The European voice of the
adhesive and **sealant industry**

SAFE ADHESIVES FOR SAFE FOOD

Migration testing approaches for adhesives

André Weiss, Manager Instrumental Analytics, Food Safety, Henkel

1. Legal Background / Risk Assessment

1.1 Framework Regulation

- Framework Regulation (EC) No 1935/2004
- Article 3
- Materials and articles [...] shall be manufactured in compliance with good manufacturing practice so that, under normal and foreseeable conditions of use, they do not transfer their constituents to food in quantities which could:
  - endager human health
  - bring about an unacceptable change in the composition of the food
  - bring about a deterioration in the organoleptic characteristics thereof
- Rationale for risk assessment

1. Legal Background / Risk Assessment

1.2 Risk Assessment

- Evaluation of adhesives via risk management

- Substance transfer from adhesive into foodstuff has to be evaluated:

  - Exposure → via worst-case **calculation**, migration **modelling**, **analytical** tests
  - Hazard → via **toxicological** assessments

1. Legal Background / Risk Assessment

1.2 Risk Assessment

- Evaluation of adhesives via risk management

- Substance transfer from adhesive into foodstuff has to be evaluated:

  - Exposure → via worst-case **calculation**, migration **modelling**, **analytical** tests
  - Hazard → via **toxicological** assessments

1. Legal Background / Risk Assessment

1.3 Worst-case calculation

- Calculate maximum transfer of substances
- Critical parameters must be known
  - Amount of substance in the adhesive
  - Amount of adhesive used in the packaging material
  - Ratio of packaging material to packed food
- Assume 100% transfer

\+ Easy and fast, no chemical analysis required

\- Difficult for reactive systems, difficult for gas phase transfer

\- No unknown components

1. Legal Background / Risk Assessment

1.4 Migration Modelling

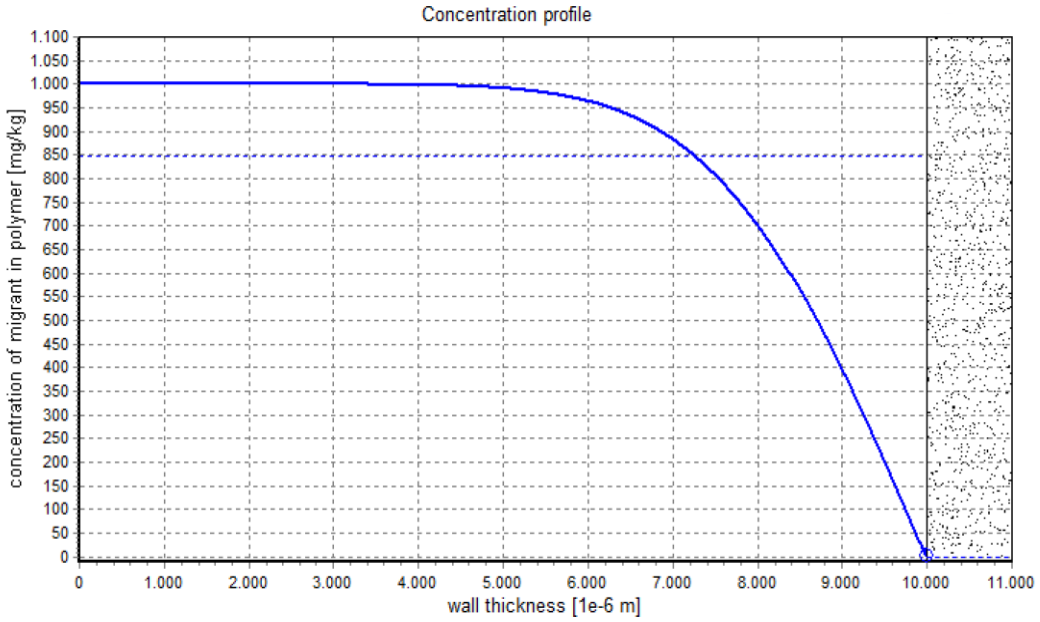
- Evaluate transfer via computer simulation
- Critical parameters must be known
  - Basic parameters (concentration, O:V ratio)
  - Layer thickness
  - Storage conditions

