

MOSH/MOAH Analysis

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

Rolf Eichelberg, SIM GmbH
Marco Nestola, Axel Semrau GmbH



in cooperation with
Axel Semrau GmbH

sim 
Scientific Instruments Manufacturer GmbH

Im Erlengrund 21-23 • D-46149 Oberhausen
Tel. +49(0)208-941078-0 • Fax +49(0)208-941078-88
www.sim-gmbh.de

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

MOSH and MOAH: What are they?

Mineral Oils in Environment

75 – 85 % MOSH (saturated)
(Mineral Oil Saturated Hydrocarbons)

- open chained, mostly branched

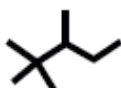
alkanes



normal octane



2-methyl-heptane

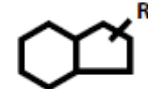


2,2,3-trimethyl-pentane
(iso-octane)

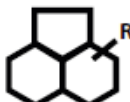
- naphthenic (cyclic)



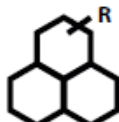
mono-naphthenes



di-naphthenes



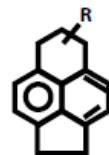
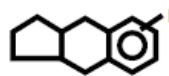
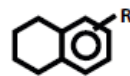
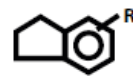
tri-naphthenes



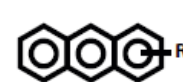
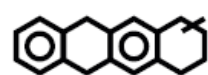
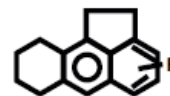
15 – 25 % MOAH (aromatic)
(Mineral Oil Aromatic Hydrocarbons)

