Oberflächenadsorption kann 3-MCPD-bildende Substanzen in Pflanzenölen reduzieren

Surface adsorption may reduce 3-monochlorpropandiol-forming substances in vegetable oils

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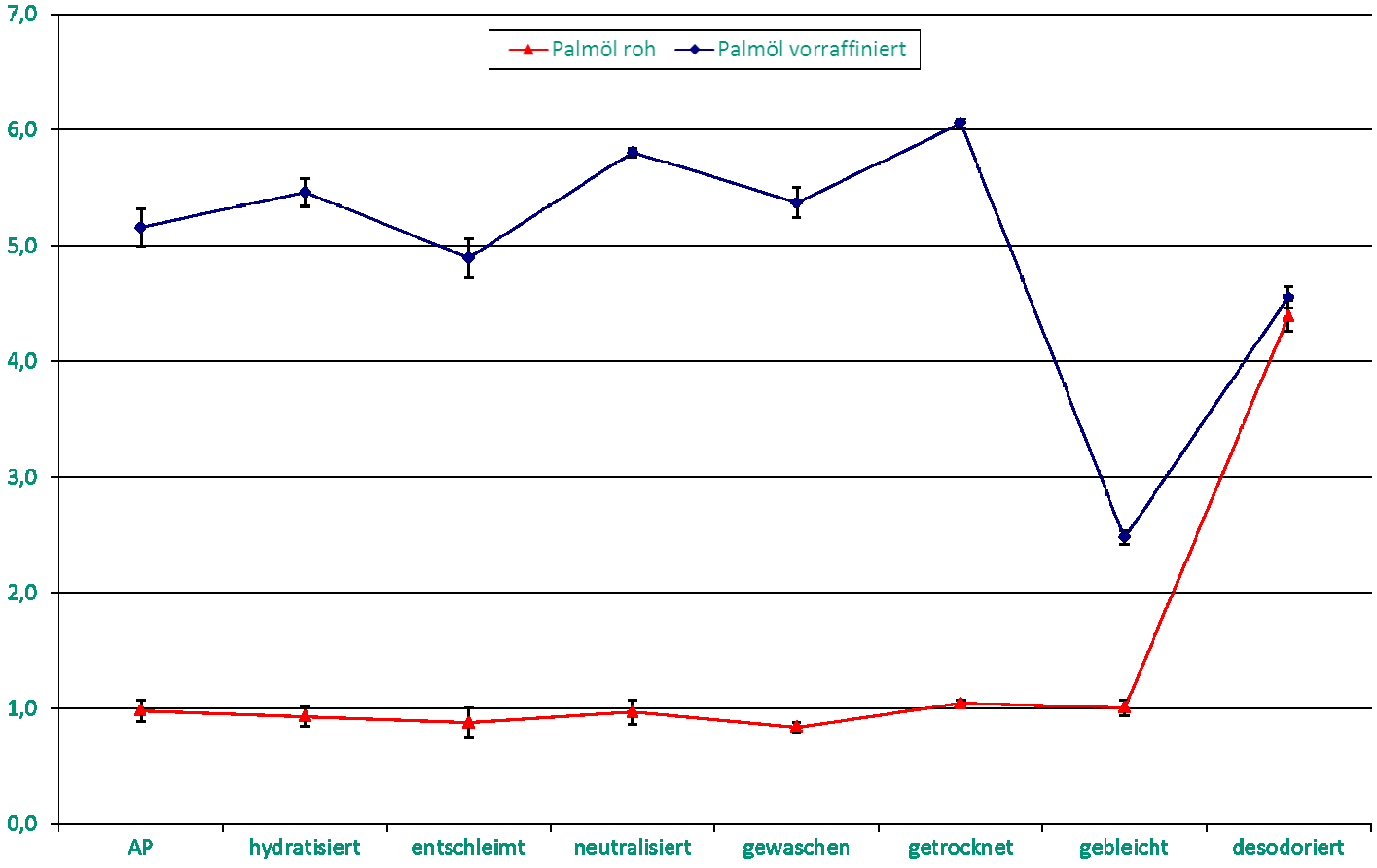
Possible starting points

- **Raw material**
  - Oil fruits are harvested at the other side of the world
  - Several factors of influence (climate, soil, fertilizer, etc.)
- **Raffination**
  - Establighed process with exact defined variables
  - No dependency on one parameter
  - Large mass flow
- **Post-treatment**
  - Further prozess step
  - Further costs
  - Presumable only for special tasks

Initial situation

- In pre-refined palmoil a reduction of 3-MCPD-fatty acid esters (Sum parameter, DGF-method A) was found



Franke et al., LWT 2009

Other possibilities

- Bleaching earth leads to sensory drawbacks
  - Second deodorisation necessary
  - Re-formation of 3-MCPD fatty acid esters

- Hypothesis:
  a) 3-MCPD- fatty acid esters and related compuonds differ in polarity and can be removed by Adsorption
     > Chlorinated substances can be removed from lipophilic plastics by adsorption (Uddin et al. 1999, Kida et al. 2008)
  b) A reaction at the surfaxce occurs leading to other substances (mono-/diacylglyceroles?)
     > Chlorine compounds and glycidoles are more reactive than acylglycerols

Adsorption material

#	Type	Supplier information
AMS1	amorphous magnesiumsilicate	> 97 %
AMS2	amorphous magnesiumsilicate	> 70 %
AMS3	amorphous magnesiumsilicate	> 40 %
Z1	Zeolithe	< 20 % Water (dried)
Z2	Zeolithe	< 1 % Water (calciniert)
SO	Silica dioxyde	> 99.9 %
SAS	Sodium alumosilikat	Perlite with citric acid
SCS	Synthetic calciumsilicate	47 % Silica dioxide 28 % Calcium oxide
SMS	Synthetic magnesiumsilicate	65 % Silica dioxide 15 % Magnesium oxid

Mode of action

Raw material: **Palm oil** (refined twice)

- Heating of 180 g of palm oil to 80 °C
- Addition of 20 g of adsorption material
- 30 min stirring (magnetic stirrer with heater)
- Removal of adsorption material by centrifugation (15 min, 2500 g)
- Analysis of oil

Characterization parameters

- Acid value
- Peroxide value, anisidine value
- Mono- and diacylglycerides (HPLC)
- Polar components (gravimetrically)
- “3-MCPD fatty esters“
  - DGF method A (3-MCPD esters and related)
  - DGF method B (only 3-MCPD)
- Color change

