# Latest developments on MOSH/MOAH methods

Dr Philipp Stolper, Dr Wolfgang Rauh

Fogra Forschungsgesellschaft Druck e.V.

www.fogra.org

# Outline

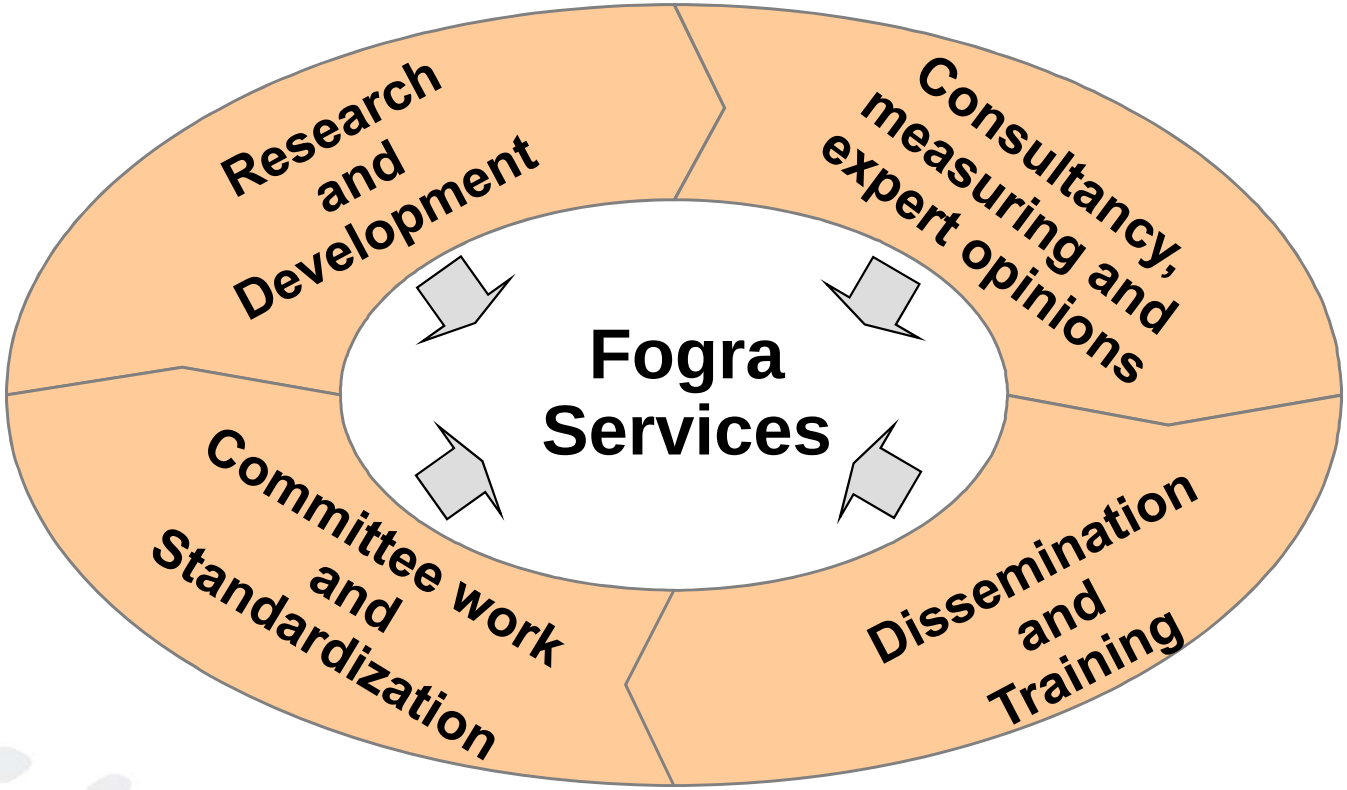
- Who is Fogra
- Overview of current BfR method
- Limits of BfR method
- Round-robin study by Fogra
- Current round-robin study
- Alternative method using GC-MS