- up to 97 % alkylated

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



di-aromatics

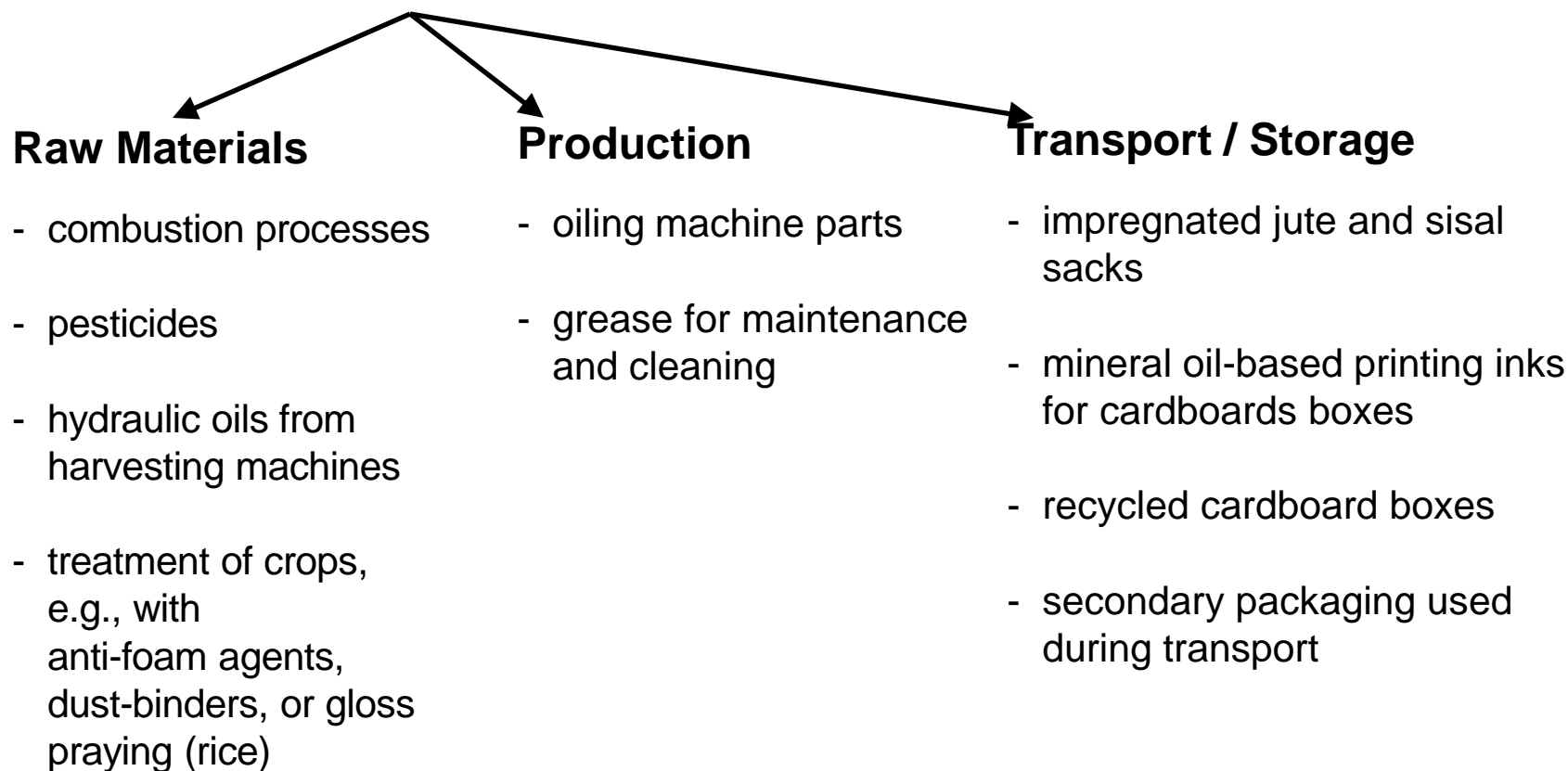


tri-aromatics



Entry Pathways into Food

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



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

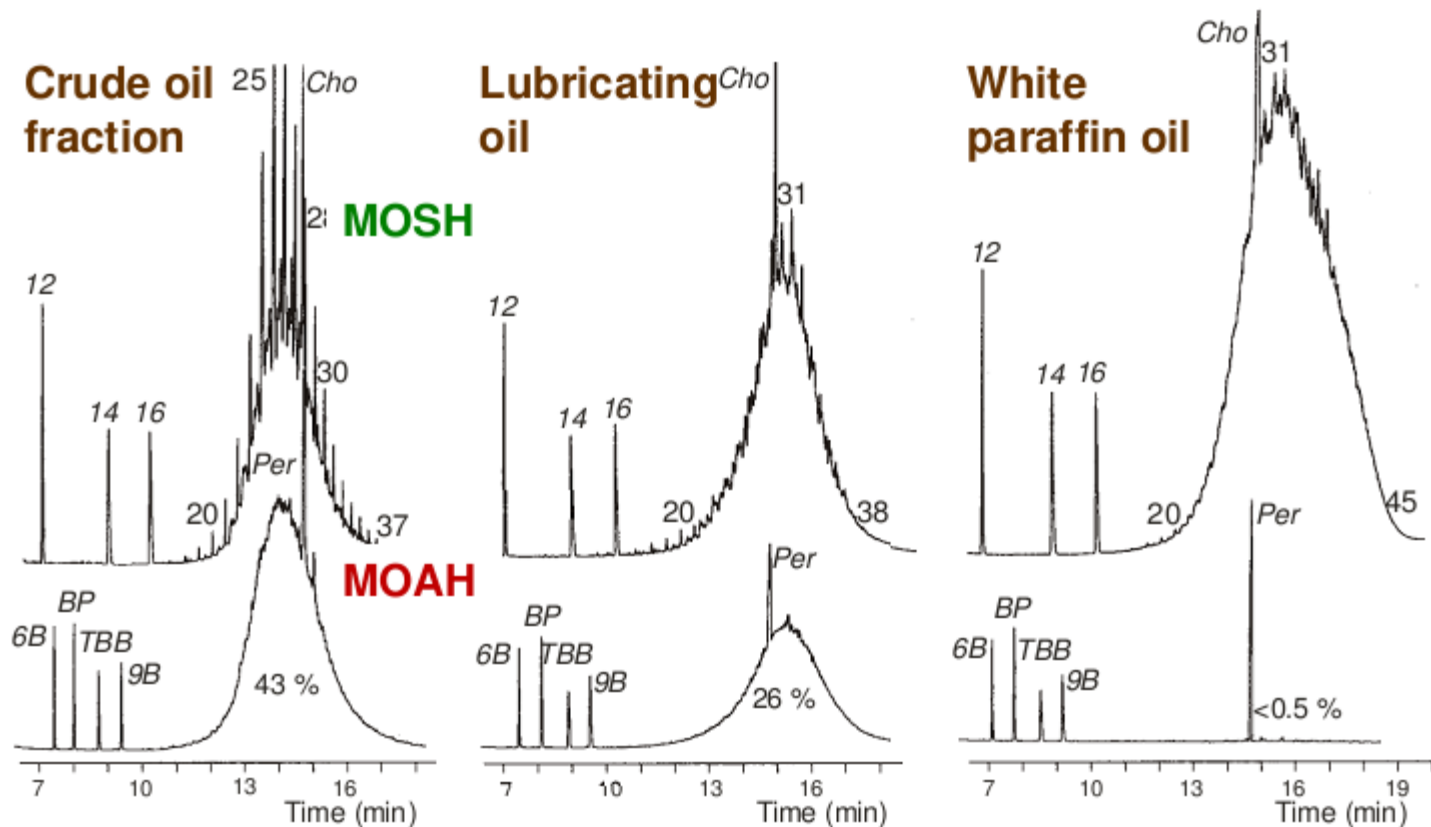
MOSH/MOAH Analyzer

- 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



Why HPLC-GC for MOSH-MOAH?