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2}$$

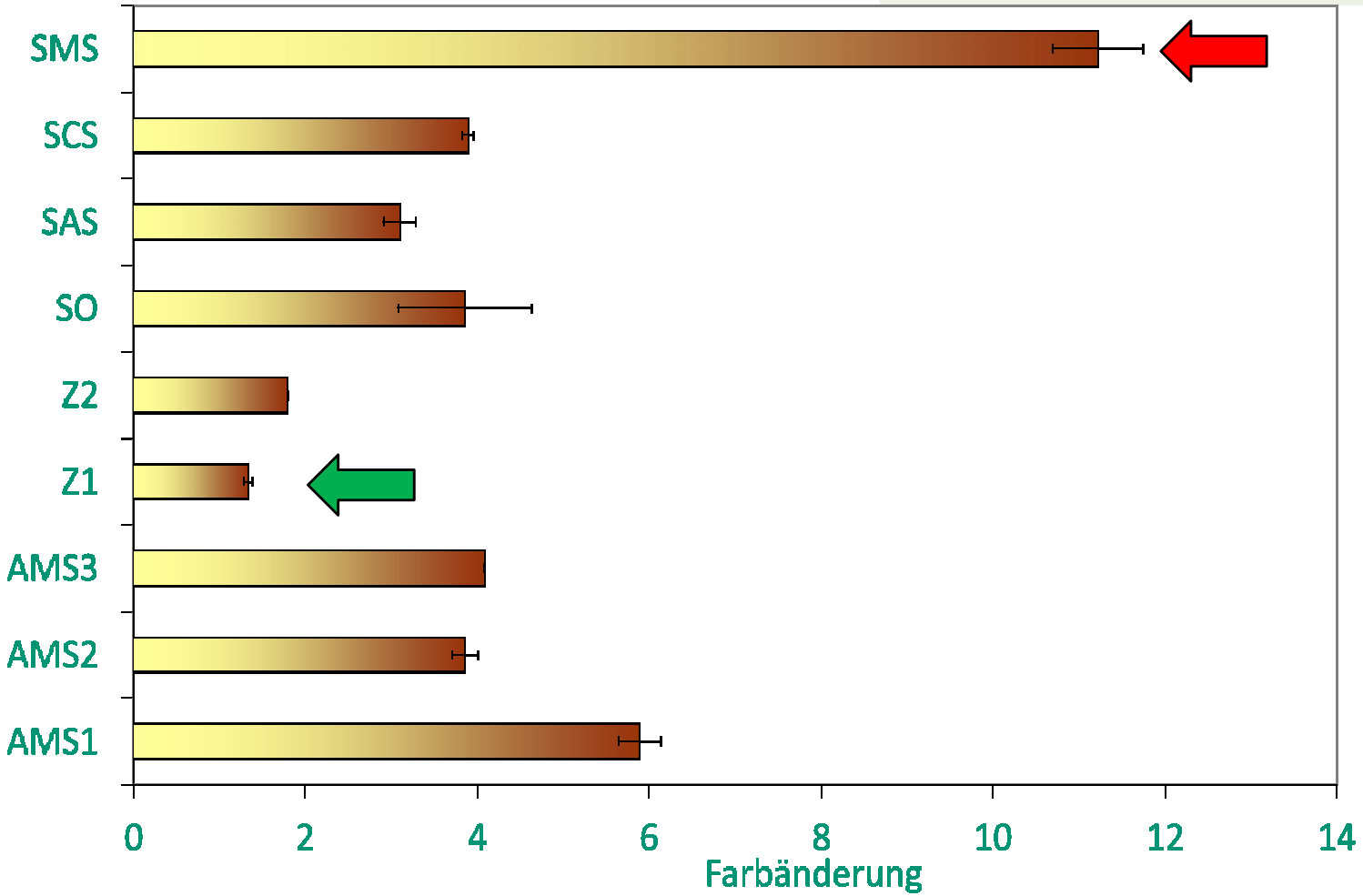
Raw material

- Color: L* = 60.3 ± 0.54
  a* = - 3.7 ± 0.08
  b* = 29.2 ± 0.81
- Acid value: 0.12 ± 0.01 mg KOH / g fat
- Peroxide value: 1.49 ± 0.46
- Anisidine value: 1.82 ± 0.04
- Mono-/diacylglycerides: 8.85 ± 0.05 g / 100 g
- Polar components: 9.41 ± 0.22

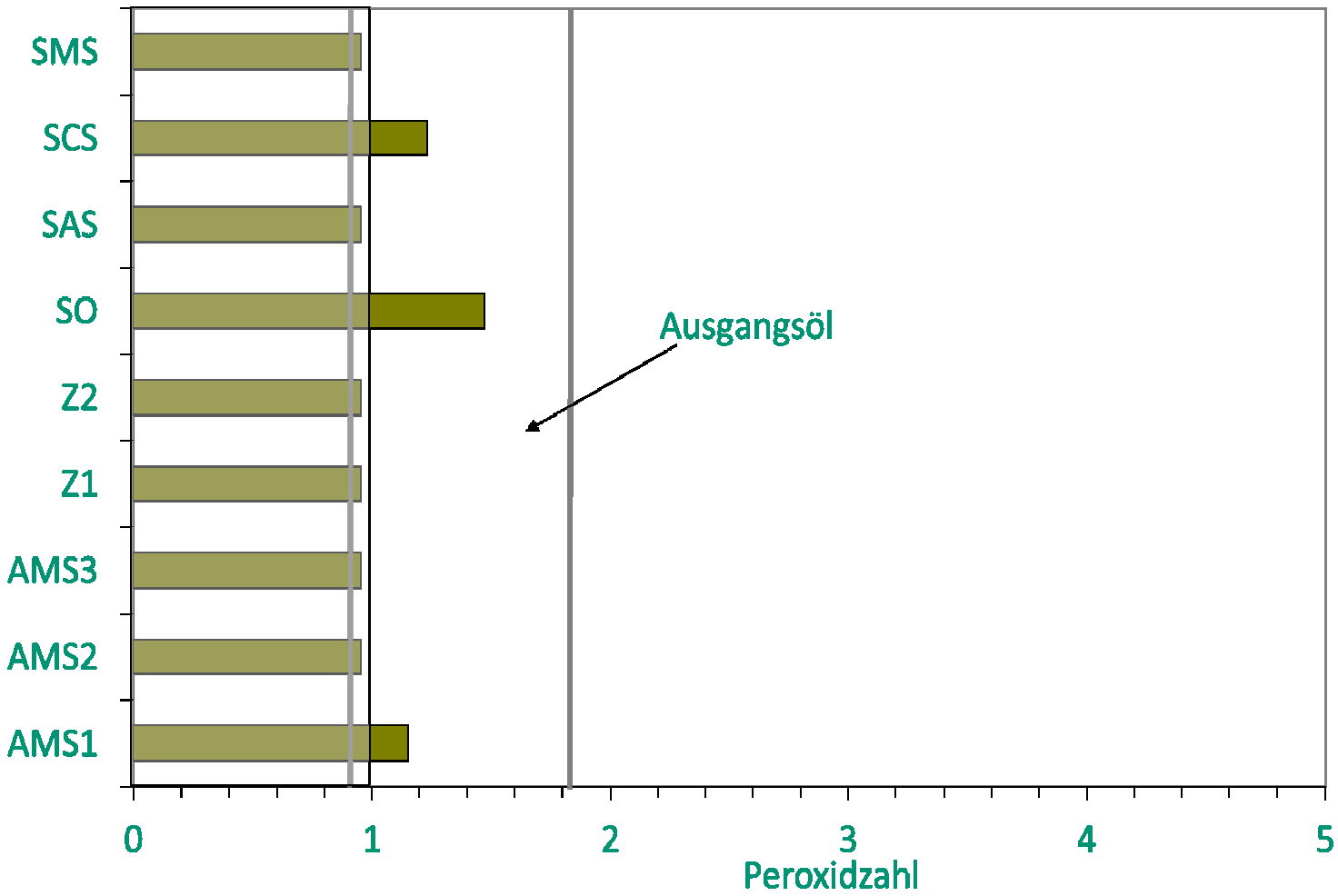
- „3-MCPD-FE“ in total: 6.59 ± 0.19 ppm
  real 3-MCPD: 4.38 ± 0.36 ppm