# Who is Fogra?

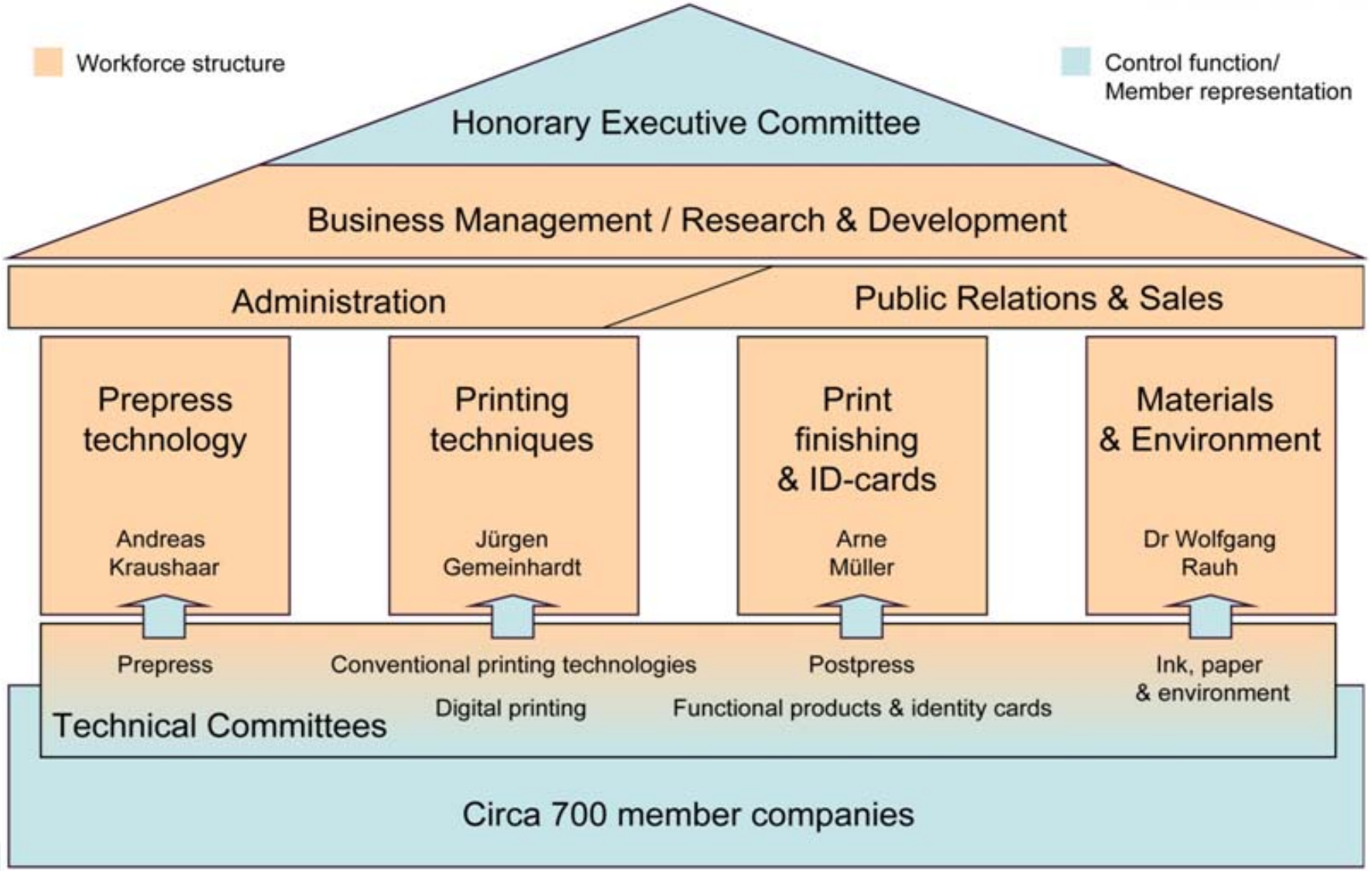
**Mission**

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

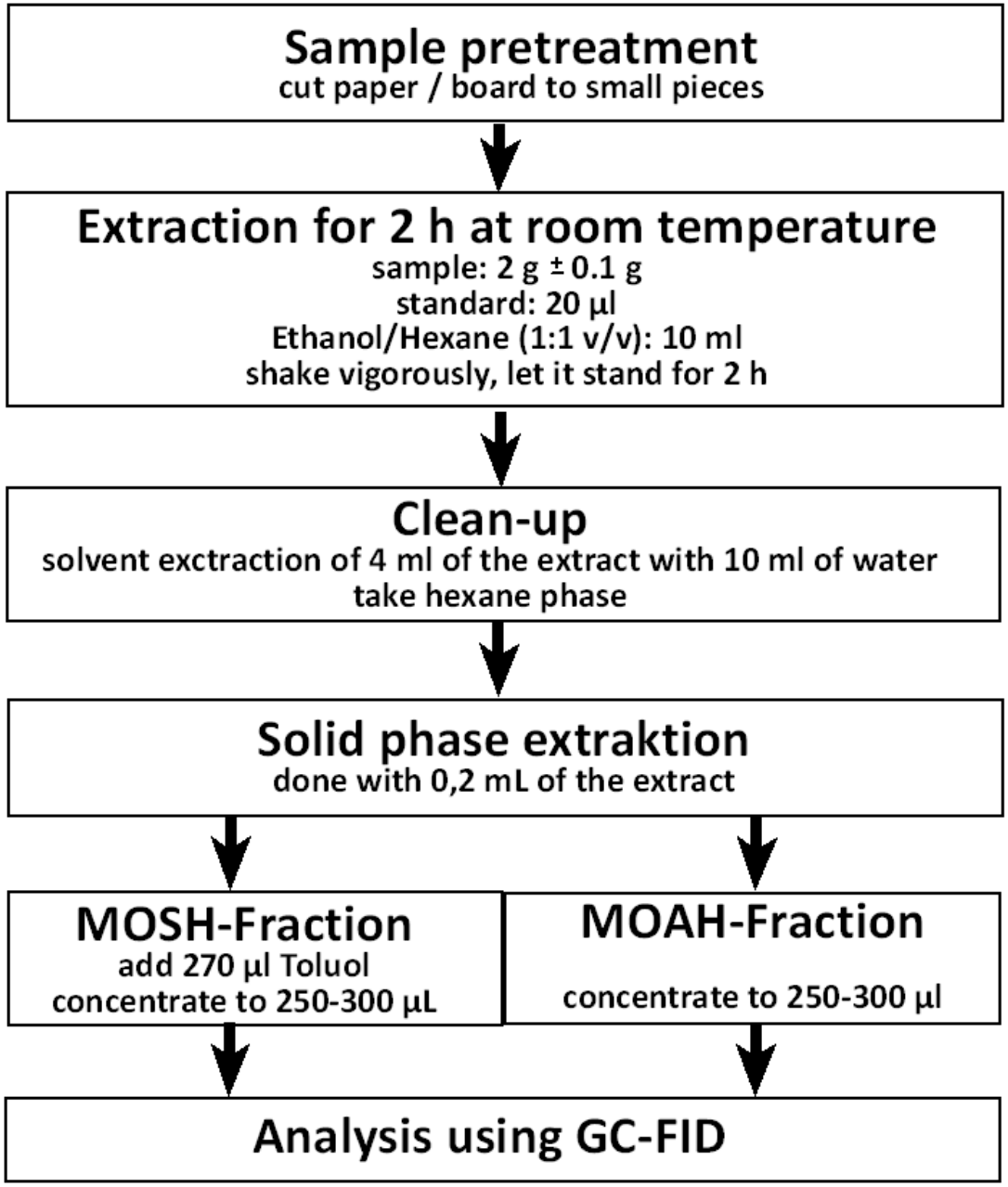
**Fields of activity**



# Who is Fogra?

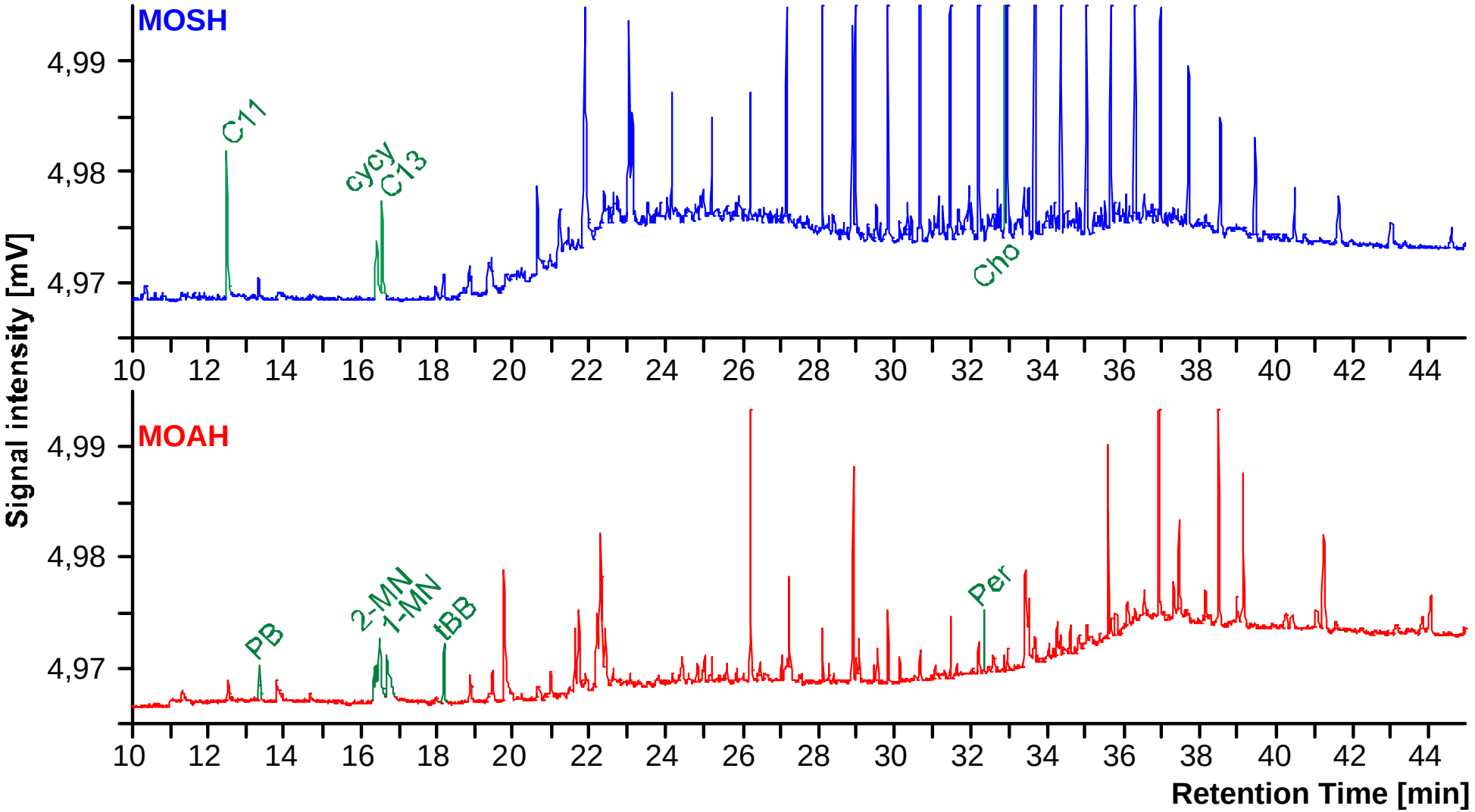

Workforce structure
Control function/
Member representation
Honorary Executive Committee
Business Management / Research & Development
Administration
Public Relations & Sales
Prepress technology
Andreas Kraushaar
Printing techniques
Jürgen Gemeinhardt
Print finishing & ID-cards
Arne Müller
Materials & Environment