\+ More realistic than worst-case calculation

\+ No chemical analysis required

\- No unknown components

Example: LDPE, Migration: 10d @ 60°C, MW 501-750 g/mol



JRC Science and Policy Reports, DRAFT for stakeholder consultaion, Technical guidelines for compliance testing – Annexes, 24/08/2016

1. Legal Background / Risk Assessment

1.5 Extraction

- Extraction under severe conditions
  - Organic solvent
  - Elevated temperature
- Analysis of extract

\+ Unknown components

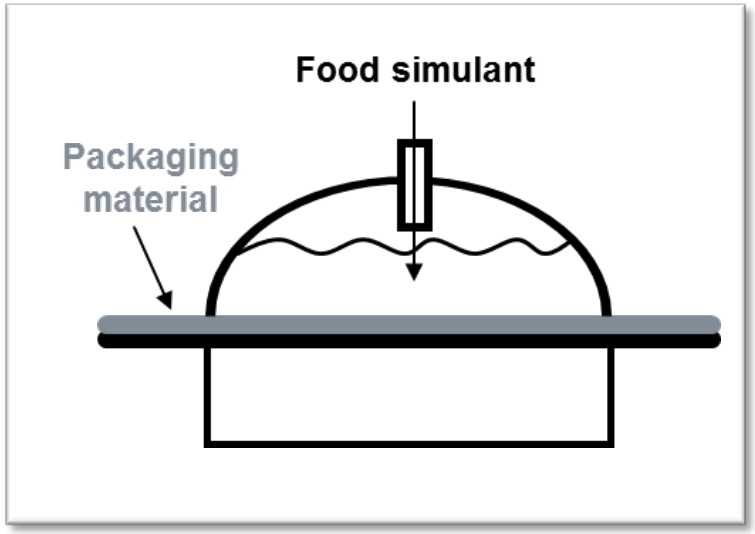
± Results overestimate real migration

\- Chemical analysis required

1. Legal Background / Risk Assessment

1.6 Migration studies

- Migration under defined conditions
- Parameters to be known
  - Storage conditions
  - Type of foodstuff
- Analysis of migration solution



\+ Most realistic results

\+ Unknown components

\- Time consuming

1. Legal Background / Risk Assessment

1.7 Plastics Regulation

- Commission Regulation (EU) 10/2011 – Plastics Regulation
- Migration testing conditions described in detail
- Often referred to as migration testing conditions for all FCM
- Only applicable for plastic materials and articles (including plastic layers in multi-material multi-layer materials)
  - Adhesives are not within the scope of the Plastics Regulation
  - JRC Technical guidelines for compliance testing: “[...] only applicable to plastic materials and articles [...]”
- Other approaches needed for non plastics!

1. Legal Background / Risk Assessment

1.8 Migration testing for non plastics

- Migration testing guidelines for non plastics
- FEICA guidance paper “Migration testing of adhesives intended for food contact materials”, 27 May 2016
  - Typical adhesive systems in food contact application
  - Material-specific properties to be considered
  - Test procedures and evaluation of test results
  - Analytical challenges

2. Approaches for adhesive testing

2.1 Overview

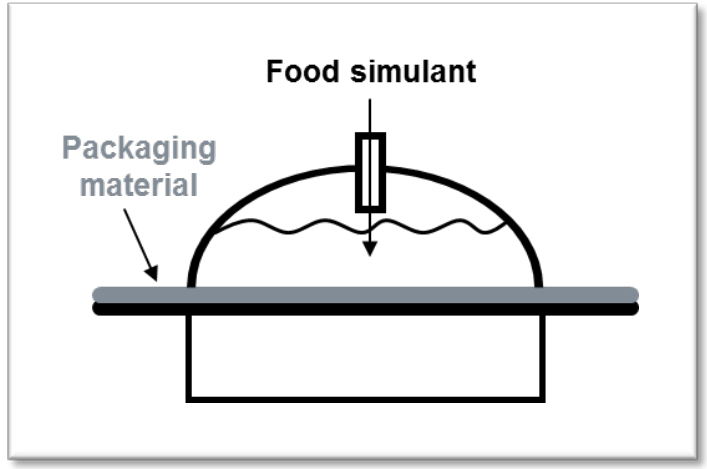
- Wide range of applications, complex chemistry

