# MOSH/MOAH Analysis

## Online LC/GC System with Chronect®-LC/GC

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# MOSH/MOAH Press Releases

Foto: dapd

November 2012:
mineral oil in chocolates of advent calenders, Stiftung Warentest (German Foundation)

Foto: Aleksandra Polski (pixabay.com)

May 2015 :
Stiftung Warentest warns of mineral oil in cosmetics, especially in lipsticks

Foto: Efes Kitab (pixabay.com)

March 2016 :
foodwatch published test about mineral oil in chocolate of Easter Bunnies

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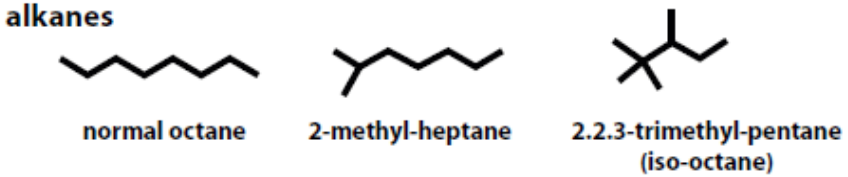
# MOSH and MOAH: What are they?

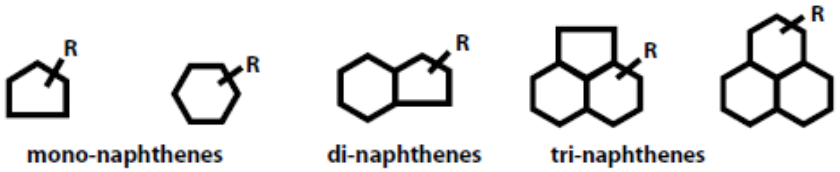
## Mineral Oils in Environment

**75 – 85 % MOSH (saturated)**
(**M**ineral **O**il **S**aturated **H**ydrocarbons)

- open chained, mostly branched



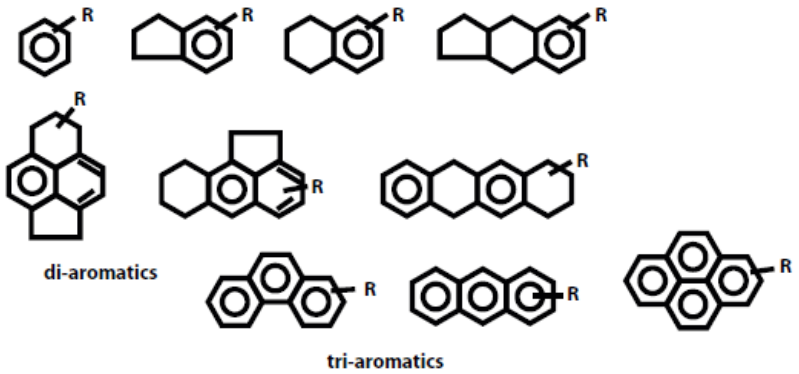

- naphthenic (cyclic)




**15 – 25 % MOAH (aromatic)**
(**M**ineral **O**il **A**romatic **H**ydrocarbons)

- up to 97 % alkylated

- different aromatic HC , mainly with 1 - 4 ring systems




reference: Matissek, R. (2014) FOOD-LAB international 1/14, 6-12

# Entry Pathways into Food

- mineral oils are widely found in the environment
- components can migrate into foods via various ways

**Raw Materials**

- combustion processes
- pesticides
- hydraulic oils from harvesting machines
- treatment of crops, e.g., with anti-foam agents, dust-binders, or gloss praying (rice)

**Production**

- oiling machine parts
- grease for maintenance and cleaning

**Transport / Storage**

- impregnated jute and sisal sacks
- mineral oil-based printing inks for cardboards boxes
- recycled cardboard boxes
- secondary packaging used during transport

# Aspects of Law

- currently,
  no validated analytical reference method
  (national/international)
  no existing limit values in the EU

- ISO is developing a standard method for determination of mineral oil in edible oil using online LC-GC

→ draft proposal of the German Federal Government (24 July 2014):

limit MOSH → 2 mg/kg foodstuff
MOAH → 0.5 mg/kg foodstuff

# MOSH/MOAH Analyzer

- Agilent 1260 Infinity LC with Degasser, bin. Pump, VWD
- Agilent 7890B GC with 2x FID
- AS Chronect® LC-GC
- CTC PAL with CHRONOS software
- OpenLAB CDS ChemStation