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



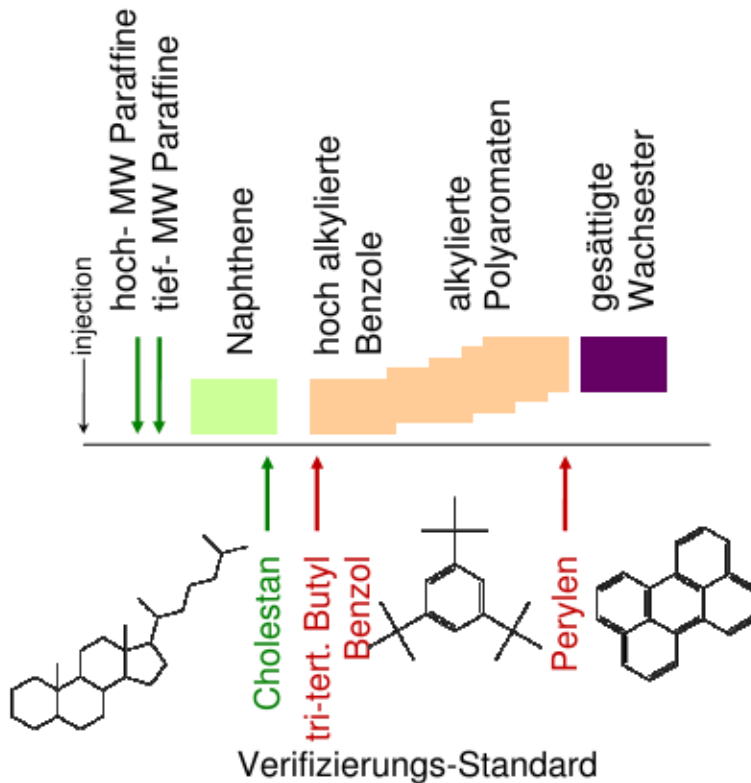
Online-LC-GC-FID Method

- 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

Sample Preparation: Internal Standard

➤ Extraction with hexane / ethanol and addition of internal standard for fractionation and quantification

- Cholestane → End of MOSH
- TBB → Beginning of MOAH
- Perylene → End of MOAH



- C₁₁ (most highly volatile compound of MOSH)
 - Pentybenzene (most highly volatile compound of MOAH)
- to monitor the non-discriminatory transfer of the MOH fractions into the GC

