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

Oudenarder Straße 16 / Carrée Seestraße
13347 Berlin Mitte

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
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 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
Analytical strategy

What is the „hump“?

online LC-GC-FID

sum MOAH

✓ 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**

- Sum MOAH

**GCxGC-TOF(MS)**

- 2D GCxGC
- Mass selective detector
- Qualitative result
- Differentation according to substances classes possible

- 1D GC
- Unspecific detector
- Response of all substances nearly the same
- Quantitative result
- Sum of MOAH
- No information about type of substances
Noodles

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

MOSH

138 ppm

high MOSH value, free of MOAH
Chocolate

Poly-alpha-Olefin synthetic lubricating oil (Production)

Oligomeres from Hexen

free of MOAH!
Online-HPLC-GC/FID

MOSH

n-C16

17 ppm

n-C50

MOAH

< 1 ppm

Soybeans
Online-HPLC-GC/FID

[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 552).

(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 202-741-6020, 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:

<table>
<thead>
<tr>
<th>Use</th>
<th>Limitation (inclusive of all petroleum hydrocarbons that may be used in combination with white mineral oil)</th>
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<tbody>
<tr>
<td>15. As a dust control agent for wheat, corn, soybean, barley, rice, rye, oats, and sorghum</td>
<td>Applied at a level of no more than 0.02 percent by weight of grain.</td>
</tr>
</tbody>
</table>
Online-HPLC-GC/FID

MOSH

coffee powder

<10 µg/l

MOSH

filter-machine

16 ppm

n-C16

coffee infusion

50 µg/l

MOSH

French Press

n-C50
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

MOSH

Purification with activated aluminium oxide

77 mg/kg
Peanut Oil

MOAH

Diterpenes

Squalens

?}

Epoxydiation

MOAH

Sterenes

4 mg/kg
Migration from the packaging 

into dry food

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.
Cornflakes

- MOSH: 5 mg/kg
- MOAH: 1.5 mg/kg
Cacao beans

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
Online-HPLC-GC/FID

**MOSH**
- 320 mg/kg
- 150 mg/kg
- 2,1 mg/kg
- 0,9 mg/kg

**MOAH**
- 150 mg/kg
- 2,1 mg/kg
- 0,9 mg/kg

Cacaobeans + Jutebag

Ghana

Jutebag

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

**Cacaobeans**

- MOSH: 2.1 mg/kg
- MOAH: 0.9 mg/kg

**Jutebag**

- MOSH: 320 mg/kg
- MOAH: 150 mg/kg

**Mono-Aromatics**

- m/z 119
  - alkyl. Benzenes

**Di-Aromatics**

- m/z 170, 184, 198, 212, 226
  - alkyl. Naphthalenes
  - alkyl. Dibenzothiophenes

**Tri-Aromatics**

- m/z 178, 192, 206, 220, 234, 248
  - alkyl. Fluorenes
  - alkyl. Anthracenes
Results

- No of the jutebags was "free of mineral oil"
- Next MOSH also always aromatics (MOAH) determinable
- Different amounts, molecular ranges and distributions

Jutebags:
- MOSH: 75–750 mg/kg
- MOAH: 10–350 mg/kg

Cacao Beans:
- MOSH: 0.6–2.7 mg/kg
- MOAH: u.B. – 0.9 mg/kg

Hypothesis: current requirements on jutebags are too low

Grob et al., 1993
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

through radicals → branched LDPE
catalytic → linear HDPE
Migration MOSH/POSH

*retained sample - end of shelf life*

- MOSH
- MOSH/POSH
- POSH
- HDPE

- Retained sample
- End of shelf life
GCxGC/TOFMS

Package

Cornflakes

m/z 260–13C alkylated Benzenes

m/z 145 159 173–nC alkylated tetrahydro Naphthalenes
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**

<table>
<thead>
<tr>
<th>Waxes</th>
<th>Resins</th>
<th>Polymers</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>- natural waxes</td>
<td>- Rosin resins</td>
<td>- PA, <strong>PE</strong>, EVA, PES, PU</td>
<td>- Antioxidants</td>
</tr>
<tr>
<td>- Synthetic waxes</td>
<td>- Terpene resins</td>
<td></td>
<td>- UV-Absorber</td>
</tr>
<tr>
<td>- Paraffin waxes</td>
<td>- Hydrocarbon resins</td>
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<td>- Chelating agent</td>
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-> **Products of petrol chemistry**

**Resins**

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<th>Fraction</th>
<th>C5 («Piperylenes»)</th>
<th>C9 («Aromatics»)</th>
<th>DCPD (Dicyclopentadienes and Cyclopentadienes)</th>
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<td><img src="image" alt="DCPD" /></td>
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→ These products can be fully or partially hydrogenated after synthesis
Online-HPLC-GC/FID

MOAH

n-C16

n-C24

GCxGC/TOFMS

Migration with Tenax ®
10 days, 40°C
GCxGC/TOFMS

Possible Structures

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→ These products can be fully or partially hydrogenated after synthesis.
Online-HPLC-GC/FID

MOAH

GCxGC/TOFMS

TIC

MOAH "peak cloud"

Per

5B

MN

TBB

n-C16

3,1%

n-C50

n-C16

3,1%

n-C50

Petrolatum
GCxGC/TOFMS

m/z 91, 92, 105, 106, 119, 120 - alkylated Benzenes

Petrolatum

m/z 302 - 16C alkylated Benzenes
GCxGC/TOFMS

m/z 145 159 173 - nC alkylated tetrahydro Naphthalenes

m/z 188 - 4C alkylated tetrahydro Naphthalenes

z.B.

MOAH

Petrolatum
GCxGC/TOFMS

m/z 210 - 2C alkylated tetrahydro Anthracenes/Phenanthrenes and/or 4C alkylated Biphenylenes

m/z 256 - 5C alkylated octahydro Anthracenes/Phenanthrenes
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!

Institut Kirchhoff Berlin GmbH
Oudenarder Straße 16 / Carrée Seestraße
13347 Berlin
Tel.: 030 – 4579893141
www.institut-kirchhoff.de   IKB@institut-kirchhoff.de