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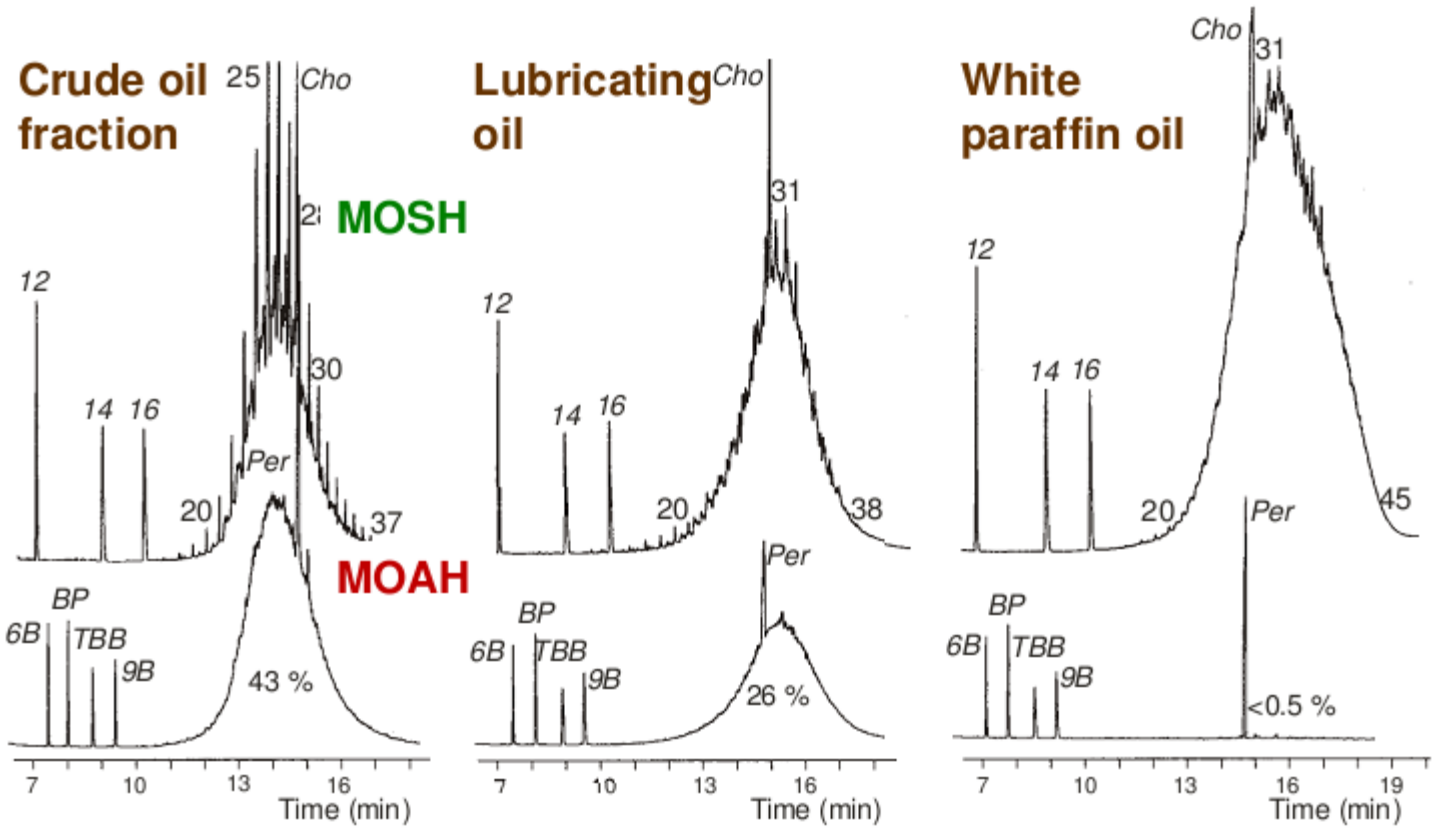
# Why HPLC-GC for MOSH-MOAH?

- GC separation between MOSH / MOAH on nonpolar GC columns not possible



# Online-LC-GC-FID Method

- challenging task due to the complex nature of foodstuffs and the unknown mixture of hydrocarbons

- single component analysis is not possible because of the high variety of substances

- originally developed by K. Grob & M. Biedermann (Cantonal Laboratory of Zurich) with separate analysis of MOAH:

1. 1st injection – MOSH cleanup → GC-FID
2. 2nd injection - MOAH cleanup → GC-FID

- optimization by Axel Semrau®: determination of the MOSH and MOAH fractions within one single analysis