Color changes after treatment

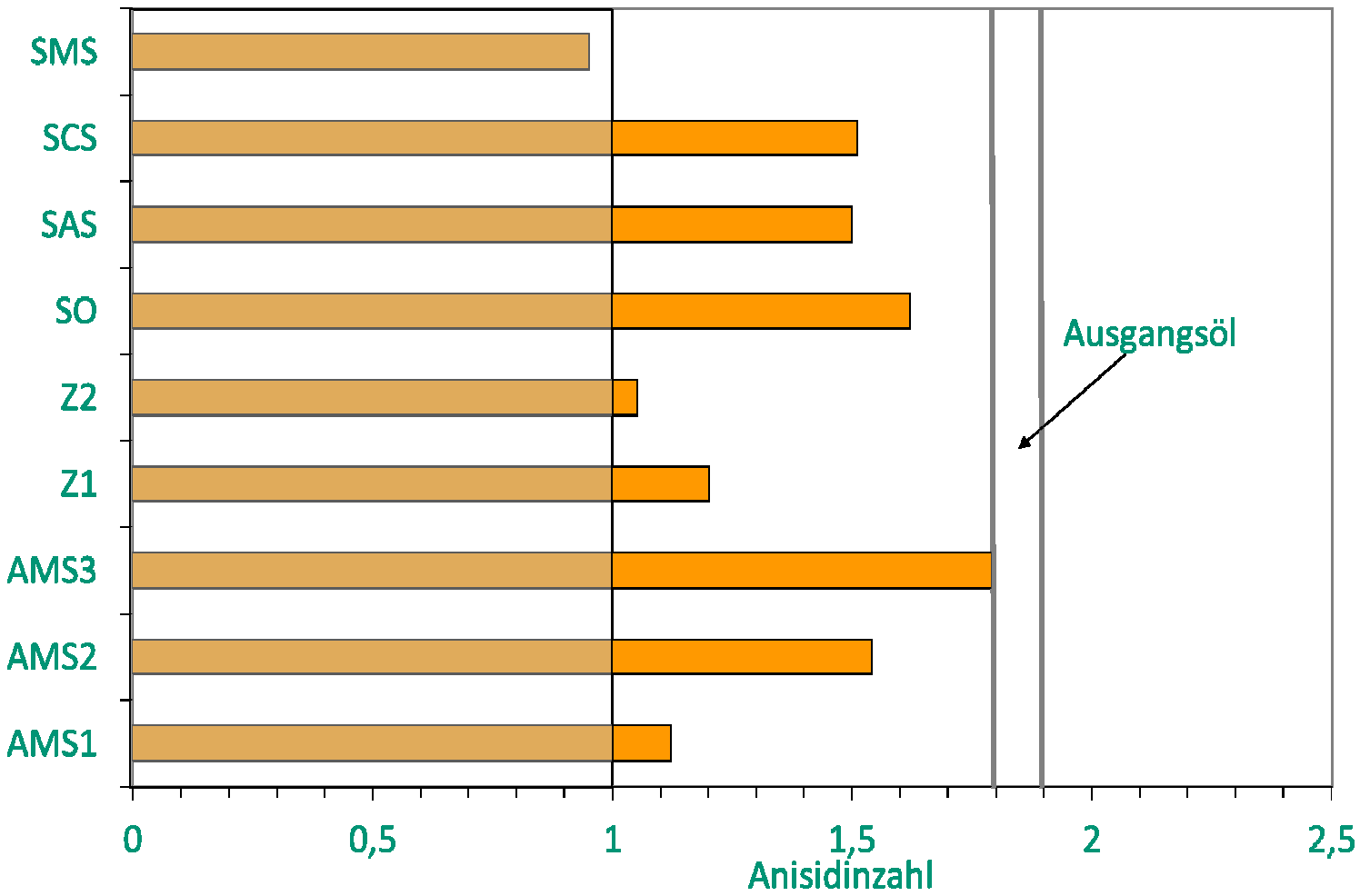
$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2}$$



