



The European voice of the
adhesive and sealant industry

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SAFE ADHESIVES FOR SAFE FOOD



Testing mineral oil and synthetic hydrocarbon from adhesives into food

Martin Lommatzsch, Analytical Chemist and Entrepreneur, Laboratory Lommatzsch

Analysis of mineral oil and synthetic hydrocarbons – Focus on adhesives

Martin Lommatzsch

FEICA Food Contact Seminar - 'Safe Adhesives for Safe Food'

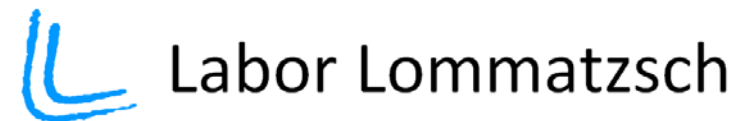


Brussels, 28.09.2017

- Diploma in Food Chemistry
- Dissertation (completion in 2017)

- Consultancy for contaminants from Food Contact Materials
- Research and Development for multidimensional chromatography

- Research laboratory since **June 2016**
 - Located in Cologne



*Consulting
Analytical Support
Research & Development*

1. Mineral oil hydrocarbons



2. Hot-melt adhesives



3. Migration testing



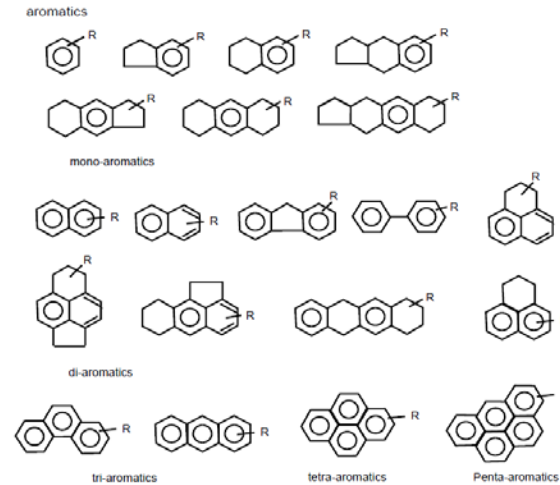
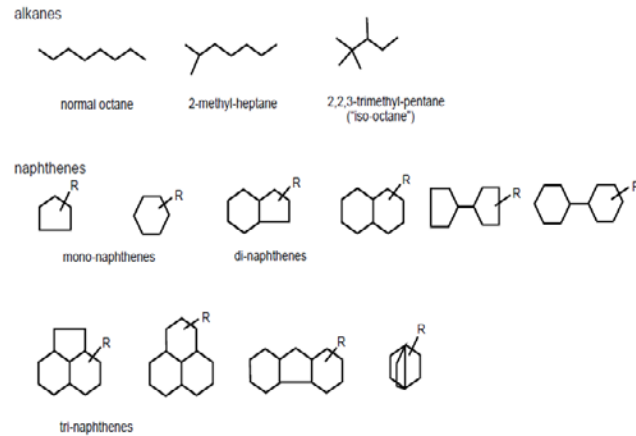
Mineral oils

Adhesives

Migration testing

MOSH: Mineral oil saturated hydrocarbons

MOAH: Mineral oil aromatic hydrocarbons



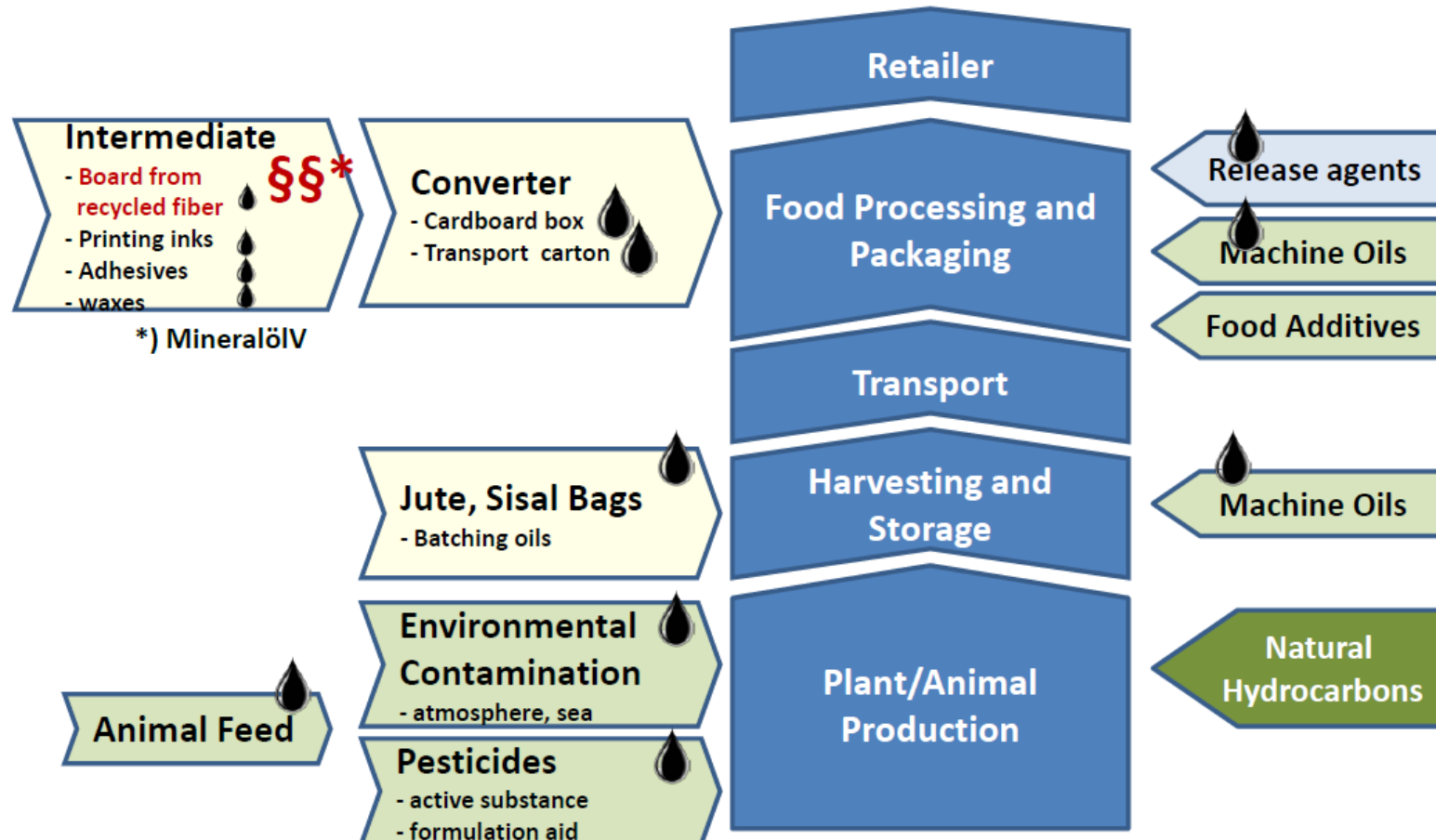
➤ Accumulation in human tissue (1-10 g per person)

➤ Partially genotoxic

- Source: mostly printing inks (recycled newspaper; printing on boxes)
- Migration into food via gas phase (5 – 50 mg/kg)
- Solutions: Functional barriers or virgin board



Sources of MOSH and MOAH

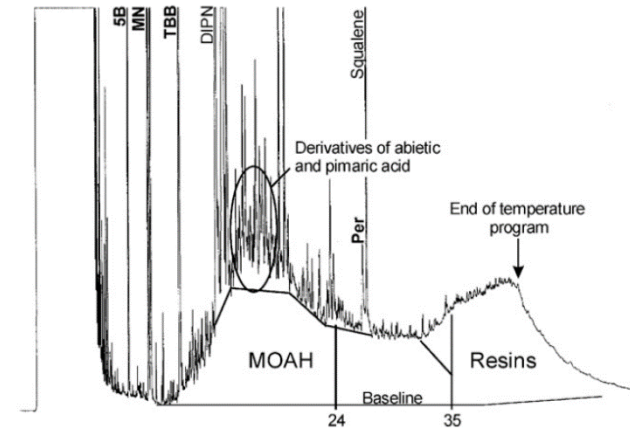
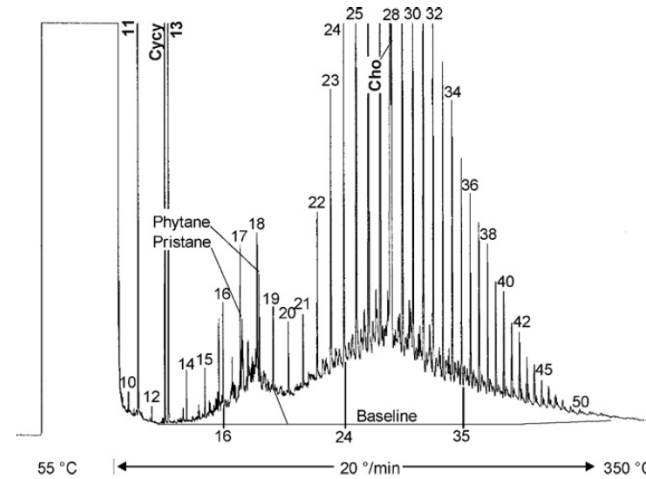


