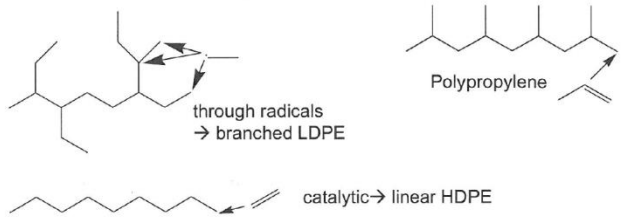
POSH - polymer oligomeric saturated hydrocarbons



MOSH-Fractions from different foil materials

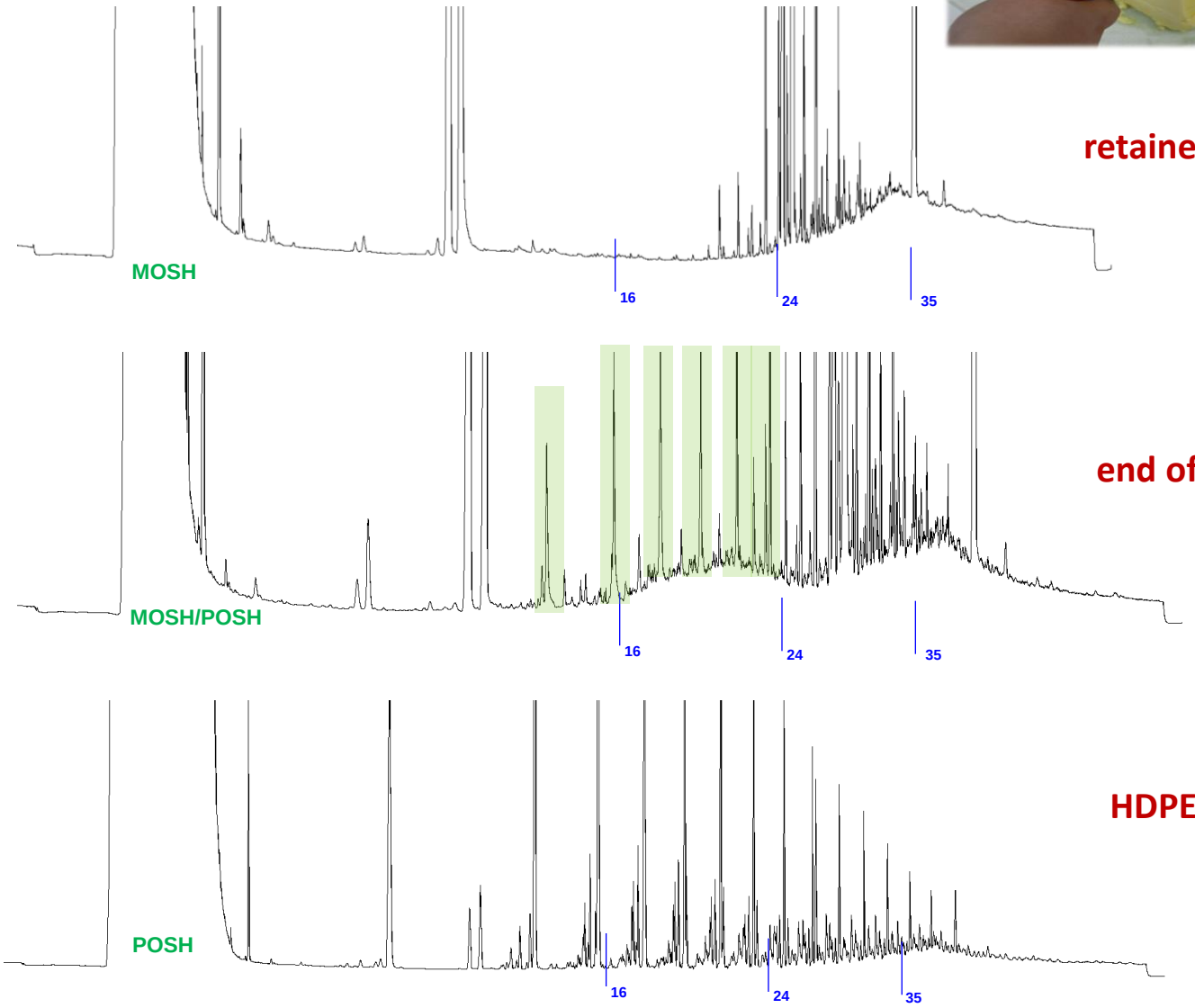
Polyethylene:
- Ziegler-Natta: irregularly branched chains → LDPE
- metallocene-catalyzed: linear, even numbered alkanes → HDPE

Polypropylene: branched open chains
- isotactic, syndiotactic, atactic: position of the methyl groups
- does not explain the complexity observed in GC