Polyurethane adhesives	**Adhesives based on natural polymers**	**Dispersions/ emulsions**
Coldseals	**Heatseals**	**Hotmelts**

2. Approaches for adhesive testing

2.2 Polyurethane adhesives

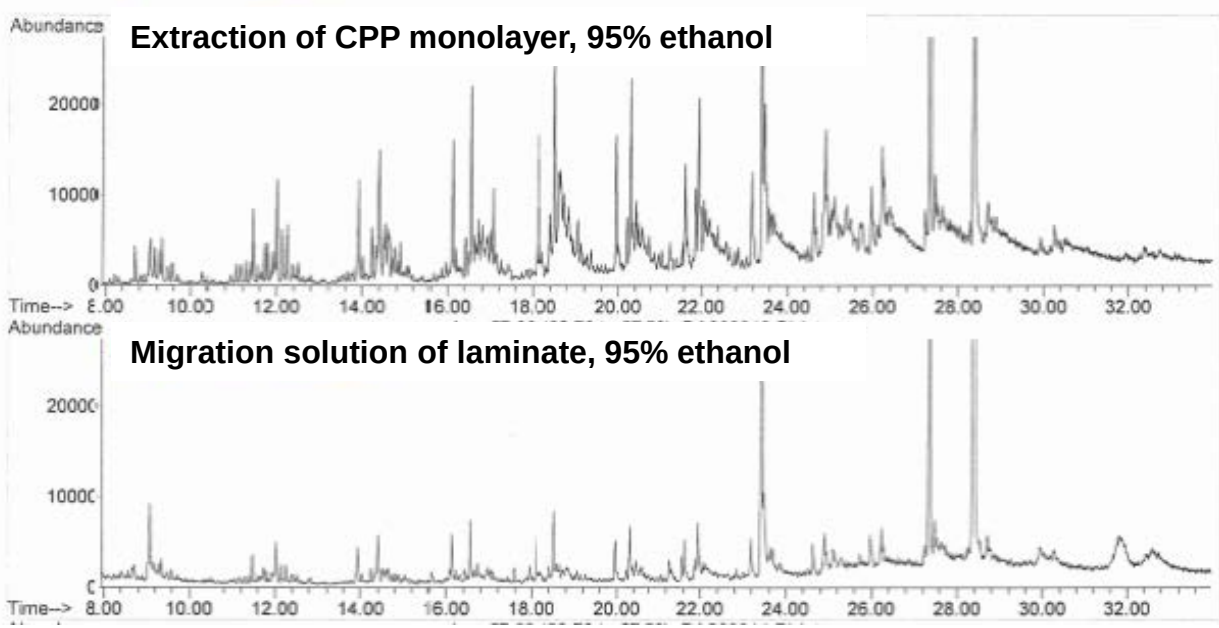
- Laminating adhesive, e.g. for flexible packaging
- Plastic multi-layer materials are subject to Plastics Regulation
  - Migration testing according to Regulation (EU) 10/2011
- Direct testing not possible (reactive adhesive system)
- Tests on final structure or model systems
  - Expected application (filling good, storage conditions)
  - Correct curing conditions