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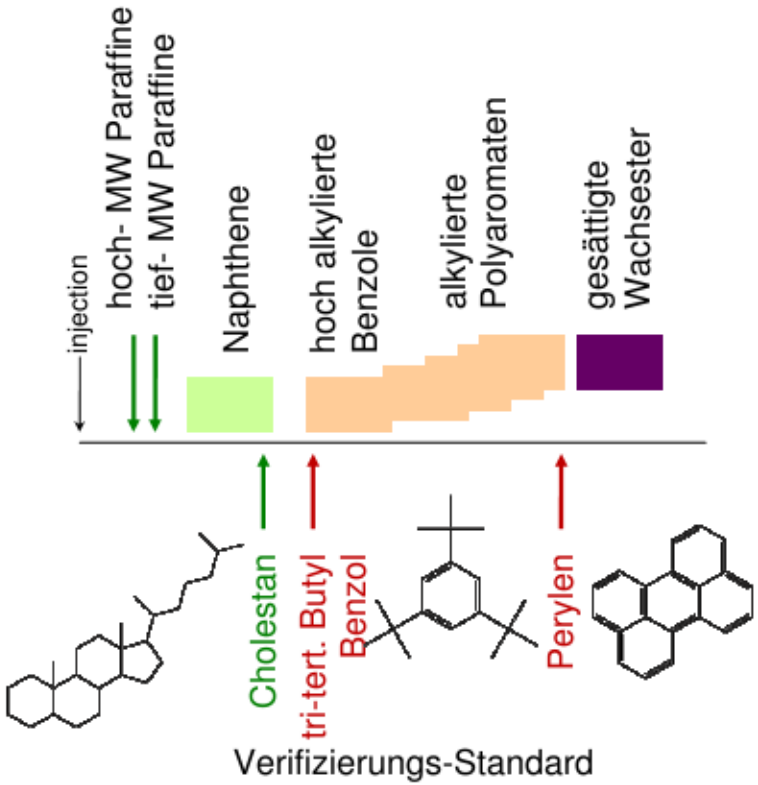
# Sample Preparation: Internal Standard




- Extraction with hexane / ethanol and addition of internal standard for <u>fractionation and quantification</u>
  - Cholestane → End of MOSH
  - TBB → Beginning of MOAH
  - Perylene → End of MOAH

- $C_{11}$ (most highly volatile compound of MOSH)
- Pentylbenzene (most highly volatile compound of MOAH)

→ to monitor the non-discriminatory transfer of the MOH fractions into the GC

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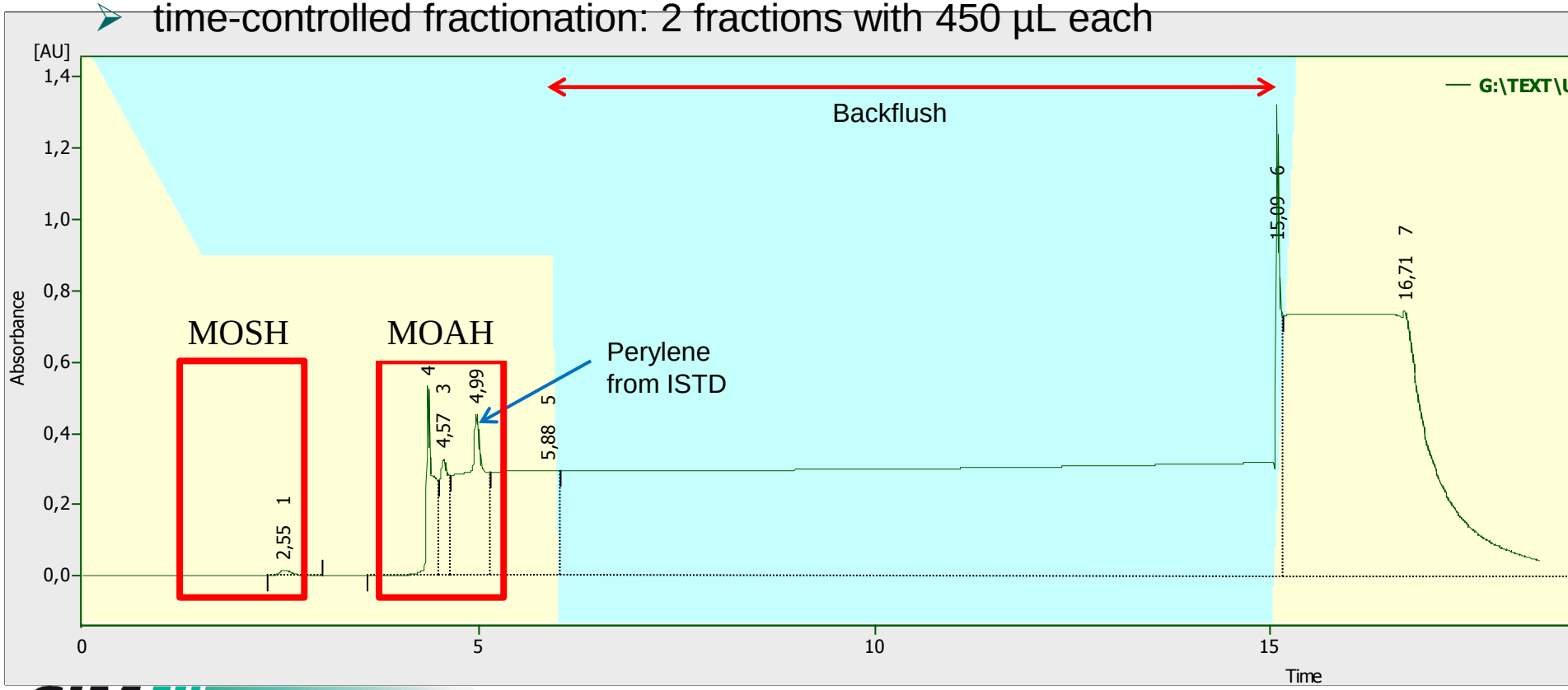
# 1. Phase: HPLC