Migration MOSH/POSH

retained sample - end of shelf life

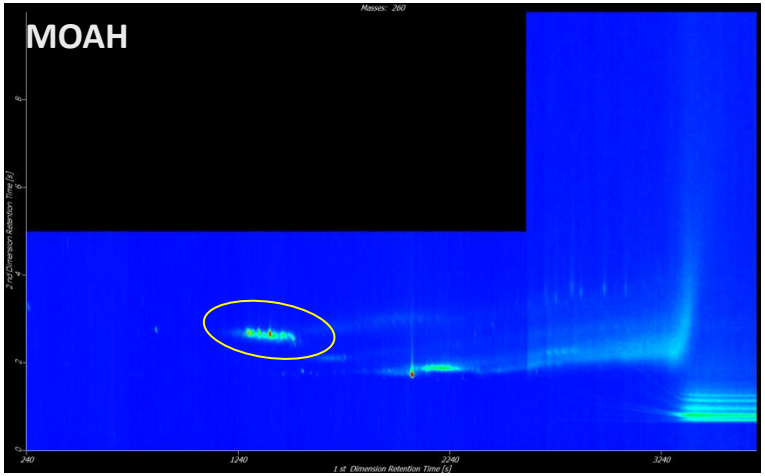


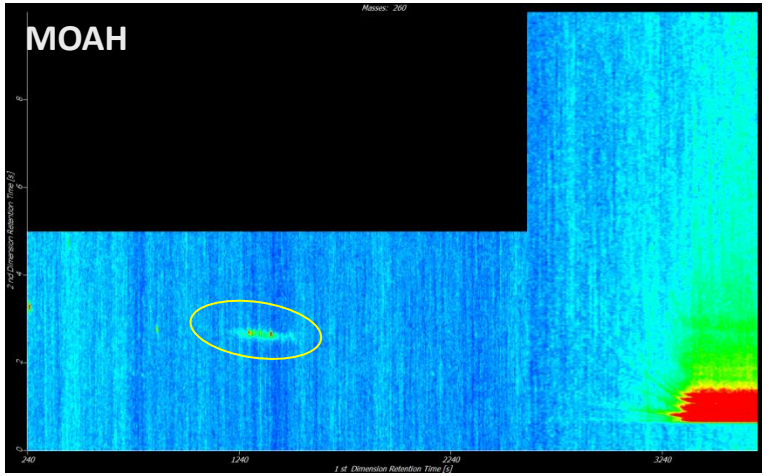
Cornflakes + Package

GCxGC/TOFMS

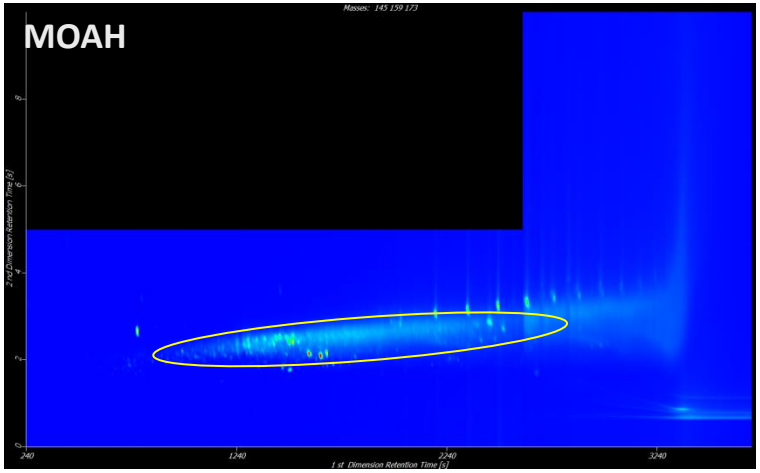
Package

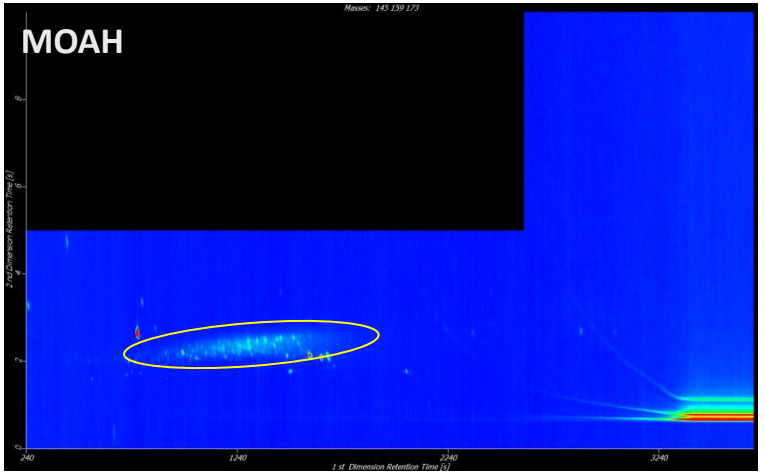
Cornflakes





m/z 260– 13C alkylated Benzenes





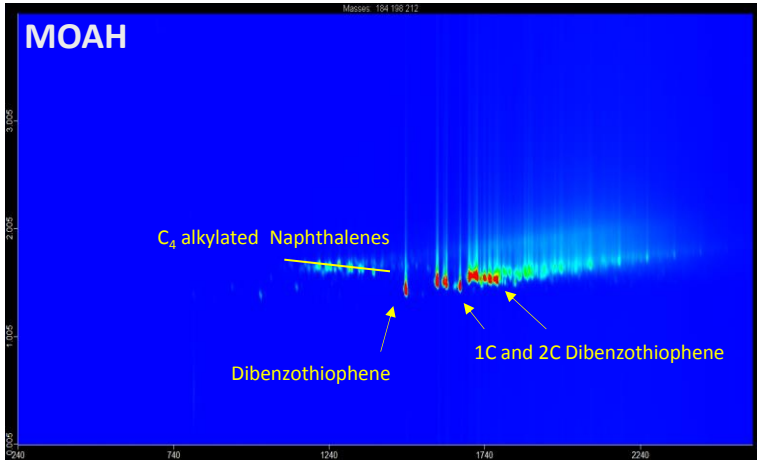
m/z 145 159 173– nC alkylated tetrahydro Naphthalenes