Dr Wolfgang Rauh
Prepress
Conventional printing technologies
Digital printing
Postpress
Functional products & identity cards
Ink, paper & environment
Technical Committees
Circa 700 member companies

# Overview of BfR method




**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)

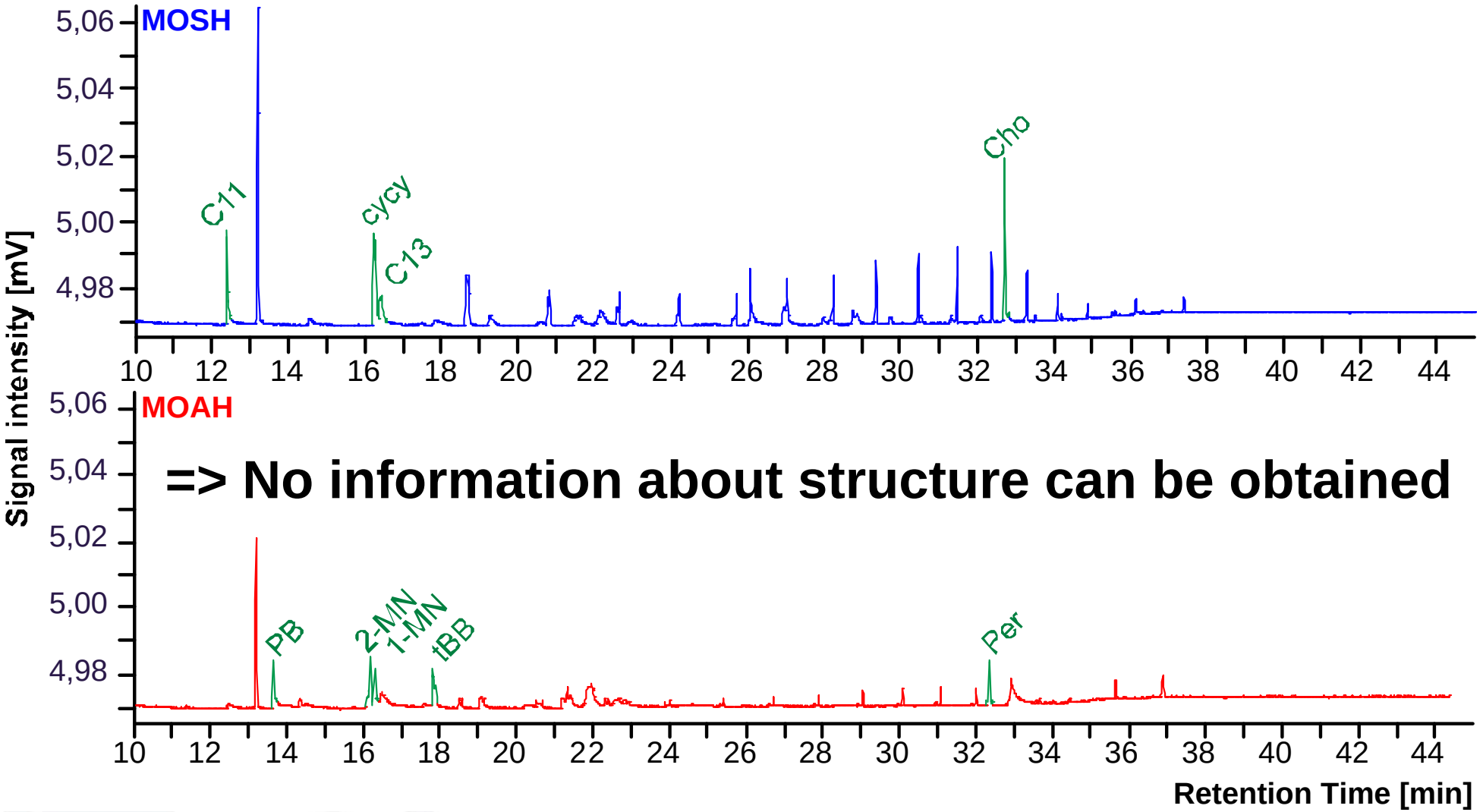
# Overview of BfR method




*C11*: Undecane, *cycy*: Bicyclohexyl, *C13*: Tridecane, *Cho*: 5α-Cholestane
*PB*: Pentylbenzene, *2-MN*: 2-Methylnaphthalene, *1-MN*: 1-Methylnaphthalene,
*tBB*: 1,3,5-tri-tert-butylbenzene, *Per*: Perylene

