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Bundesinstitut für Risikobewertung

BUNDESINSTITUT FÜR RISIKOBEWERTUNG

Mineral Oil at the Focus of Consumer Health Protection: General Introduction to the Topic

Dr. Christoph Hutzler

German Federal Institute for Risk Assessment (BfR)

Department for Chemical and Product Safety

Mineral Oil: selected activities of the BfR

2009

- BfR opinion on the migration of mineral oil from packaging material into food.

BfR
Risiken erkennen – Gesundheit schützen

Übergänge von Mineralöl aus Verpackungsmaterialien auf Lebensmittel

Stellungnahme Nr. 008/2010 des BfR vom 09. Dezember 2009

Karton für Verpackungen wird aus ökologischen Erwägungen zu einem großen Teil aus recykliertem Altpapier hergestellt. Untersuchungen aus der Schweiz zeigen, dass Recyclingkartons hohe Mineralölanteile enthalten können. Ursprung der Mineralöle sind Druckfarben, wie sie üblicherweise im Zeitungsdruck verwendet werden. Werden Lebensmittel wie zum Beispiel Reis in derartigen Kartons verpackt, können Mineralöle aus dem Karton in größeren Mengen in das Lebensmittel übergehen. Wegen des hohen Anteils an Mineralölfraktionen mit kürzerkettigen und aromatischen Kohlenwasserstoffen sind derartige Kontaminationen von Lebensmitteln unerwünscht. Kürzerkettige Kohlenwasserstoffe werden vom Körper leicht aufgenommen, so dass bei häufigerem Verzehr derart belasteter Lebensmittel die toxikologischen Grenzwerte überschritten werden können. Aus tierexperimentellen Studien ist bekannt, dass Mineralölgemische mit niedriger Viskosität im Körper gespeichert werden und zu Ablagerungen und Schäden in der Leber, den Herzklappen und den Lymphknoten führen können. Aufgrund dieser Daten kam das Bundesinstitut für Risikobewertung (BfR) in seiner Bewertung zu dem Schluss, dass der Übergang von Mineralölen auf Lebensmittel dringend minimiert werden sollte.

2010

- Workshop on analytics of MOSH and MOAH.

BfR
Risiken erkennen – Gesundheit schützen

KANTONALES LABOR ZÜRICH

Workshop
des Bundesinstituts für Risikobewertung (BfR) Berlin
und des
Kantonalen Labors Zürich

Mineralölanalytik im Lebensmittelbereich

Methoden für MOSH und MOAH (GC-FID, on-line HPLC-GC-FID, GCxGC), Vorkommen und Risikobewertung

Donnerstag 10. Juni 8 Uhr bis Freitag 11. Juni ca. 16:30 Uhr,
Kantonales Labor Zürich, Fehrenstrasse 15, CH-8032 Zürich, Schweiz

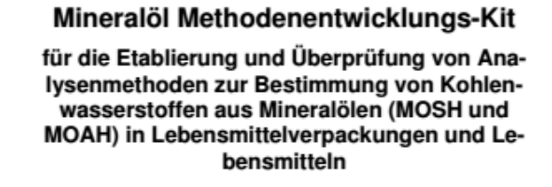
Mineral Oil: selected activities of the BfR

2011

- BfR conference on mineral oils in food packaging.
- Development of the manual method.
- Assisting OCLs in establishing the analysis of MOSH and MOAH by providing characterized samples and accompanying documents.

2012

- 120 “Mineral oil method development kits“ were shipped world wide.




Journal of Chromatography A, 1271 (2013) 192–200

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

Development of a manual method for the determination of mineral oil in foods and paperboard

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ABSTRACT

So far the majority of the measurements of mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH) were obtained from on-line high performance liquid chromatography–gas chromatography–flame ionization detection (on-line HPLC–GC–FID). Since this

Mineral Oil: selected activities of the BfR

2015

- BfR Opinion on mineral oil in cosmetic products
- Authority/expert meeting on the issue of certain mineral oil components in different regulatory areas.

2016

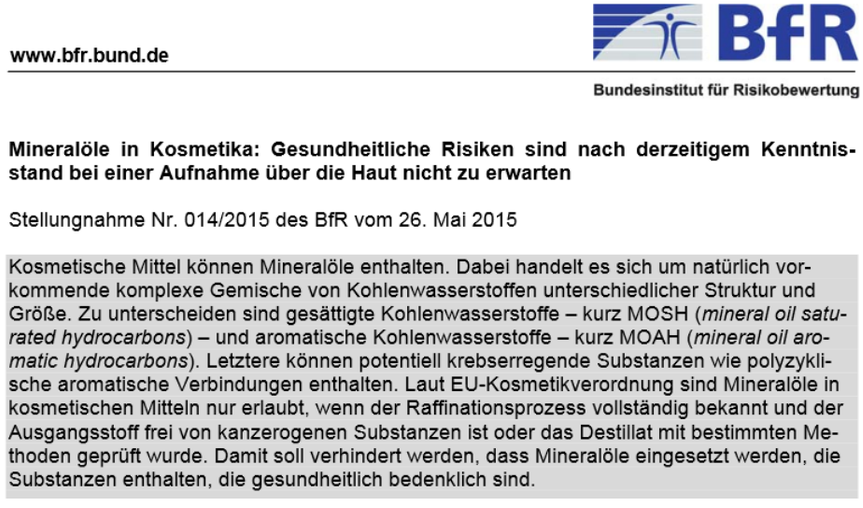
- Expert meeting on MOAH in cosmetics.

2017

- BfR consumer protection forum: mineral oil at the focus of consumer health protection.

ongoing

- Committee work on analytics and assessment of MOSH and MOAH.
- On-hand lab training for OCLs and NRLs (Germany and European).
- MOSH and MOAH data from Total Diet Study (Exposure) - MEAL.



www.bfr.bund.de

Bundesinstitut für Risikobewertung

Mineralöle in Kosmetika: Gesundheitliche Risiken sind nach derzeitigem Kenntnisstand bei einer Aufnahme über die Haut nicht zu erwarten

Stellungnahme Nr. 014/2015 des BfR vom 26. Mai 2015

Kosmetische Mittel können Mineralöle enthalten. Dabei handelt es sich um natürlich vorkommende komplexe Gemische von Kohlenwasserstoffen unterschiedlicher Struktur und Größe. Zu unterscheiden sind gesättigte Kohlenwasserstoffe – kurz MOSH (*mineral oil saturated hydrocarbons*) – und aromatische Kohlenwasserstoffe – kurz MOAH (*mineral oil aromatic hydrocarbons*). Letztere können potentiell krebserregende Substanzen wie polyzyklische aromatische Verbindungen enthalten. Laut EU-Kosmetikverordnung sind Mineralöle in kosmetischen Mitteln nur erlaubt, wenn der Raffinationsprozess vollständig bekannt und der Ausgangsstoff frei von kanzerogenen Substanzen ist oder das Destillat mit bestimmten Methoden geprüft wurde. Damit soll verhindert werden, dass Mineralöle eingesetzt werden, die Substanzen enthalten, die gesundheitlich bedenklich sind.

Definition: Mineral Oil

Wikipedia: Mineral oil is any of various colorless, odorless, light mixtures of higher alkanes from a mineral source, particularly a distillate of petroleum. The name *mineral oil* by itself is imprecise, having been used for many specific oils over the past few centuries. Other names, similarly imprecise, include *white oil*, *liquid paraffin*, *paraffinum liquidum*, and *liquid petroleum*. Baby oil is a perfumed mineral oil.

Petroleum Industry: Complex substances of hydrocarbon components. Consists of alkanes (isoparaffinics), saturated cyclic alkanes (naphtenics) and alkylated aromatics.

IARC: Complex and variable mixtures of straight and branched-chain paraffinic, naphtenic (cycloparaffinic) and aromatic hydrocarbons.

Mineral Oil: terms often used

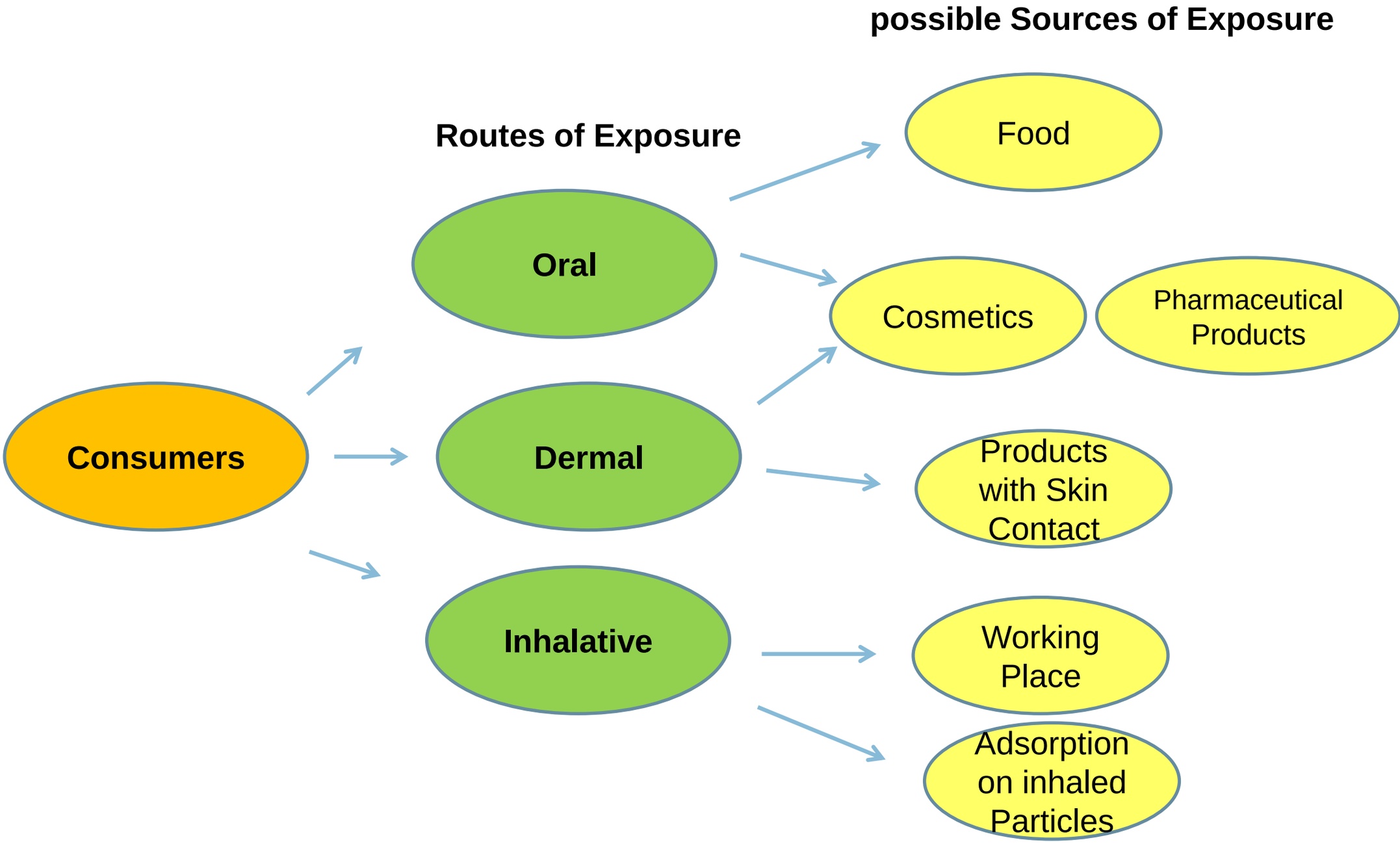
petroleum, crude oil, raw oil,

Erdöl, Rohöl, (Mineralöl ??)