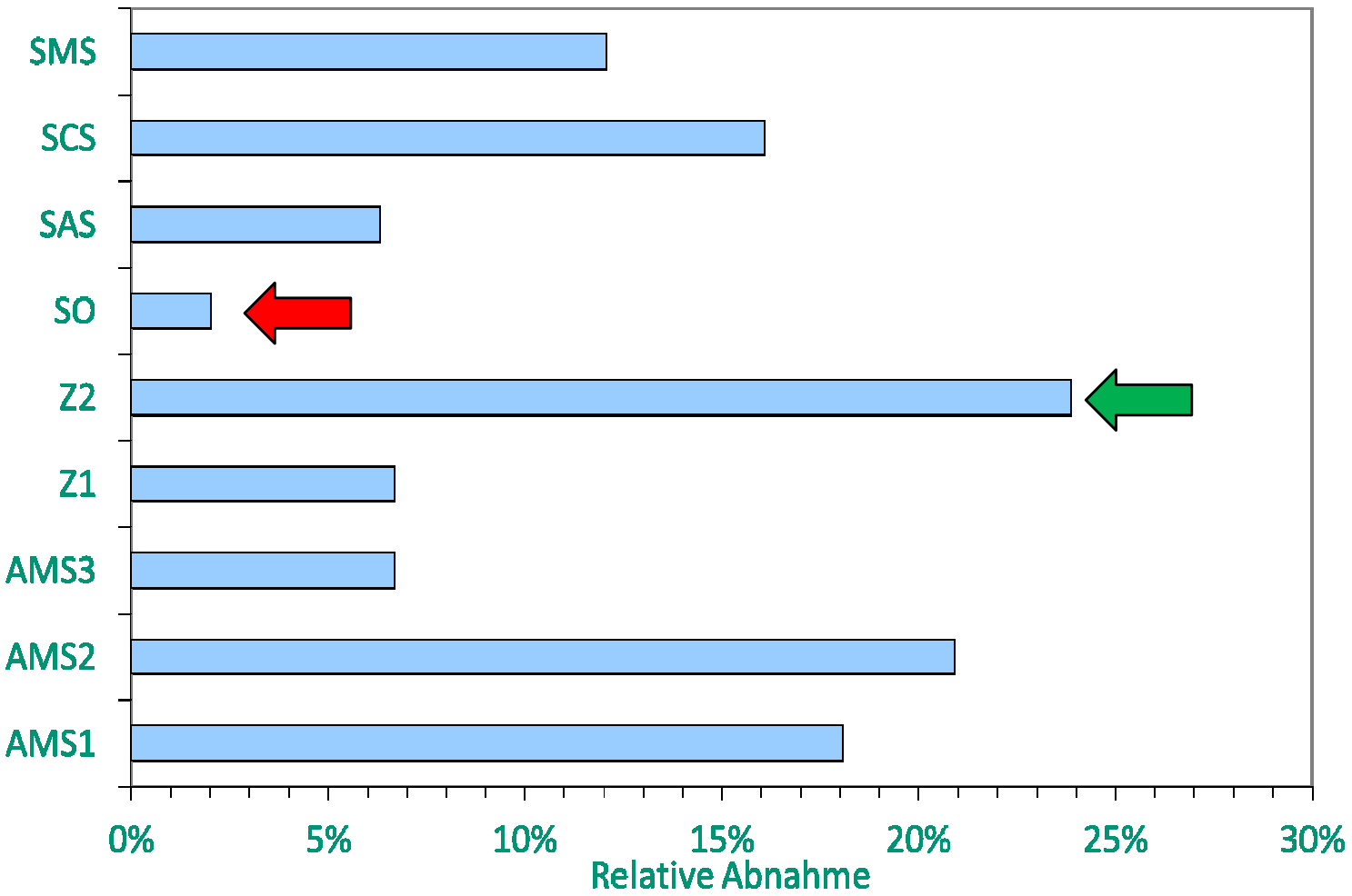
Peroxid value



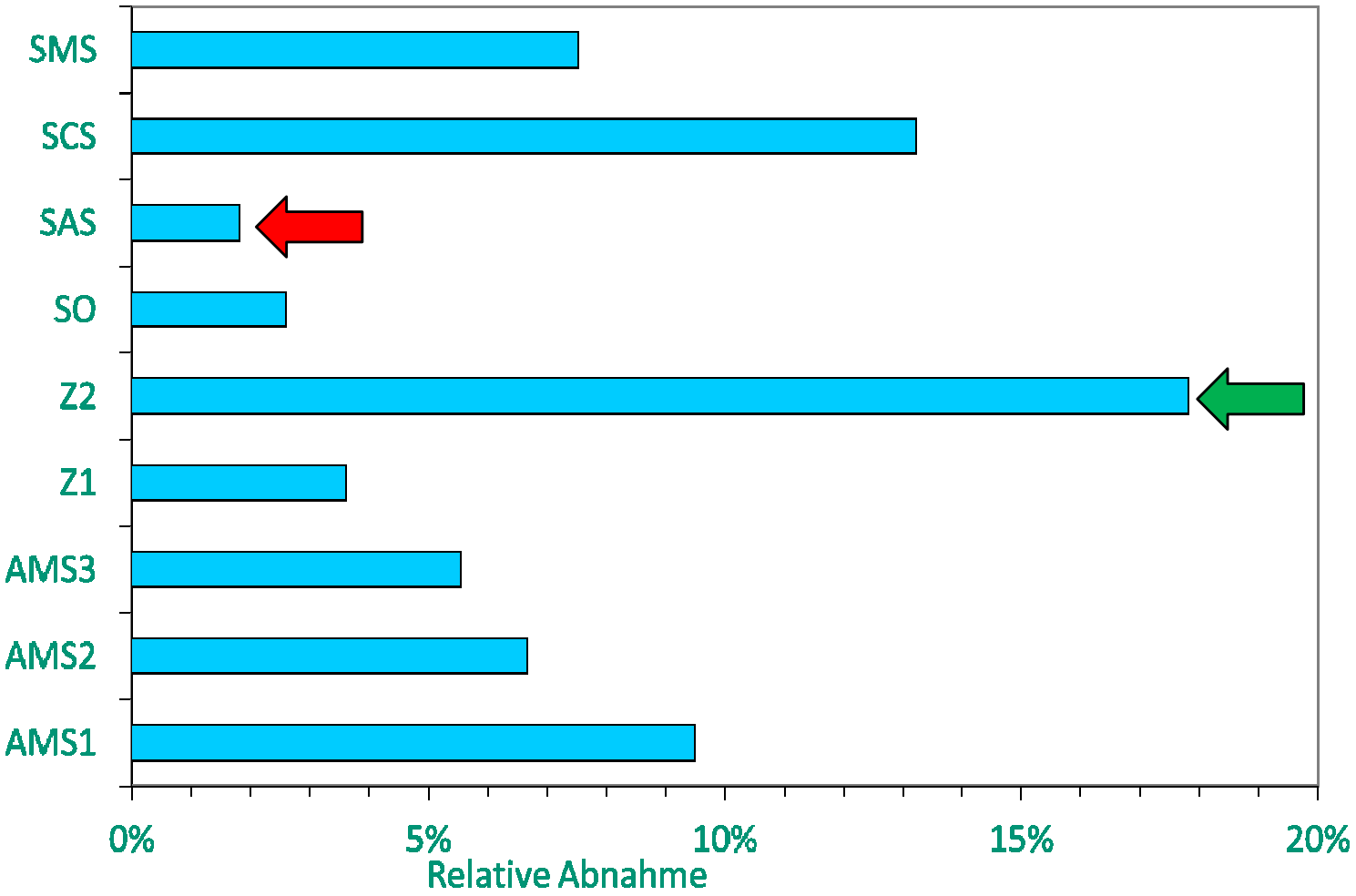
Anisidine value



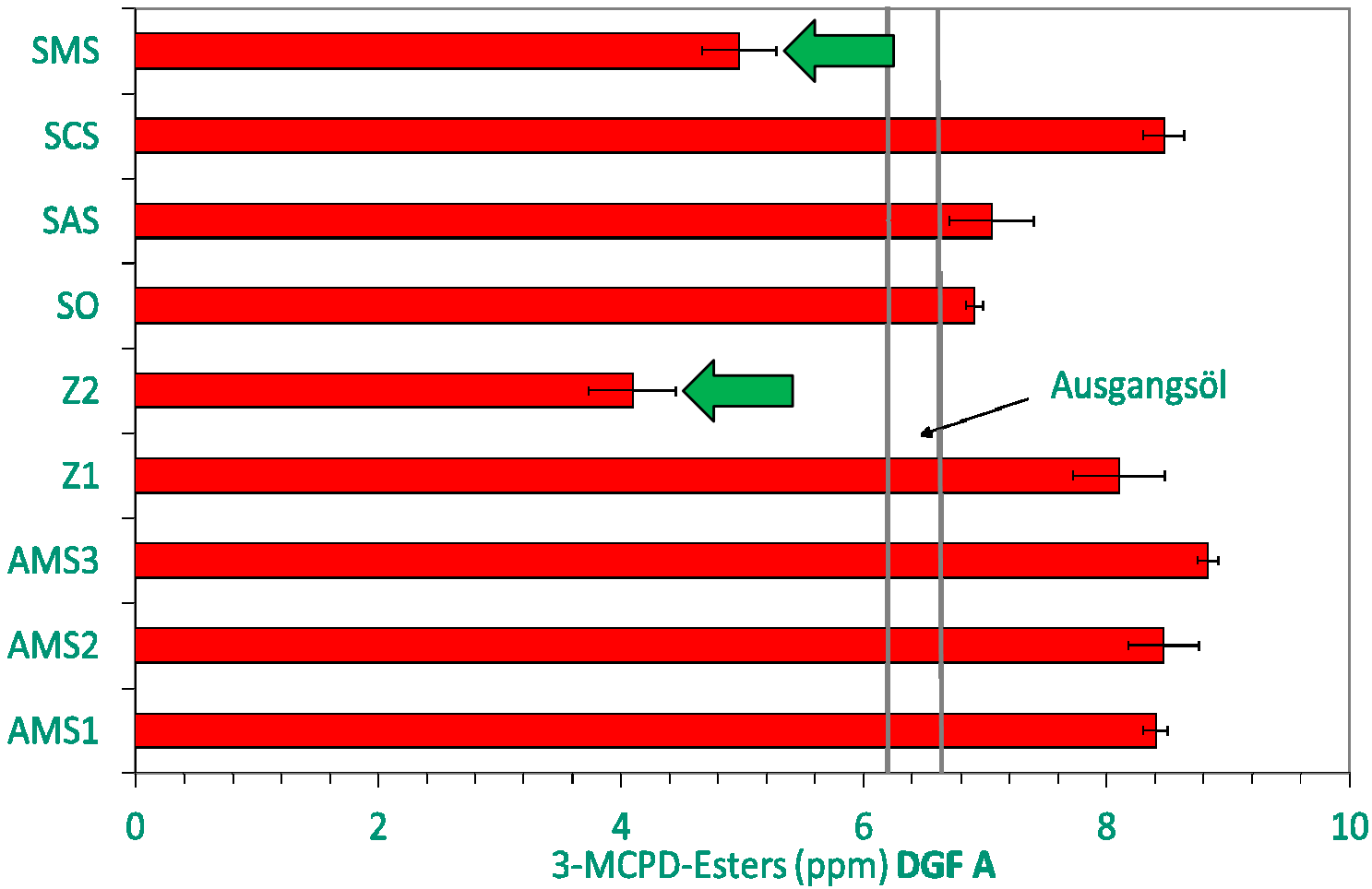
Polar components



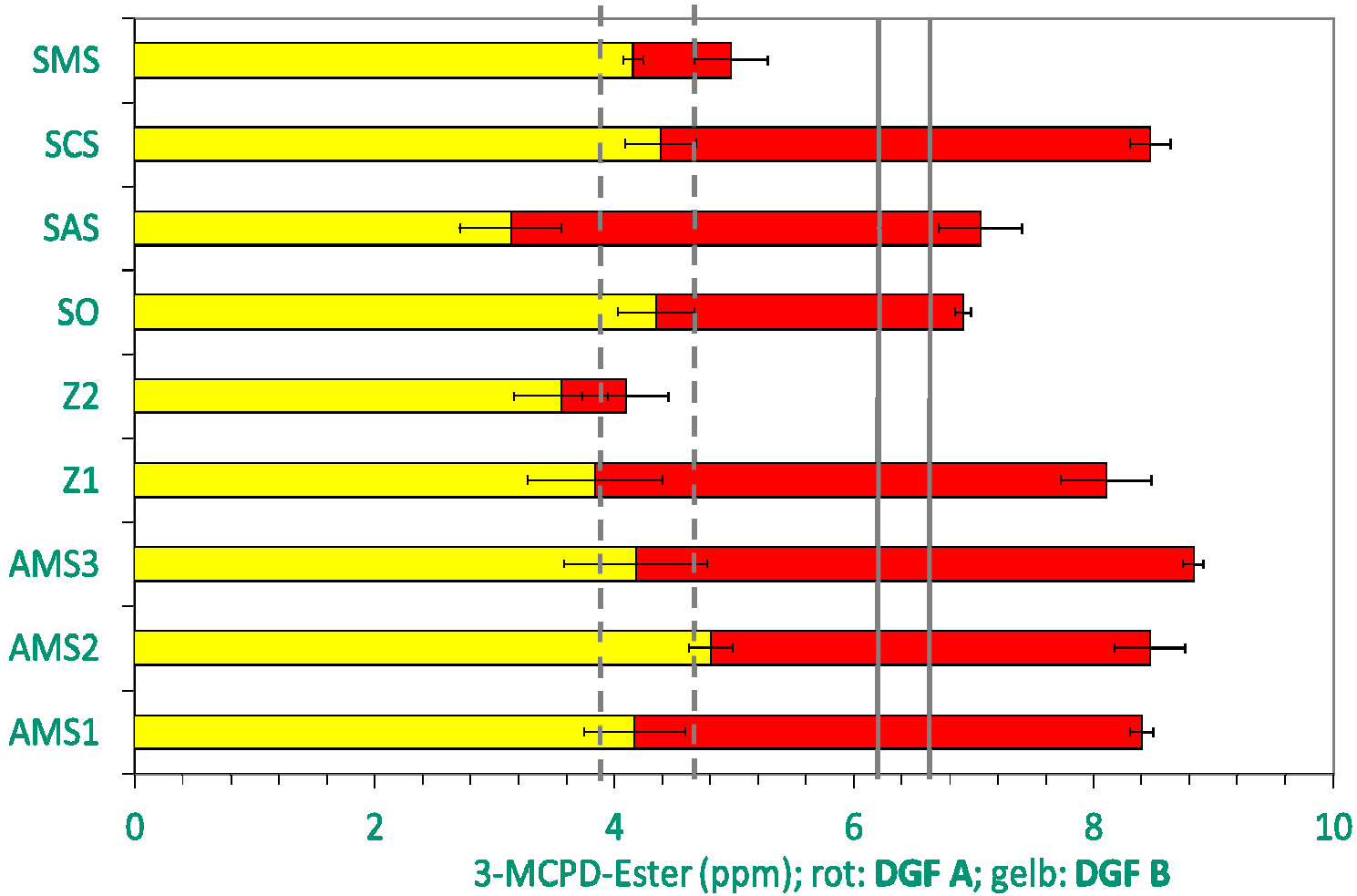