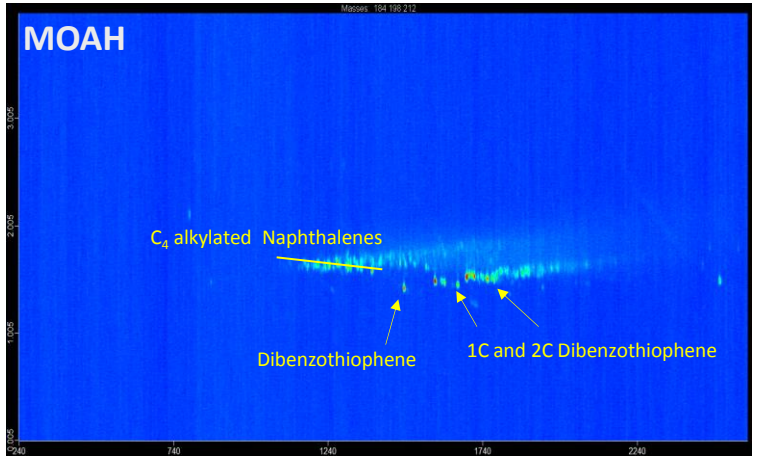
Coffee + Jutebag

GCxGC/TOFMS

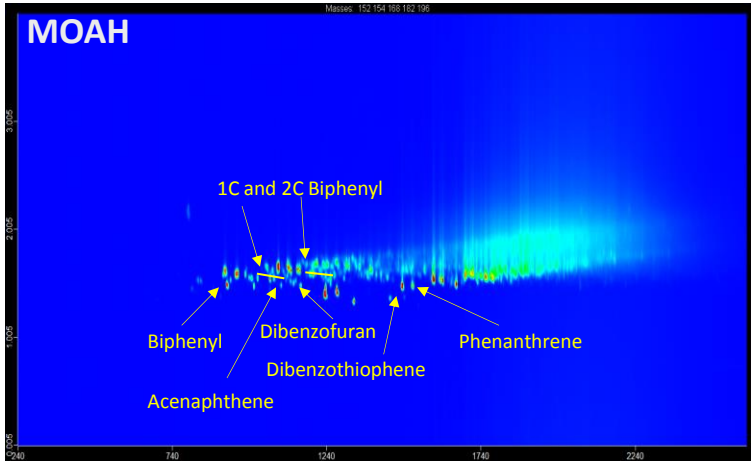
jutebag

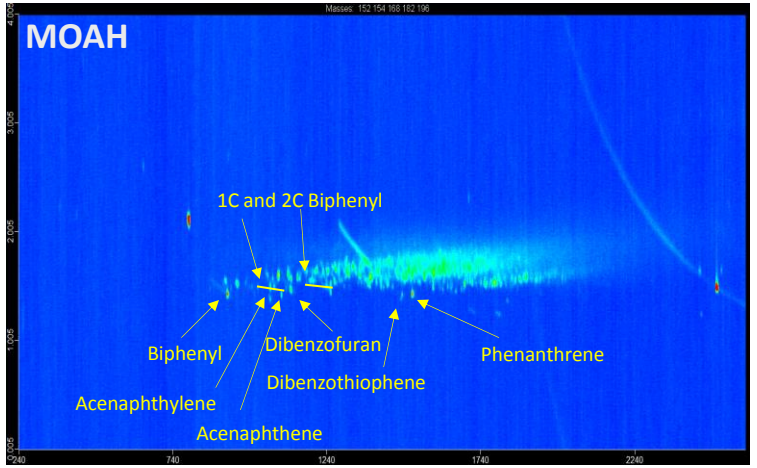
coffee





m/z 184 198 212 – Dibenzothiophene, 1-2C alkylated Dibenzothiophenes, 4C alkylated Naphthalenes





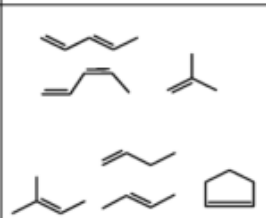
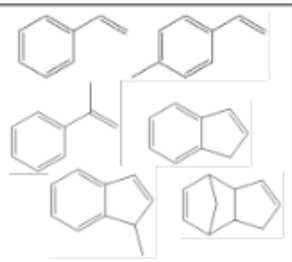
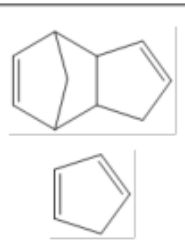
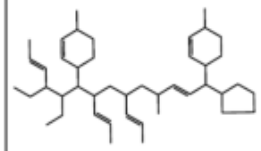
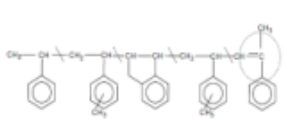
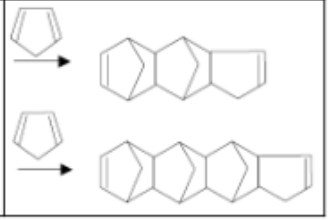
m/z 152 154 168 182 196 Biphenyl, 1-2C Biphenyl, Acenaphtylene, Acenaphtene, Dibenzofuran, Dibenzothiophene, Phenanthrene

Hotmelts - Composition

Waxes	Resins	Polymers	Additives
-natural waxes	- Rosin resins	- PA, PE, EVA, PES, PU (elatomers/copolymers)	- Antioxidants
- Synthetic waxes	- Terpene resins		- UV-Absorber
- Paraffin waxes	- Hydrocarbon resins		- Chelating agent

-> Products of petrol chemistry

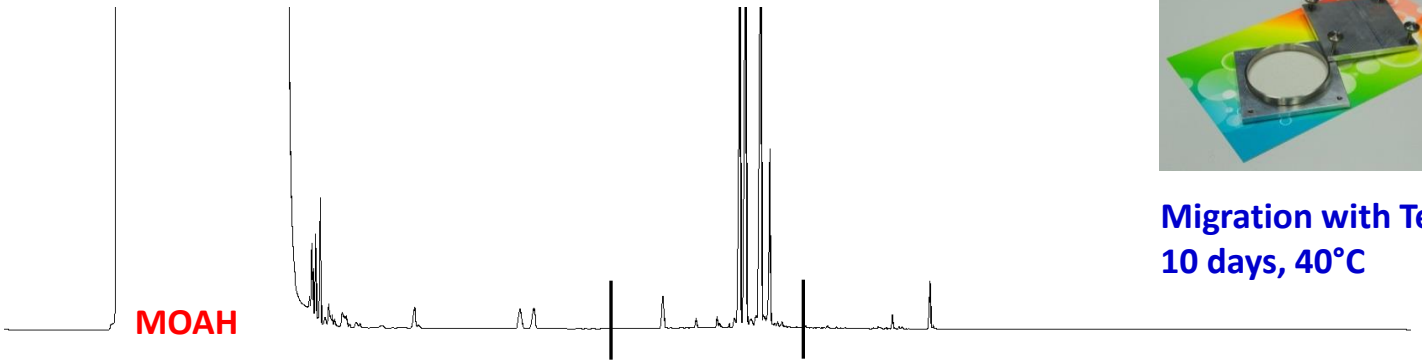
Resins

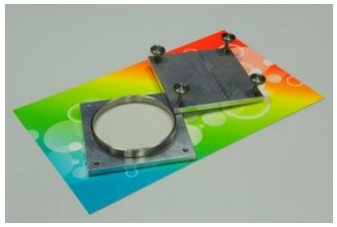
Fraction	C5 *(«Piperylenes»)*	C9 *(«Aromatics»)*	DCPD *(Dicyclopentadienes and Cyclopentadienes)*
Educts			
Products			