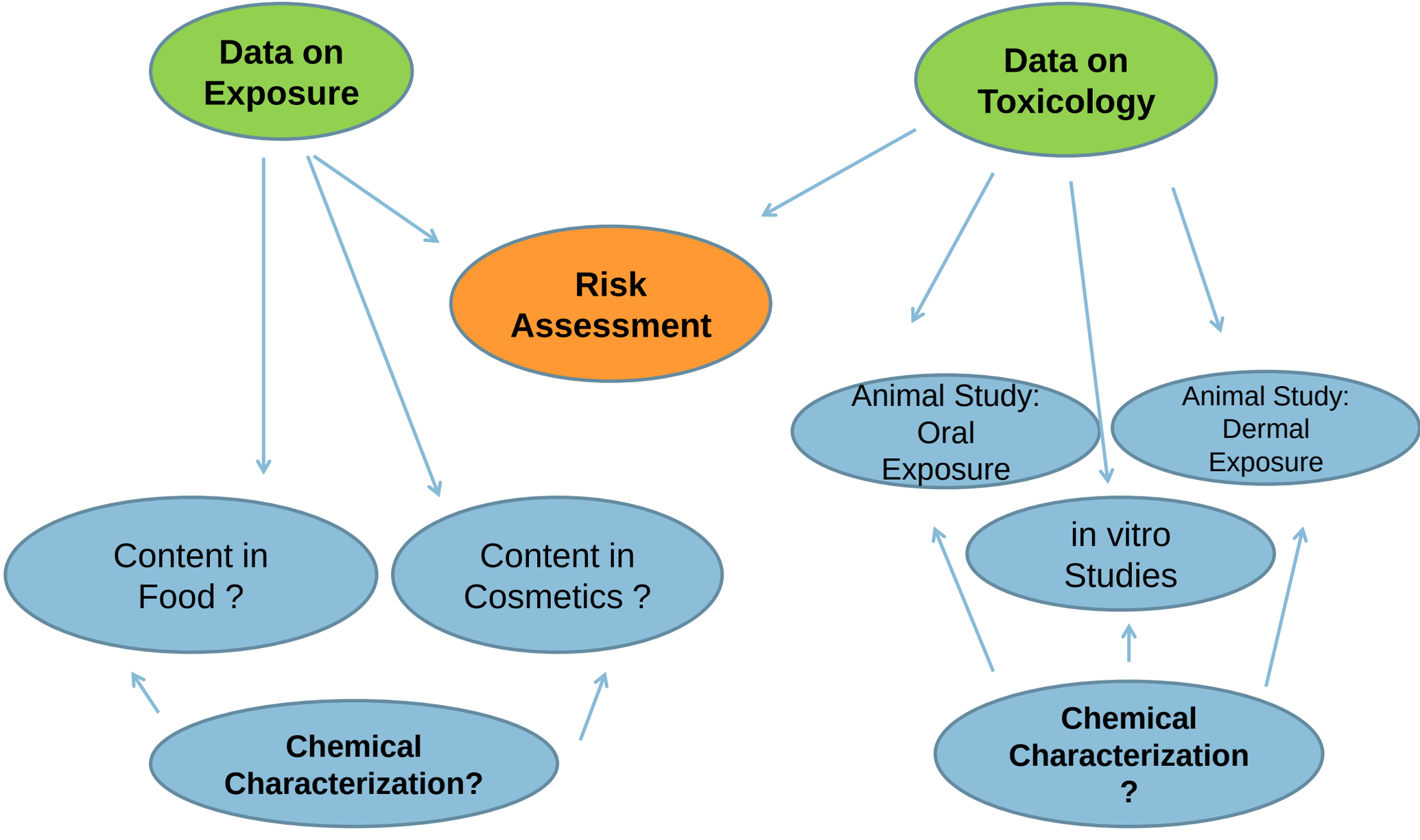
mineral oil, white oil

Mineralöl, Paraffin, Weißöl, Mineralparaffin

MOSH and MOAH: Possible Routes and Sources of Exposure



MOSH and MOAH: Data needed for proper risk assessment



Possible sources for MOSH and MOAH in food (not exhaustive)

• food additives: intentionally added in the entire production line (e.g. food grade oil)

• packaging material (e.g. jute badges, cardboard, recycling cardboard, adhesives, printing inks)

• environment

• transport processes

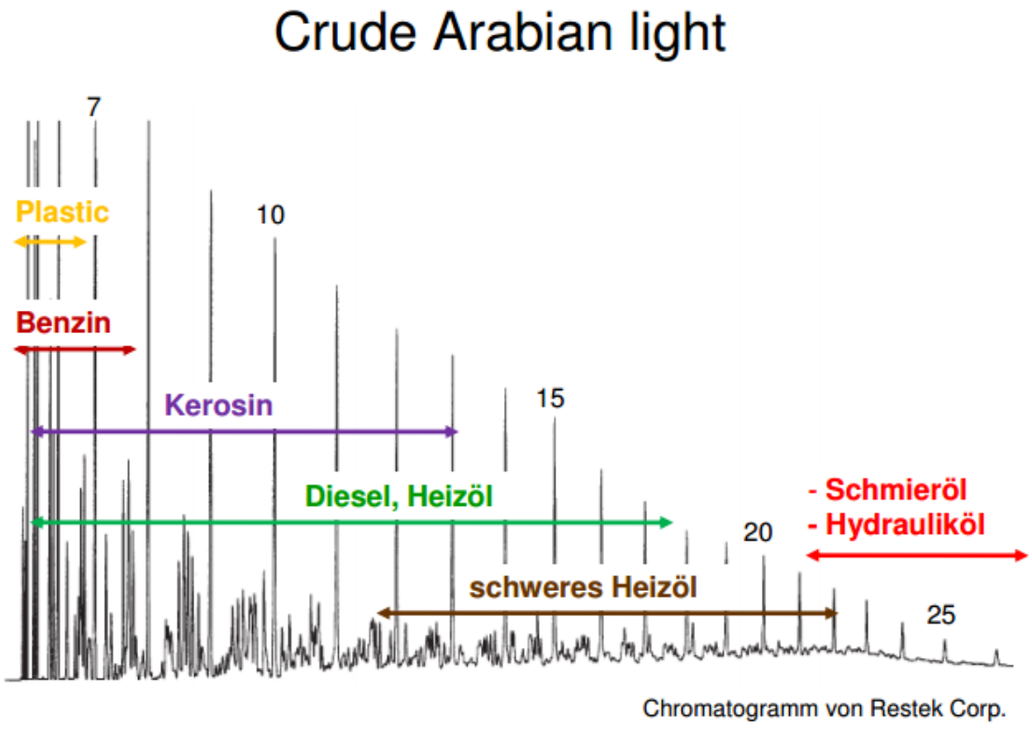
• accident (e.g. leakage of lubrication circulation)

• contaminated feed for animals

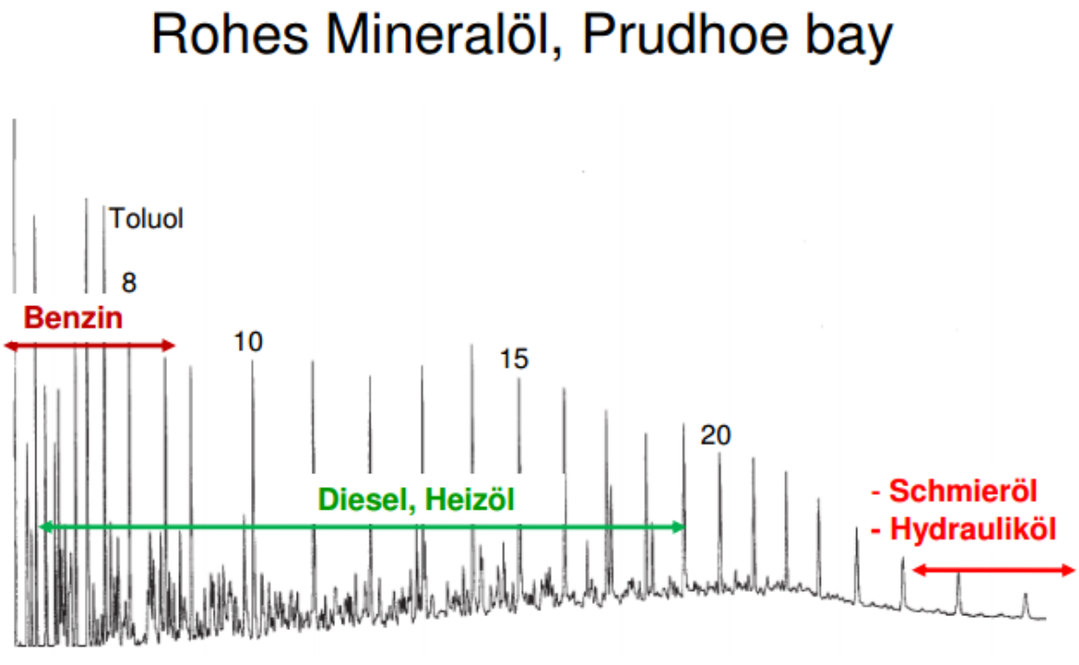
• component of veterinary medicinal products

- **urgent need for further knowledge about possible entry sources**
- **monitoring data for food, concepts for reduction**

GC-Chromatograms of different Crude Oils



Chromatogramm von Restek Corp.