# 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

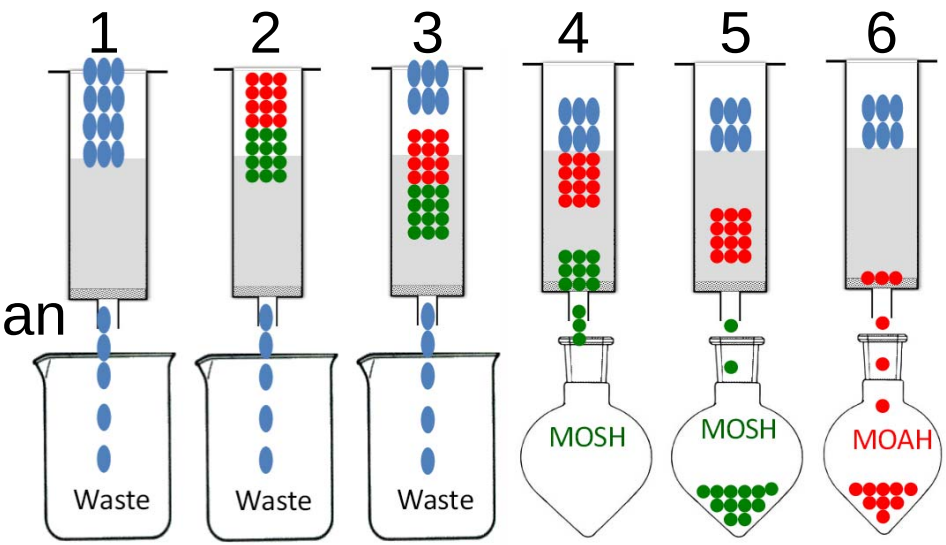
## Solid phase extraction (SPE)

- Generating MOSH/MOAH fraction using the following scheme:

Solvents:

1-4: Hexane

5,6: Hexane, Toluene, Dichloromethan




Source => slide 5 : Determination of hydrocarbons … (BfR, May 2012)

## 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

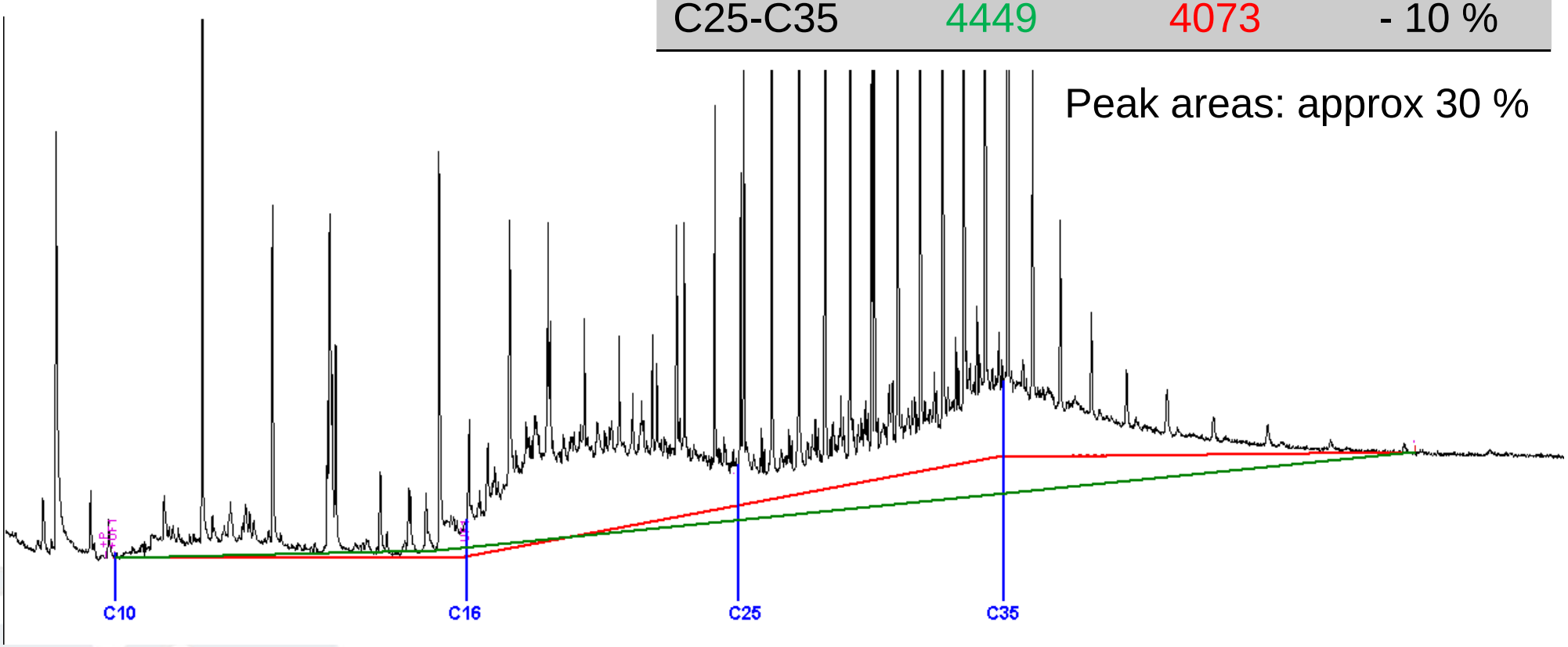
- Discrimination of low-boiling components
- Overestimation of high-boiling components