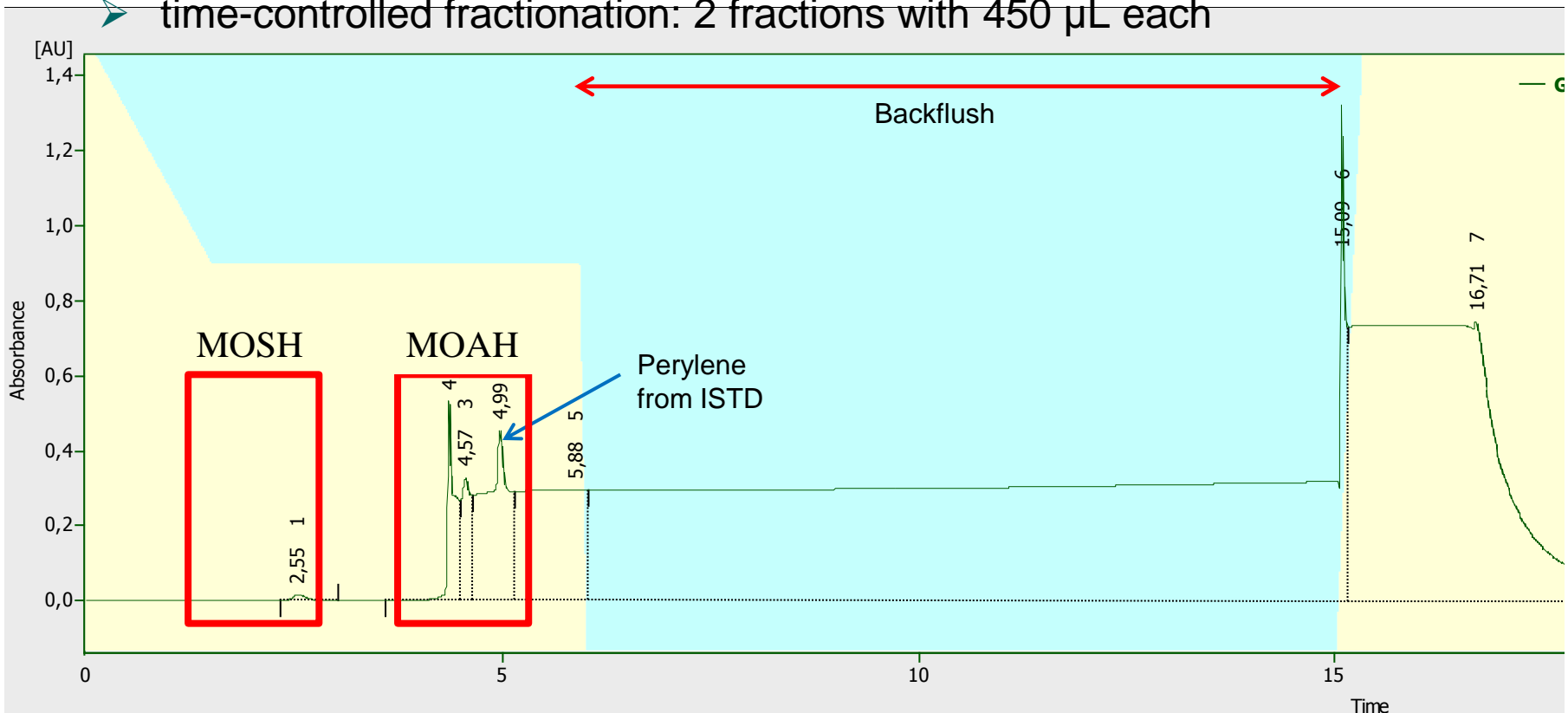
1. Phase: HPLC



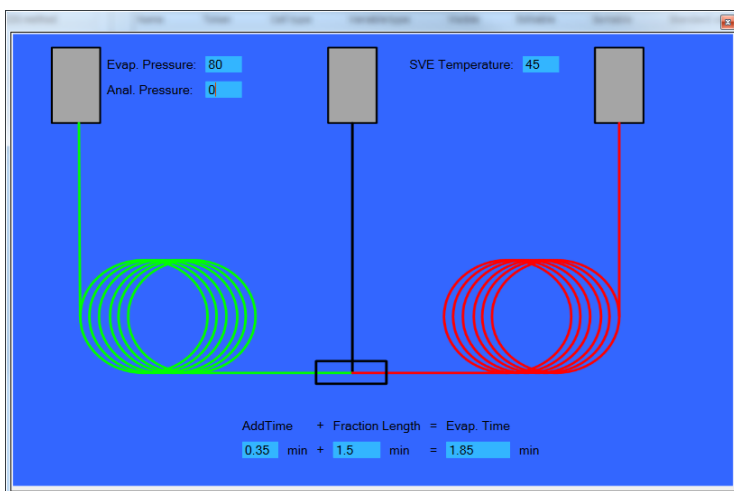
- **Agilent 1260 Infinity LC**
for high separation efficiency and reproducibility
- fractionation of MOSH and MOAH;
separation of interfering matrix compounds
(e. g., lipids)
- high sensitivity as the entire fractions
(each 450 µl) are transferred into the GC
- contaminations due to the use of column
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/CH₂Cl₂ 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

