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FAST QUANTITATIVE DETECTION OF MICROPLASTICS USING TED-GC/MS, AN INNOVATIVE THERMOANALYTICAL METHOD

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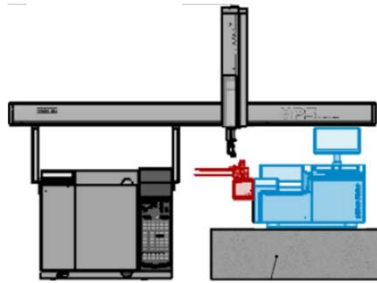


AGENDA

> Motivation



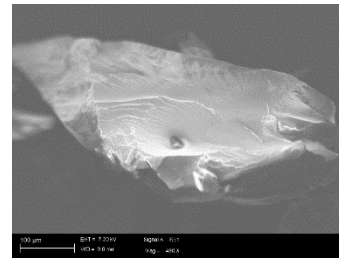
> TED-GC/MS



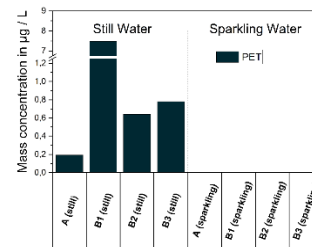
> Reference Material



What's a  BAM?



> Microplastic

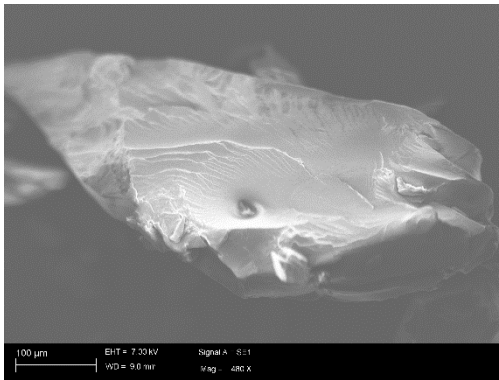


> Selected results

Summary <



Microplastic (MP)



Single particle



WWTP effluent
(concentrate from 1 m³)

Expected amount of MP in 1 m³



- Microplastic:
Main compound: synthetic polymer,
Particle size: 1-1.000 μm [ISO/TC 21960]
- Analytical challenge:
Few MP beside majority of natural particles
Volatility, solubility

Working principle TED-GC/MS

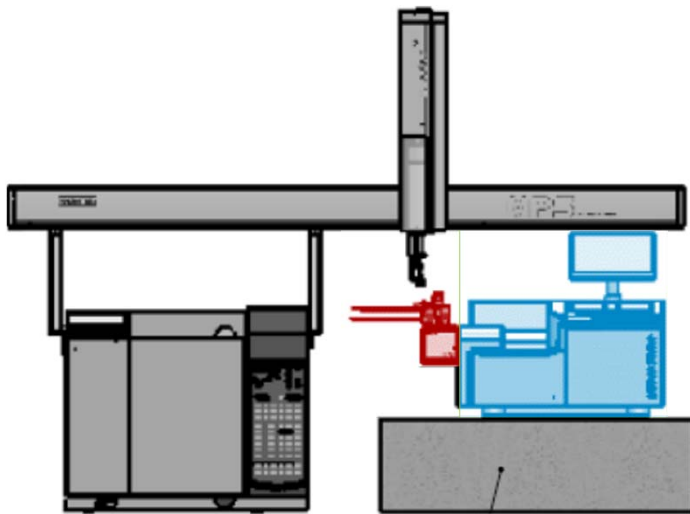


TED-GC/MS



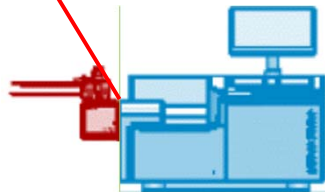
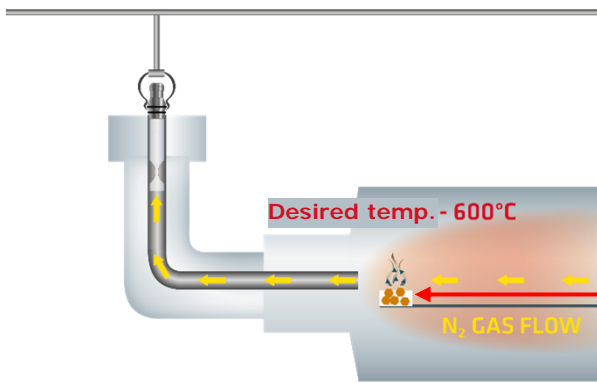
Thermo Extraktion Desorption-Gas Chromatography-Mass Spectrometry
TED-GC/MS

- > Fully automated method in 2 steps
- > 2,4 h/measurement
- > Main application:
MP in environmental samples
- > Only marginal sample preparation required
(most of the time)