➤ **HPLC-GC-FID method for mineral oils according to Grob & Biedermann (2012)**

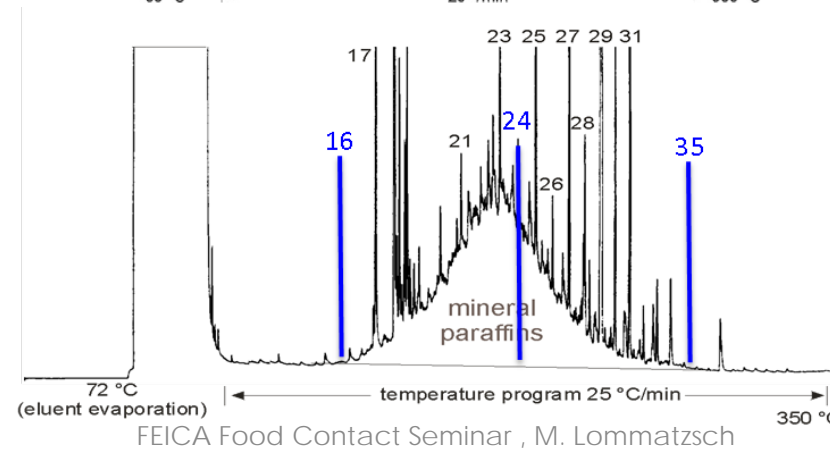
Recycled cardboard:

MOSH fraction (Saturates)

MOAH fraction (Aromatics)



Human tissue:

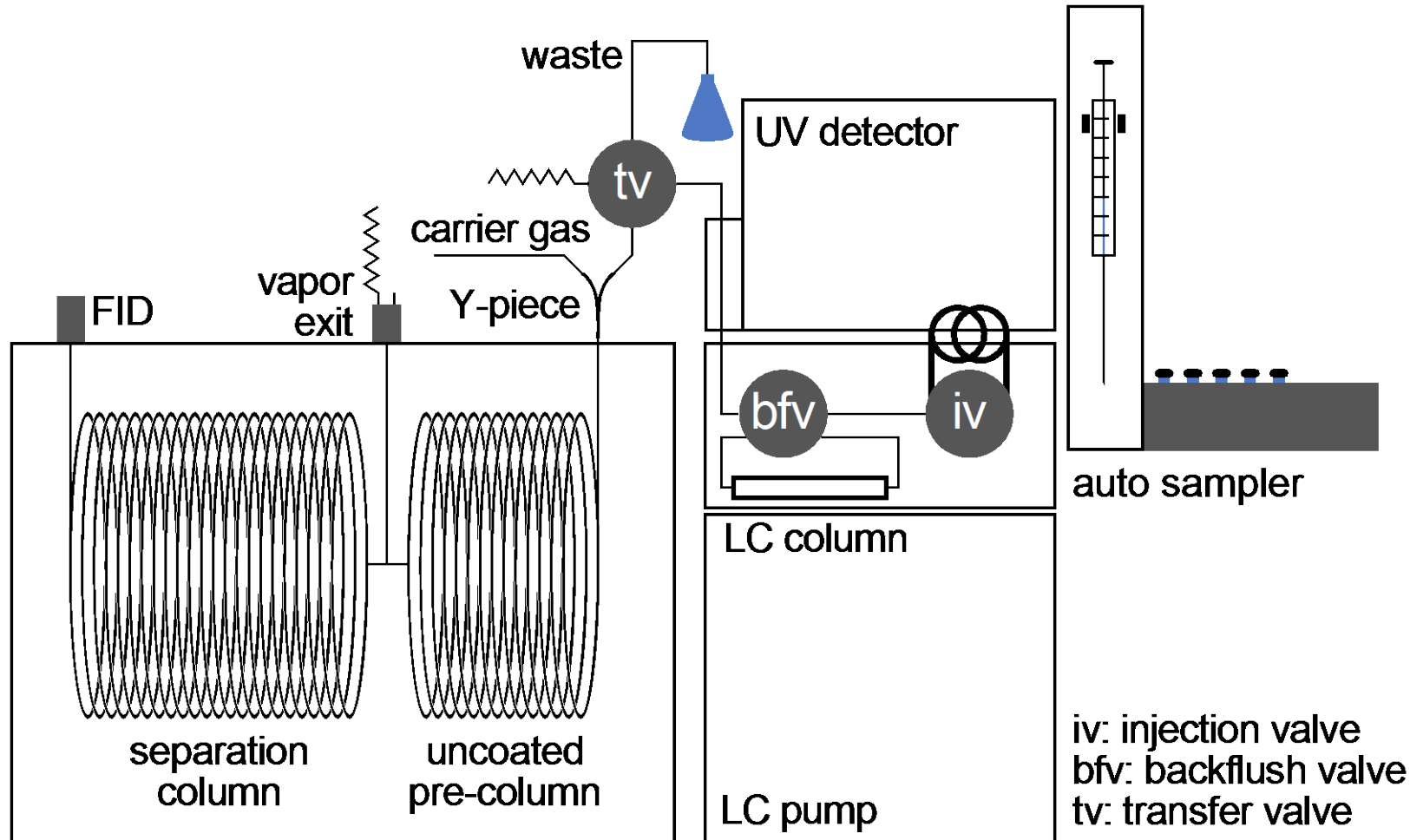


Internal standards are used for quantification and validation

Mineral oils

Adhesives

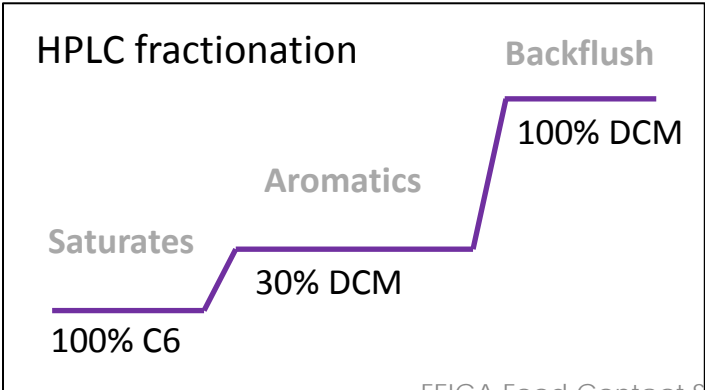
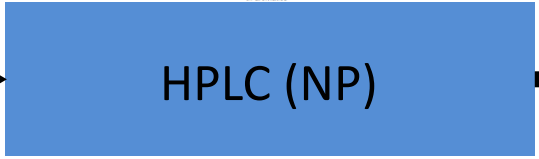
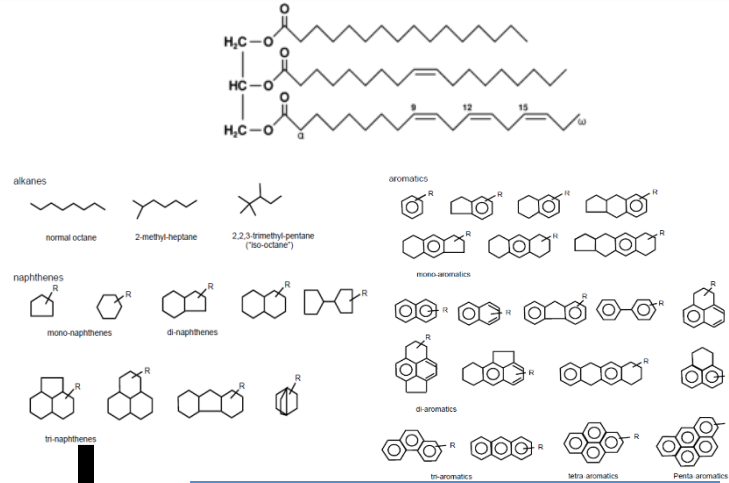
Migration testing