Chromatogramm von Restek Corp.

Processing of Crude Oils

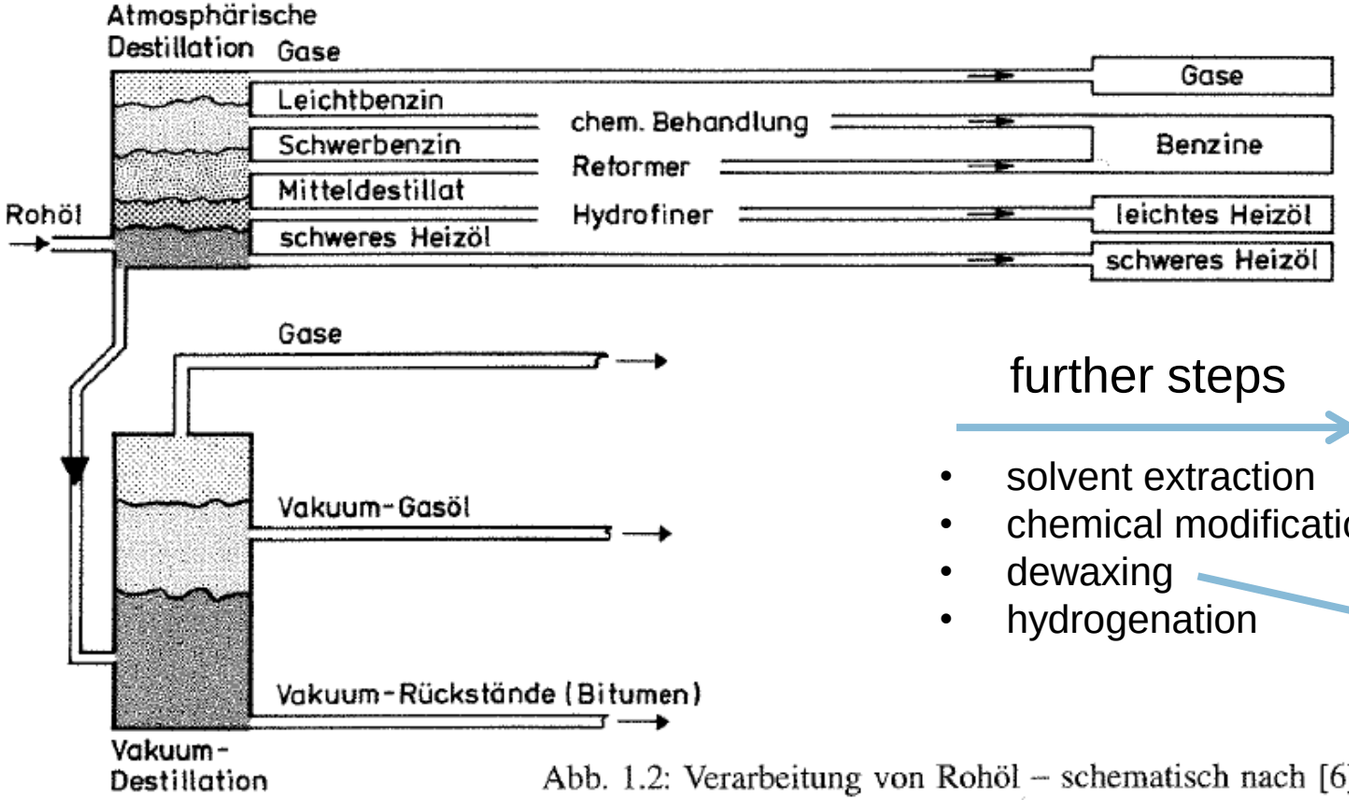


Abb. 1.2: Verarbeitung von Rohöl – schematisch nach [6].

further steps

- solvent extraction
- chemical modification
- dewaxing
- hydrogenation

mineral oil

wax

Source: Hellmann, 1995

Distillation of Crude Oils

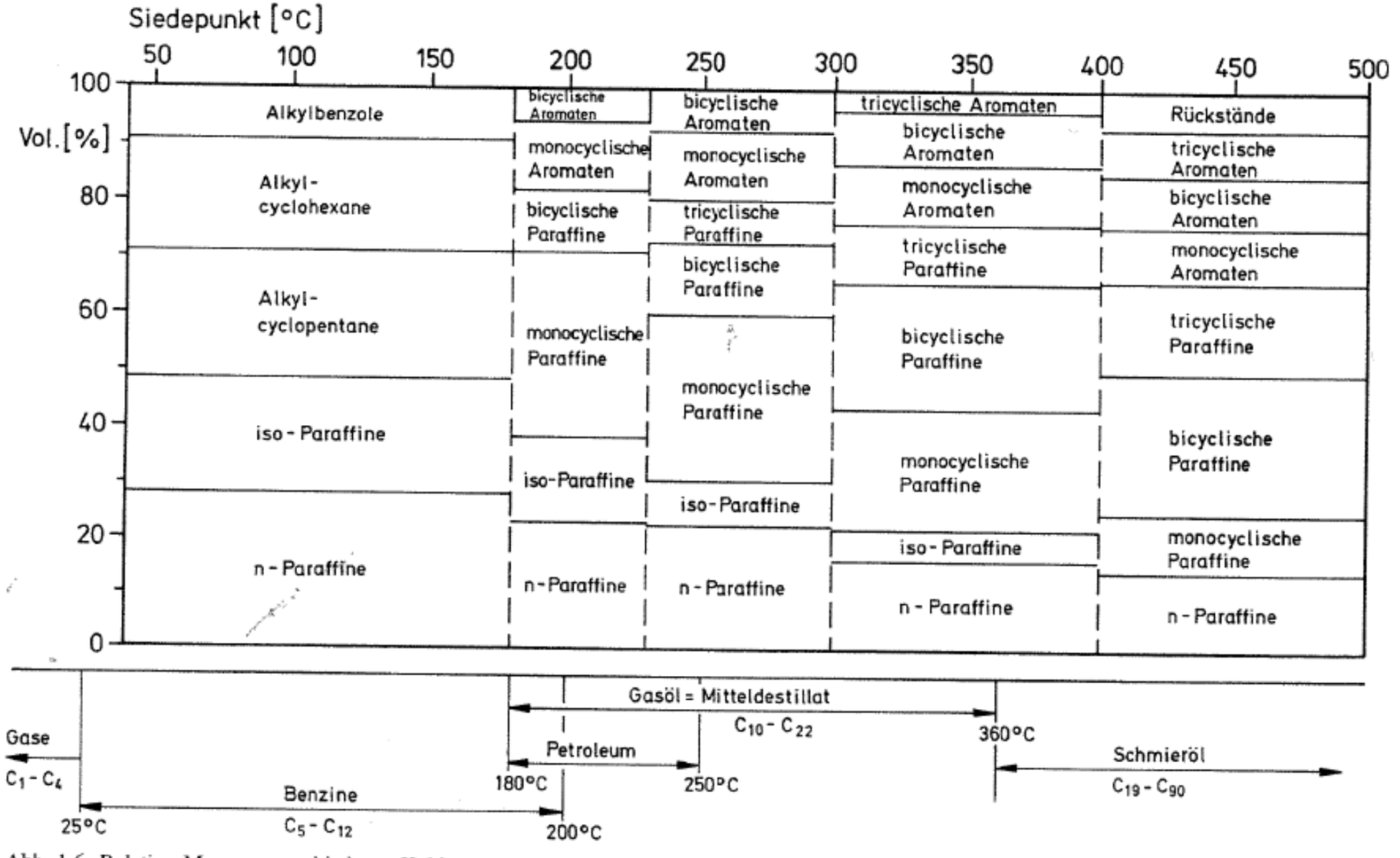


Abb. 1.6: Relative Mengen verschiedener Kohlenwasserstoff-Verbindungen in fünf Fraktionen eines repräsentativen Rohöls nach [22] und deren Zuordnung zu Mineralölprodukten.

Source: Hellmann, 1995

Mineral Oil:

- **Consists predominantly of aliphatic and aromatic hydrocarbons (MOSH and MOAH).**

- **Is produced from crude oil by different steps (e.g. distillation, chemical modification).**

- **Is designed to fulfill certain physico-chemical properties (e.g. viscosity, mass distribution, boiling point range) related to its final use.**

- **Often characterized by standard methods with respect to its physico-chemical properties (e.g. viscosity, mass distribution, boiling point range).**

Quelle: EFSA, 2012

Background: Origin of the acronyms MOSH and MOAH

Acronyms MOSH and MOAH introduced by Biedermann and Grob 2009

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

J. Agric. Food Chem. **2009,** *57,* 8711–8721 **8711**
DOI:10.1021/jf901375e

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

MAURUS BIEDERMANN, KATELL FISELIER, AND KONI GROB*

Kantonales Labor (Official Food Control Authority of the Canton of Zurich), Fehrenstrasse 15, CH-8032 Zurich, Switzerland