# Limits of BfR method

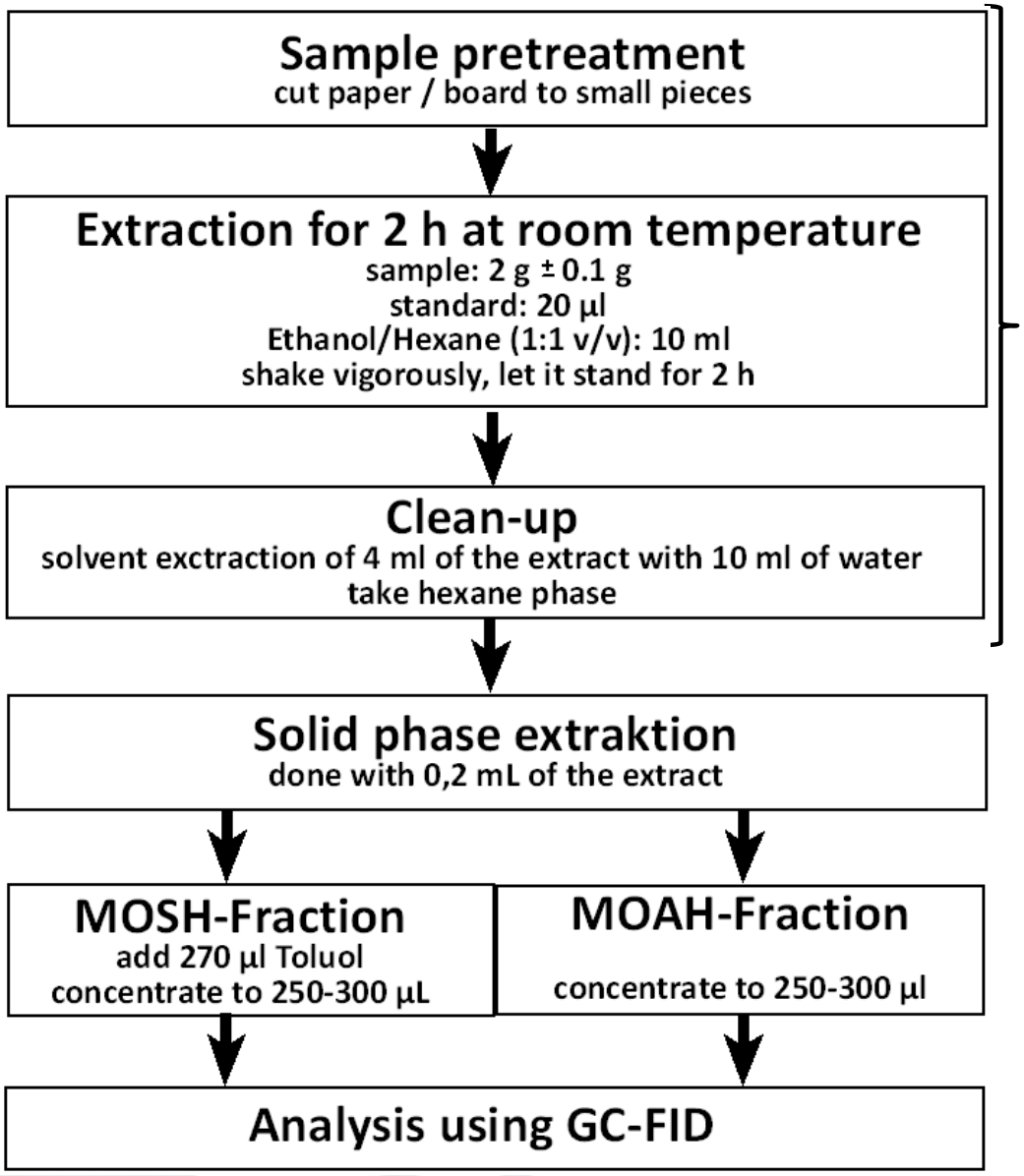
## Analysis / Evaluation using GC-FID

| Range | Integral 1 | Integral 2 | ΔIntegral |
|---|---|---|---|
| C10-C16 | 1174 | 1298 | + 10 % |
| C16-C25 | 3599 | 3148 | - 13 % |
| C25-C35 | 4449 | 4073 | - 10 % |

Peak areas: approx 30 %



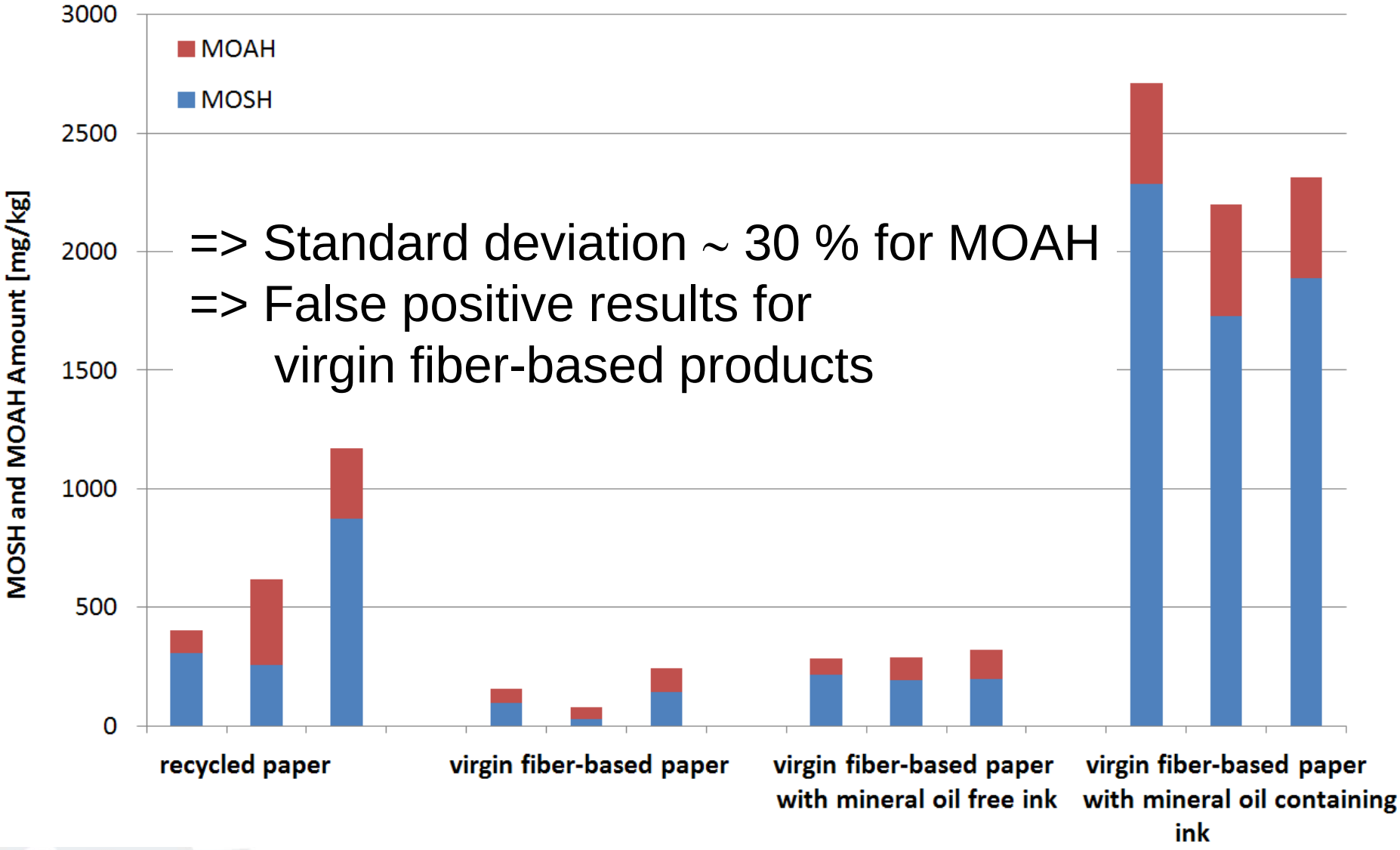
# Limits of BfR method




| | Manual | Online |
|---|---|---|
| Sample pretreatment, Extraction, Clean-up | ~ 5 % | ~ 5 % |
| Solid phase extraktion | ~ 10 % | |
| MOSH-Fraction / MOAH-Fraction | ~ 10 % | |
| Analysis using GC-FID | ~ 20 % | ~ 20 % |