→ These products can be fully or partially hydrogenated after synthesis

Hotmelt

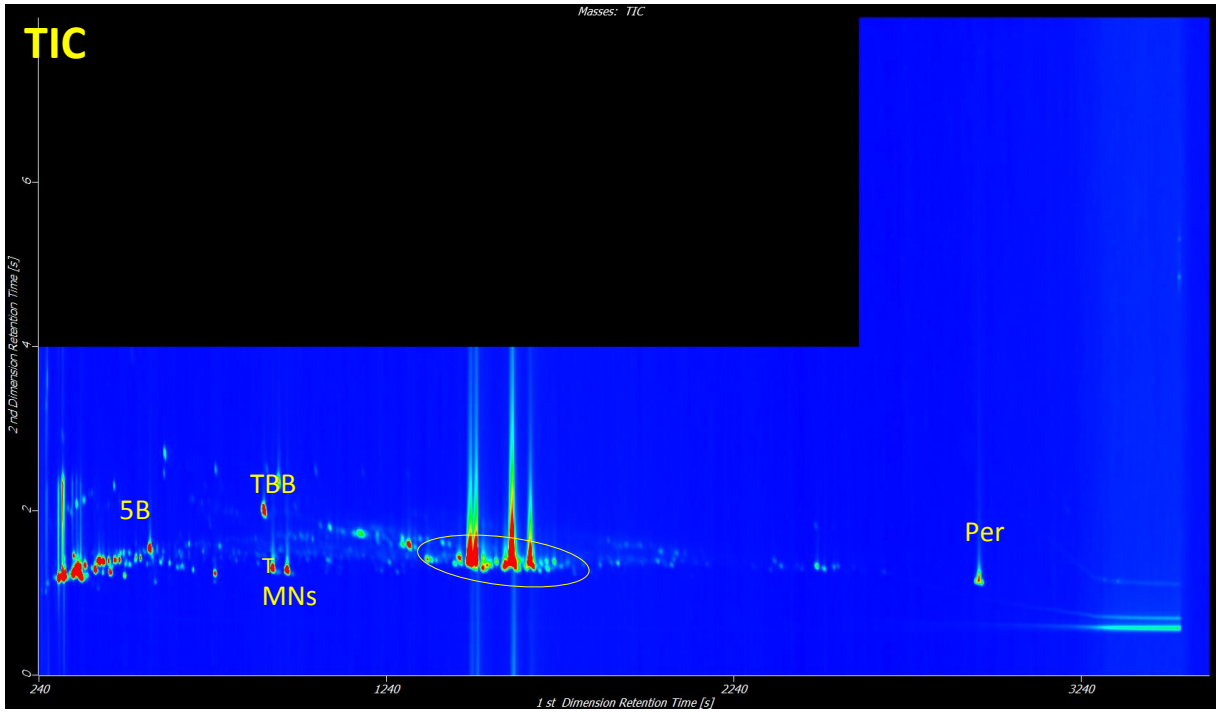
Online-HPLC-GC/FID





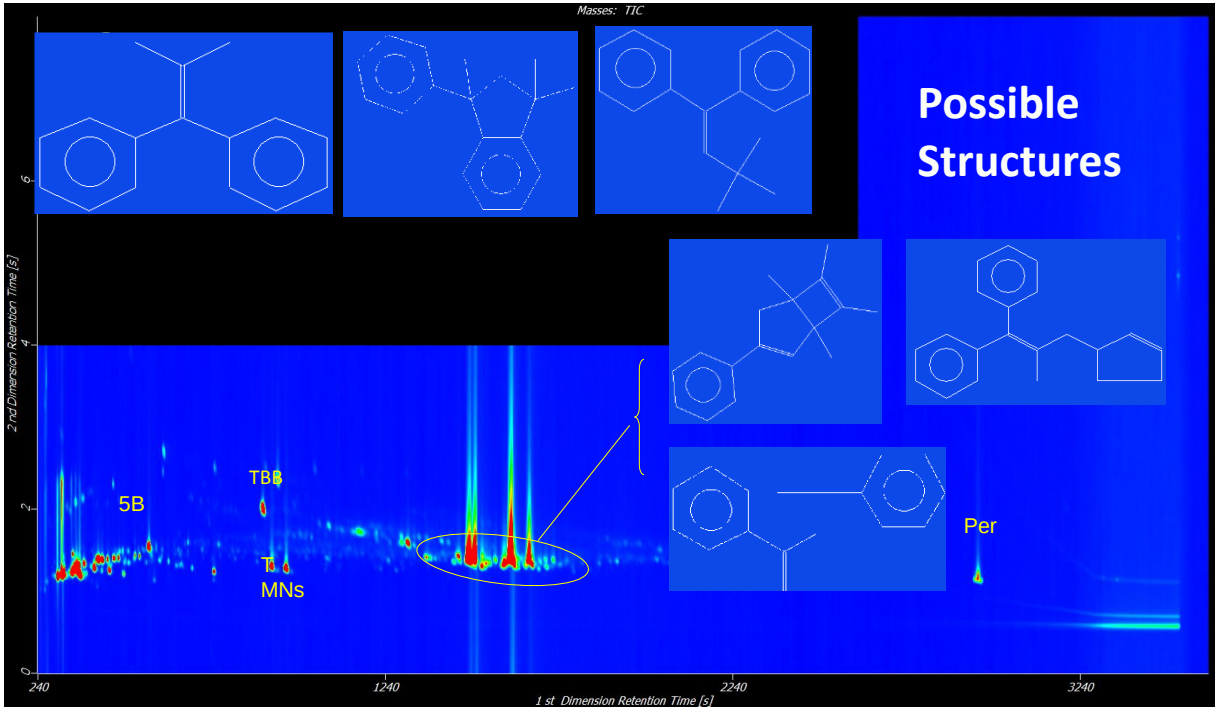
Migration with Tenax ®
10 days, 40°C

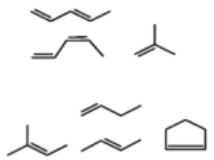
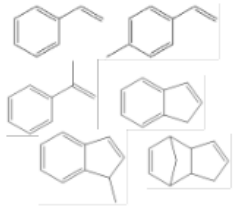
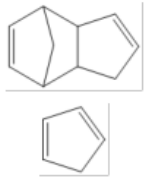
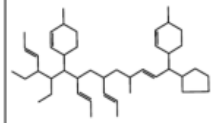
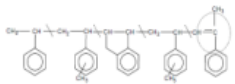
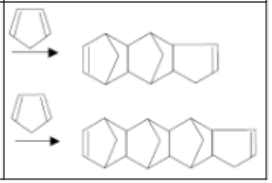
GCxGC/TOFMS