Published on Web 09/03/2009

J. Sep. Sci. 2009, *32*, 3726–3737

Research Article

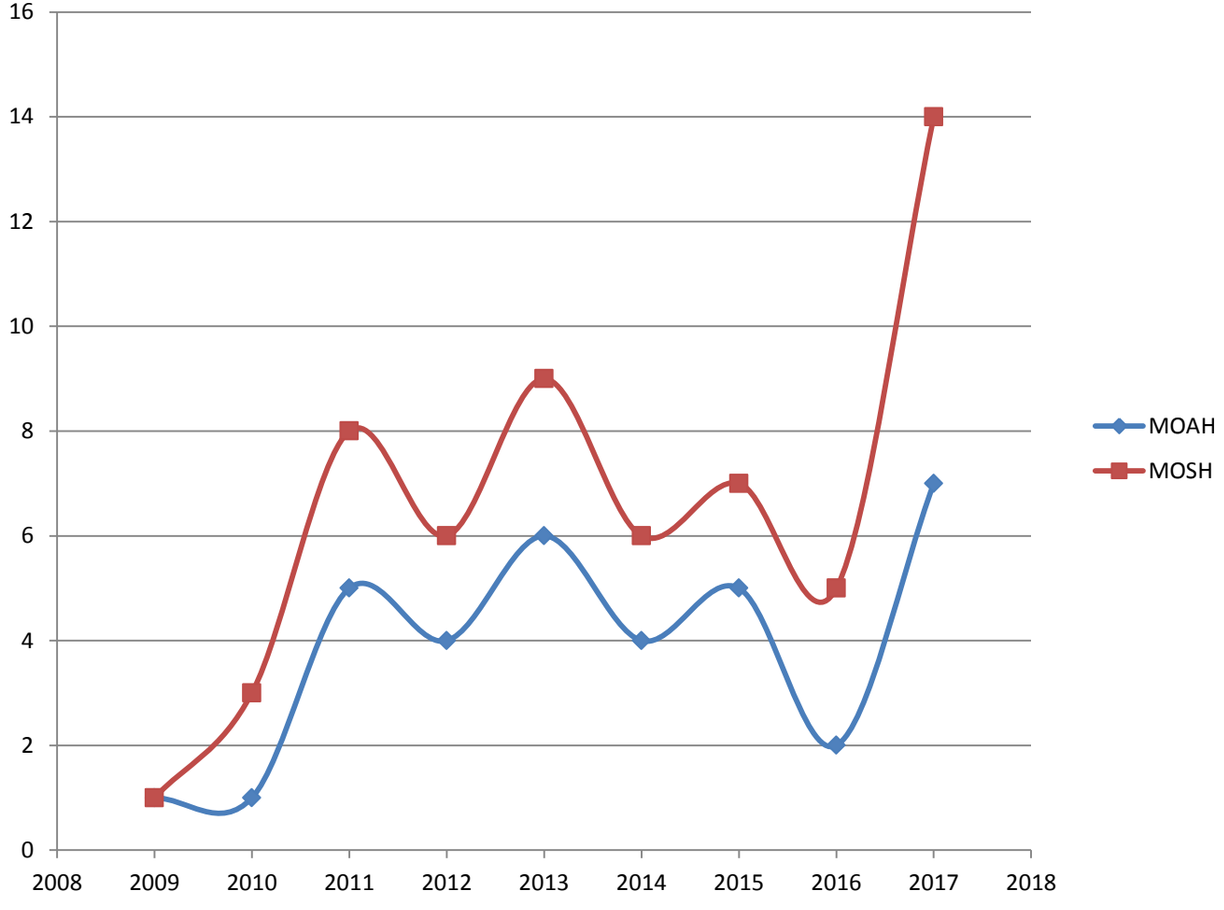
Comprehensive two-dimensional GC after HPLC preseparation for the characterization of aromatic hydrocarbons of mineral oil origin in contaminated sunflower oil

Maurus Biedermann
Koni Grob

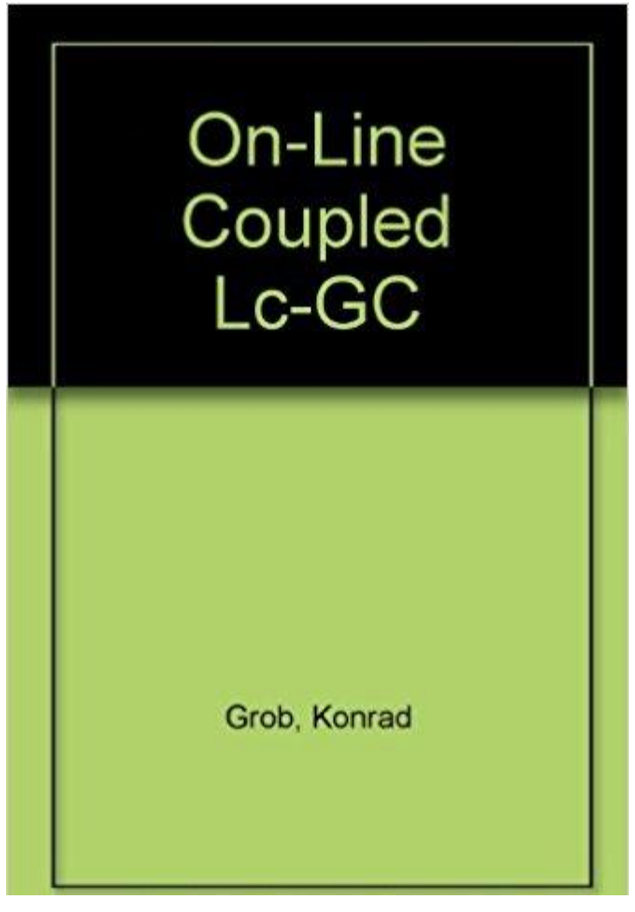
Official Food Control Authority of the Canton of Zurich, Zurich, Switzerland

Received May 23, 2009
Revised August 3, 2009
Accepted August 5, 2009

MOSH and MOAH in Scientific Literature



Number of Publications found in Scopus



Published in 1991

MOSH and MOAH: Definitions from Biedermann et al.,

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

- We use the more general term **"mineral oil saturated hydrocarbons" (MOSH;** instead of "white paraffinic mineral oil") and in this way also distinguish them from the hydrocarbons of plant origin.

- The **mineral oil aromatic hydrocarbons (MOAH)** differ from the widely analyzed polycyclic aromatic hydrocarbons (PAH) formed by pyrolysis at elevated temperature and present in, for example, roasted or smoked food: PAH consist of a limited number of largely nonalkylated ring systems, whereas the MOAH are alkylated to 97-99% and consist of an enormous number of components.

- **In the past, mineral oil analysis in foods referred to the MOSH.** However, not all mineral oils contaminating foods are white, and the MOAH might well be more of concern than the MOSH.

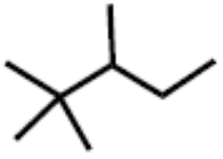
- **The neglect of the MOAH is primarily due to the lack of a method for their analysis.**

Mineral oil – structures MOSH

alkanes

normal octane

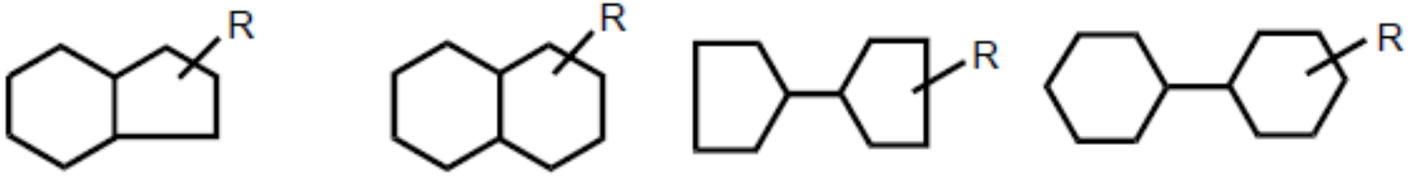
2-methyl-heptane



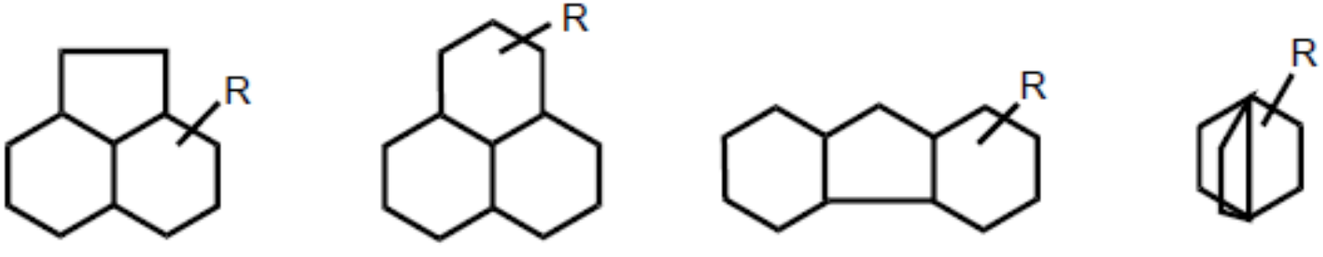
2,2,3-trimethyl-pentane
("iso-octane")