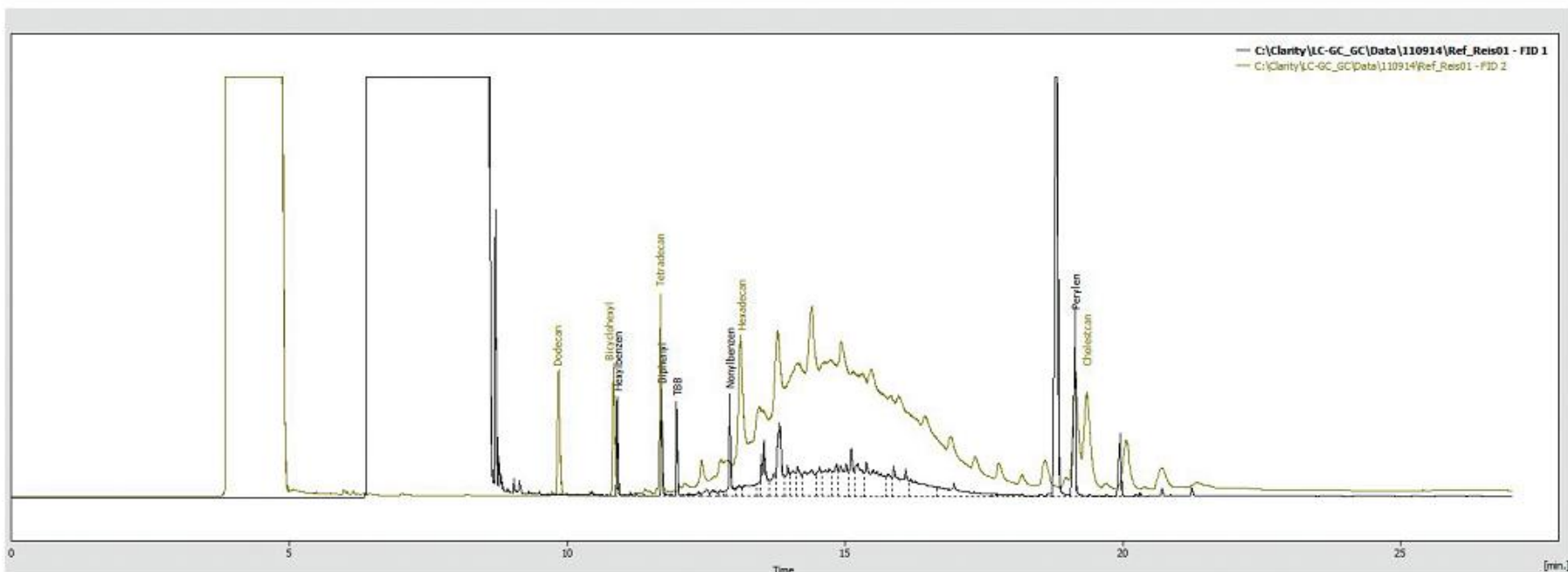
2. Phase: GC



- **Agilent 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
- ➔ doubling of sample throughput

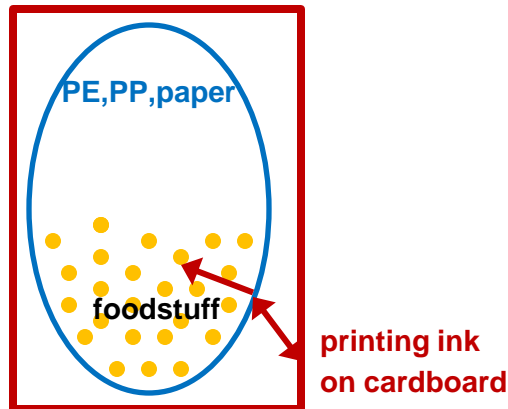


Mineral Oil Transfer from Packaging to Food



Foto: Marie Beaucaire (pixabay.com)

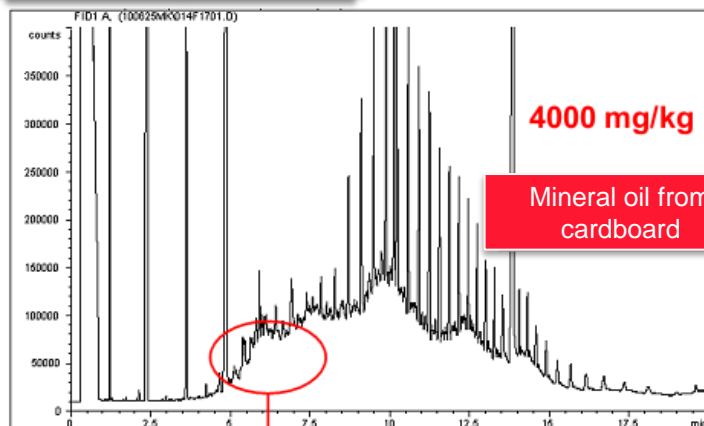
- input through printing ink and recycled cardboard boxes (unless mineral oil free ink is used)
- high risk for food with high surface (e.g. rice, semolina, cereals)