# Round-robin study by Fogra

## in October 2012

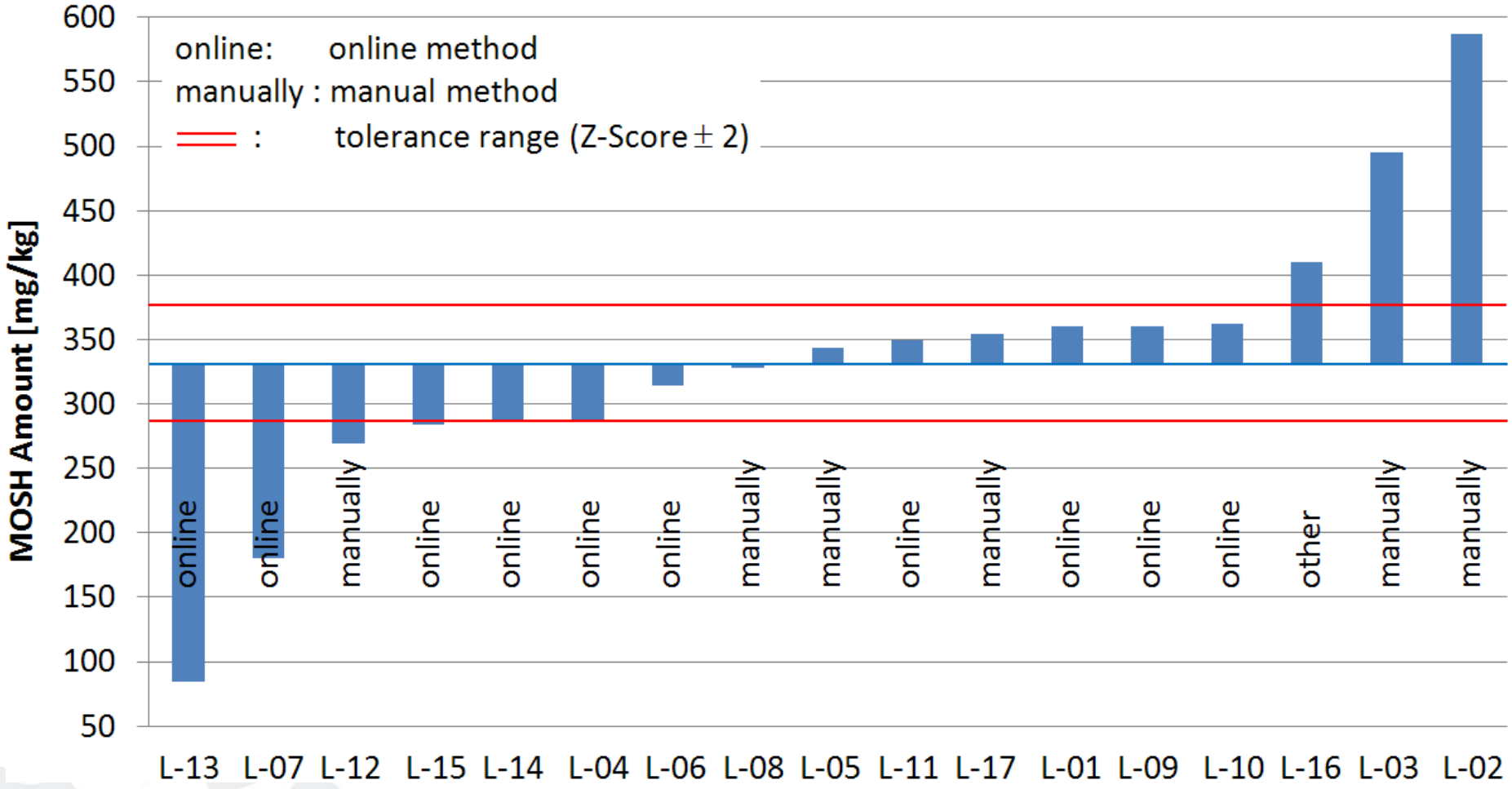


# Current round-robin study

- 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

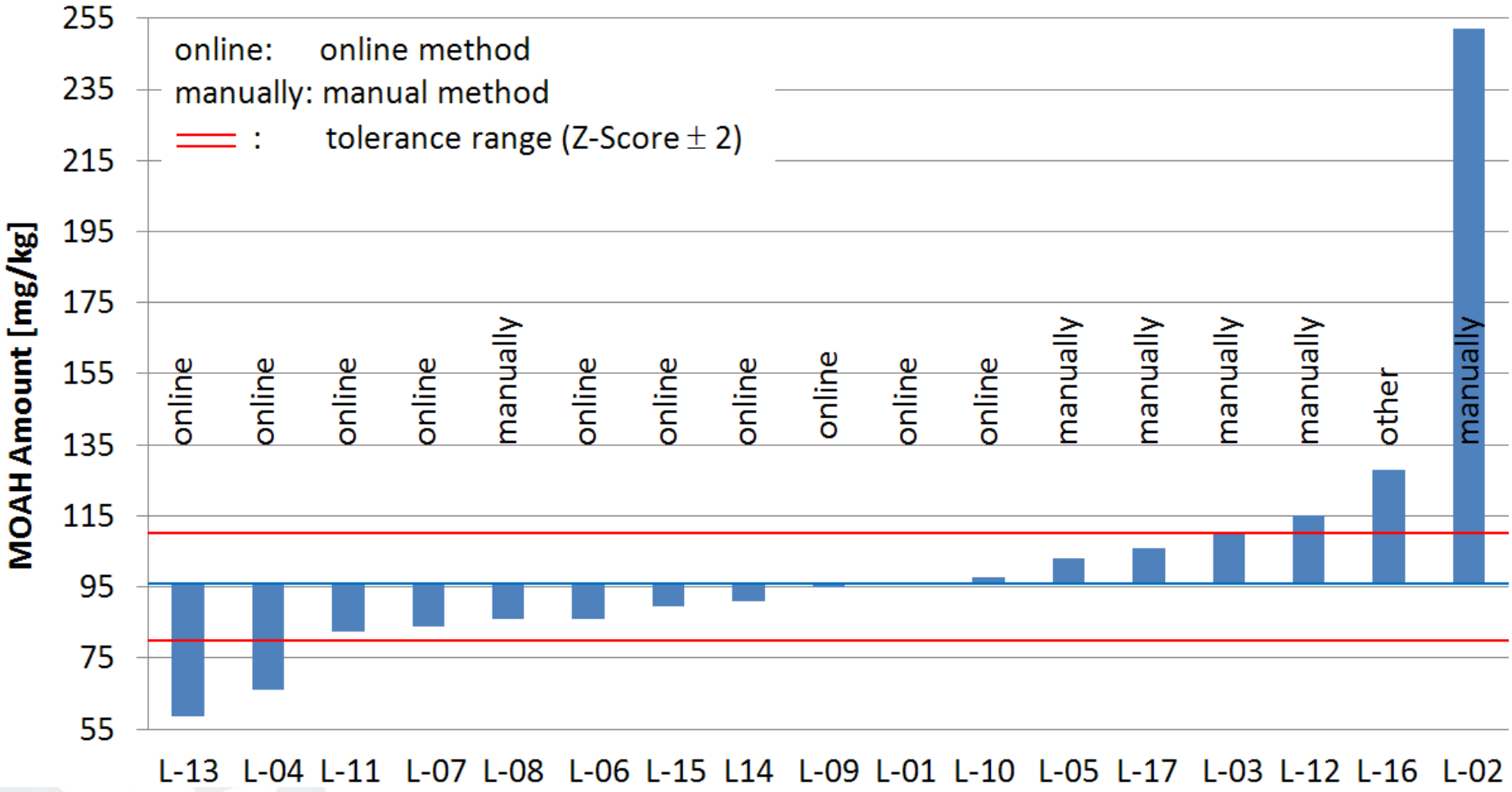
- MOSH fraction (recycled board)
- Mean value: 332 mg/kg  Standard deviation: 23 %