naphthenes

mono-naphthenes



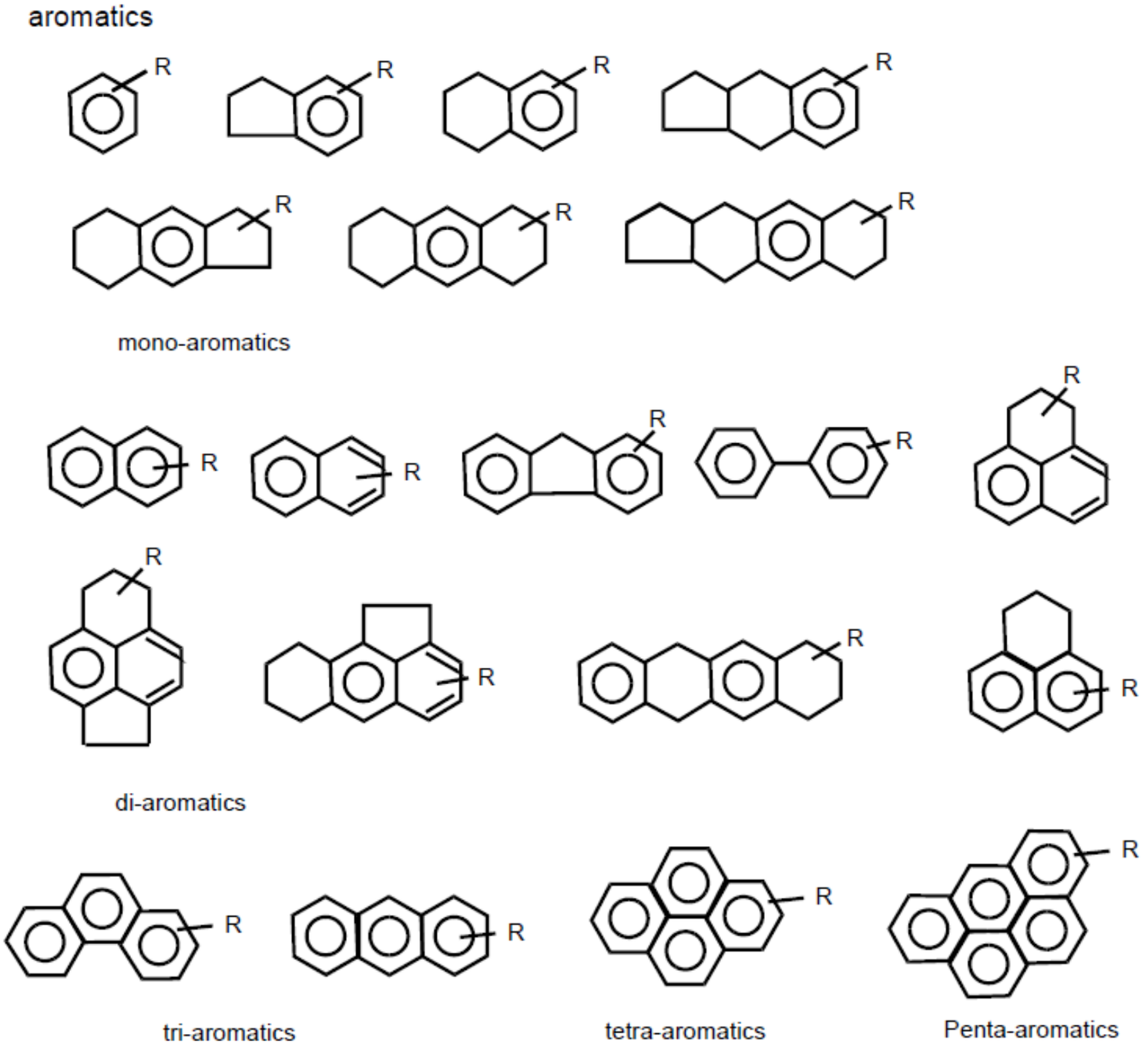
di-naphthenes



tri-naphthenes

Source: EFSA, 2012

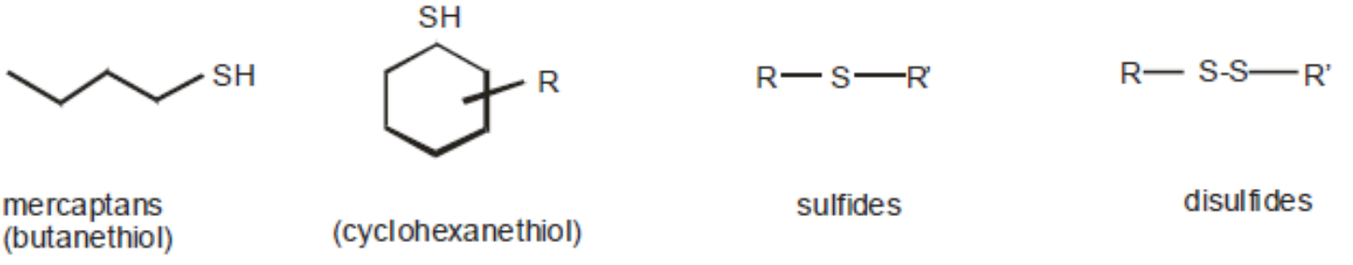
Mineral oil – structures MOAH



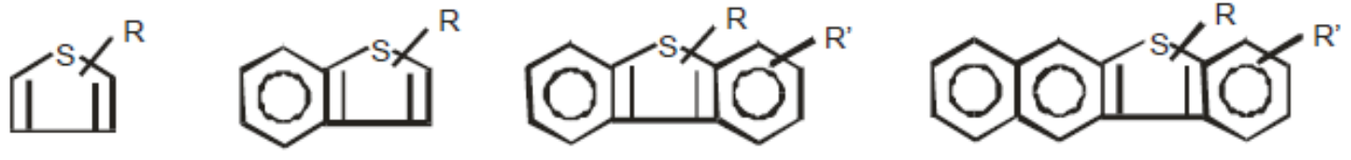
Source:
EFSA, 2012

Mineral oil – further compounds in crude oil

sulphur compounds

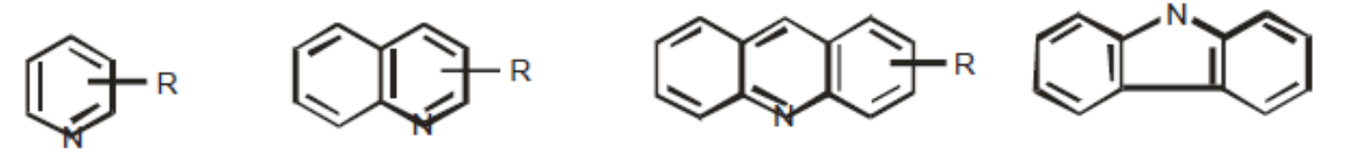


mercaptans (butanethiol) | (cyclohexanethiol) | sulfides | disulfides

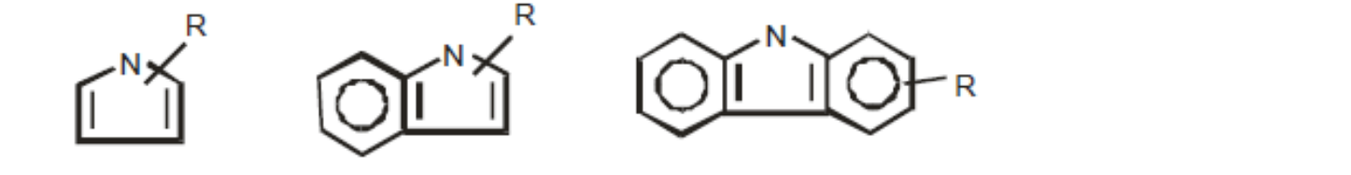


thiophenes | benzothiophenes | dibenzothiophenes | benzonaphthothiophenes

nitrogen compounds



basic pyridines | quinolines | benzoquinolines | azacarbazoles



neutral pyroles | indoles | carbazoles

Source:
EFSA, 2012

MOSH and MOAH: Background

- Inconsistent use of acronyms MOSH and MOAH may lead to confusion. Clear description necessary if acronyms are used not in the way like they were introduced in literature.
- The “historical” background of the acronyms MOSH and MOAH has to be considered (context: analysis of contaminations in edible oils).
- Further knowledge about possible interferences and synthetic hydrocarbons (after 2009).
- Use of MOSH/MOAH analysis in other fields / product groups (e.g. food, food packaging material, cosmetics).
- The analytical methods provided in scientific literature provide tools for the quantitative analysis of aliphatic and aromatic hydrocarbons (e.g. online-LC-GC-FID) and qualitative characterization/verification (e.g. GCxGC-ToF-MS) were developed and published.
- Knowledge about the sample and training on chromatogram interpretation is necessary for correct data analysis – MOSH and MOAH chromatogram library needed!
- Auxiliary techniques were provided (e.g. enrichment, removal of n-alkanes, epoxidation).

Separation of MOSH and MOAH with online-LC-GC-FID:

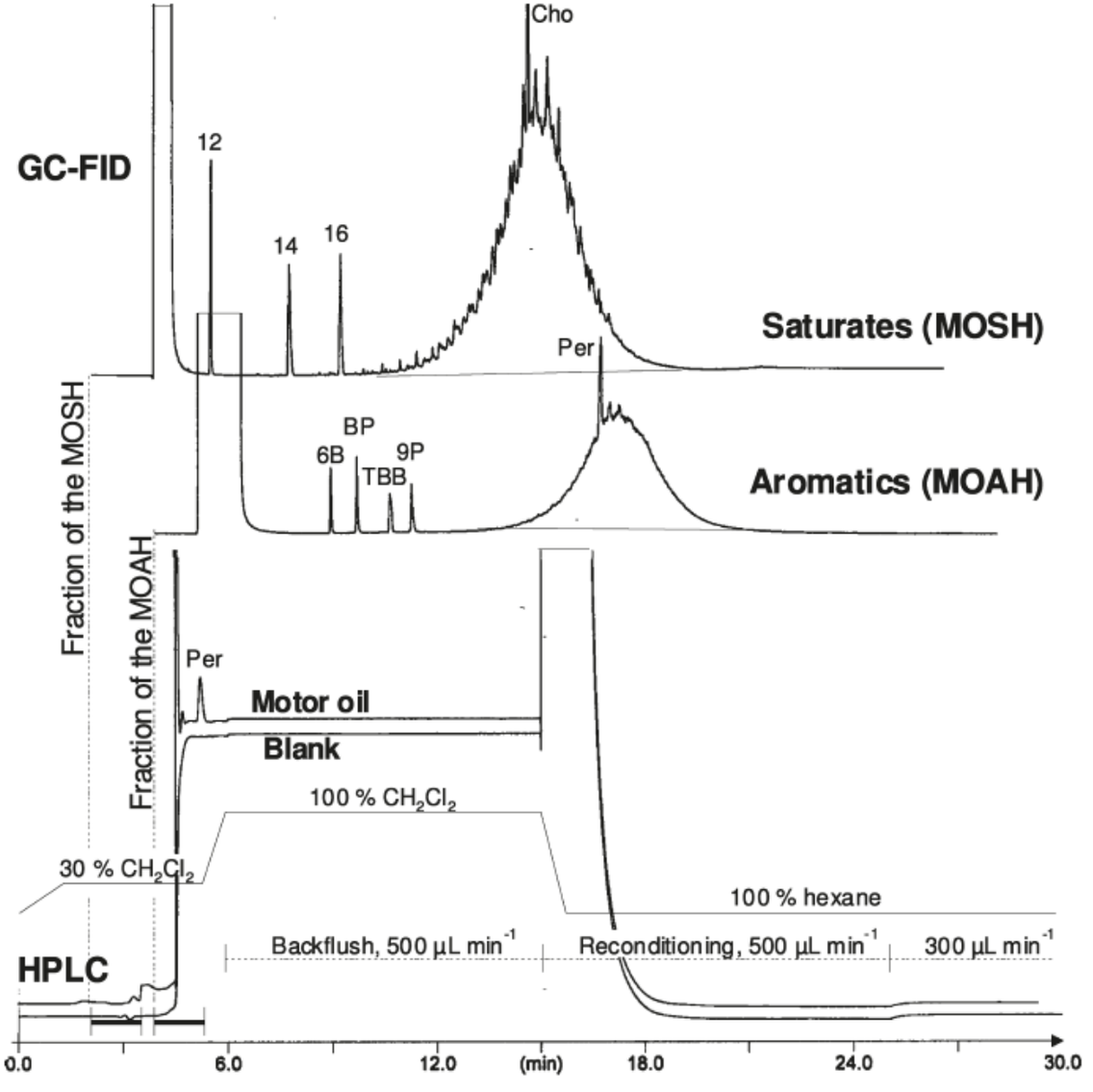


Figure 1. Analytical procedure visualized by the chromatograms of a motor (lubricating) oil. Labeled peaks indicate internal standards for determining concentrations and verification of the performance.