Hotmelt

GCxGC/TOFMS

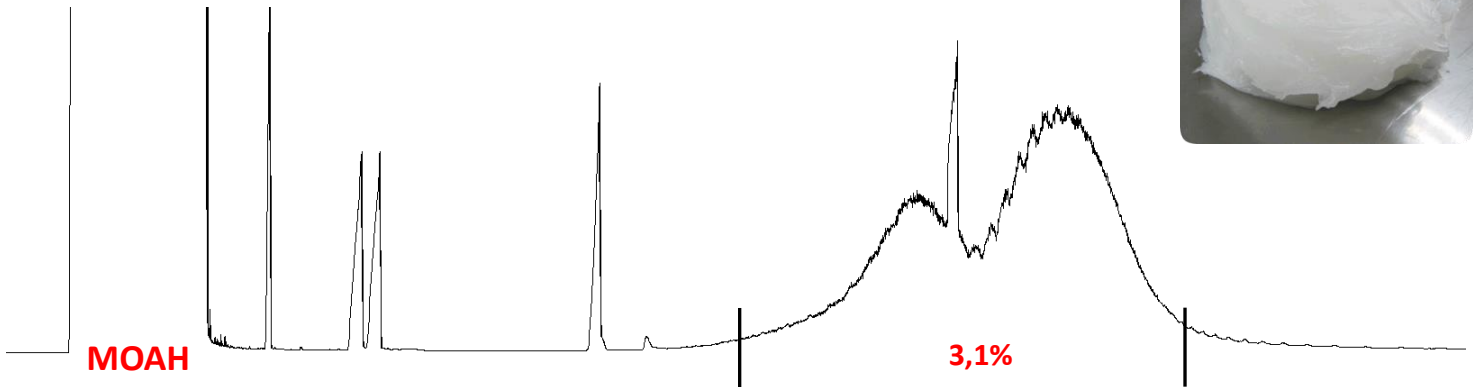


Fraction	C5 *(«Piperylenes»)*	C9 *(«Aromatics»)*	DCPD *(Dicyclopentadienes and Cyclopentadienes)*
Educts			
Products			

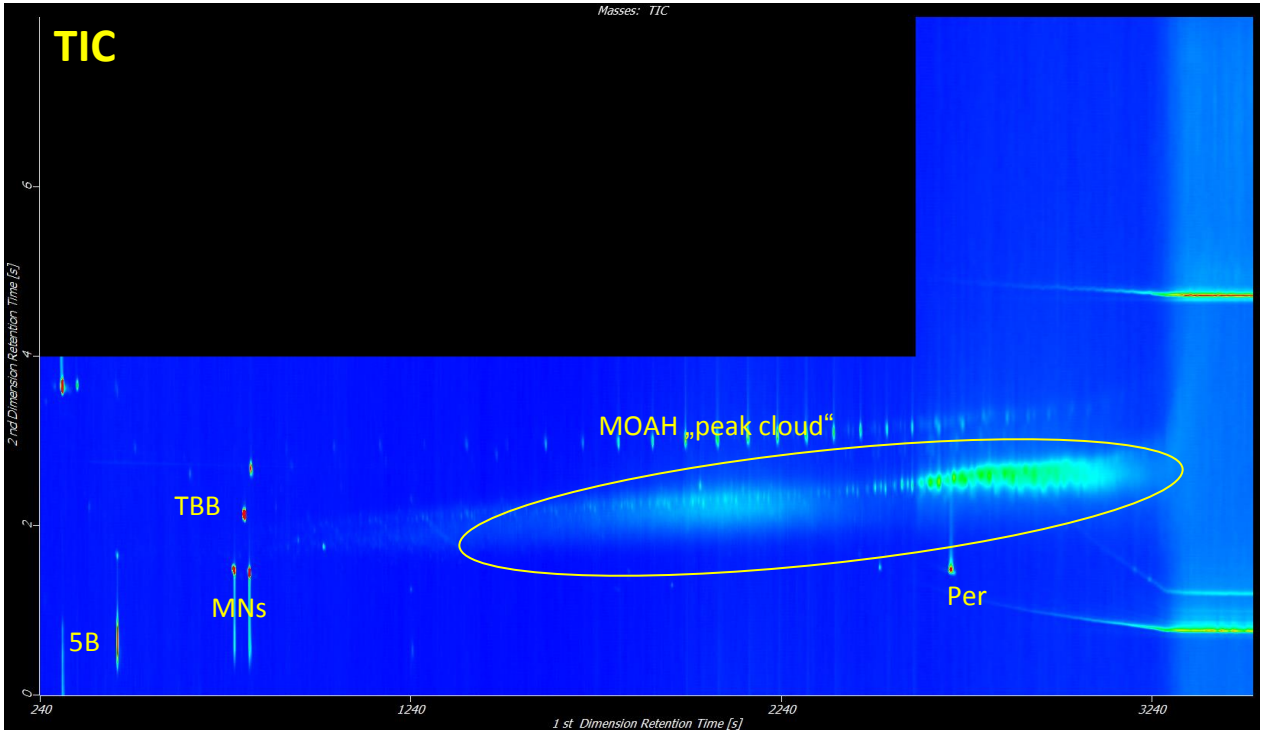
→ These products can be fully or partially hydrogenated after synthesis