Mineral oils

Adhesives

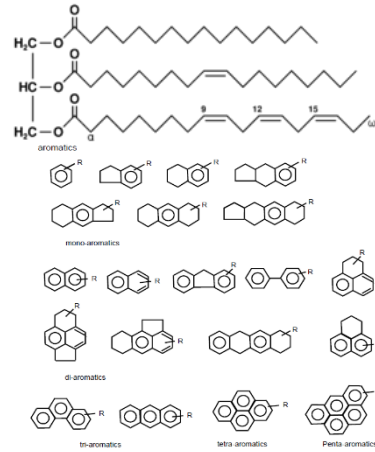
Migration testing



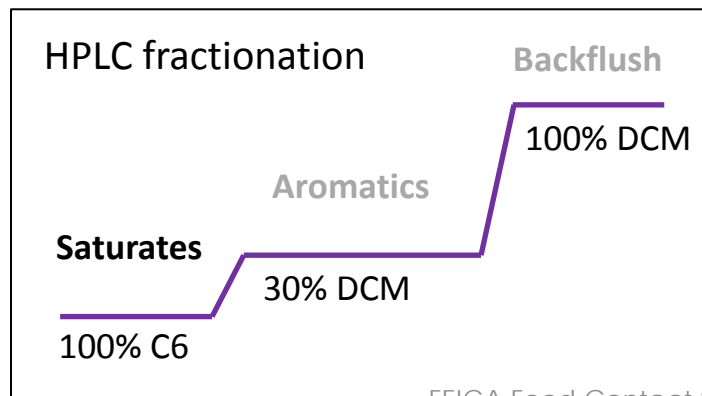
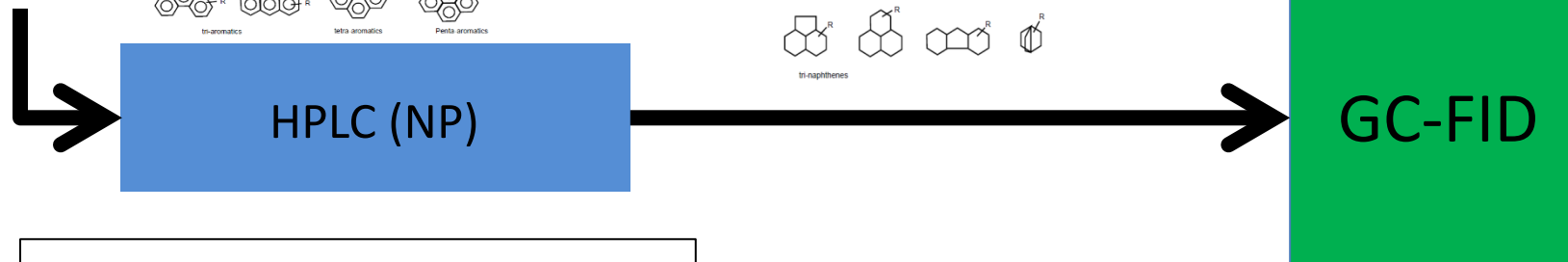
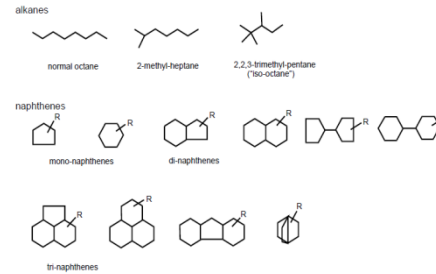
Mineral oils

Adhesives

Migration testing



1st Fraction (aliphatic hydrocarbons – MOSH fraction)

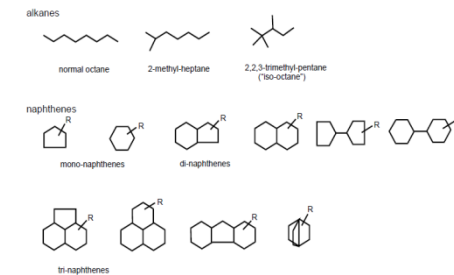
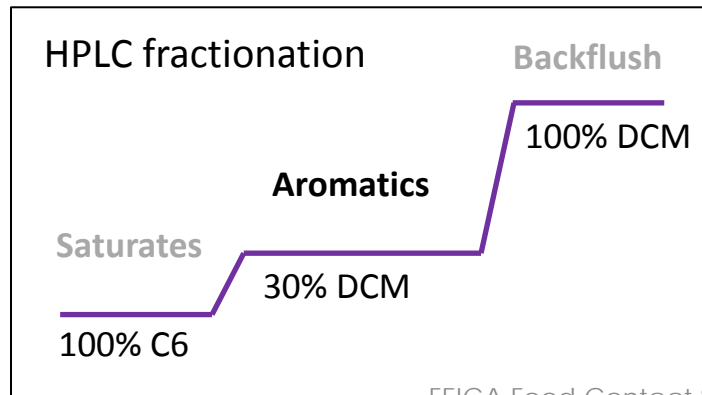
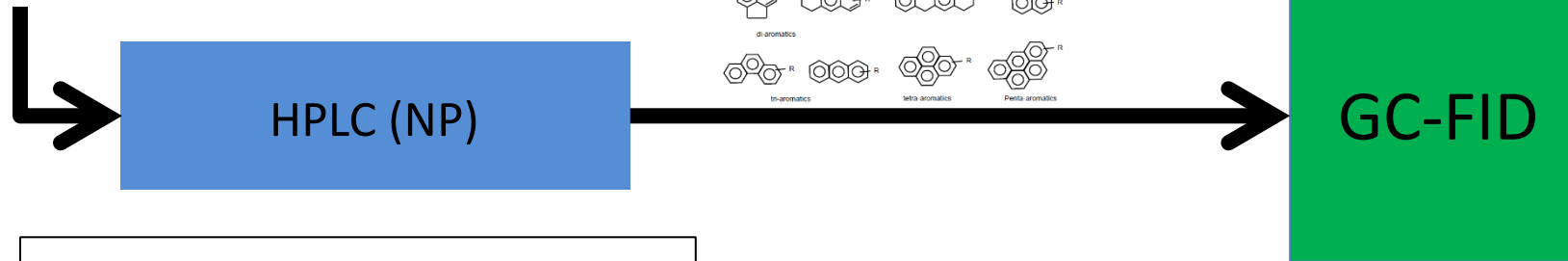
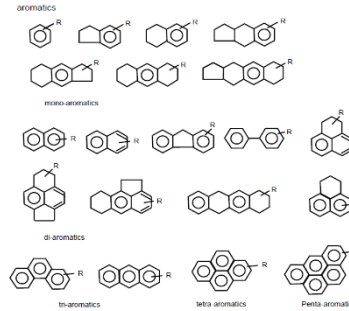
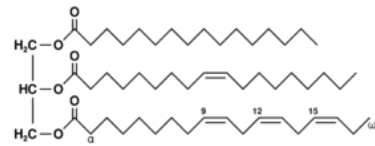


Mineral oils

Adhesives

Migration testing

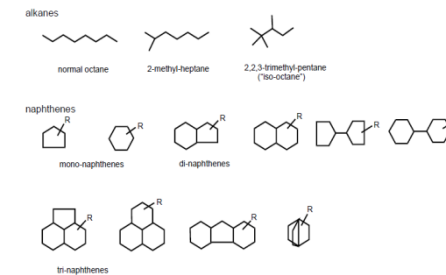
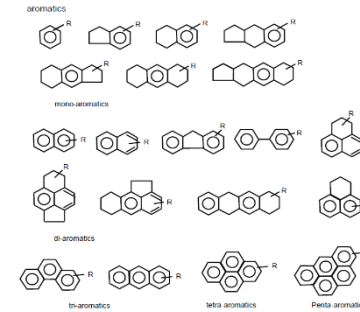
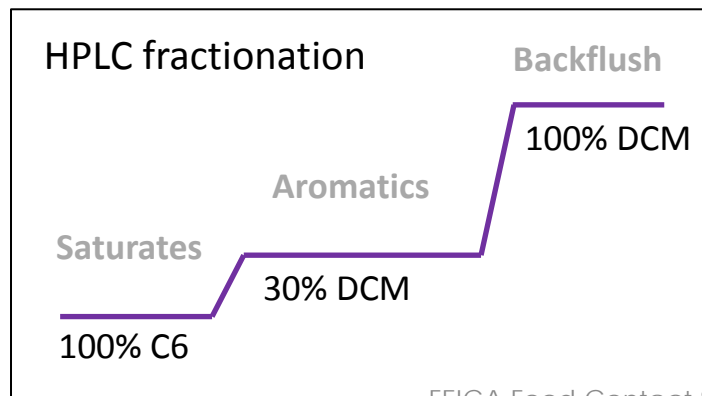
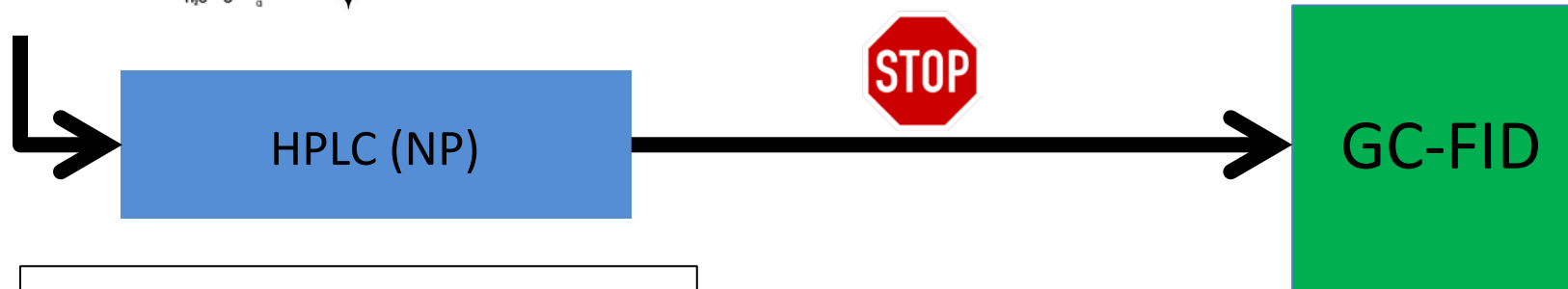
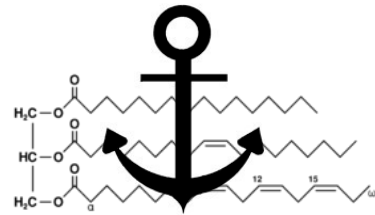
2nd Fraction (aromatic hydrocarbons – MOAH fraction)