2. Approaches for adhesive testing

2.2 Polyurethane adhesives

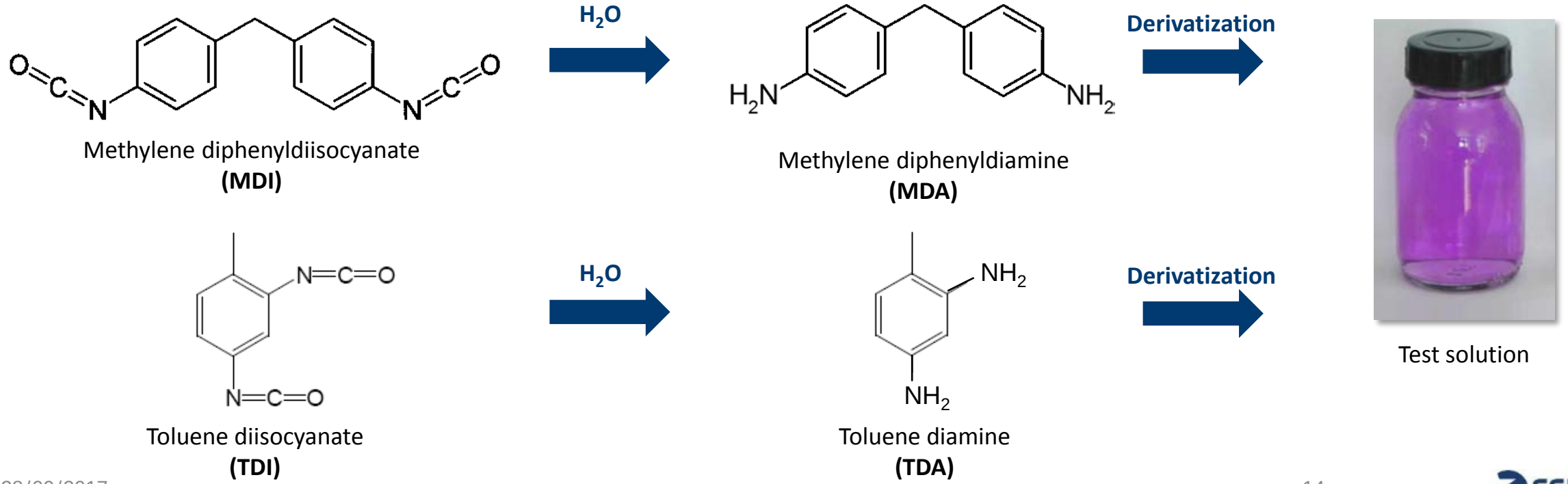
- Monolayers should be tested separately
  - Distinguisch between migration of adhesive and monolayer compounds
- Example
  - Polyolefin Oligomeric Saturated Hydrocarbons (POSH) from CPP monolayer



2. Approaches for adhesive testing

2.2 Polyurethane adhesives

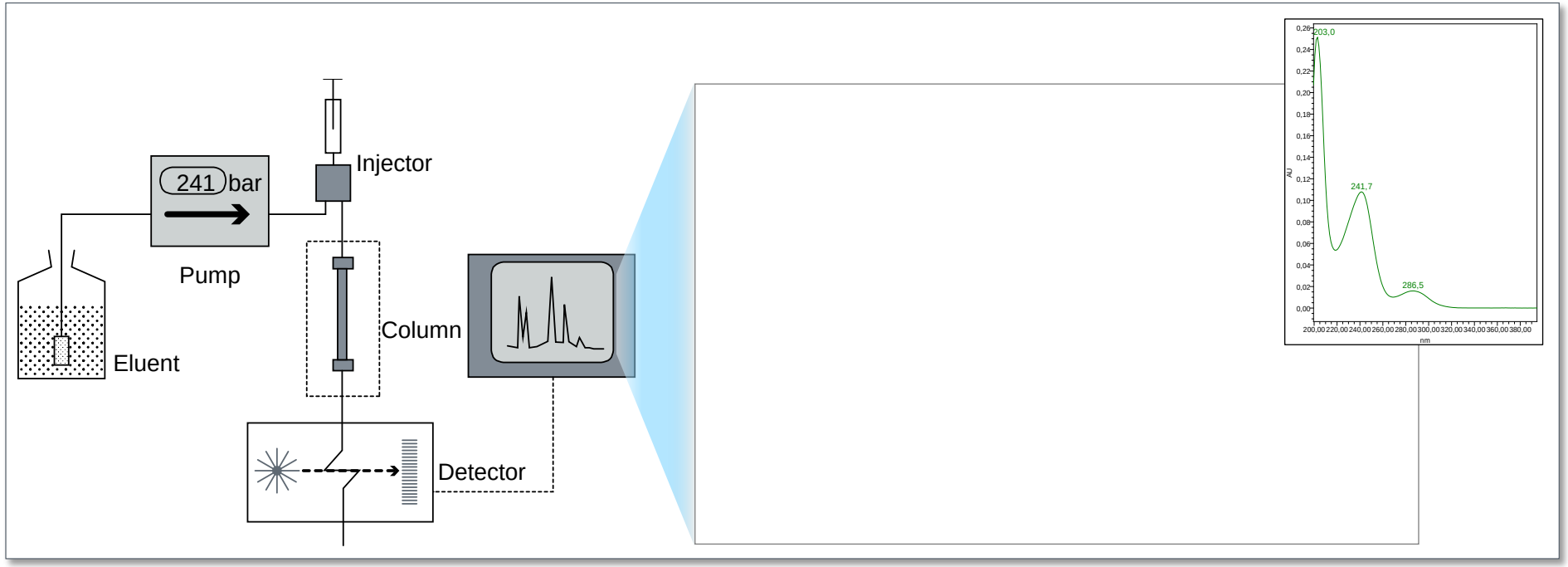
- False-positive results/analytical artefacts
  - Primary aromatic amines (PAA) via photometric method
  - Sum parameter