Mono- and Diacylglycerides



3-MCPD fatty acid esters (DGF A)



3-MCPD fatty acid esters (DGF A + B)



Variation of treatment conditions

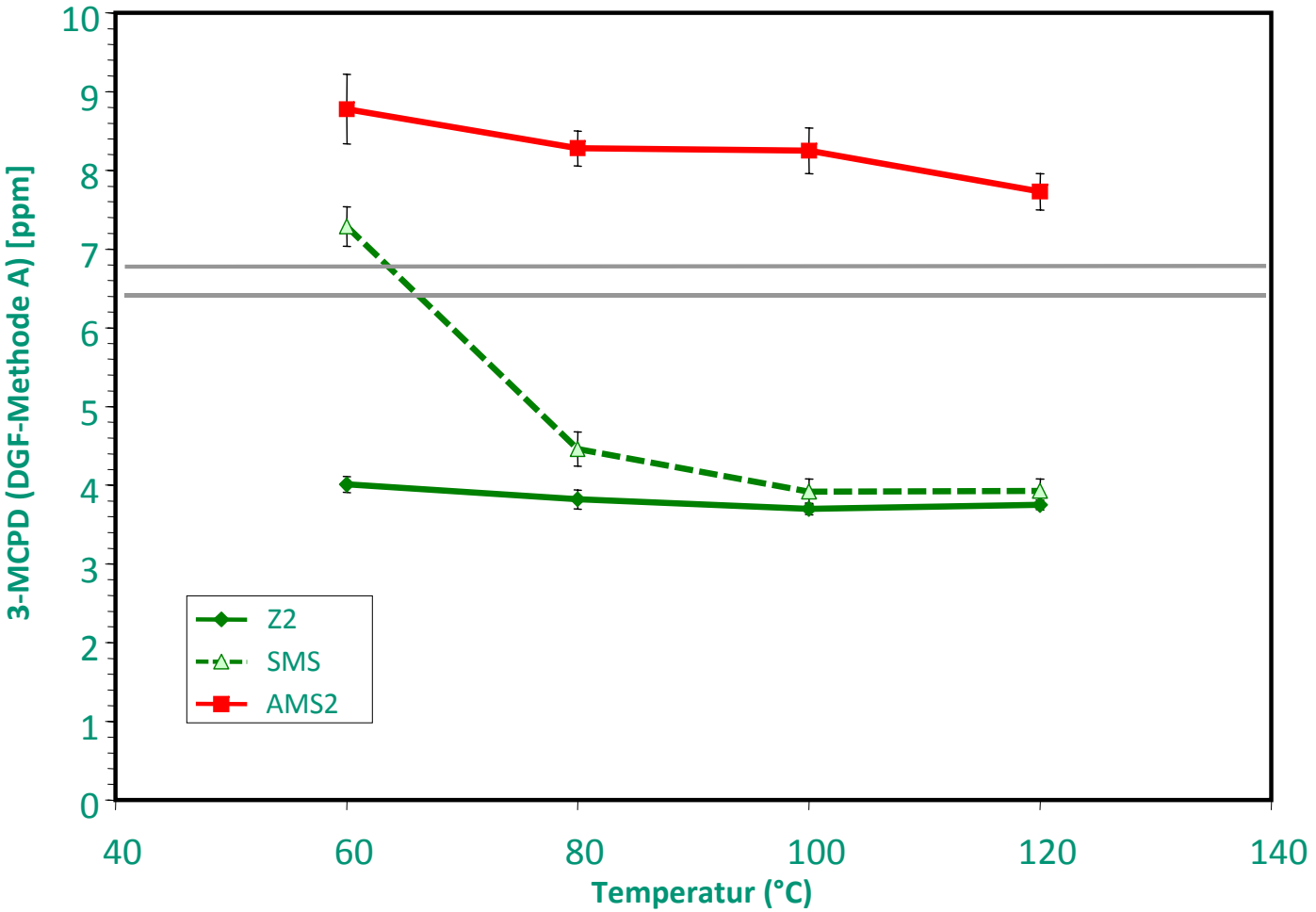
Used materials:

- Z2 zeolite with < 1 % water
- SMS synthetic magnesium silicate
- AMS2 amorphous magnesium silicate (negative control)

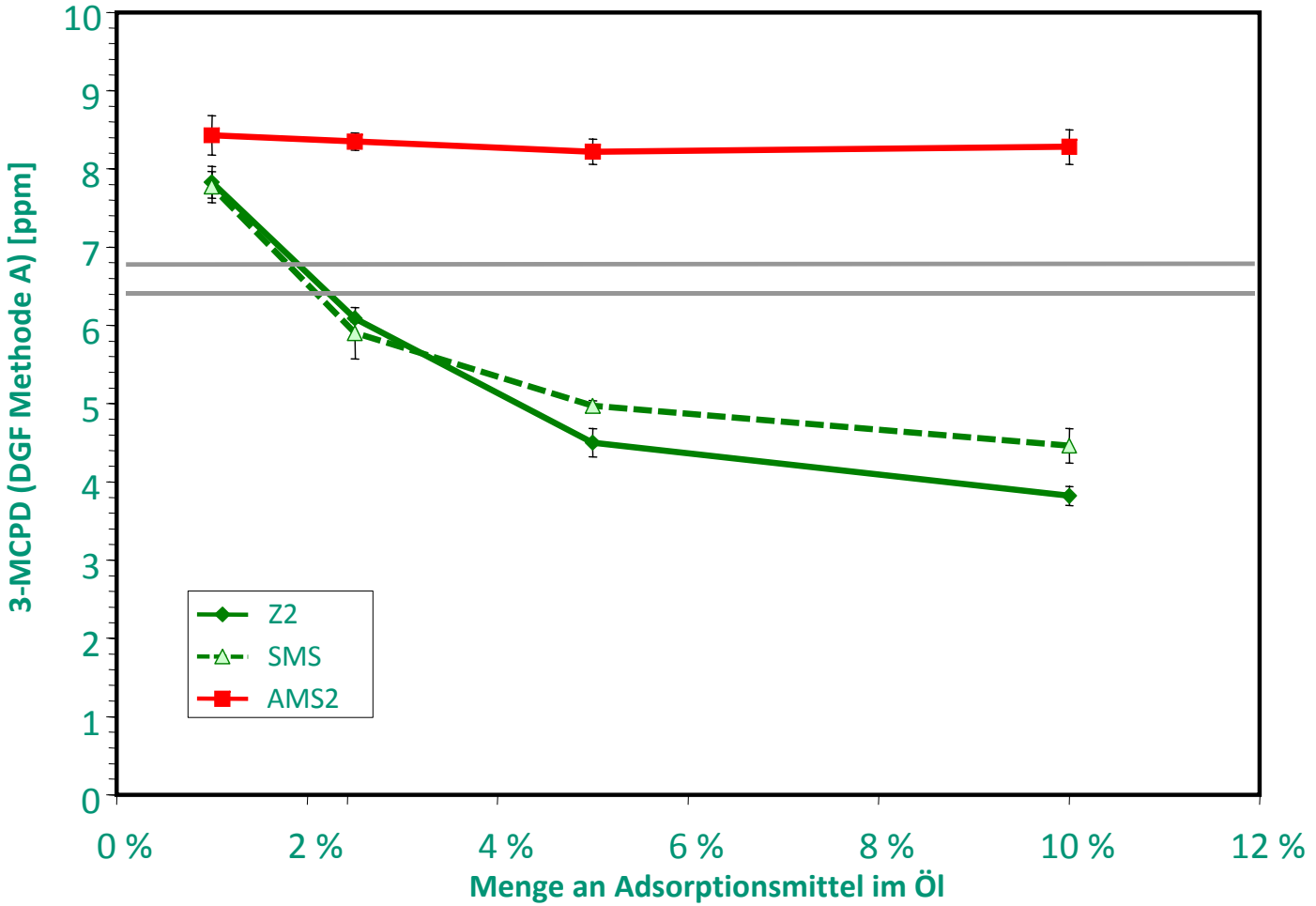
Variation

- Temperature: 60 80 100 120°C
- Proportion AM/oil: 0.1 0.05 0.025 0.01
- Duration: 1 5 10 15 30 60 120 min