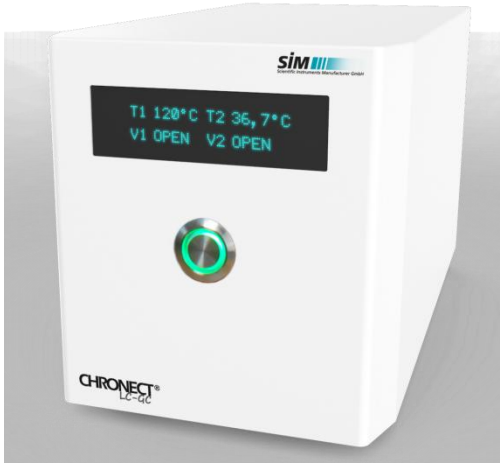
- **Agilent 1260 Infinity LC**
  for high separation efficiency and reproducibility
- fractionation of MOSH and MOAH; separation of interfering matrix compounds (e. g., lipids)
- high sensitivity as the entire fractions (each 450 µl) are transferred into the GC
- contaminations due to the use of column chromatography, evaporation steps, etc. (as with the manual method) are impossible

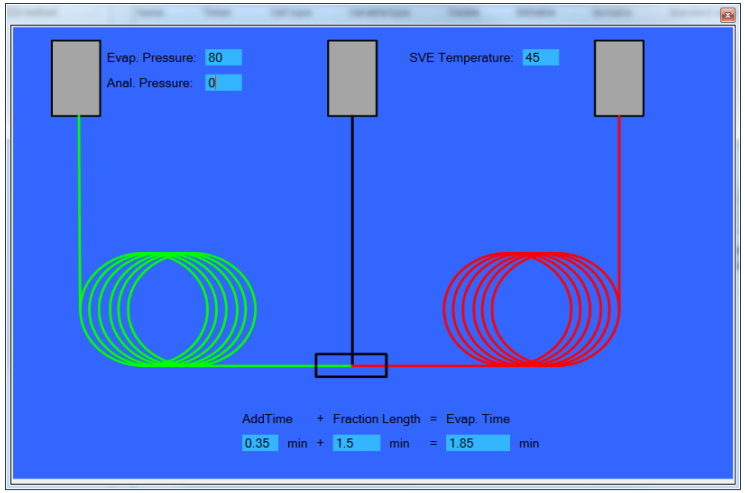
# LC Gradient

- column: 2-mm normal phase silica column
- separation of MOSH and MOAH with hexane/$CH_2Cl_2$ gradient
- UV detection (230 nm)
- gradient tracking
- time-controlled fractionation: 2 fractions with 450 µL each



# Interface – CHRONECT®LC-GC




- transfer of the MOSH and MOAH fractions (450 µl each) into the GC
- On-column transfer with partially concurrent solvent evaporation
- 1 or 2 channel operation (MOSH and/or MOAH)
- complete integration into CHRONOS (PAL-Software)
- user-friendly input mask for transfer parameters

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# 2. Phase: GC


- **Agient 7890B GC** with 2 FIDs
- **FID** (but not MS!): approx. same response for all hydrocarbons → quantitation possible
- GC-FID on nonpolar columns also enables characterization of the sample related to its molar mass distribution
- Two independent on-column channels with “retention gaps“ for simultaneous determination of MOSH and MOAH

# MOSH und MOAH in Parallel

- normally, two injections of a sample needed
- with CHRONECT®LC-GC: MOSH + MOAH in the same GC run
  (green: MOSH, black: MOAH)

→ adjusted temperature, special transfer valve, separate gas regulations, two columns, SVEs, FIDs