Petrolatum

Online-HPLC-GC/FID



GCxGC/TOFMS



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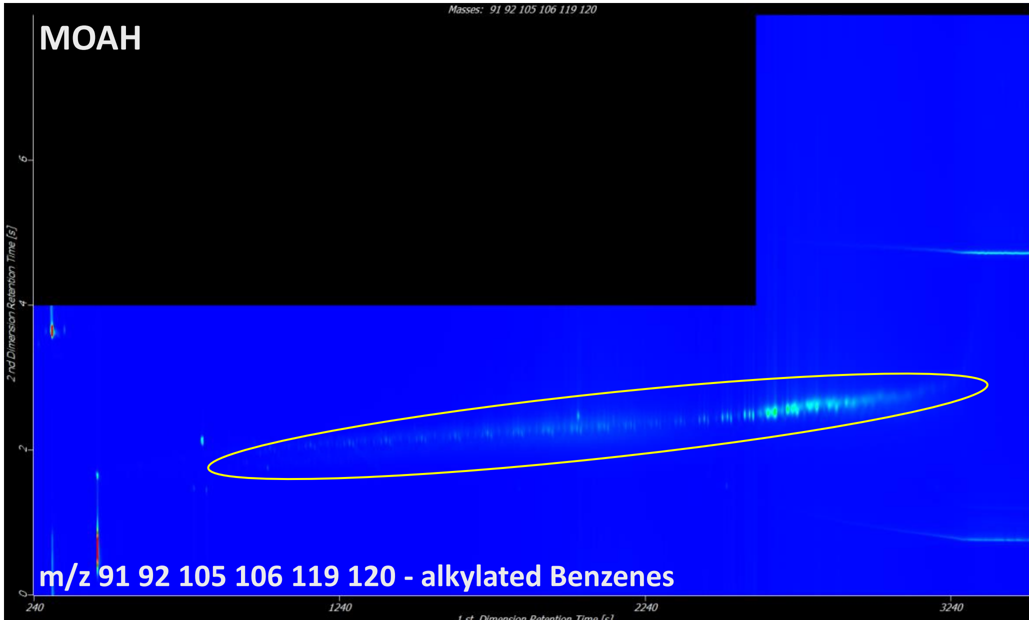

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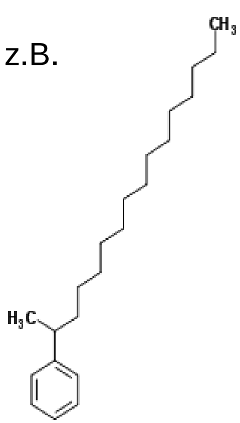
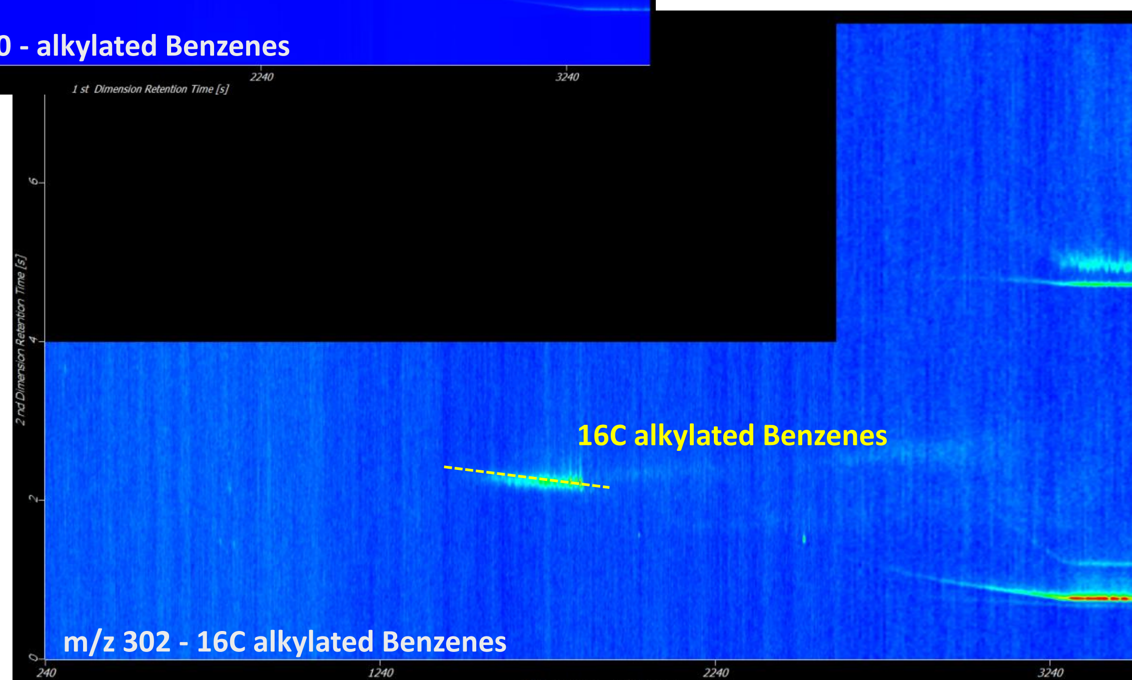
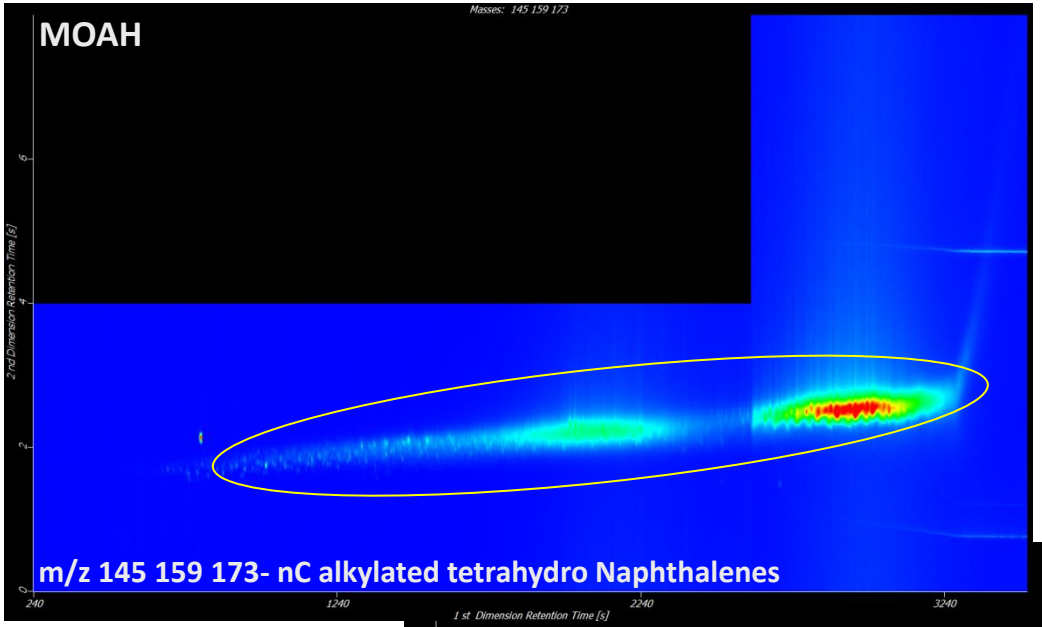