Working principle

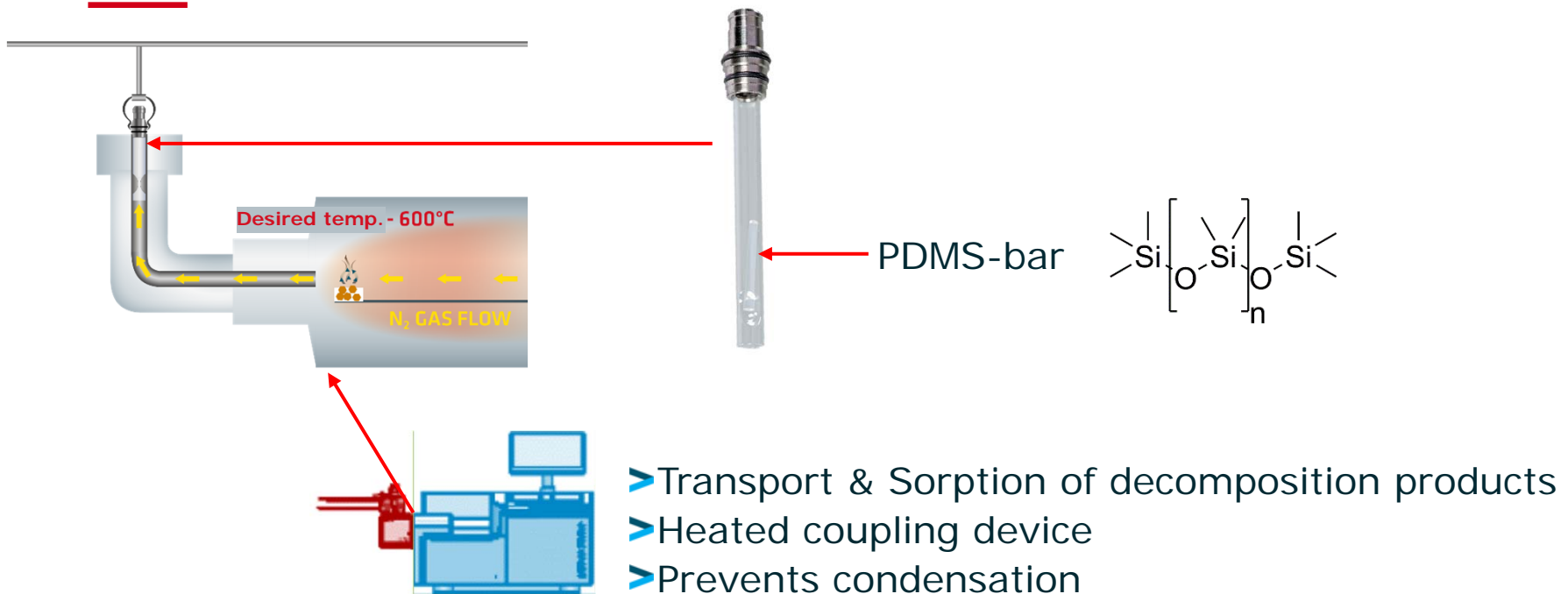
-1st step: Thermo Extraction



- Generation & transport of decomposition products
- 0-700 mg (solid) sample
- 25-600 °C
- N₂-gas flow

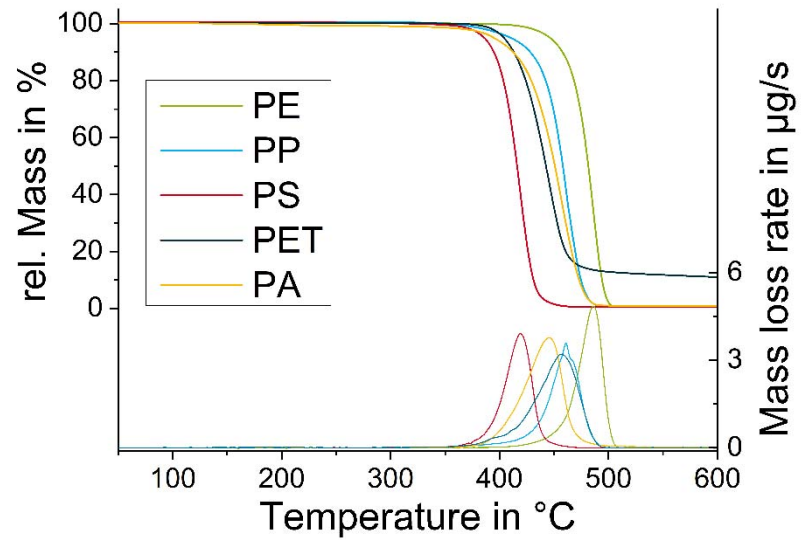
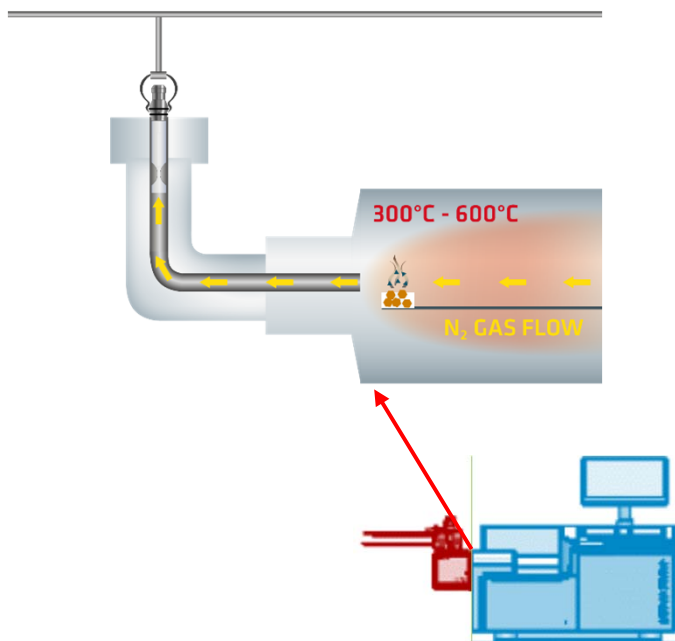
Working principle