→ no loss of highly volatile components

→ doublication of sample throughput

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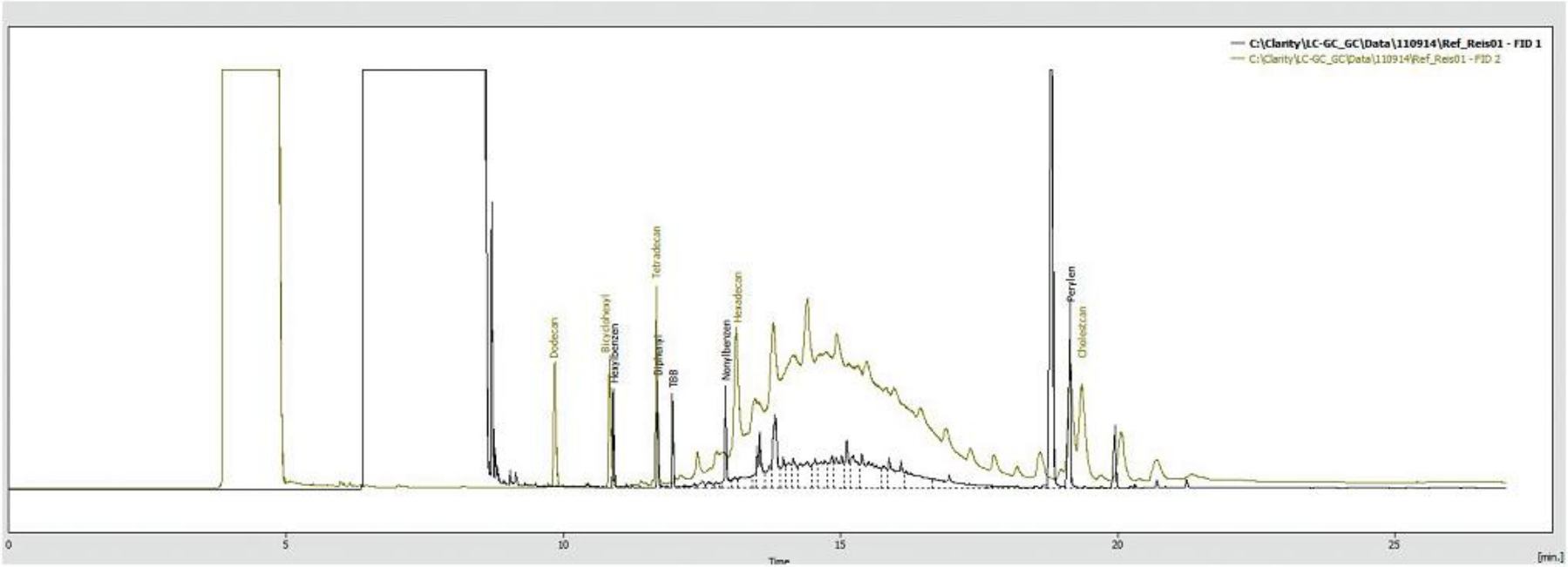
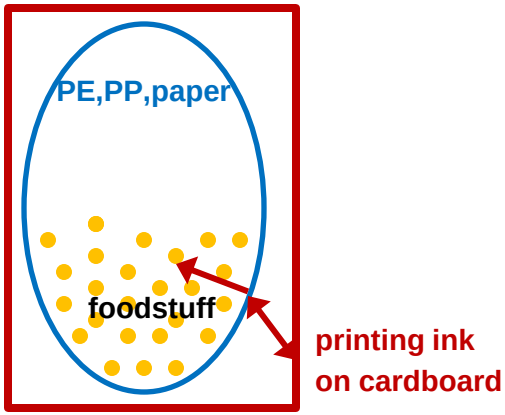


# Mineral Oil Transfer from Packaging to Food

Foto: Marie Beaucaire (pixabay.com)

- input through printing ink and recycled cardboard boxes
  (unless mineral oil free ink is used)
- high risk for food with high surface (e.g. rice, semolina, cereals)

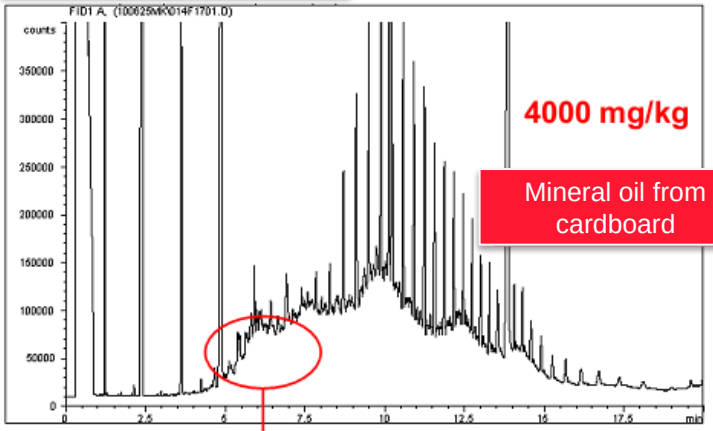



- migration of printing ink from cardboard
- cardboard → inner packaging (PE, PP)
  via gaseous phase
- (delayed) migration from inner packaging
- inner packaging → foodstuff
  via gaseous phase

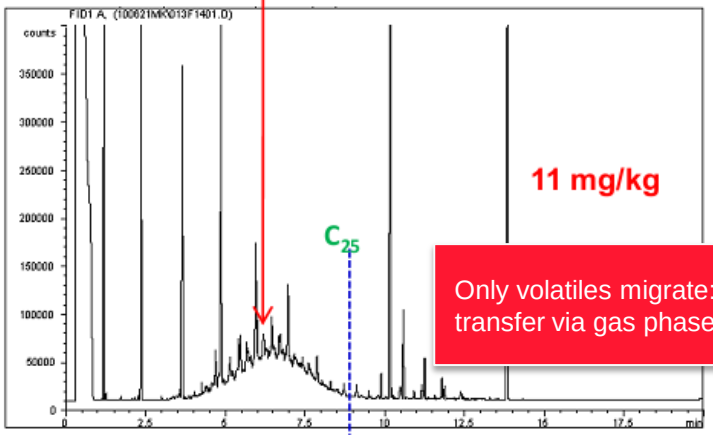
reference (figure): http://www.institut-kirchhoff.de/fileadmin/user_upload/de/download/mineraloel.pdf