Mineral oils

Adhesives

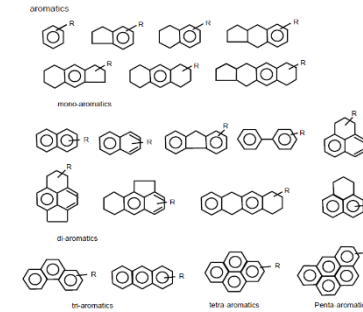
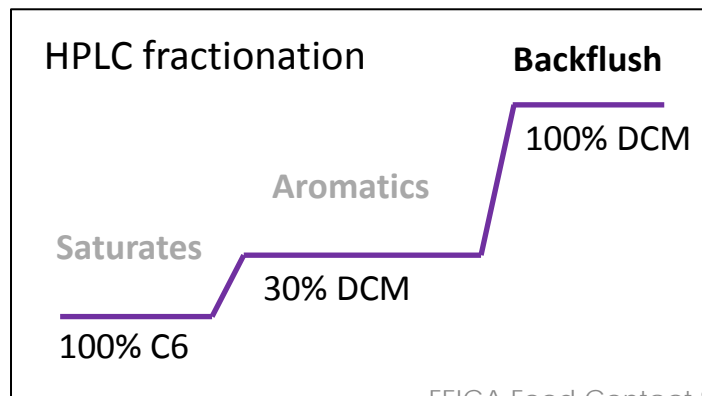
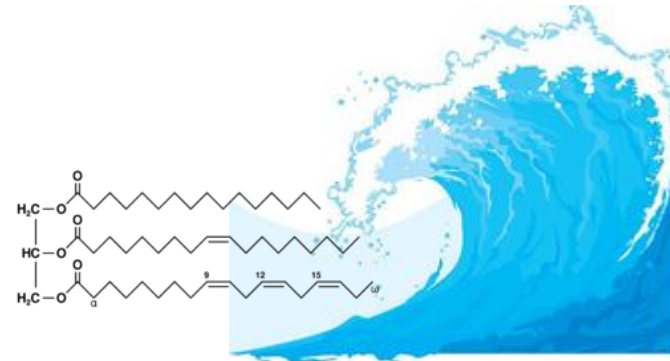
Migration testing



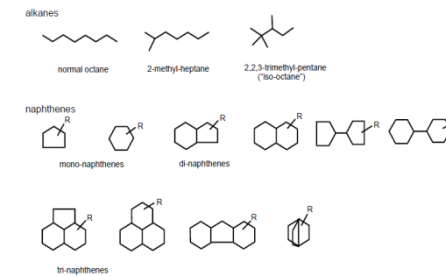
Mineral oils

Adhesives

Migration testing



GC-FID



Mineral oils

Adhesives

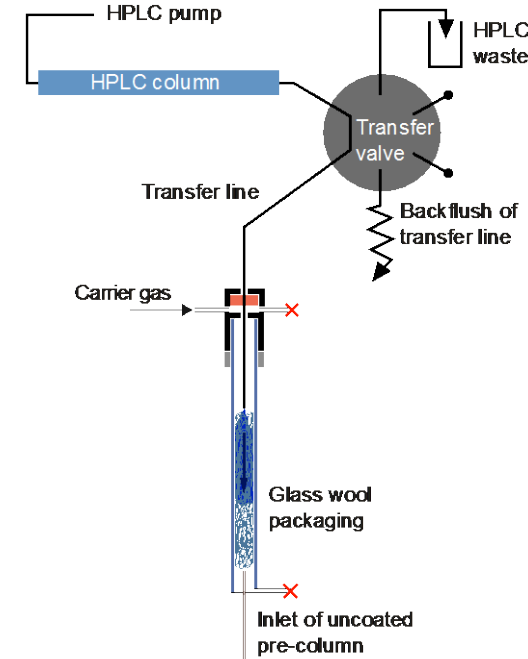
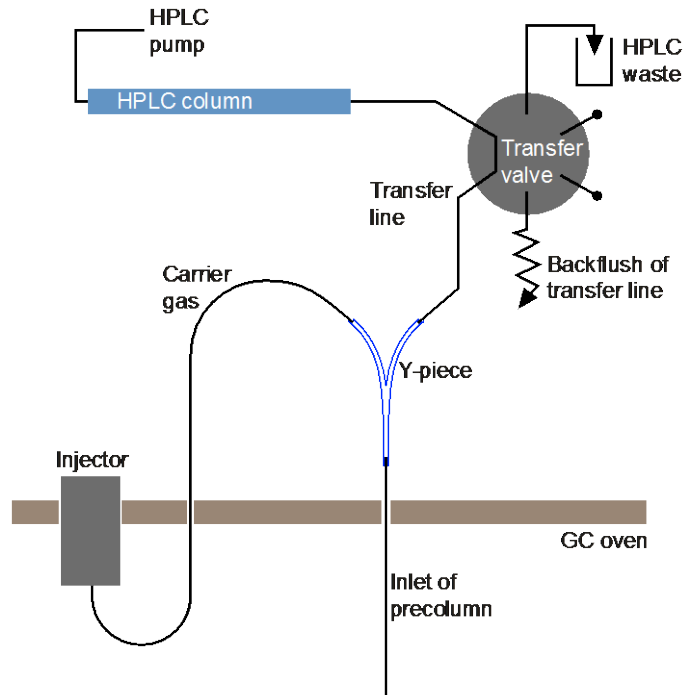
Migration testing

Y-Pressfit replaces the on-column injector

- Solvent and carrier gas mix without dead volume

PTV injector as filter for high-boiling matrices

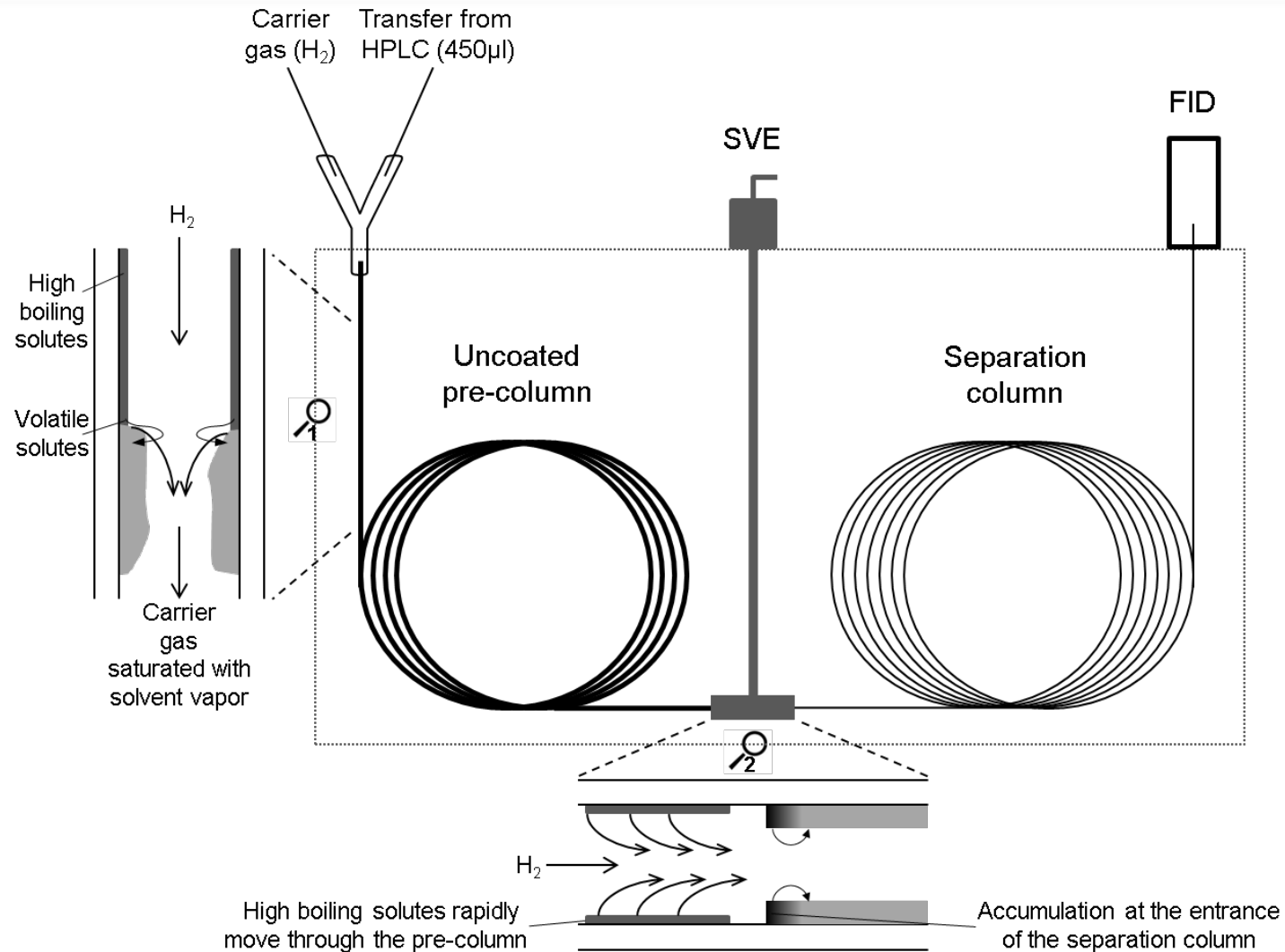
- Splitless transfer
- Concurrent solvent recondensation (CSR)
- Same conditions analogous to on-column injection



