Latest developments on MOSH/ MOAH methods

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Outline

- Who is Fogra
- Overview of current BfR method
- Limits of BfR method
- Round-robin study by Fogra
- Current round-robin study
- Alternative method using GC-MS
Who is Fogra?

Mission

- Promoting print engineering and its future-oriented technologies
- Enabling printing industry to utilise the results

Fields of activity

- Research and Development
- Committee work and Standardization
- Consultancy, measuring and expert opinions
- Dissemination and Training
Who is Fogra?

2013-09-10, MOCRINIS Workshop  |  Dr Philipp Stolper
Overview of BfR method

Sample pretreatment
- cut paper / board to small pieces

Extraction for 2 h at room temperature
- sample: 2 g ± 0.1 g
- standard: 20 µl
- Ethanol/Hexane (1:1 v/v): 10 ml
- shake vigorously, let it stand for 2 h

Clean-up
- solvent extraction of 4 ml of the extract with 10 ml of water
- take hexane phase

Solid phase extraktion
- done with 0,2 mL of the extract

MOSH-Fraction
- add 270 µl Toluol
- concentrate to 250-300 µl

MOAH-Fraction
- concentrate to 250-300 µl

Analysis using GC-FID

According to:
Determination of hydrocarbons from mineral oil (MOSH & MOAH) or plastics (POSH & PAO) in packaging materials and dry foodstuffs by solid phase extraction and GC-FID (BfR, May 2012)
Overview of BfR method

Overview of BfR method

Virgin fiber-based board

=> No information about structure can be obtained
Limits of BfR method

Sample pretreatment, Extraction step, Clean up step

- Adding 20 µl of internal standard to 2 g of cut paper
- Extraction with 10 ml Hexane/Ethanol (1:1)
- Work at room temperature
- Remove Ethanol with 15 ml water

Possible Problems

- „Normal“ analytical failure (syringe, room temperature,...)
- Recovery rate of internal standard
Limits of BfR method

Solid phase extraction (SPE)

- Generating MOSH/MOAH fraction using the following scheme:

  Solvents:
  1-4: Hexane
  5,6: Hexane, Toluene, Dichloromethane

Possible Problems

- SPE columns and material not commercially available
- No visible control about quality of fraction
- Possible impurities (DIPN, olefinic species,...)
Limits of BfR method

Concentration step
- Reduce volume to ~ 500 µl by rotary evaporator
- Use 270 µl Toluene as keeper
- Use vacuum, elevated temperature

Possible Problems
- Discrimination of low-boiling components
- Overestimation of high-boiling components
## Limits of BfR method

### Analysis / Evaluation using GC-FID

<table>
<thead>
<tr>
<th>Range</th>
<th>Integral 1</th>
<th>Integral 2</th>
<th>ΔIntegral</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10-C16</td>
<td>1174</td>
<td>1298</td>
<td>+ 10 %</td>
</tr>
<tr>
<td>C16-C25</td>
<td>3599</td>
<td>3148</td>
<td>- 13 %</td>
</tr>
<tr>
<td>C25-C35</td>
<td>4449</td>
<td>4073</td>
<td>- 10 %</td>
</tr>
</tbody>
</table>

Peak areas: approx 30 %
Limits of BfR method

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add 270 μl Toluol
concentrate to 250-300 μL

MOAH-Fraction
concentrate to 250-300 μL

Analysis using GC-FID

Manual
~ 5 %
~ 10 %
~ 20 %

Online
~ 5 %
~ 10 %
~ 20 %
in October 2012

=> Standard deviation ~ 30 % for MOAH
=> False positive results for virgin fiber-based products
Current round-robin study

- Performed by Institut Kirchhoff Berlin
- Conditions:
  - 17 laboratories (German and Swiss labs)
  - 4 matrices (recycling board, oil, rice, chocolate)
  - No specification concerning method and evaluation
Current round-robin study

- MOSH fraction (recycled board)
- Mean value: 332 mg/kg  Standard deviation: 23%

Data taken from report on the round-robin study by Institut Kirchhoff, 19.07.2013
Current round-robin study

- MOAH fraction (recycled board)
- Mean value: 96 mg/kg  
  Standard deviation: 20%

Data taken from report on the round-robin study by Institut Kirchhoff, 19.07.2013
Current round-robin study

Position paper was suggested:

- Integration
  => take single peaks into account?

- Clean-up steps
  => standards to use
  => clean-up steps before separation?

- Methodical approach
  => which method to use?
  => determining

- Limit of detection

- **standard deviation:** $\pm 25 \%$

- **Measurement uncertainty:** $\pm 50 \%$
Alternative method using GC-MS

Background:

- Original method proposed by FABES for testing on recycled paper
- Modifications proposed after first discussions with BfR
- Tested in current joint research project together with Fogra
Alternative method using GC-MS

Sample pretreatment

- cut paper / board to small pieces

Extraction for 72 h at 40°C

- sample: 2 g ± 0.1 g
- Ethanol / Hexene (1:1 v/v): 10 ml
- shake vigorously, let it stand for 2 h

Clean-up

- obtain extract in a quantitative way
- filtration of extract, concentrate to 1 ml
- add standard: 15 µl of tridecane standard
- fill up to exactly 2 ml

GC-FID

quantification

GC-MS

determination of MOAH amount using m/z 50-52, 63-66, 75-78
Alternative method using GC-MS
Alternative method using GC-MS

Comparison to BfR method:

- **Fogra round-robin study:**

- **Kirchhoff round-robin study:**

![Graph showing comparison]

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Alternative method using GC-MS

Advantages:
- Detection of (relevant) aromatic compounds only
- Structural information obtained by GC-MS
- Determination of real MOAH components possible
- No LC-GC online system necessary
- Slight overestimation => save with regards to health

Disadvantages:
- Slight overestimation
- Method not yet accepted by BfR
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