Petrolatum

GCxGC/TOFMS



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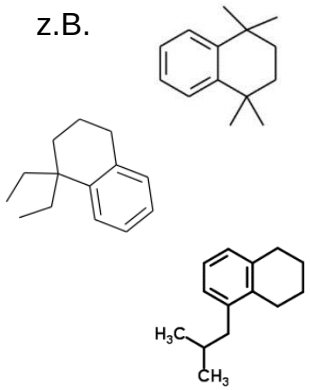
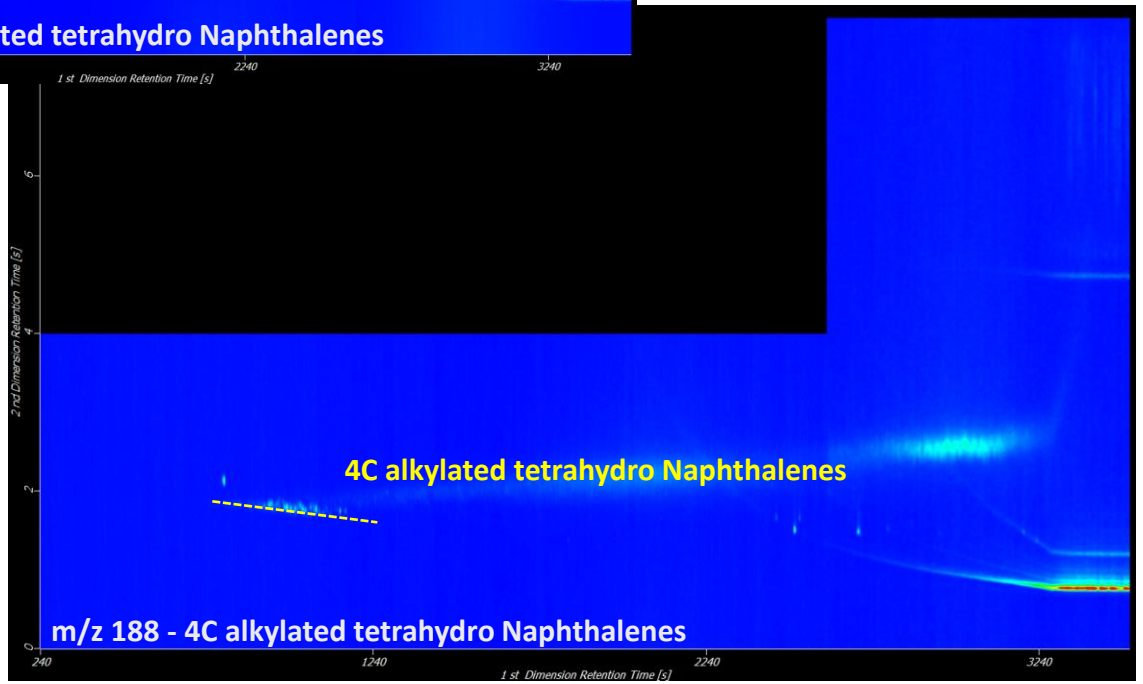
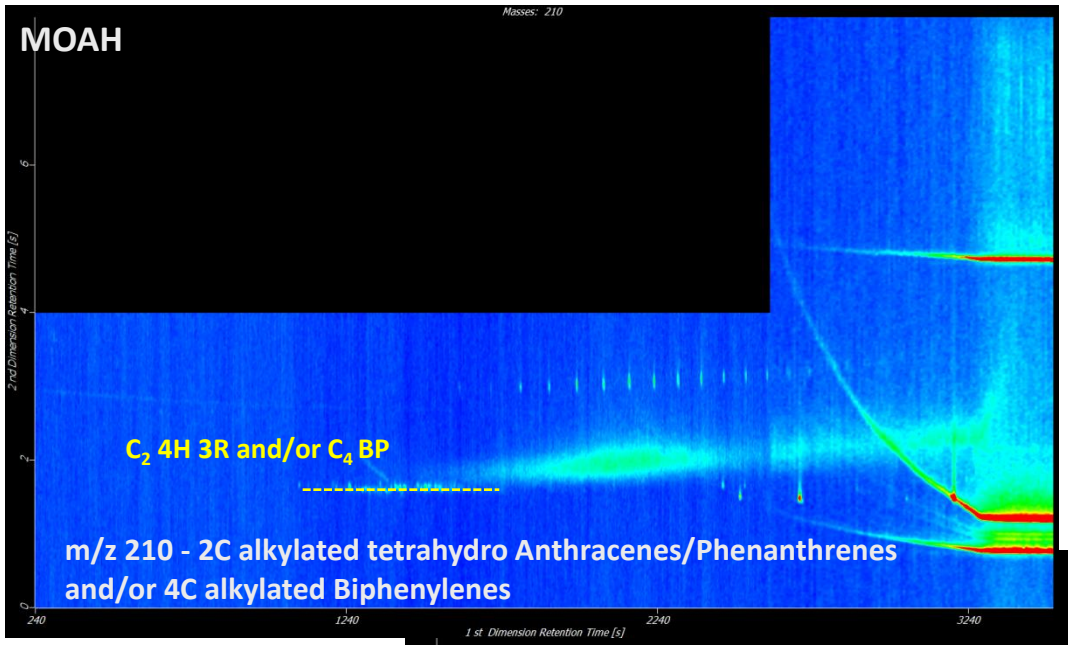
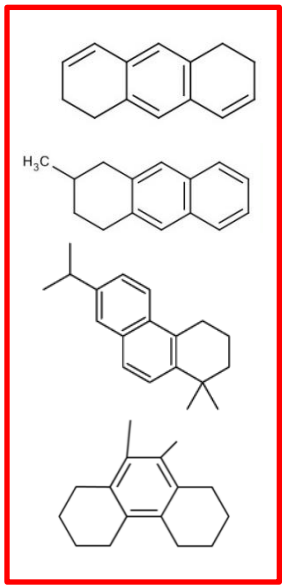