Mineral oils

Adhesives

Migration testing



1. Mineral oil hydrocarbons



2. Hot-melt adhesives

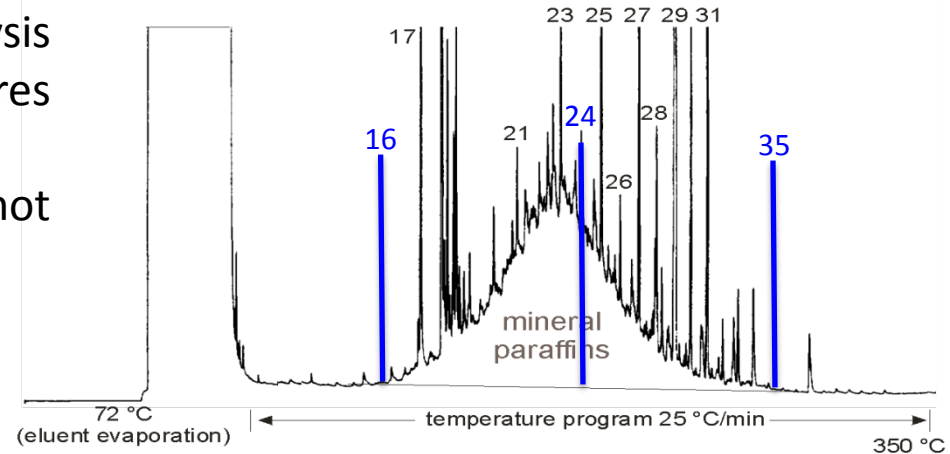


3. Migration testing

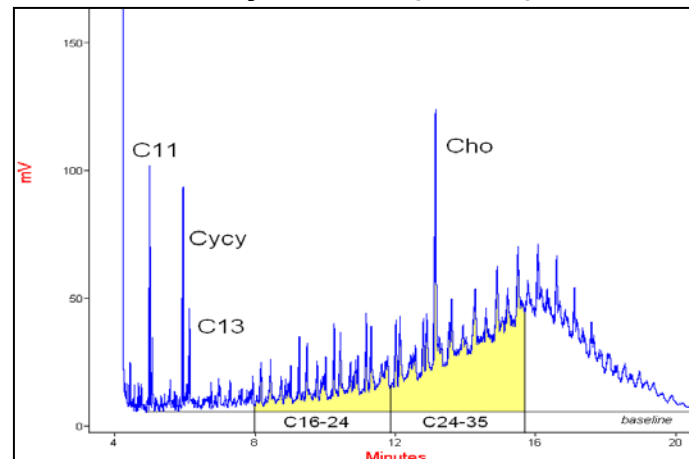


- In general, the HPLC-GC-FID analysis determines hydrocarbon mixtures **... not only MOSH and MOAH**
- The source of the hydrocarbons is not displayed during analysis
- Synthetic hydrocarbons (oligomers):

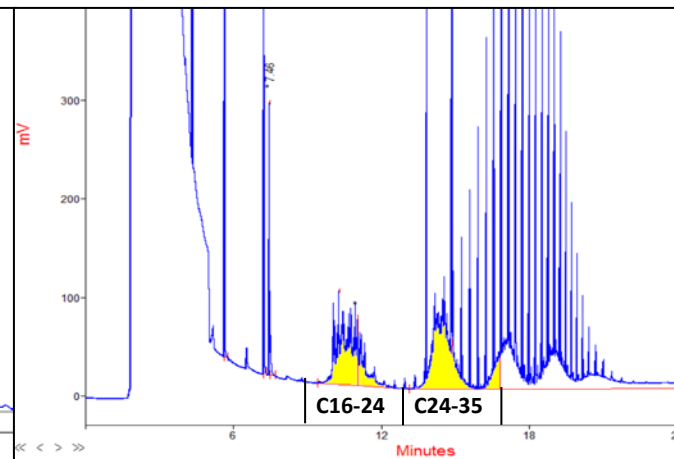
Extract of human tissue:



Polyolefins (LDPE)



Hot-melt adhesives (HMA)



Mineral oils

Adhesives

Migration testing



Reference: reka-klebetchnik.de

Waxes	Resins	Polymers	Additives
<ul style="list-style-type: none"> - <i>Natural waxes</i> - <i>Synthetic waxes</i> - <i>Paraffinic waxes</i> 	<ul style="list-style-type: none"> - <i>Rosin resins</i> - <i>Terpene resins</i> - Hydrocarbon resins 	<ul style="list-style-type: none"> - <i>PA, PE, EVA, PES, PU (elastomers/ copolymers)</i> 	<ul style="list-style-type: none"> - <i>Antioxidants</i> - <i>UV-absorber</i> - <i>Chelating agent</i>

Mineral oils

Adhesives

Migration testing

Hot-melt adhesives (HMA) mainly consist of various types of waxes, resins and polymers. The main individual types were investigated:

	Paraffinic waxes	Hydrocarbon resins	PE copolymers
Saturated Hydrocarbons [g/kg; C ₁₆₋₂₄]	<0.1 – 20	10 – 120	0.2 – 0.5
Aromatic Hydrocarbons [g/kg; C ₁₆₋₂₄]	<0.1	<0.1 – 60	<0.1
Amount in the HMA formulation	20 – 30 %	30 – 50 %	20 – 50 %
Regulation 10/2011	FCM 93: 0.05 mg/kg FCM 94: no SML <i>FCM 95: no SML*</i>	FCM 97: no SML	---

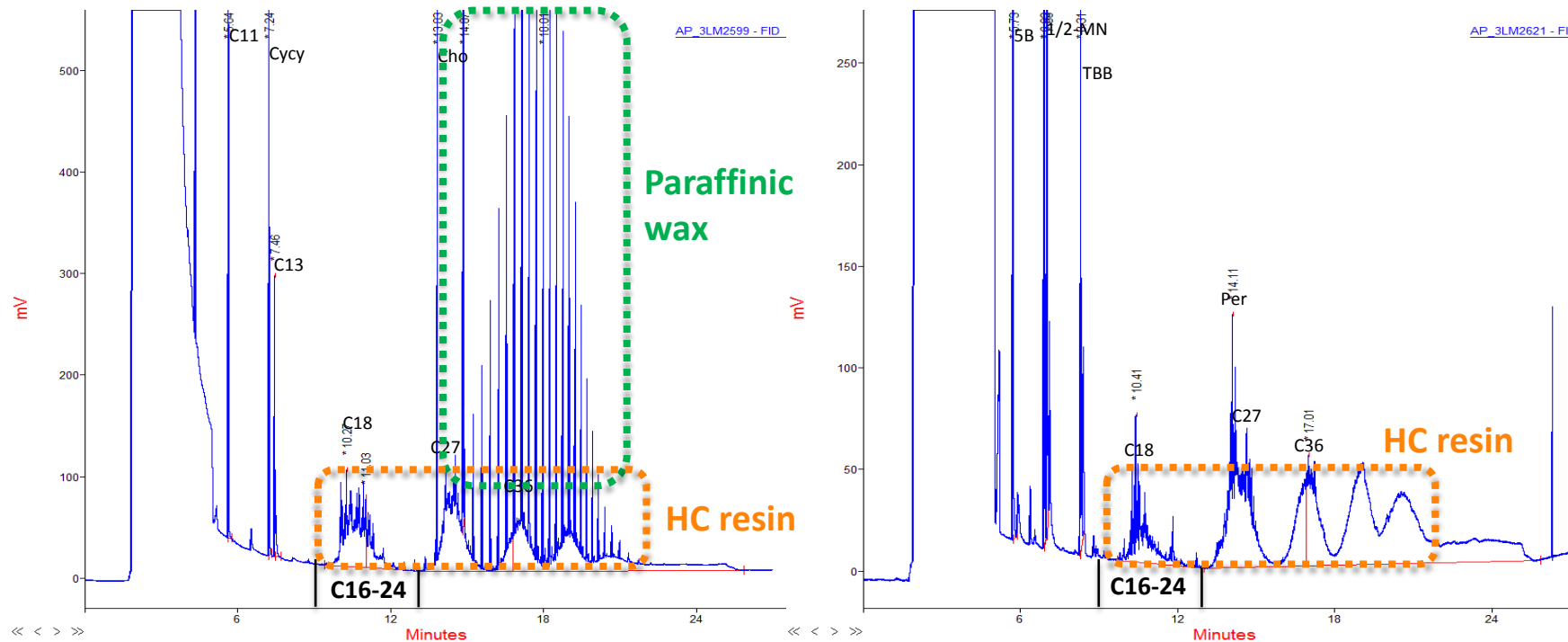
* *White mineral oils (paraffinic)*

Disclaimer: The origin and potential SMLs of hydrocarbon mixtures is not displayed during analysis