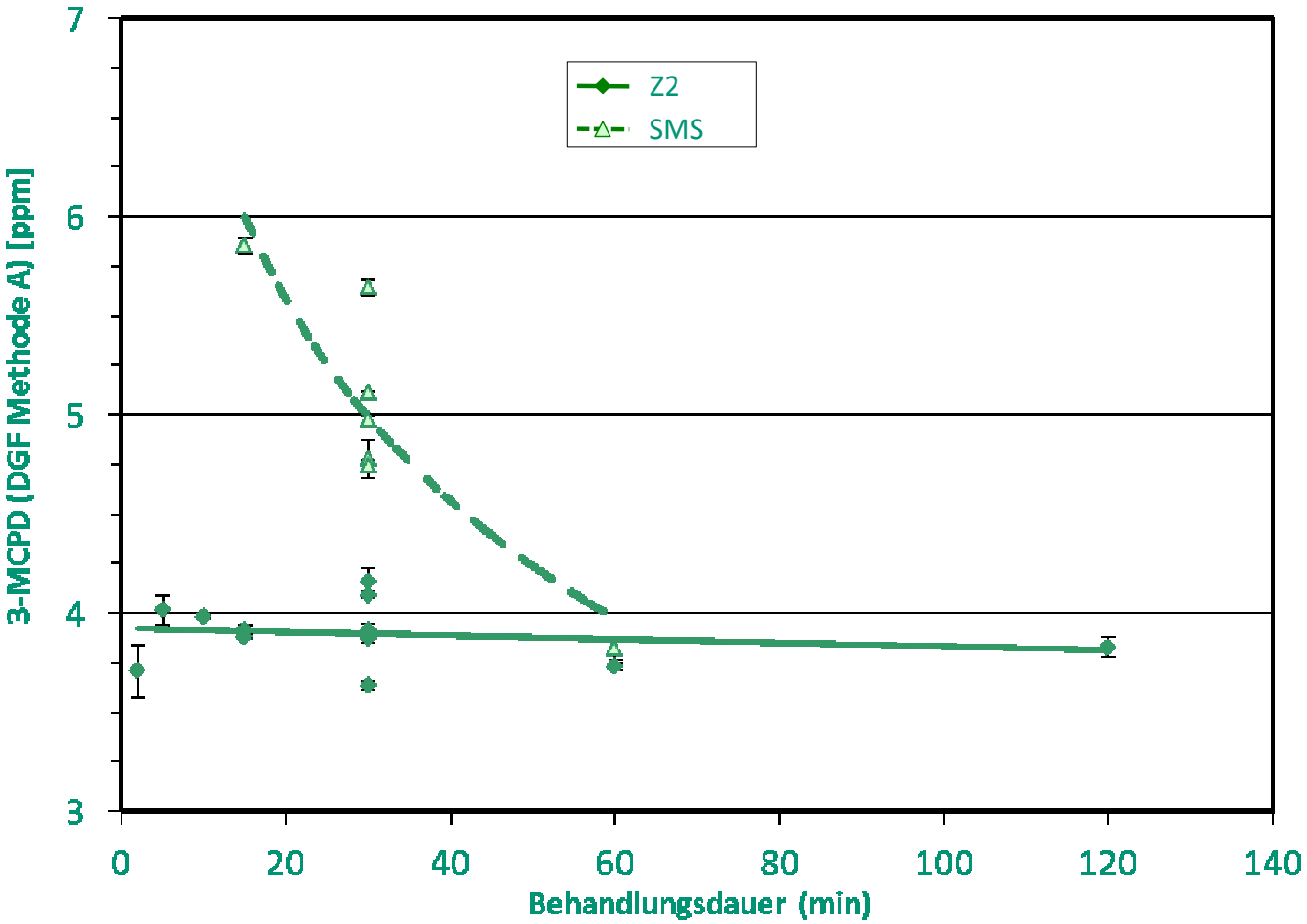
Temperature



Amount of adsorption media

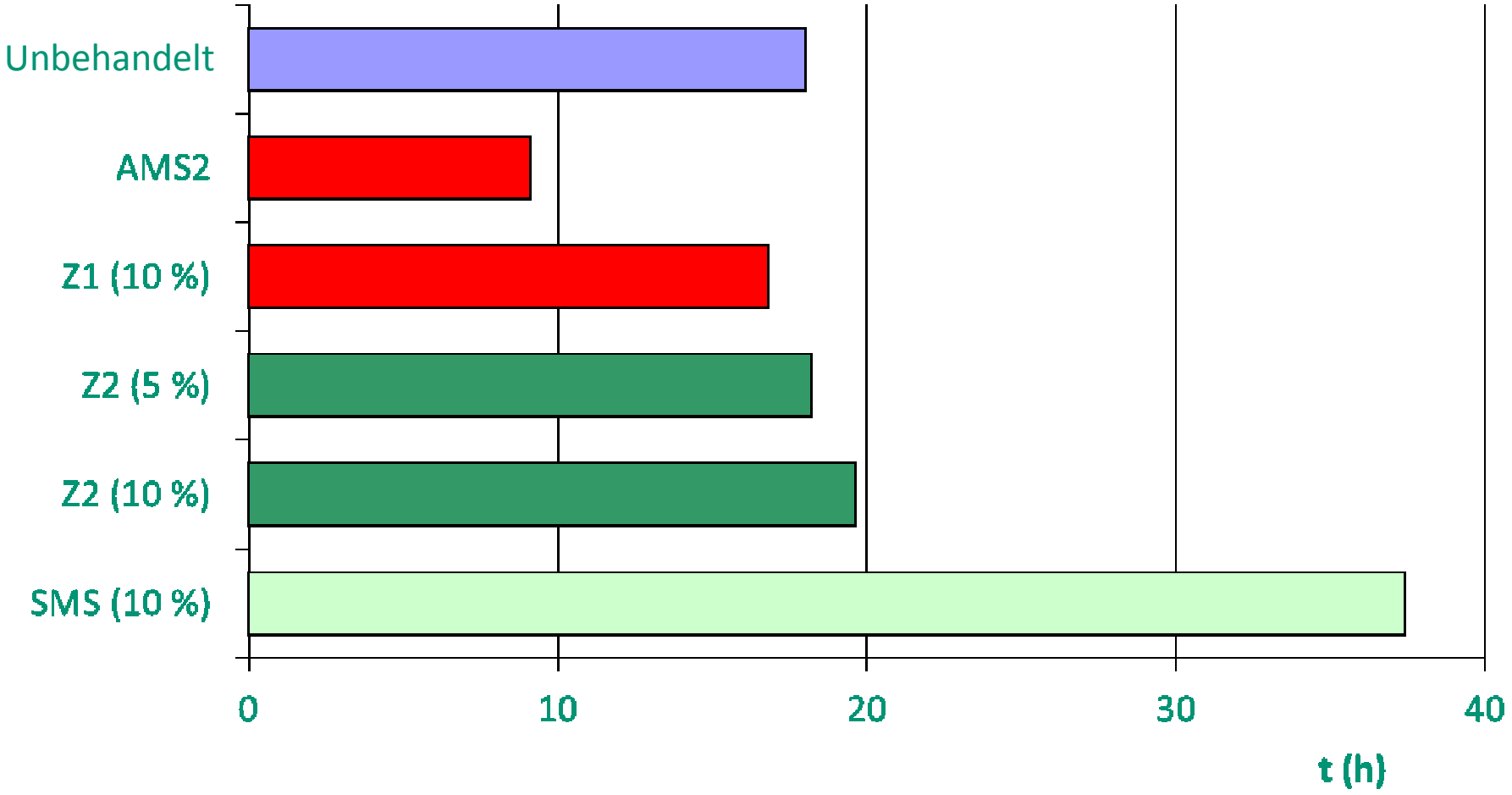


Treatment time



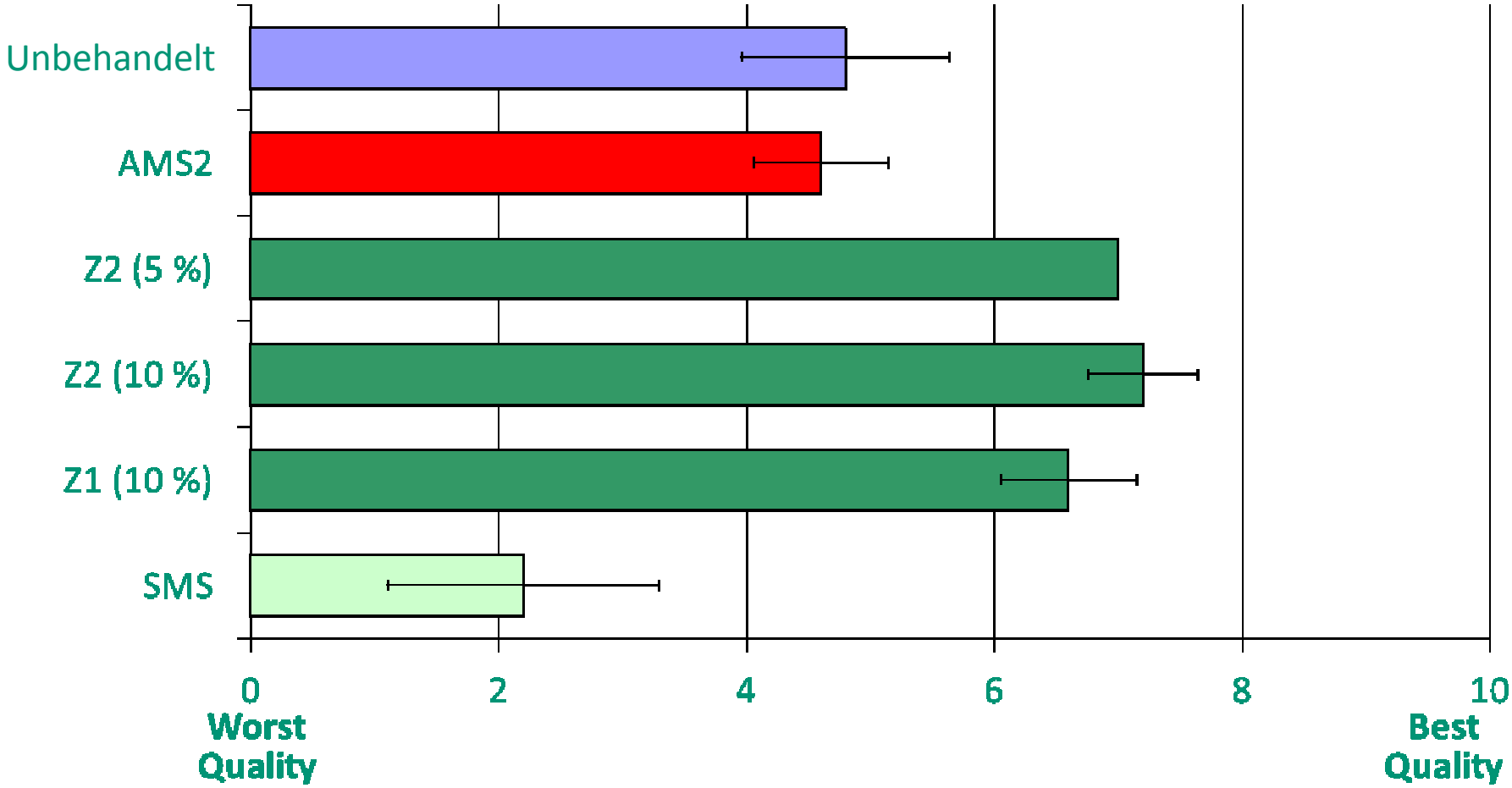
Oxidation stability

- Ranzimat, 110 °C



Sensory evaluation

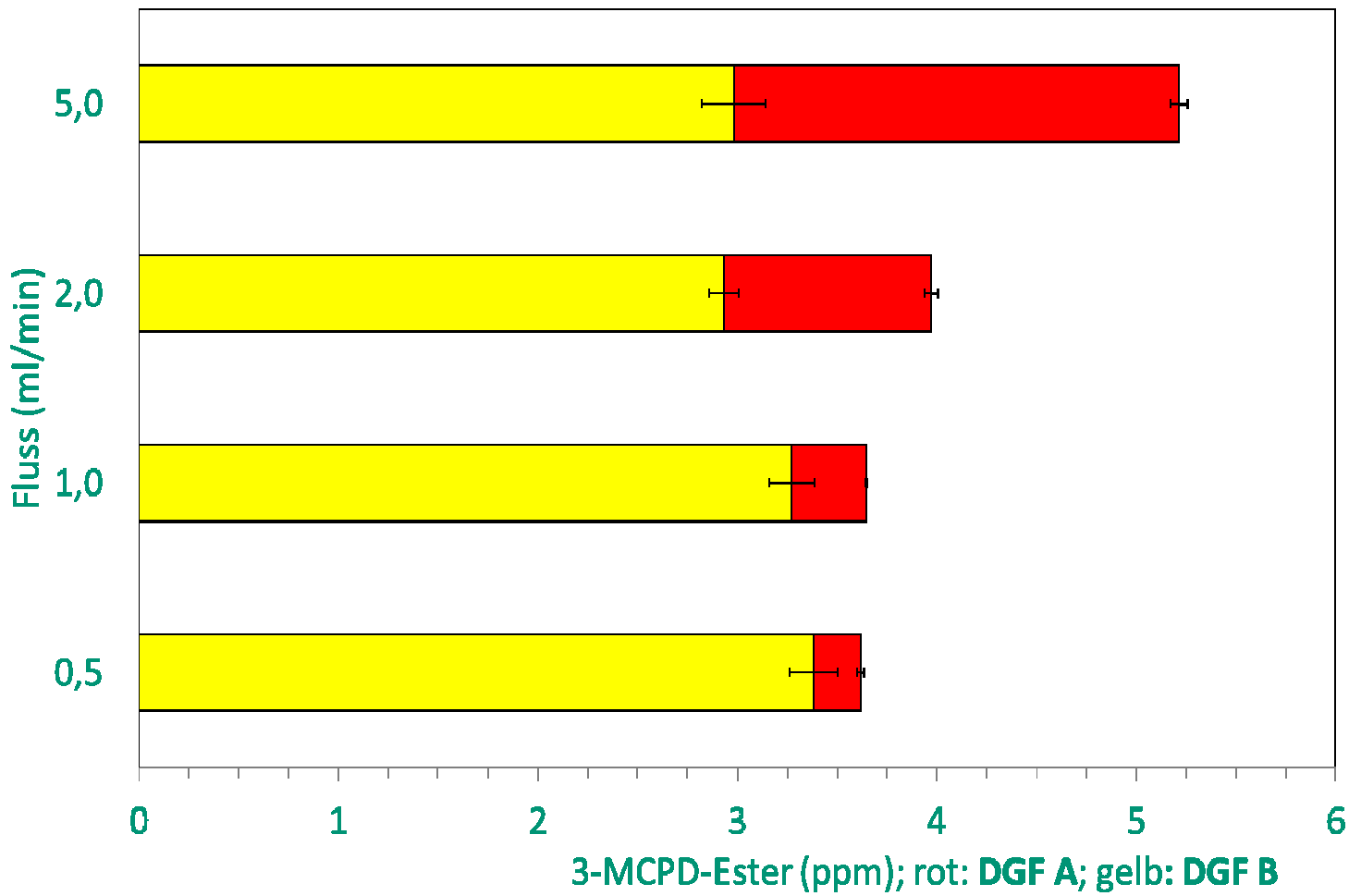
- Independent panel from oil industry, blind taste testing



Continuous reduction

- Batch procedure has drawbacks
- Not possible for industrial scale
  - To much adsorption material (min. 5 %)
  - Volume of stirrer vessel
  - Separation (centrifugation? filtration?)
- Development of a continuous
- „bypass “ of oil at adsorption media
- Flow rates inversely proportional to contact duration
- Also possible for pilot plant scale

3-MCPD fatty acid esters (DGF A + B)



Conclusions

- Two successful substances (Z2, SMS) for removal were identified
- Removal of 3-MCPD forming components, not of the 3-MCPD fatty acid esters
- Temperatures > 80 °C do not lead to better removal during adsorption
- A minimum of 5 % of adsorption media seems to be required for sufficient reduction in batch processing
- Z2 reduces after very short treatment time totally
- Oxidation stability of treated oils remains constant (Z2) or is even improved (SMS)
- Sensory damage is found after treatment with SMS, whereas Z2 improves sensory properties
- Z2 is able to reduce 3-MCPD-forming substances in a continuous procedure
- Mechanism of reduction still under investigation