*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

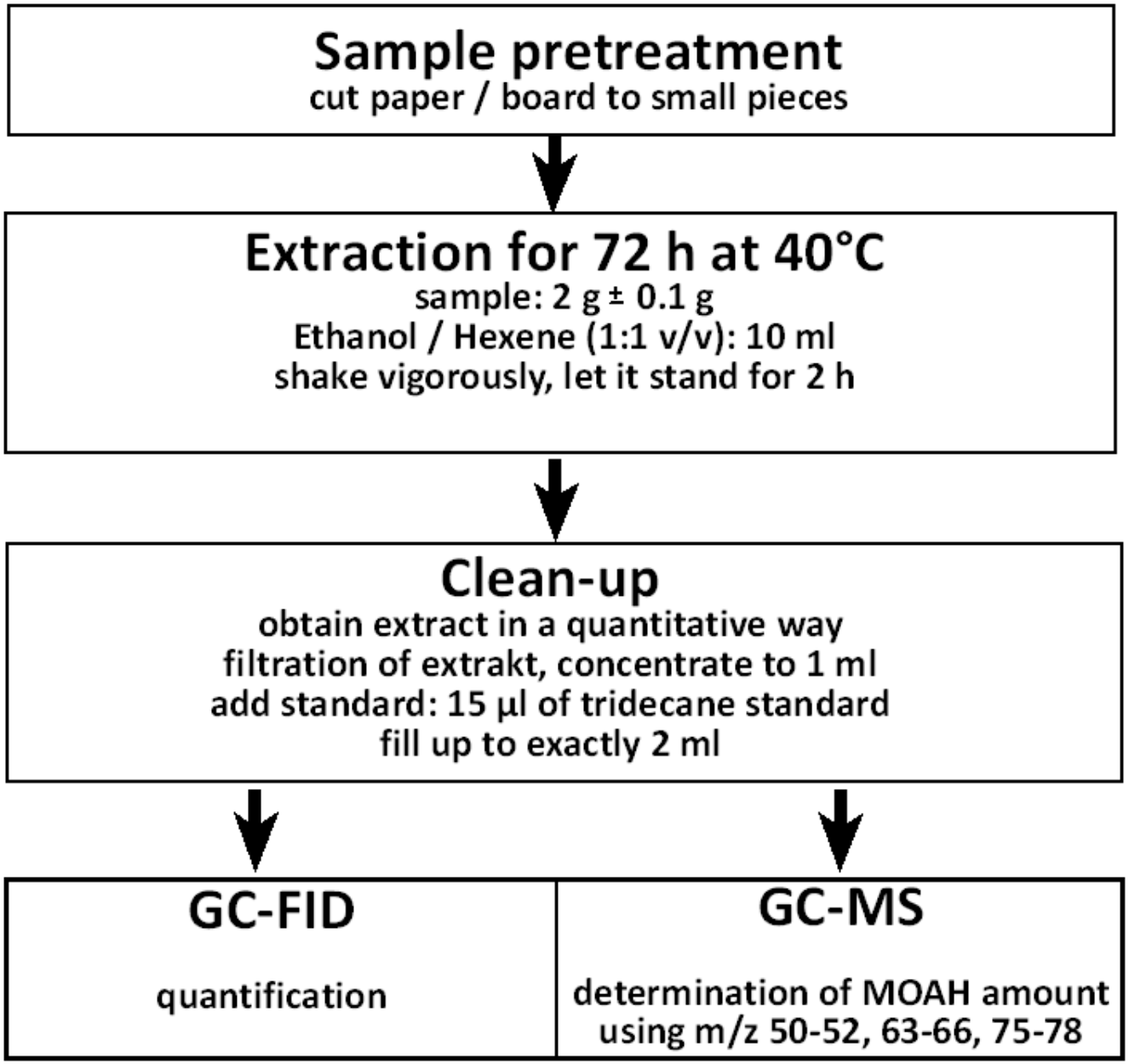
- Limit of detection
- **standard deviation: ± 25 %**
- **Measurement uncertainty : ± 50 %**