Chromatograms of a hexane extract of a hot-melt adhesive from a commercial rice (risotto) sample packed in virgin board folding box

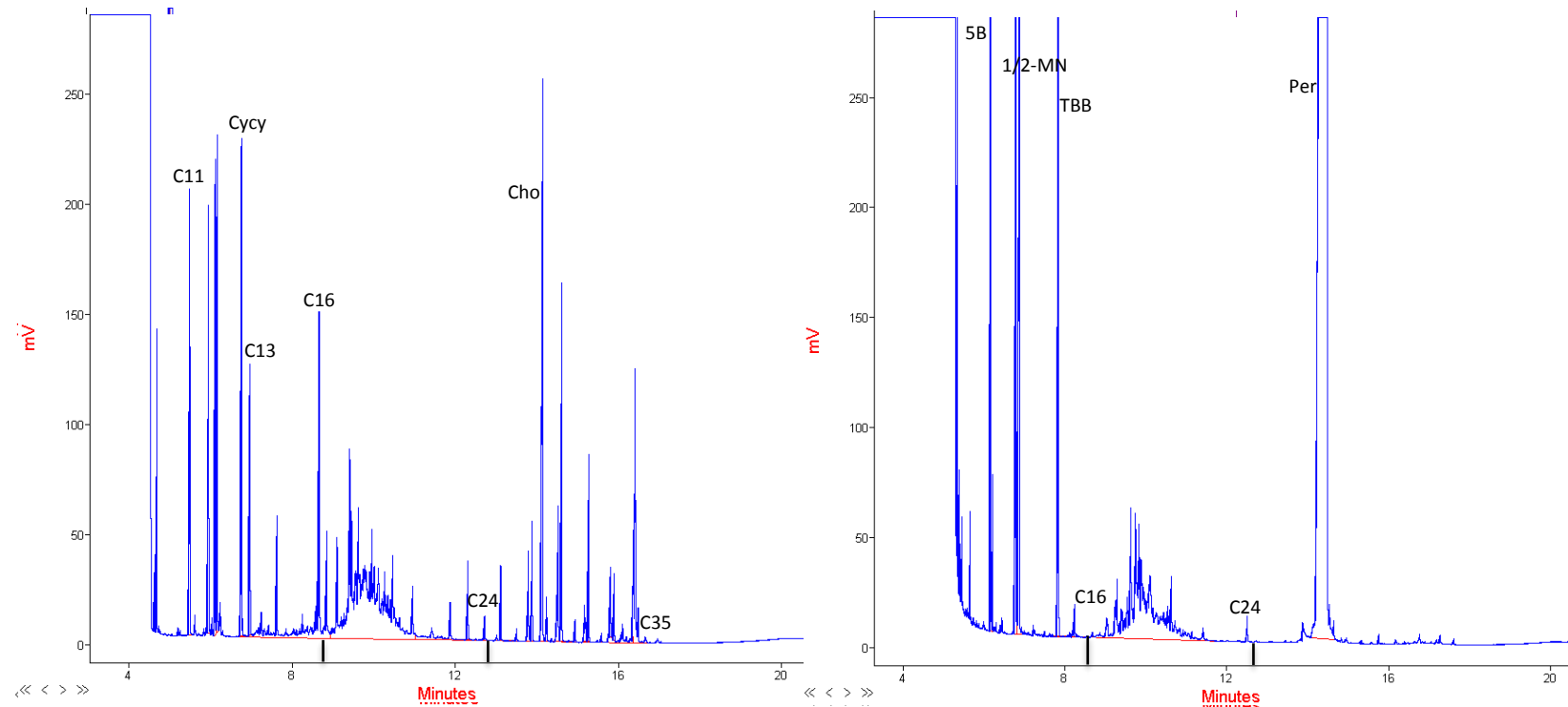
MOSH fraction C_{16-24} : 20 g/kg HMA

MOAH fraction C_{16-24} : 6 g/kg HMA



➤ Migration via gaseous phase (C_{16-24})

- 500g rice (risotto) packed in 7.5 dm² virgin board and closed with 1 g hotmelt
- Hexane extract (24h, RT) of 1 cm rice **bottom layer** (25g)



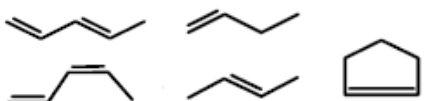
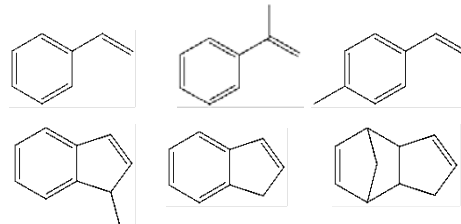
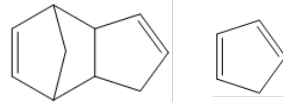
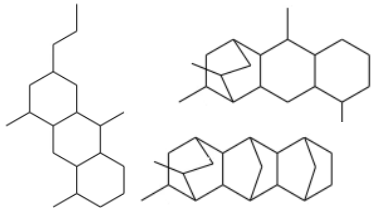
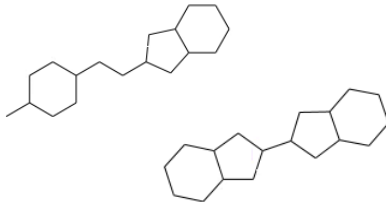
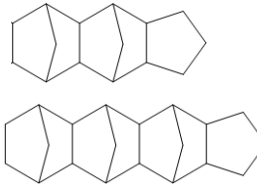
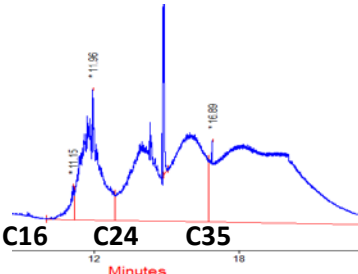
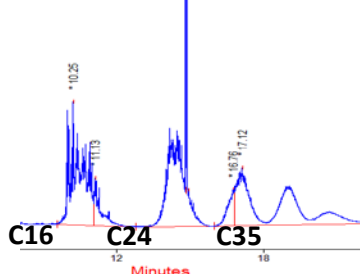
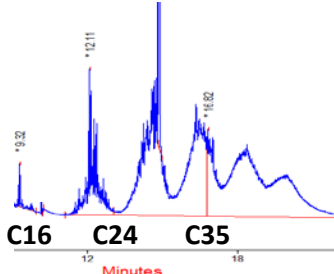
MOSH fraction: 2.7 mg/kg C₁₆₋₂₄

MOAH fraction: 0.7 mg/kg ≤C₂₄

Mineral oils

Adhesives

Migration testing

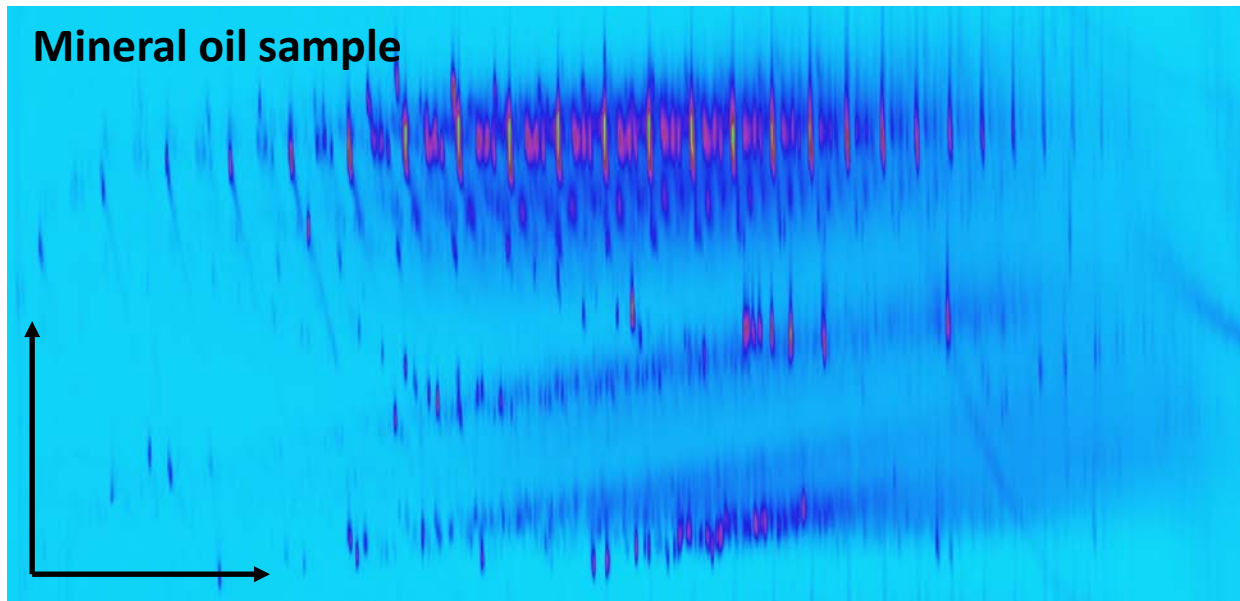
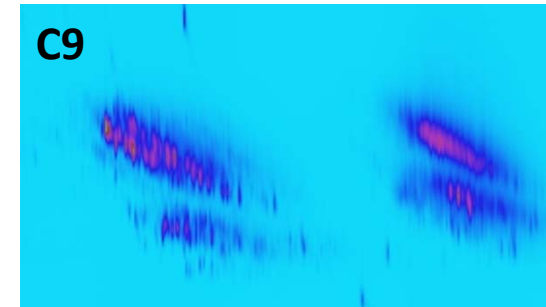
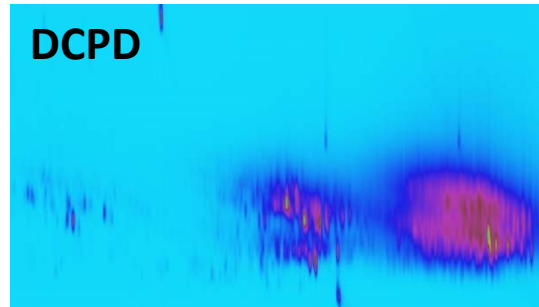
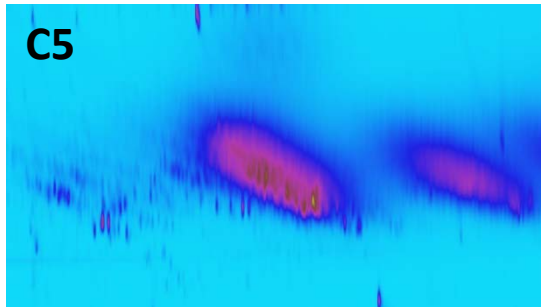
Fraction	C5 («Piperylenes»)	C9 («Aromatics»)	DCPD (Dicyclopentadienes)
Monomers			
Oligomers (saturated) C ₁₆₋₂₄			
GC			