2. Approaches for adhesive testing

2.2 Polyurethane adhesives

- False-positive results/analytical artefacts
  - PAA via specific HPLC method
  - Retention time and UV spectrum allow for unequivocal assignment



2. Approaches for adhesive testing

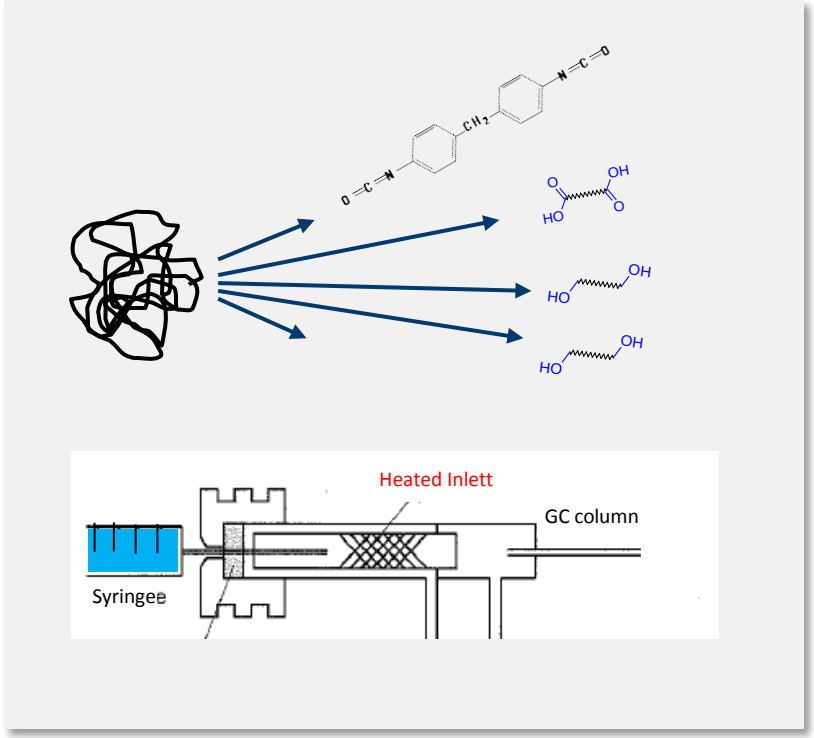
2.2 Polyurethane adhesives

- False-positive results/analytical artefacts
  - PAA: Comparison between photometric and HPLC method
  - Example
    - CPP monolayer, 3% acetic acid, retort conditions
    - Photometric: >> 10 µg/kg
    - HPLC: not detectable