# Migration Example: Rice Packaged in Cardboard

Recycled cardboard – sample 1



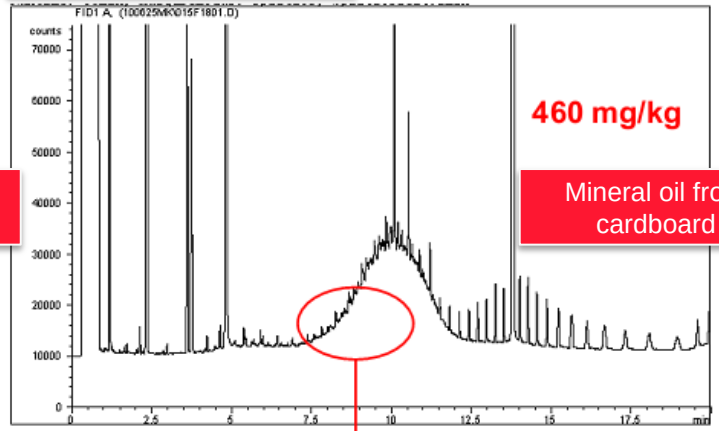

Mineral oil from cardboard



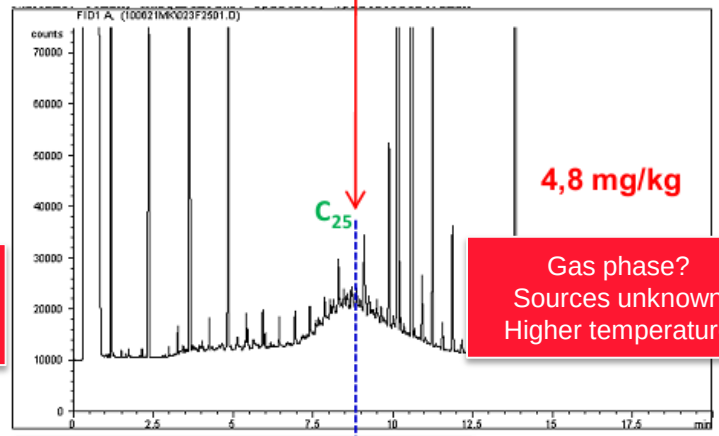

Only volatiles migrate: transfer via gas phase

Rice packaged in sample 1

Recycled cardboard – sample 2