# Alternative method using GC-MS

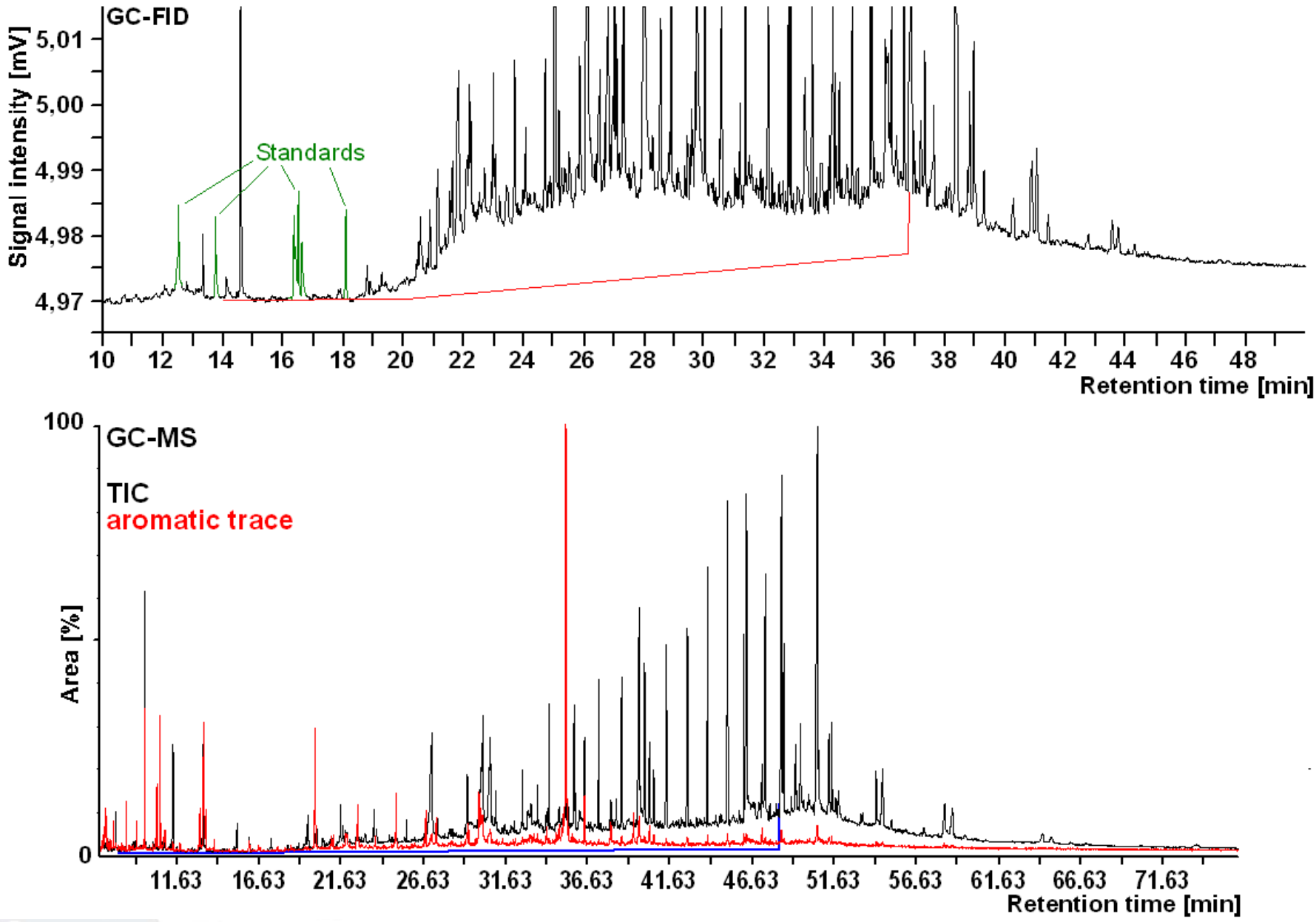
**Background:**

- 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



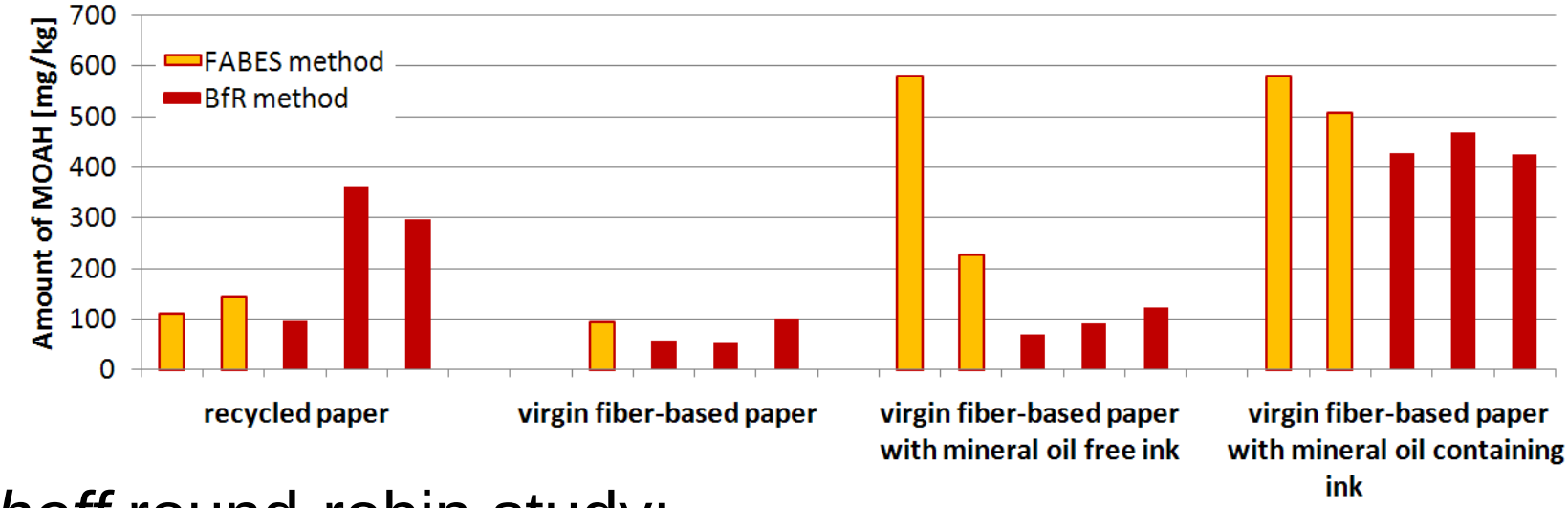
# Alternative method using GC-MS



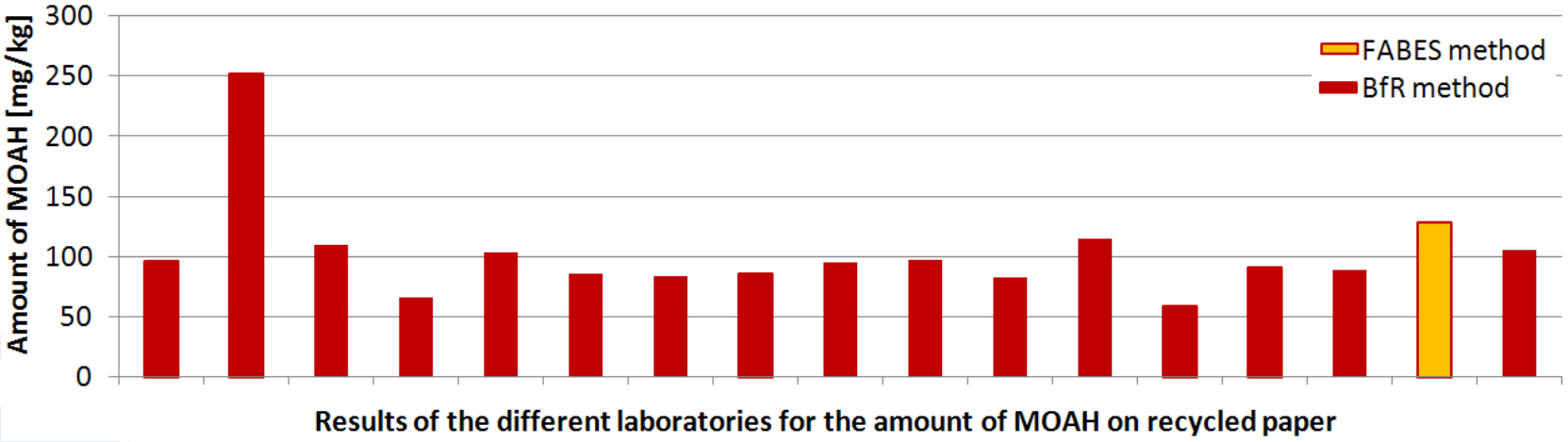
# Alternative method using GC-MS

## Comparison to BfR method:

- *Fogra* round-robin study:




- *Kirchhoff* round-robin study:



# 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

# Contact


## Dr Philipp Stolper

Fogra Forschungsgesellschaft Druck e.V.
Streitfeldstraße 19
81673 München, Germany

Tel. +49 89. 431 82 - 354
E-Mail stolper@fogra.org

www.fogra.org