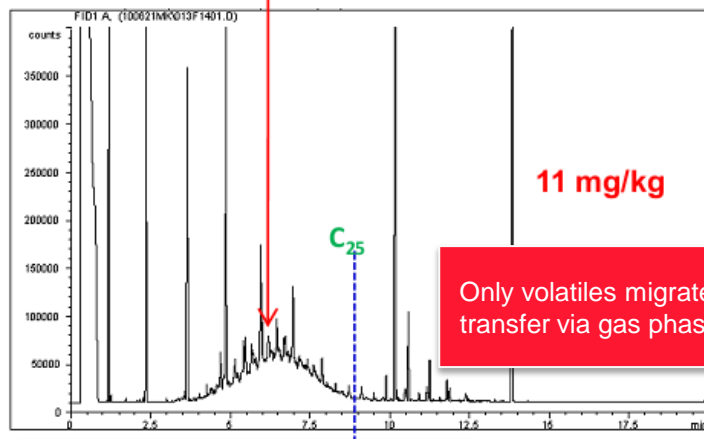
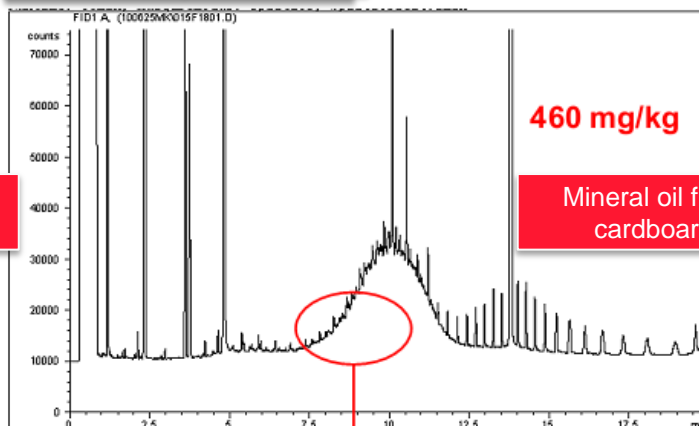
- migration of printing ink from cardboard
- cardboard → inner packaging (PE, PP) via gaseous phase
- (delayed) migration from inner packaging
- inner packaging → foodstuff via gaseous phase