2. Approaches for adhesive testing

2.2 Polyurethane adhesives

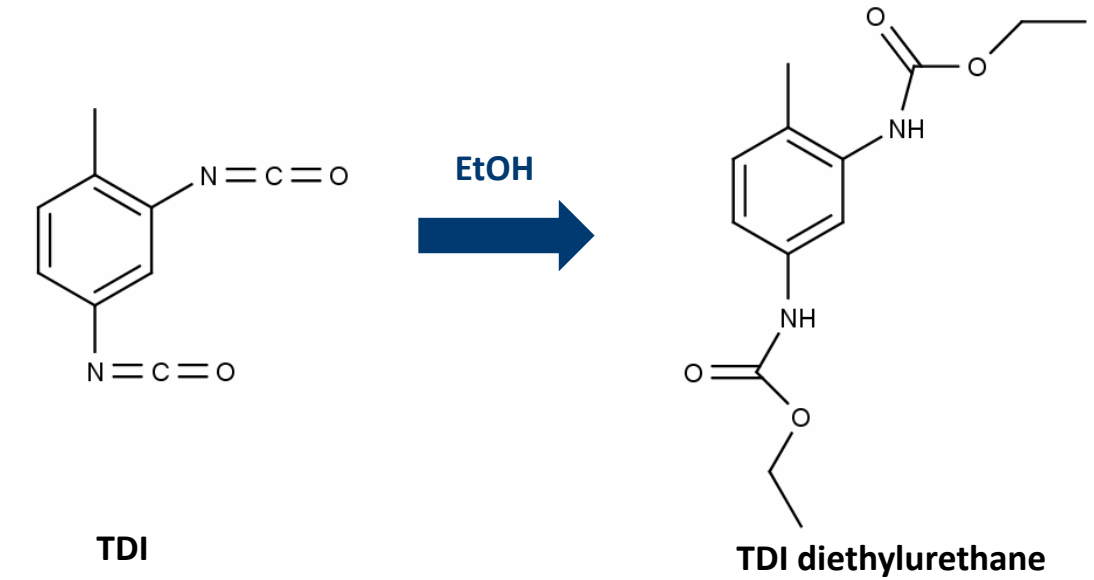
- False-positive results/analytical artefacts
  - Example
    - Free isocyanate monomers in a 3 week old laminate
  - Reason
    - Migration of (pre)polymers
    - High GC injector temperature may cause breakdown of polymers
    - Formation of free isocyanates and diols/diacids
  - Solution
    - Analytical alternatives (e.g. LC-MS)
    - Correlation between injection temperature and detected monomer content?



2. Approaches for adhesive testing

2.2 Polyurethane adhesives

- False-negative results
  - Reaction of isocyanates with food simulants
    - 3% acetic acid: PAA formation
    - Ethanol: urethane formation
    - Vegetable oil: amide formation
  - Solution
    - Determination of reaction products
    - Determination of free isocyanates after extraction with an inert solvent