→ These products can be fully or partially hydrogenated after synthesis

Mineral oils

Adhesives

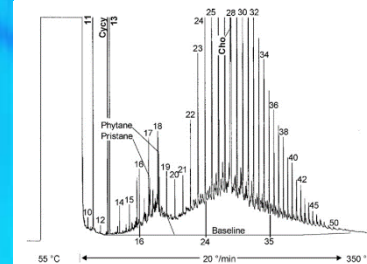
Migration testing



2nd Dimension
(polarity)

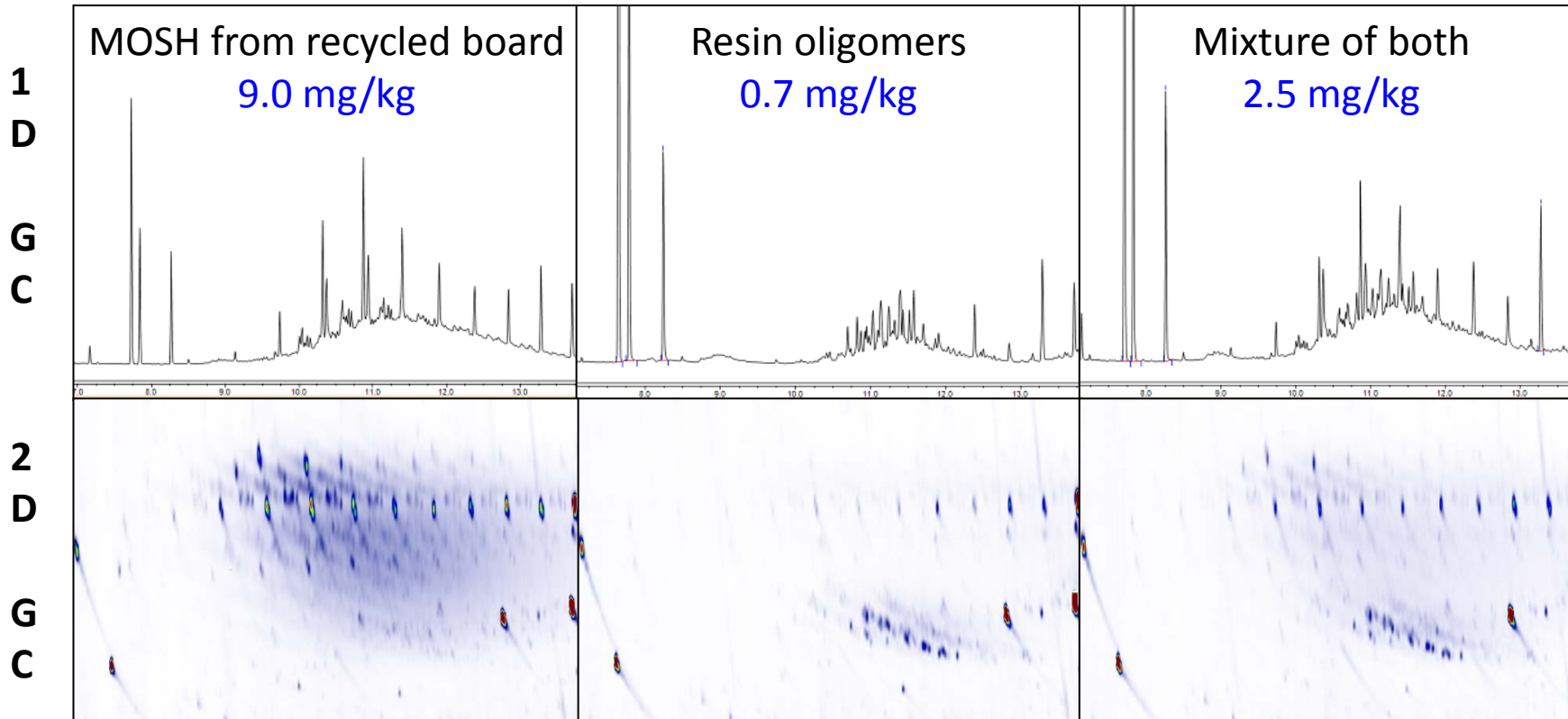
1st Dimension (volatility)

Bird's-eye view of the mineral oil hump



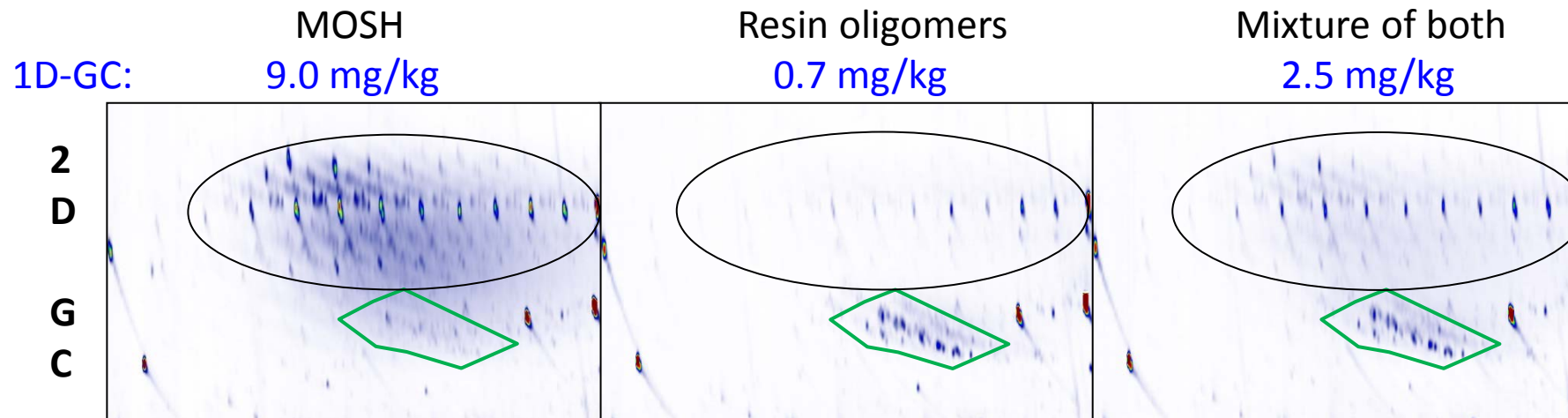
Model: Cereals were incubated with recycled cardboard or hydrocarbon resin (*hydrogenated*)

➤ Migration via gaseous phase ($\leq C_{24}$): **GC sections C_{13-24} are displayed**



Model: Cereals were incubated with recycled cardboard or hydrocarbon resin (*hydrogenated*)

➤ Migration via gaseous phase ($\leq C_{24}$): **GC sections C_{13-24} are displayed**



<5% of MOSH are located in the **oligomer region**

➤ **0.4 ppm of 9.4 ppm**

>90% of oligomers are located in **this region**

➤ **0.6 ppm**

20% of hydrocarbons in the **oligomer region**

➤ **0.5 ppm of 2.4 ppm**

- **Quantification has to be validated by using both methods**
- **Calculated values correspond to measured concentrations in this case**
- **Identification can be ensured by the help of mass spectra**