Migration Example: Rice Packaged in Cardboard

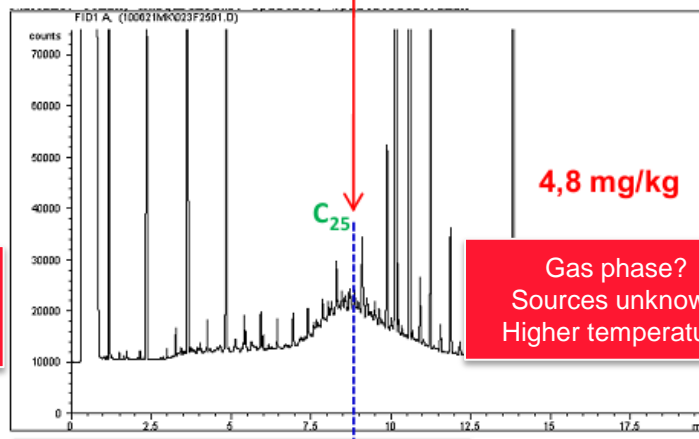
Recycled cardboard –
sample 1



Recycled cardboard –
sample 2



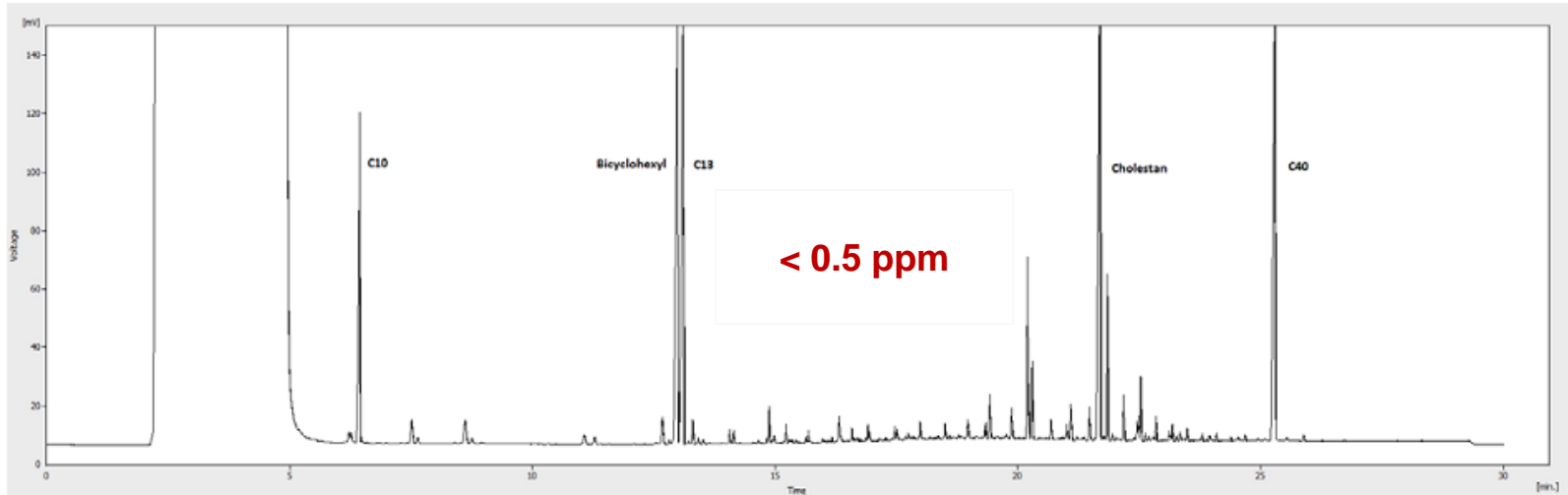
Rice packaged in sample 1



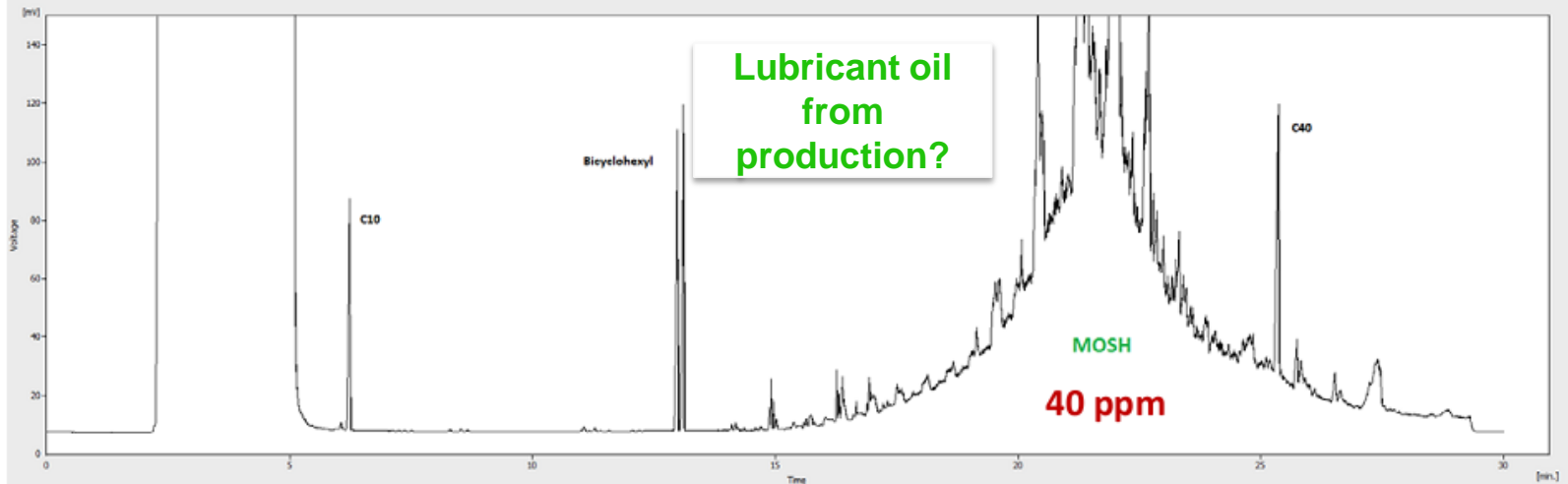
Rice packaged in sample 2

Contamination in Production Process: Nut Nougat Cream

uncontaminated sample:

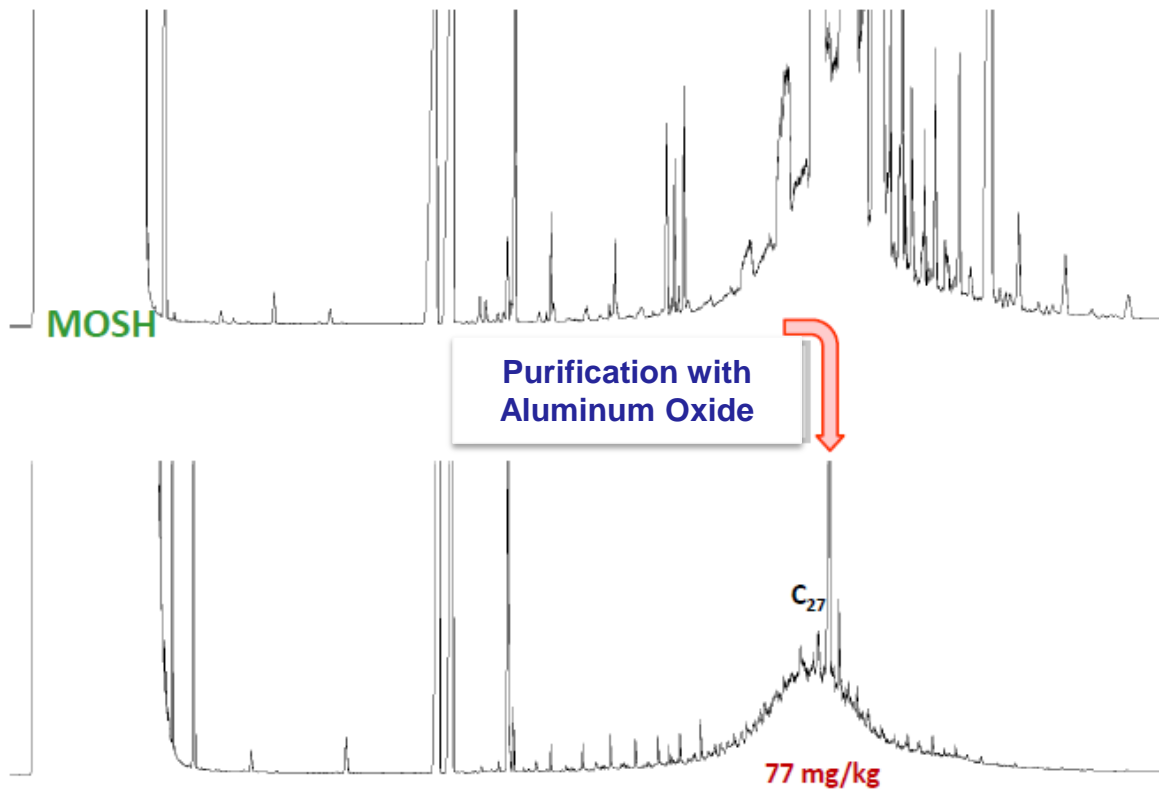


contaminated sample:



MOSH Fraction: Interfering Compounds

Sunflower oil



Interference:

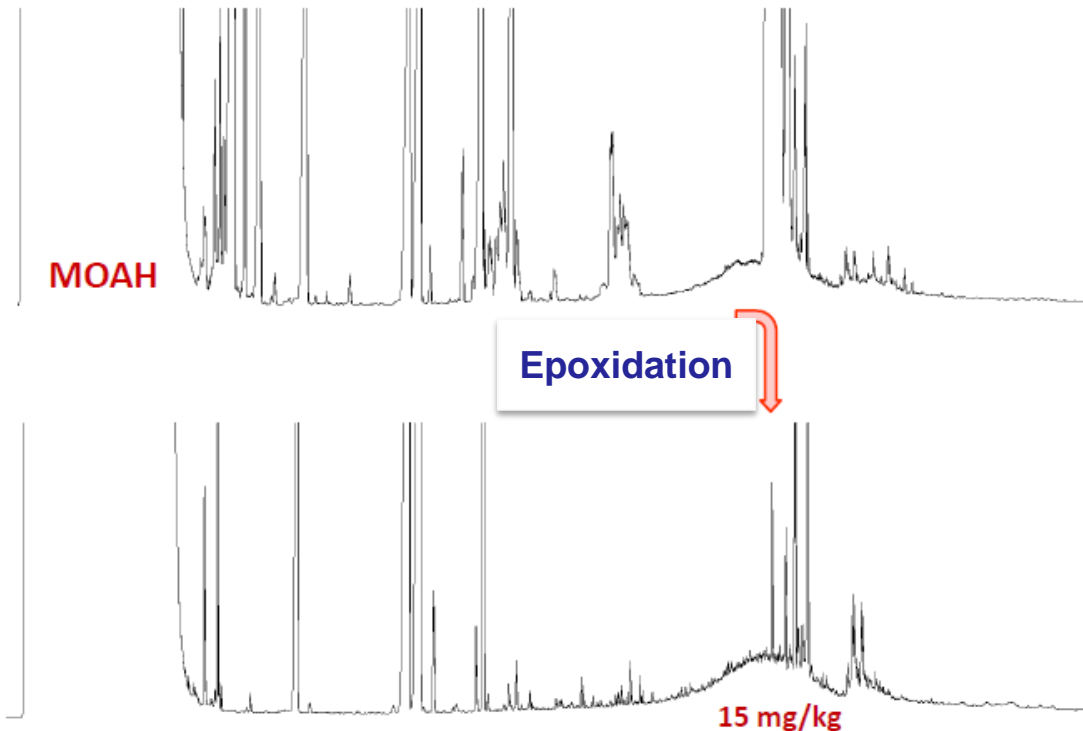
biogenic hydrocarbons

→ column chromatography with activated aluminum oxide:

- biogenic long-chained odd-numbered *n*-alkanes (C₂₃ – C₃₅) are removed
- *iso*-alkanes (branched, from MOSH fraction) remain

MOAH Fraction: Interfering Compounds

Sunflower oil



Interference:

olefins (squalene and isomers, sterenes, etc.)

- ➔ polar modification using epoxidation
- separation by LC possible
- reliable identification

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

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**