Gas phase migration of MOSH and MOAH from recycled cardboard to rice

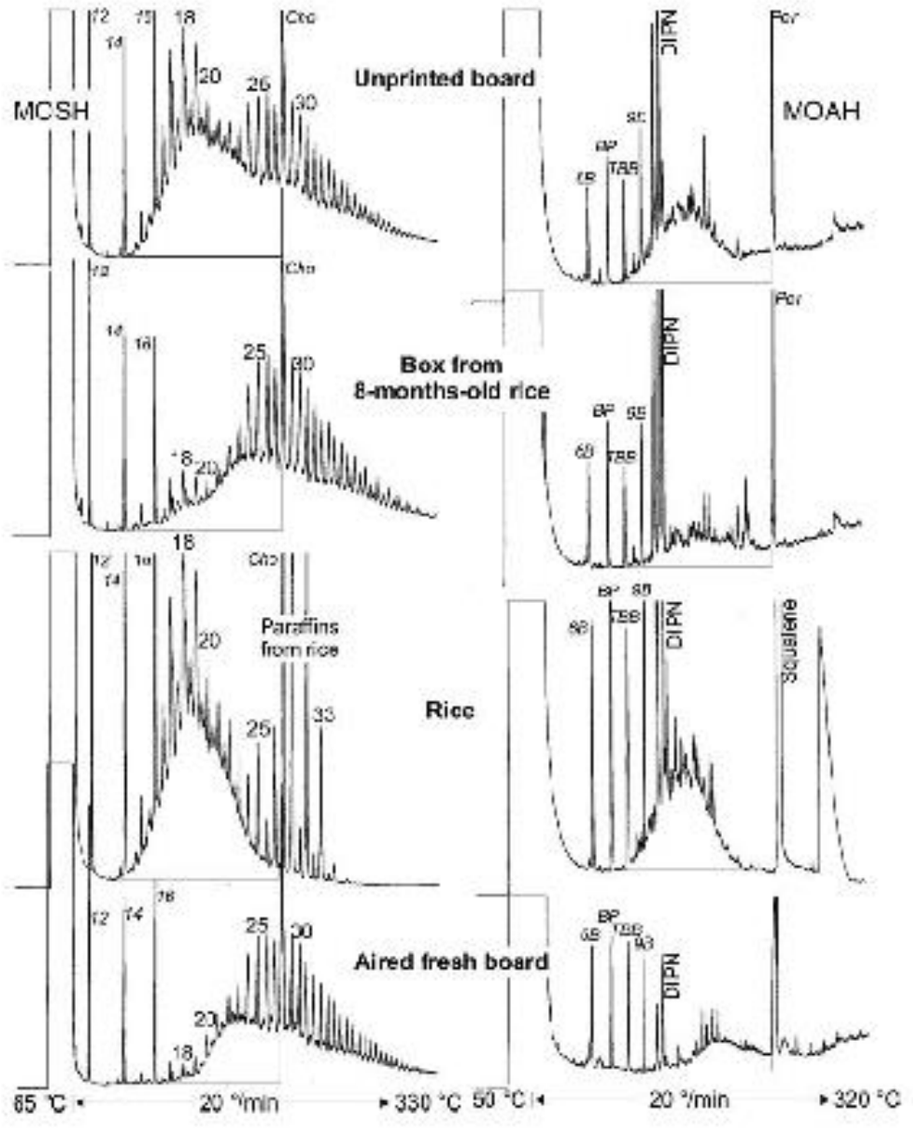


Fig. 6 HPLC-GC-FID chromatograms of the MOSH (*left*) and the MOAH (*right*) of samples related to rice packed into a cardboard box during 8 months. Areas integrated up to n-C_{28}

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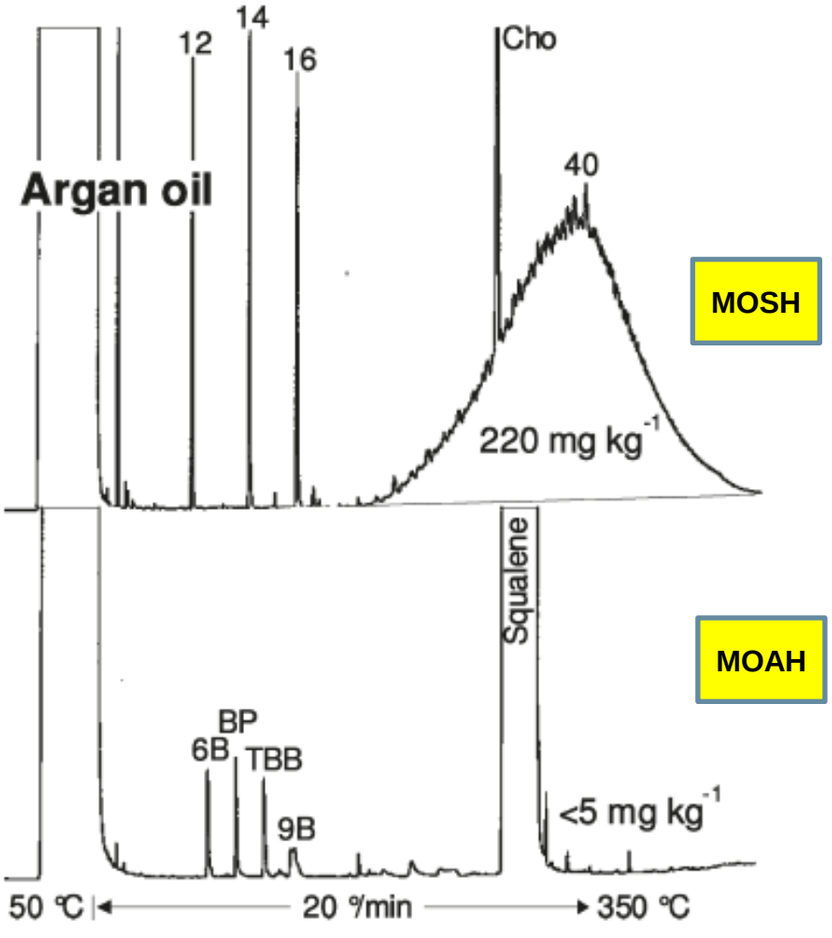
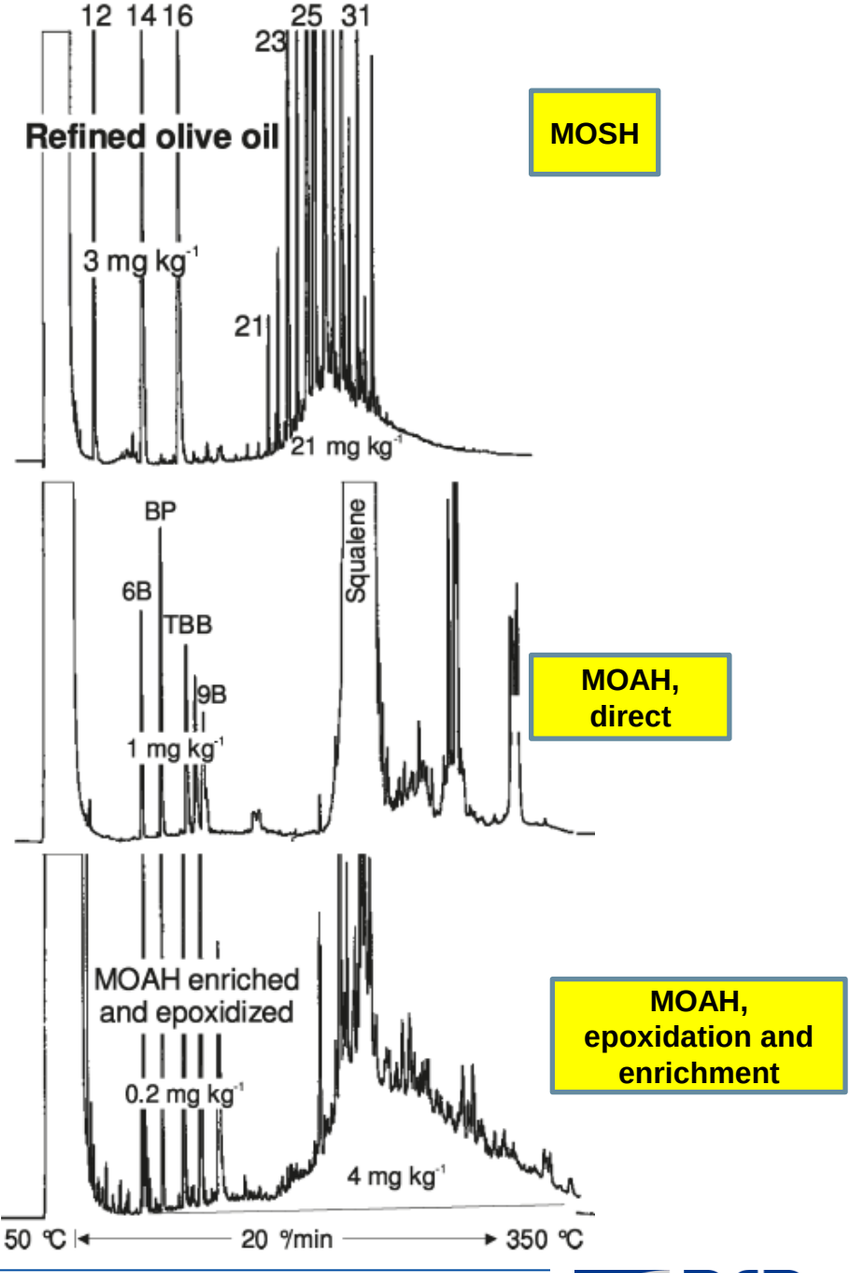
Biedermann und Grob,
Eur Food Res Technol. 2010