2. Approaches for adhesive testing

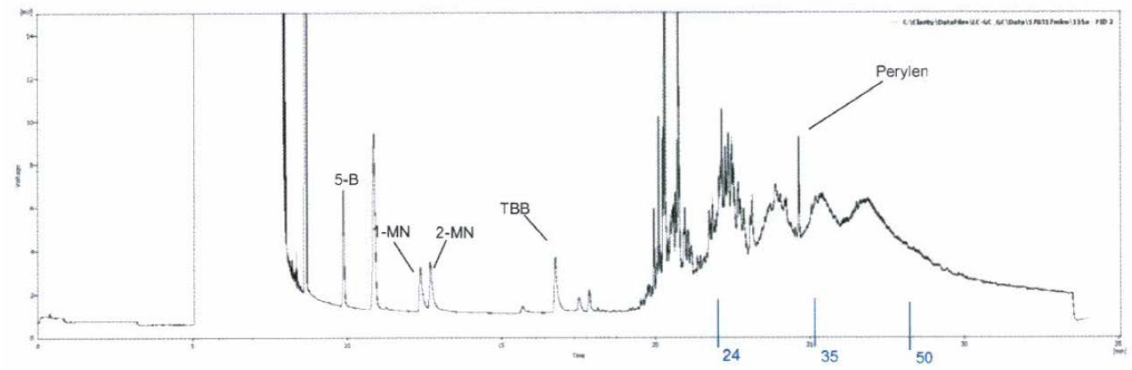
2.3 Choice of detector

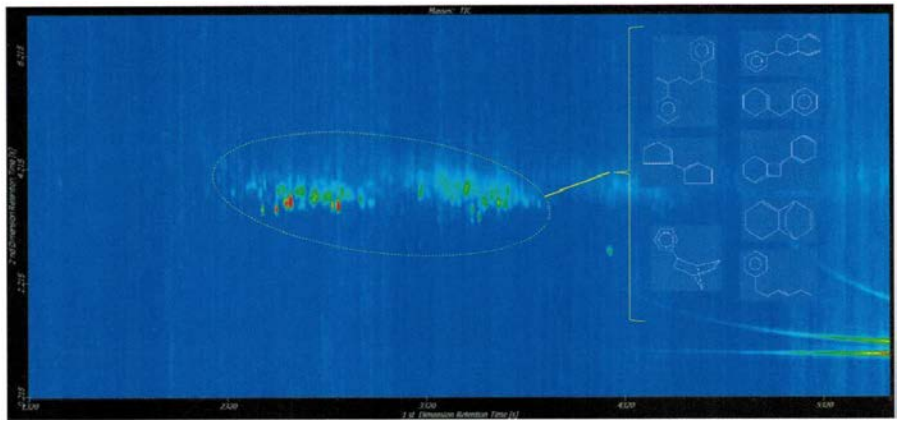
- Example 1: PAA analysis
- Unspecific detector (photometer)
  - Easy to handle
  - Sum parameter
  - No structural information
- Specific detector (HPLC-PDA)
  - Instruments required
  - Distinguish between substances
  - No false-positives

2. Approaches for adhesive testing

2.3 Choice of detector

- Example 2: MOSH/MOAH
- Unspecific detector (LC-GC-FID)
  - Proper quantification
  - Sum parameter
  - No structural information
- Specific detector (GCxGC-MS)
  - Technical expertise required
  - Structural information
  - Distinguish between MOAH and other hydrocarbons

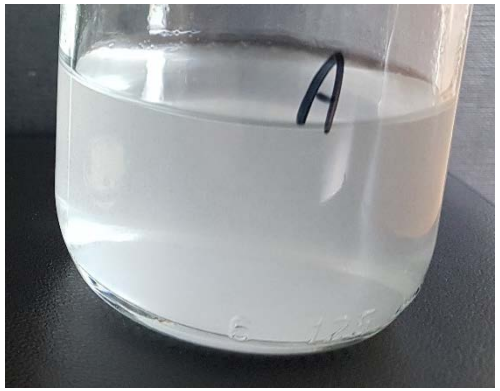




2. Approaches for adhesive testing

2.4 Adhesives other than polyurethane adhesives

- Dissolution of aqueous dispersions and hotmelts in liquid simulants
  - Predominant use of liquid simulants according to Plastics Regulation
  - Liquid simulants may re-dissolve the adhesive
  - Extraction rather than migration (worst case)
- High temperature during migration
  - Softening point < 60°C
- Change of physical properties