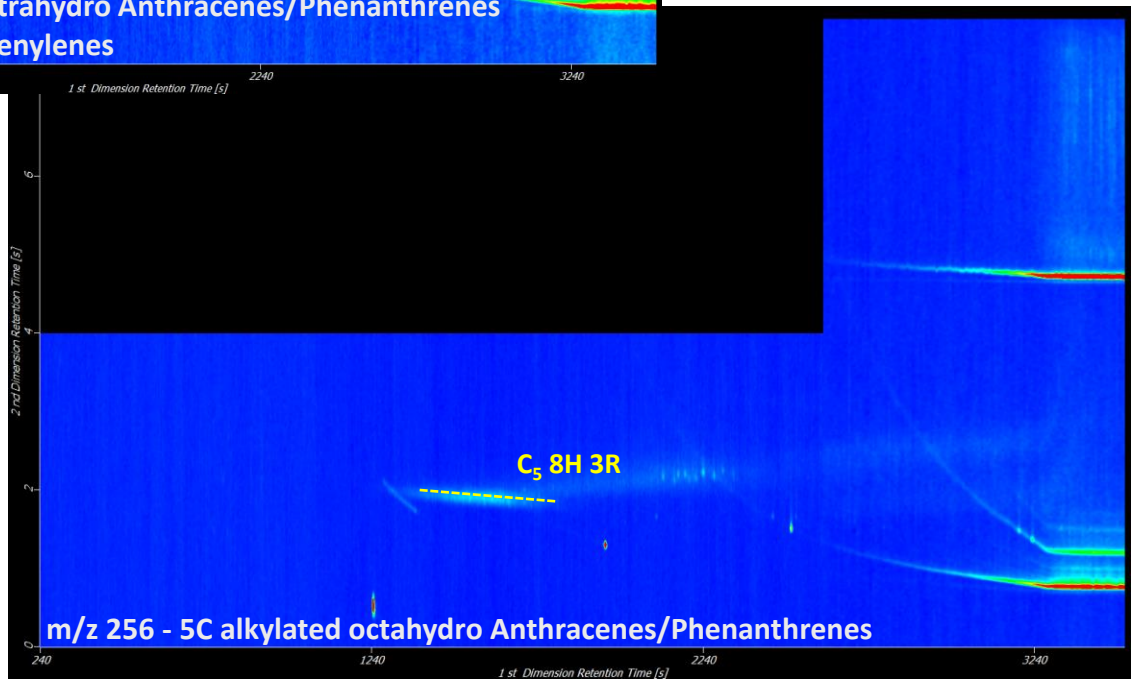


Petrolatum

GCxGC/TOFMS



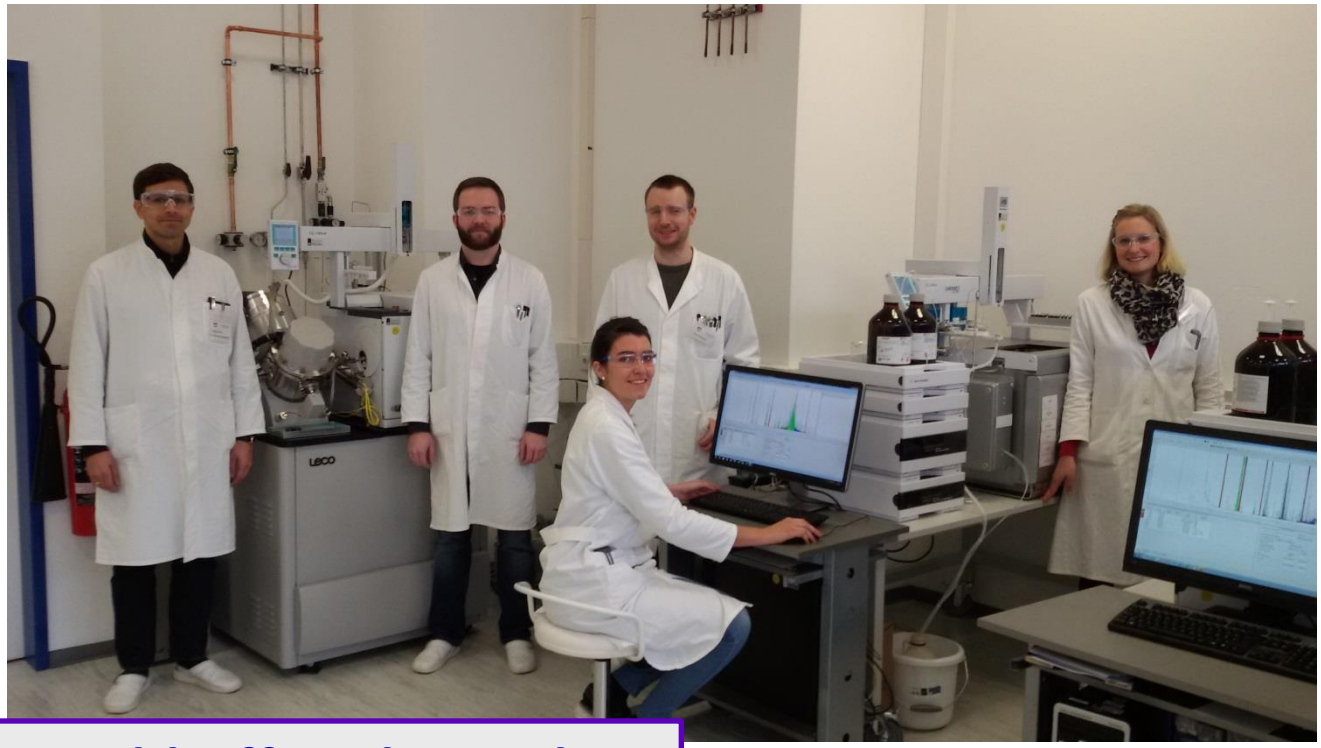




Results

- in the period from 06/10 bis 10/15 appr. **9200 samples** for residues of mineral oils (MOSH/POSH and MOAH) are examined
- from that appr. **600** samples **packaging material** (cardboard, foils)
- in appr. **30 %** of all **food samples** residues of mineral oils detectable
- concentration of mineral oil in packed foods **up to 60 mg/kg**
- all **recycling cardboards** contained aromatics (MOAH-Fraktion); highest **3300 mg/kg**
- **lubricating oils** from production (40 – 300mg/kg), usually no MOAH
- in many foodstuffs a **„environmental backround contamination“** with mineral oil hydrocarbons (only MOSH-Fraction) was found

Thank you for your kind attention!



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