Online-LC-GC-FID: Chromatograms of edible oils

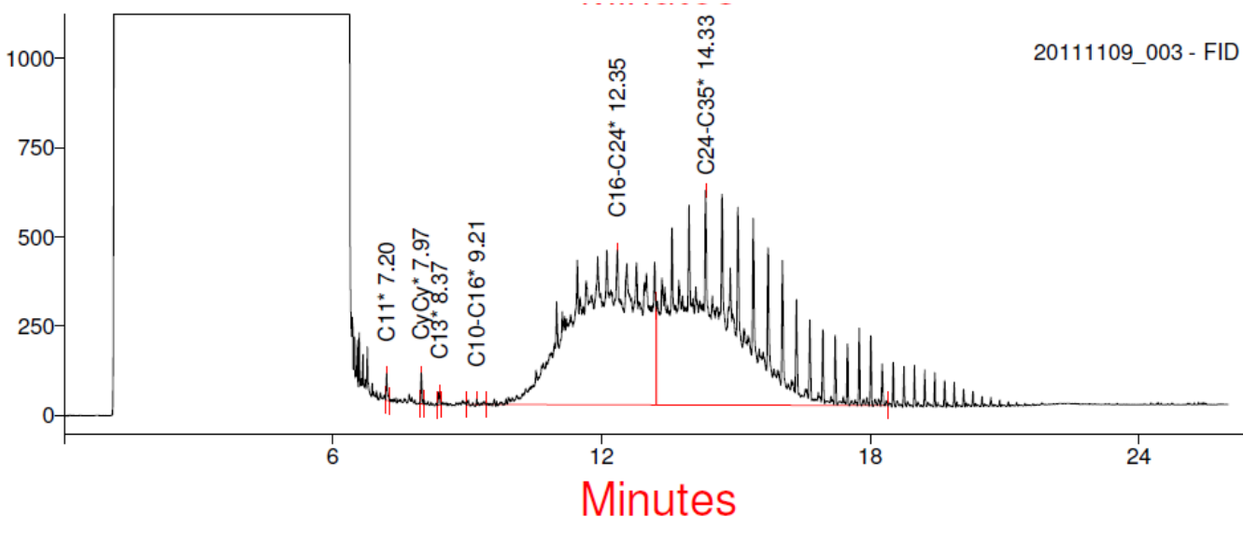


MOSH but “no“ MOAH



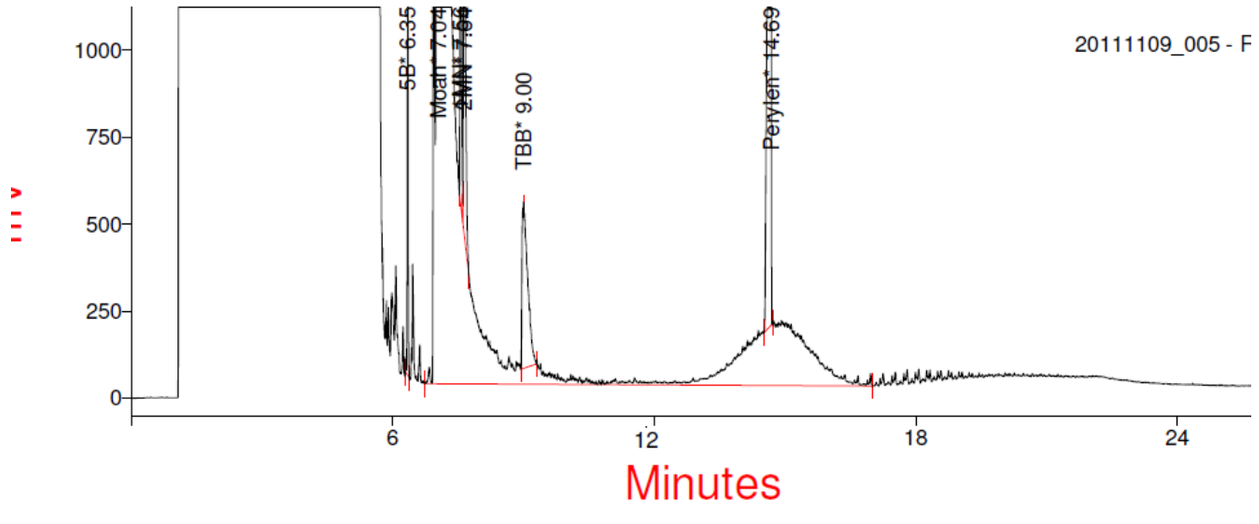
Source: Biedermann et al., 2009

Online-LC-GC-FID: Chromatograms of Real Samples



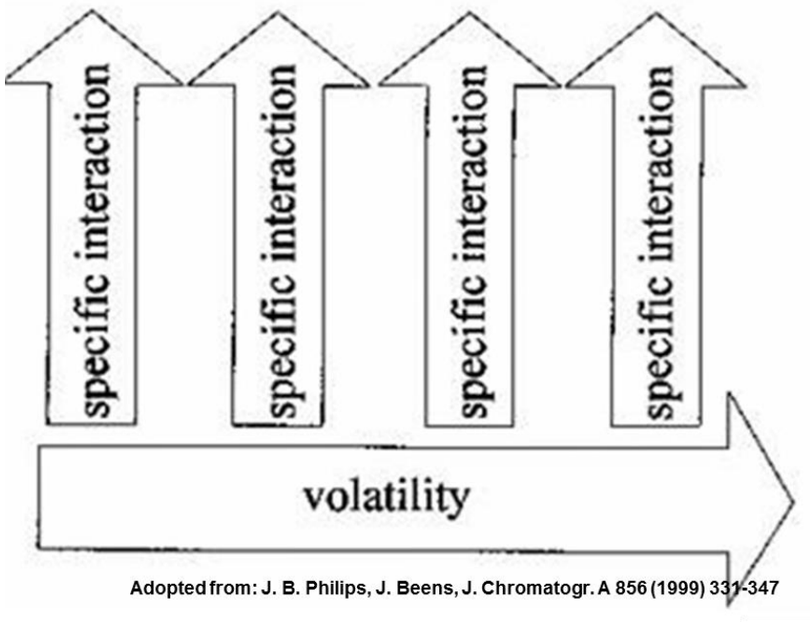
MOSH (21 %)

Baby care cream

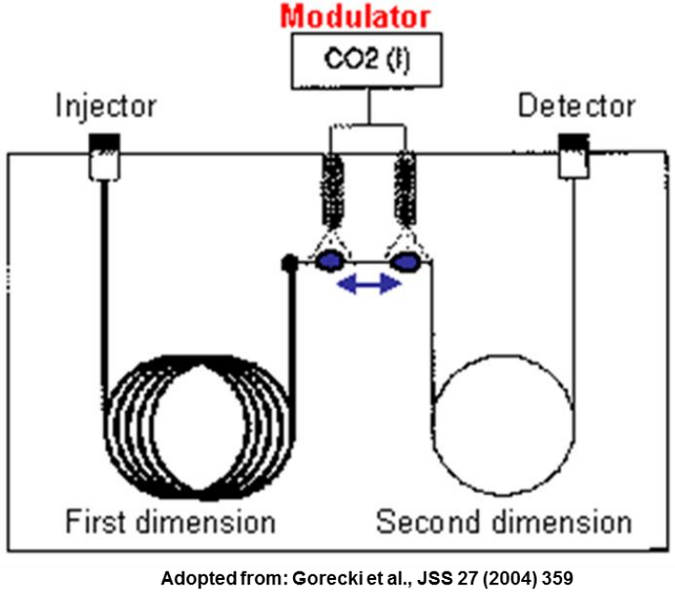


MOAH
(250 ppm = 0.025%)

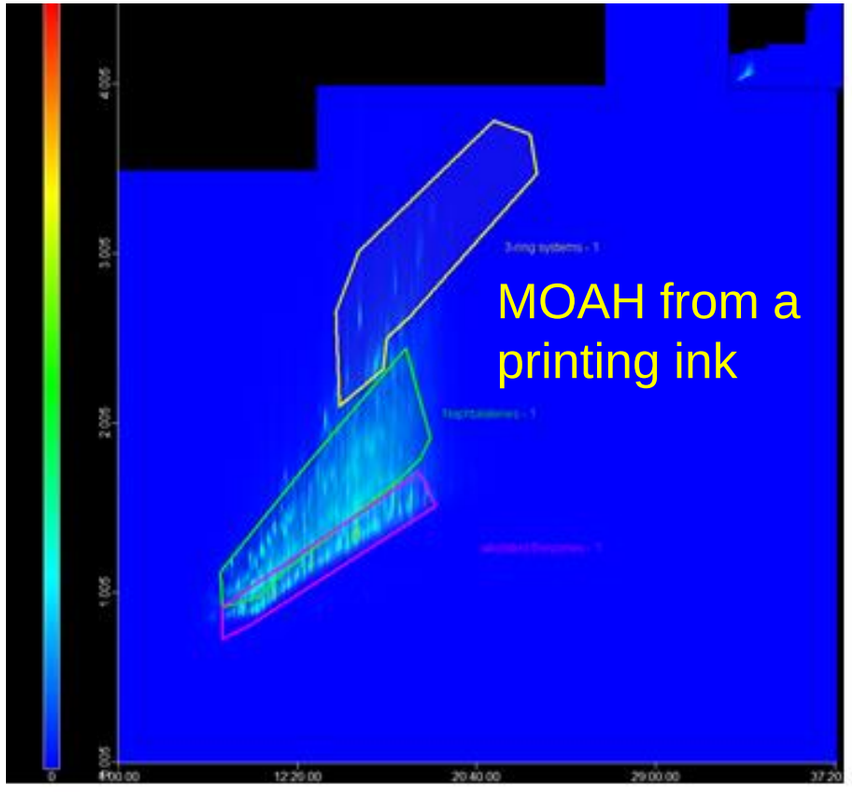
MOAH: Visualization of the Complexity by GCxGC