EVA based adhesive
95% ethanol

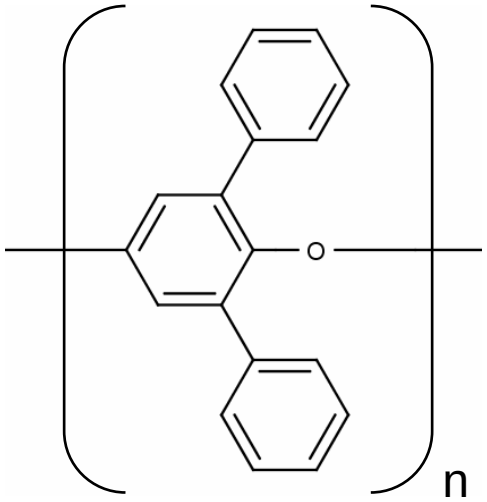
Hotmelt
40°C

Hotmelt
60°C

2. Approaches for adhesive testing

2.4 Adhesives other than polyurethane adhesives

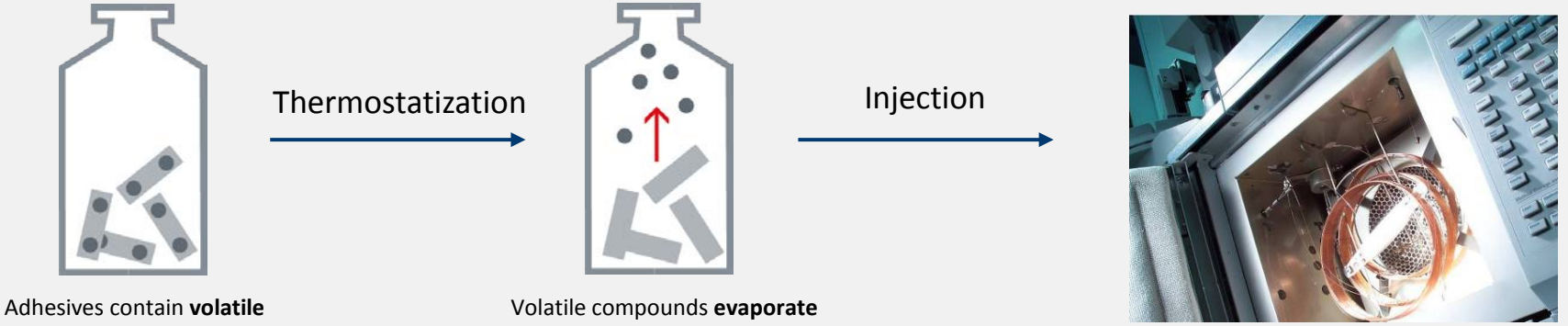
- Typical applications
  - Paper and cardboard
  - Secondary/tertiary packaging
- Gas phase transfer
  - Tenax
  - Stored within a distance
- Direct contact on seams and edges
  - Adhesive may be applied on a substrate
  - Tenax in direct contact



2. Approaches for adhesive testing

2.4 Adhesives other than polyurethane adhesives

- Typical applications
  - Paper and cardboard, secondary/tertiary packaging
- Gas phase transfer
  - Headspace analysis as a first screening tool



2. Approaches for adhesive testing

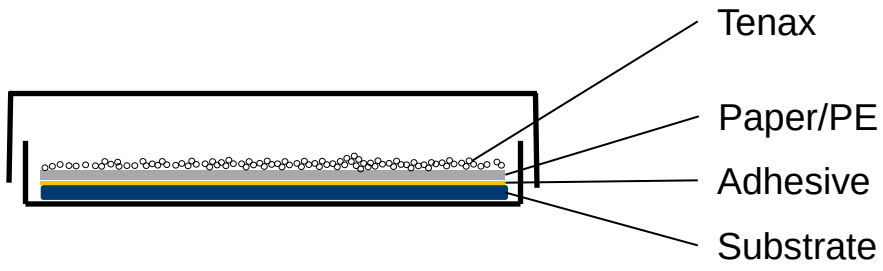
2.4 Adhesives other than polyurethane adhesives

- Heatseals or coldseals may be applied on a substrate and direct food contact cannot be excluded
- Example
  - Heatseal on aluminium substrate
  - Acidic foodstuff
  - Testing with 3% acetic acid
  - Physical change of substrate
  - For testing purposes, an alternative substrate should be selected (e.g. PET)

2. Approaches for adhesive testing

2.4 Adhesives other than polyurethane adhesives

- Pressure sensitive adhesives
  - e.g. dispersions based on acrylic polymers or hotmelts
  - Very tacky, Tenax will stick to the adhesive
  - To test direct contact (e.g. direct labelling), the PSA may be applied on a substrate with no or low barrier properties (paper, thin PE)
  - Migration through substrate, Tenax can be removed easily



3. Summary

- Wide range of applications, complex chemistry of adhesives
- Migration conditions of Regulation (EU) 10/2011 only apply to plastic materials, other approaches are needed for adhesives
- All layers of the FCM should be tested
- False-positives and false-negatives should be considered
- Dissolution of adhesives in liquid food simulants
- Tenax as suitable alternative
- In case of doubt the real application has to be tested