Mineral oil from cardboard




Gas phase?
Sources unknown
Higher temperature

Rice packaged in sample 2

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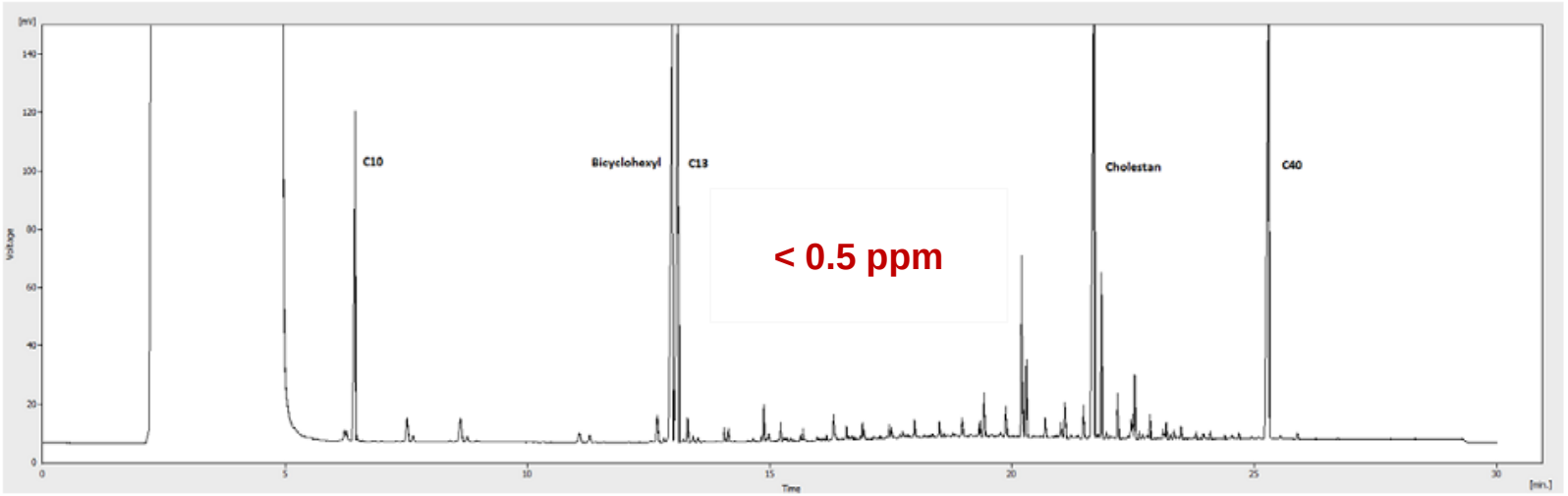
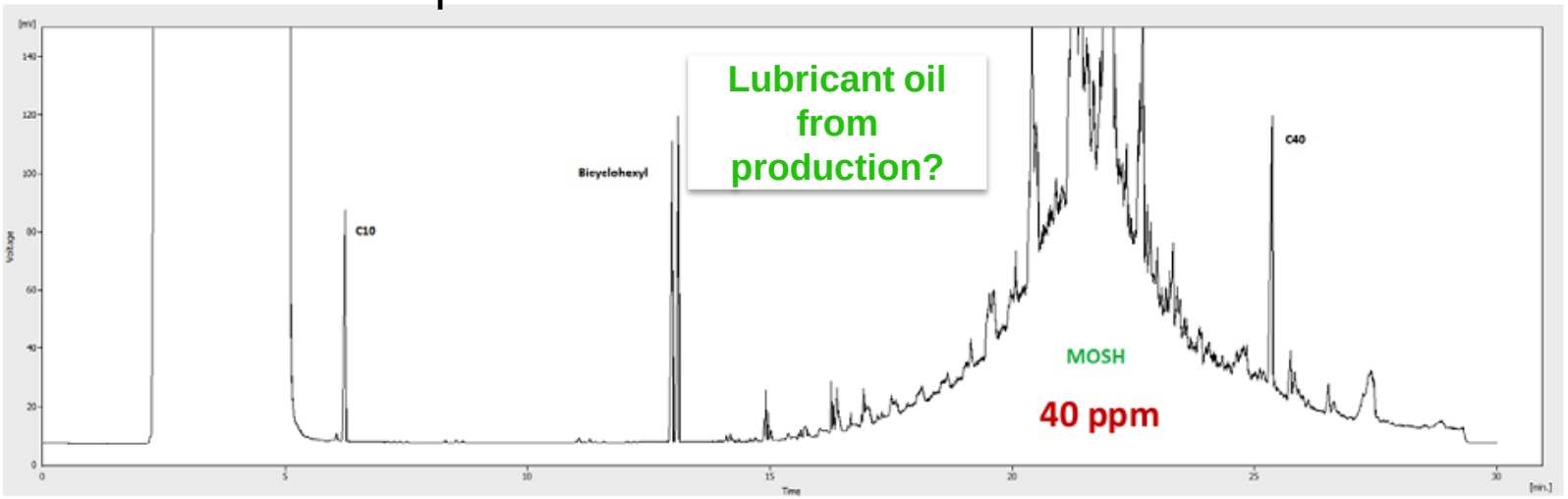
# Contamination in Production Process: Nut Nougat Cream

uncontaminated sample:

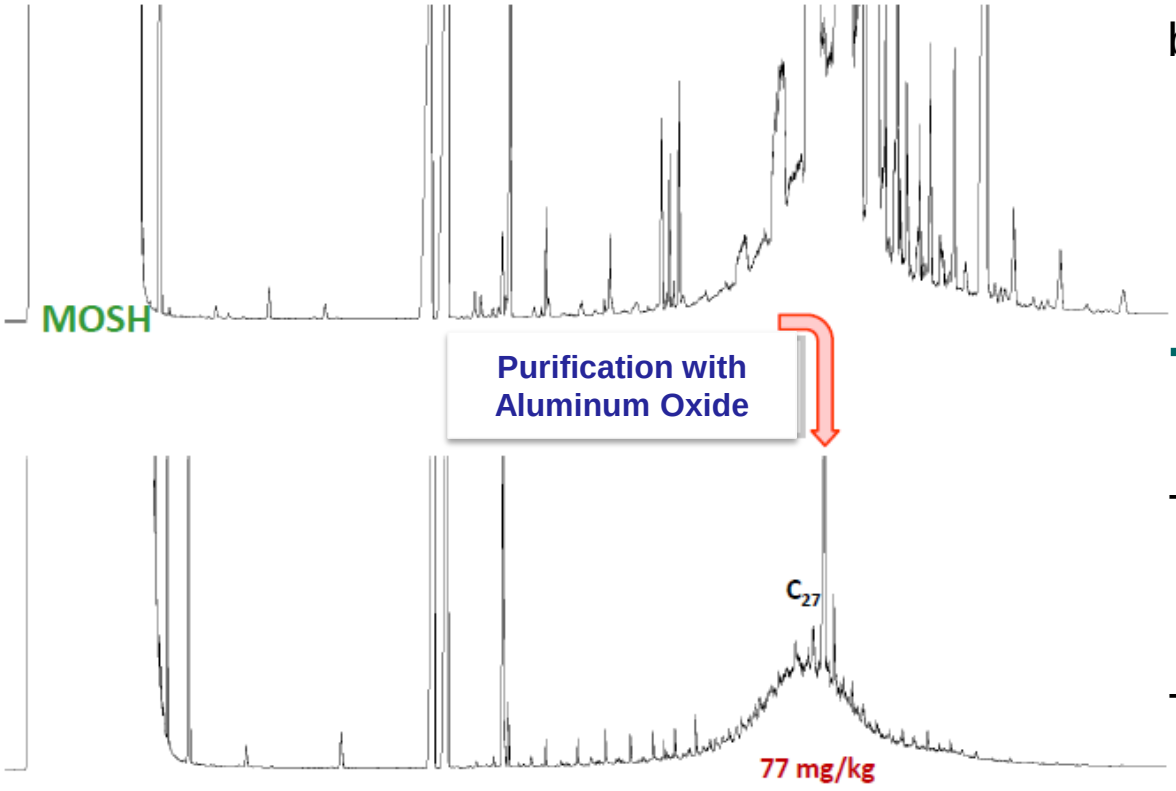



contaminated sample:



# MOSH Fraction: Interfering Compounds

**Sunflower oil**




**Interference:**

biogenic hydrocarbons

➔ column chromatography with <u>activated aluminum oxide:</u>

- biogenic long-chained odd-numbered *n*-alkanes ($C_{23}$ – $C_{35}$) are removed
- *iso*-alkanes (branched, from MOSH fraction) remain

reference: Nestola, M., Becker, E., Ernährung aktuell, November/Dezember 2012, 25-27

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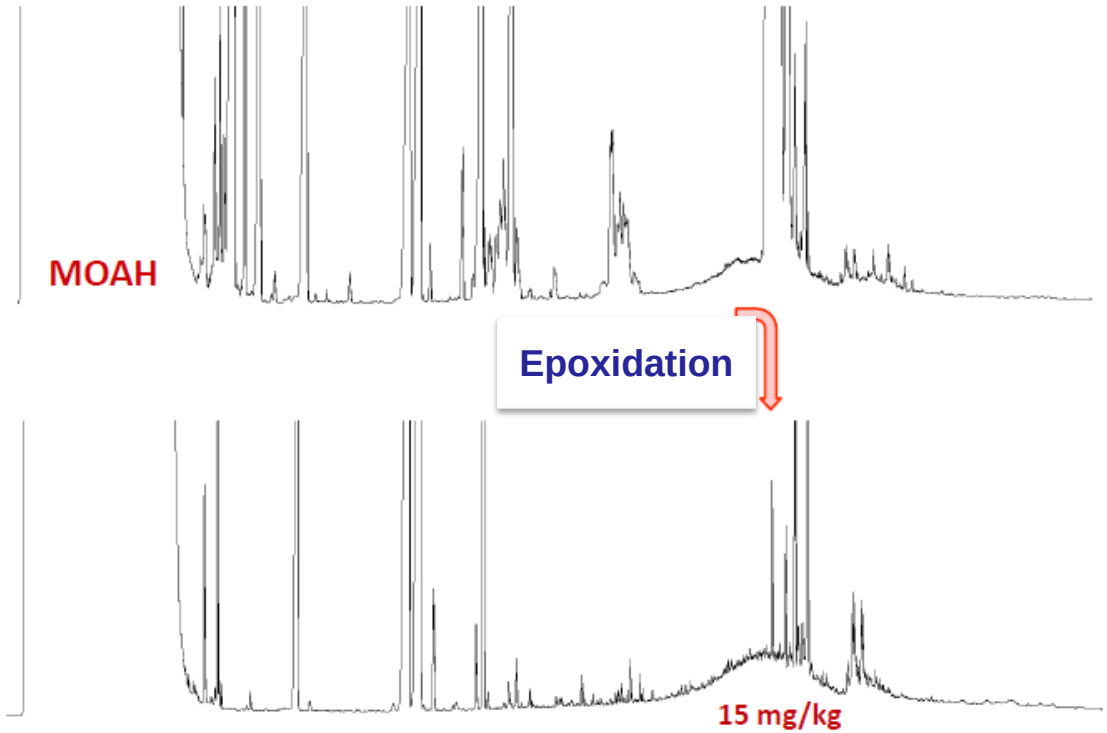
# MOAH Fraction: Interfering Compounds

**Sunflower oil**




**Interference:**

olefins (squalene and isomers, sterenes, etc.)

➔ polar modification using <u>epoxidation</u>

- separation by LC possible
- safe identification

➔ various kinds of sample preparation depending on food matrix: highest sensitivity by elimiation of interfering compounds

reference: Nestola, M., Becker, E., Ernährung aktuell, November/Dezember 2012, 25-27

# MOSH/MOAH Analyzer: Features

- optimization of the original method by K. Grob: simultaneous determination of MOSH and MOAH within one chromatographic run (30 min)
- direct LC-GC coupling prevents from contamination
- high degree of automation for excellent reproducibility
- optimum sensitivity due to lossless transfer into GC

- 24/7 routine analysis, expandable to further applications (sterols, PAHs)
- installed base: 30 units

→ MOSH/MOAH Analyzer is preassembled, configured with columns, and analytical method, tested and delivered

→ **ready-to-analyze**

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