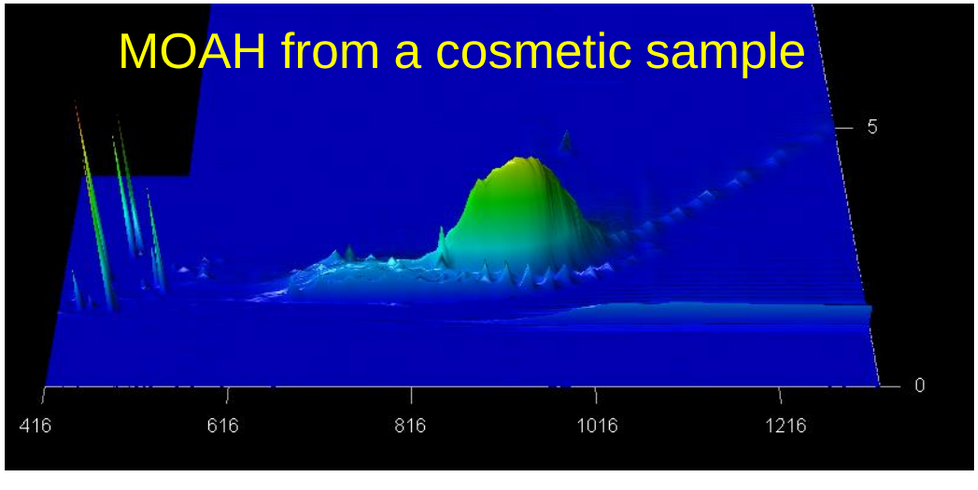


Adopted from: J. B. Philips, J. Beens, J. Chromatogr. A 856 (1999) 331-347

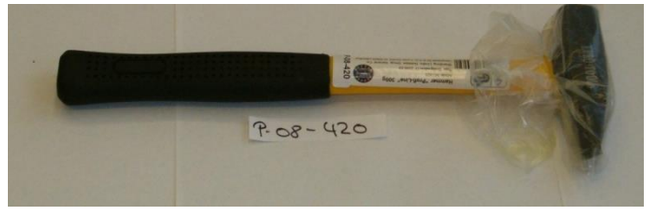


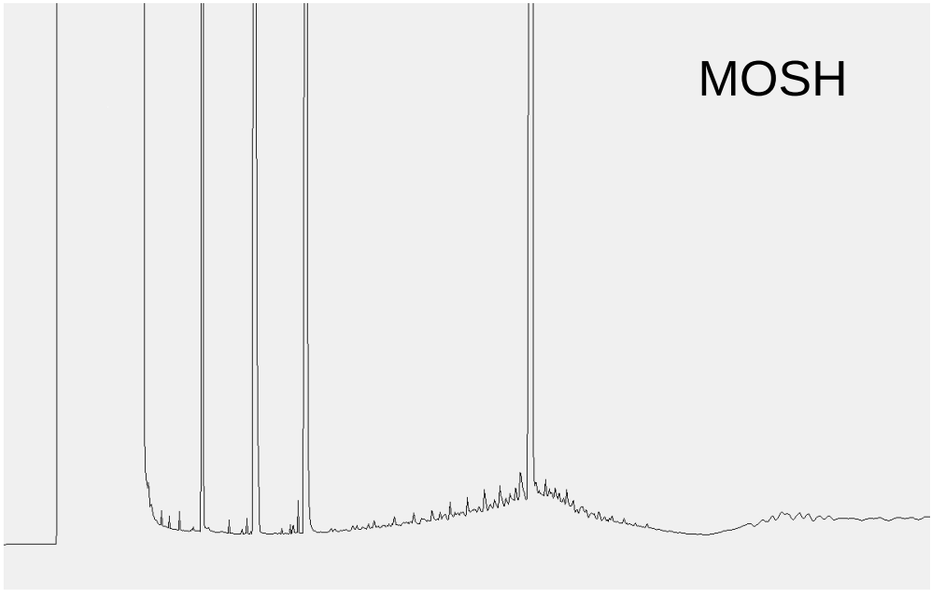
Adopted from: Gorecki et al., JSS 27 (2004) 359

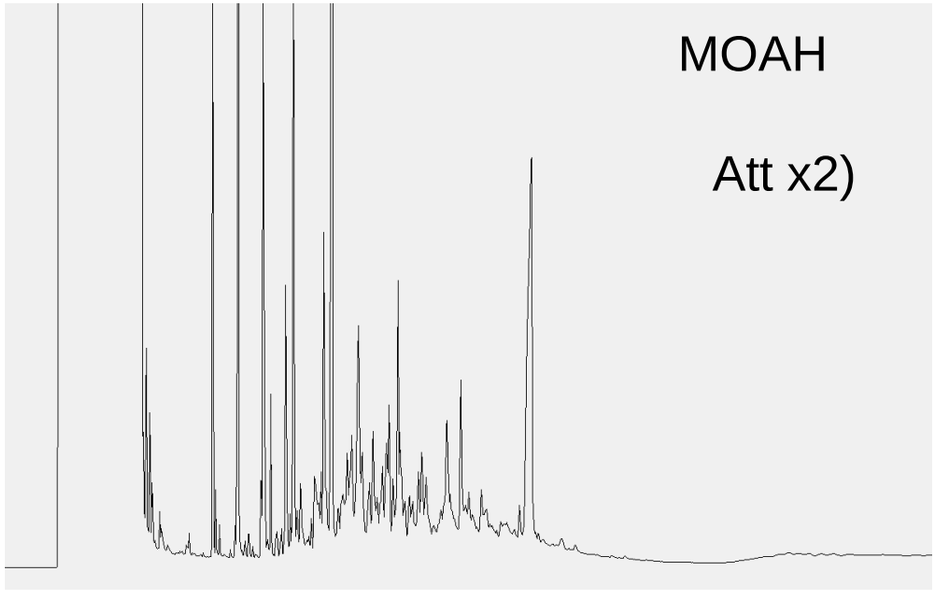




MOSH and MOAH in consumer products







MOSH: 1.0 %
MOAH: 3.8 %

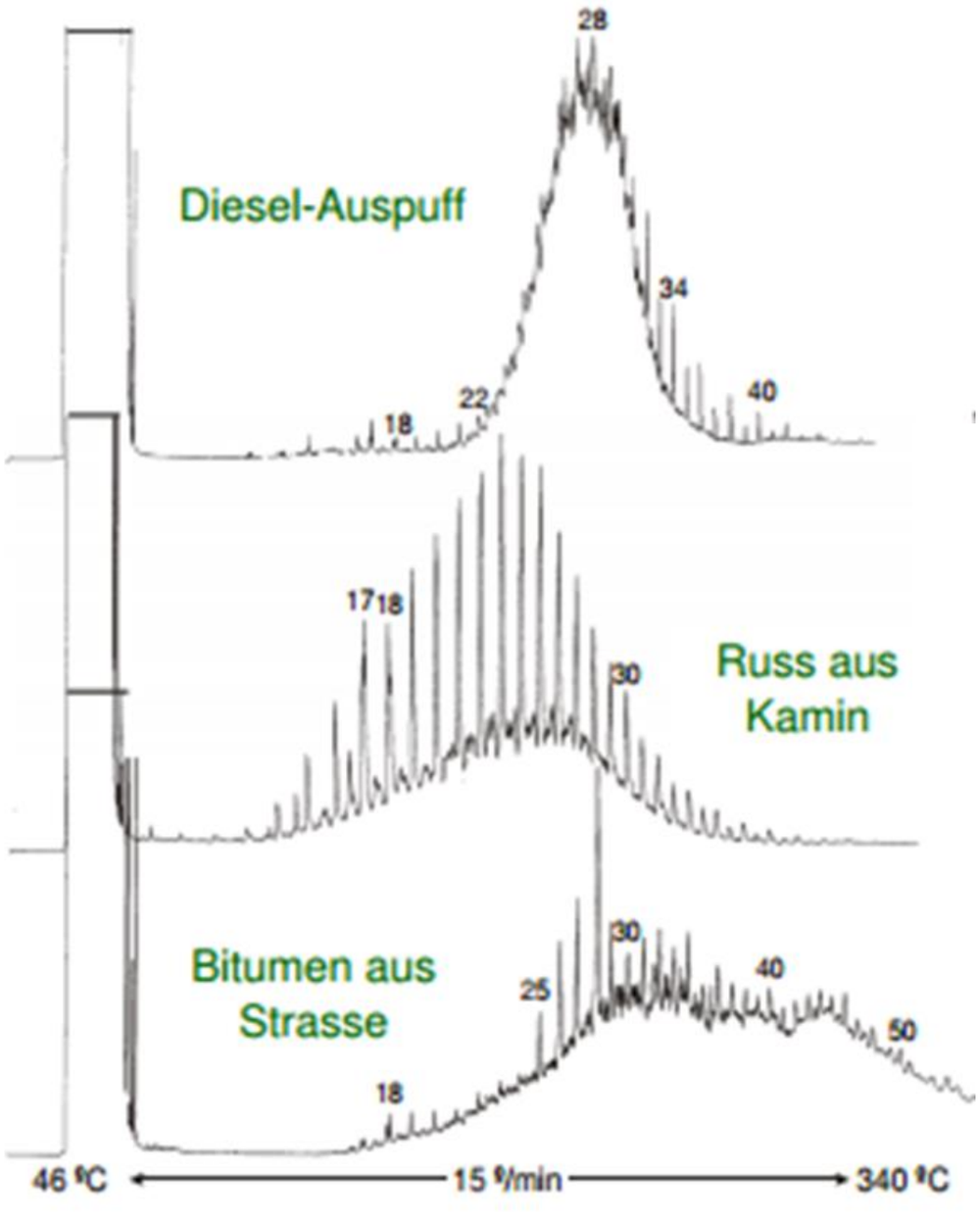
volatility range of MOSH and MOAH does not match

PAK-Source: next to Soot
DAE as softener?

KANTONALES LABOR ZÜRICH

Elastomers and Rubbers can be sources for MOSH and MOAH.
Bartsch et al, 2017

Mineral Hydrocarbons in the Environment



Quelle: K. Grob, 2002

Summary

- **Consumers get into contact with MOSH and MOAH from different sources via different exposure routes.**
- **Different petroleum products are always complex mixtures.**
- **Analytical methods for quantification and verification of MOSH and MOAH are already available.**
- **Two cases have to be clearly distinguished: intended legal use of evaluated highly refined products vs. contamination via unknown source of unevaluated products.**
- **Lack of data - Monitoring data needed for all exposure routes, chemical composition, reduction strategies. --> Work started and still in progress.**

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Thank you for your attention!

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