1. Mineral oil hydrocarbons



2. Hot-melt adhesives



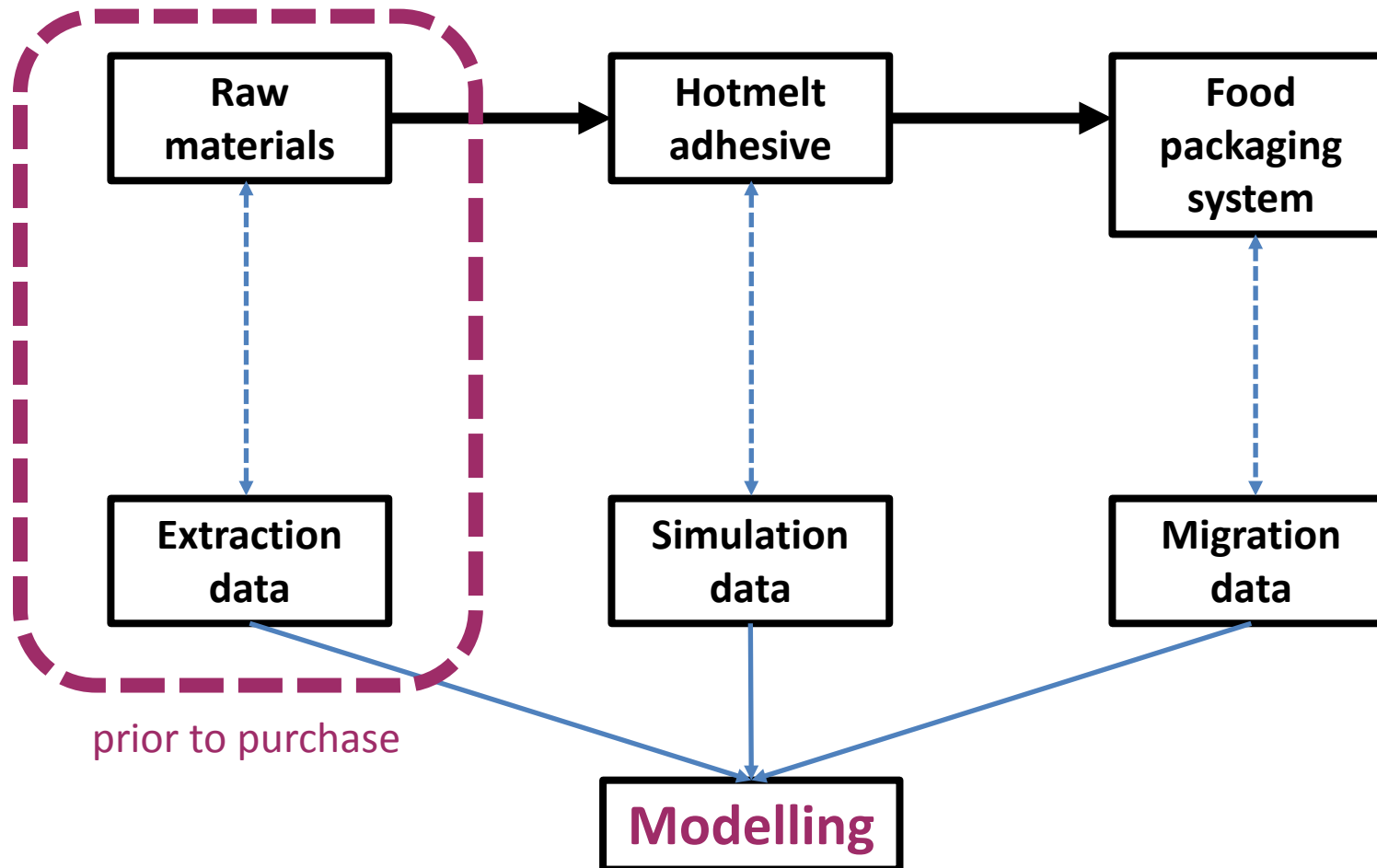
3. Migration testing



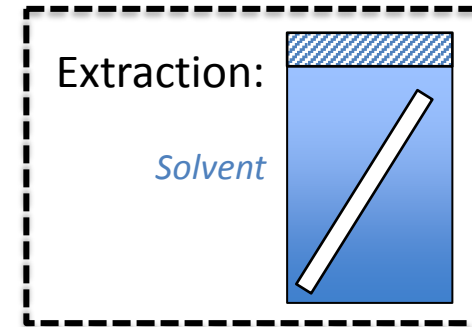
Mineral oils

Adhesives

Migration testing



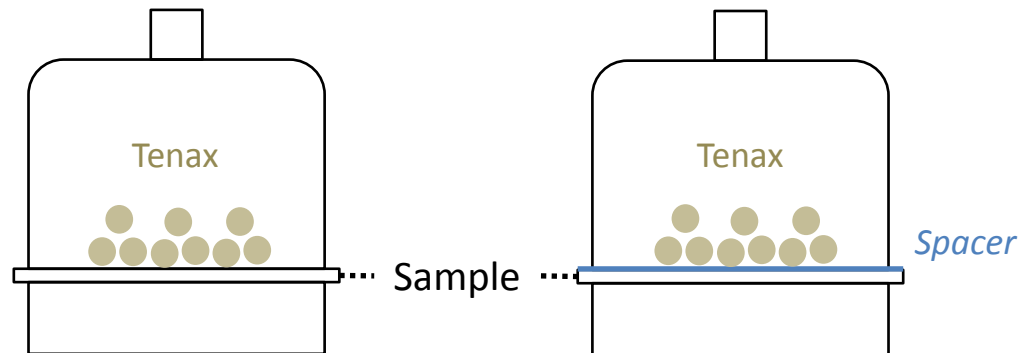
- **Extraction of adhesives and polymers (granulates/films)**
 - Solvent: n-Hexane
 - Conditions: 24h at 60°C



- **“Extraction” of tackifier resins and paraffinic waxes**
 - Most of them are soluble in n-hexane
 - 10min ultrasonic bath

Caution! A PTV injector is often necessary for the analysis of extracts

- **Migration via gaseous phase**
 - Analogous to EU 10/2011 or EN 14338:2003
 - Simulant: Tenax or adequate food stuff
- Migration cell:



Reference: gassner-glastechnik.de

Conditions: 10d at 40°C (\equiv 47-82d at ambient temp)
or 10d at 60°C (\equiv roughly 1 year at ambient temp)

Examples: Hot-melt adhesives (folding boxes)

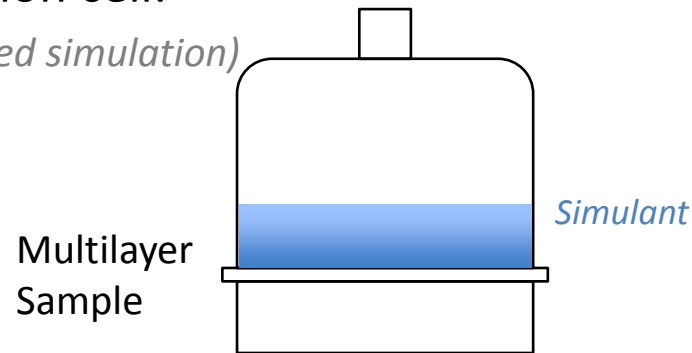
Mineral oils

Adhesives

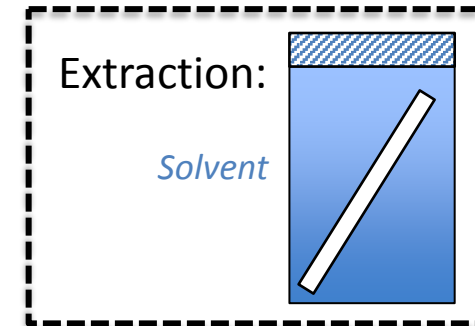
Migration testing

- **Migration via direct contact**
 - Analogous to EU 10/2011
 - Polar-apolar simulants
- Migration cell:

(one-sided simulation)



Food simulant	Abbreviation
Ethanol 10 % (v/v)	Food simulant A
Acetic acid 3 % (w/v)	Food simulant B
Ethanol 20 % (v/v)	Food simulant C
Ethanol 50 % (v/v)	Food simulant D1
Vegetable oil (*)	Food simulant D2



Conditions: 10d at 40-60°C (≡ 2-12 months at ambient temp)
or under pasteurization conditions (e.g. 1h at 95°C)

Examples: Multilayer packaging involving adhesives

- Indirect or direct contact
- Model foods, such as rice or sunflower oil
- Produced under industrial conditions
 - Applied adhesive (amount, surface, application conditions)
- Parameters:
 - Temperature
 - Time
 - Humidity
 - Secondary packaging (transport box)
 - Environment (warehouse, store, ...)

Storage box:

C		C
C		C

Corner samples

➤ **Simulations should be validated with the reality from time to time**



HARRPA

➤ Tackifier resins (identification of oligomers)



➤ Migration of hydrocarbon mixtures from different hot-melt adhesive formulations

for your attention!

Thomas Simat
Konrad Grob
Maurus Biedermann



**TECHNISCHE
UNIVERSITÄT
DRESDEN**



Kanton Zürich
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Cooperation with
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