-1st step: Thermo Extraction



Working principle

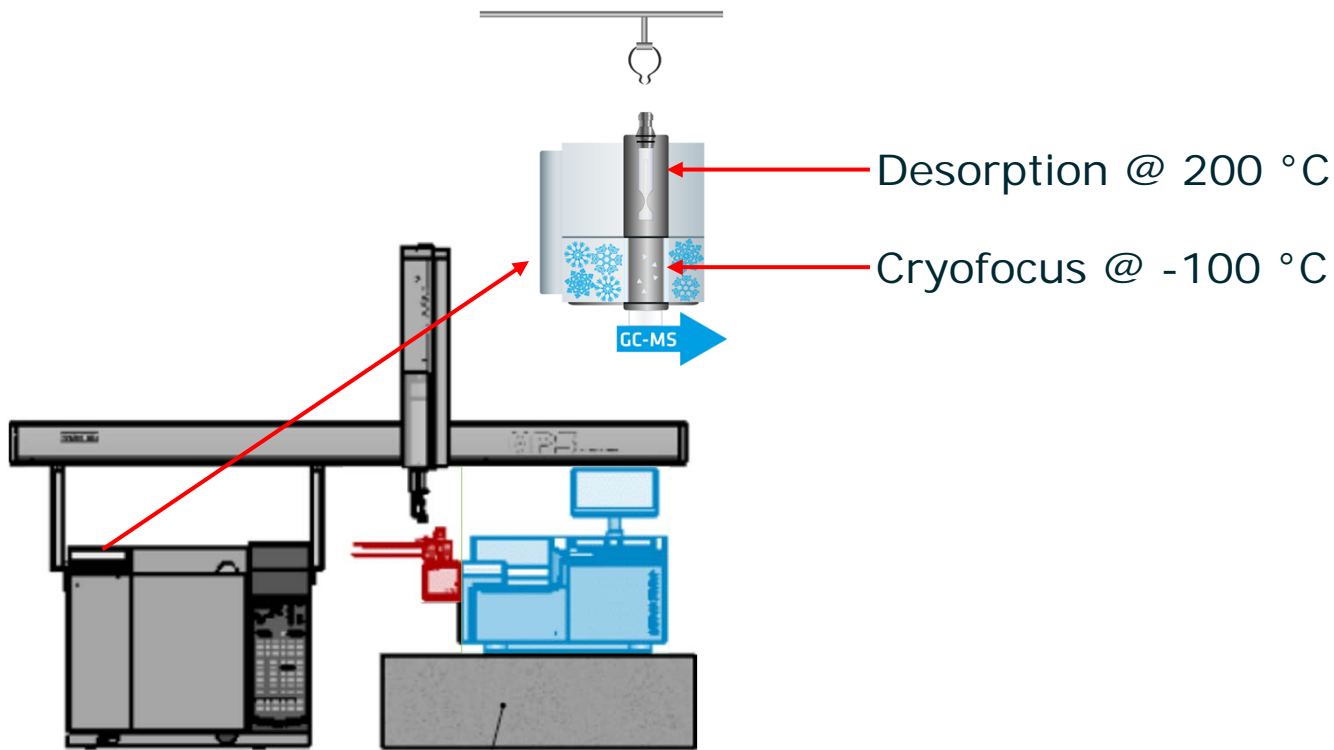
-1st step: Thermo Extraction



- Variable temperature range
- Matrix components can be excluded

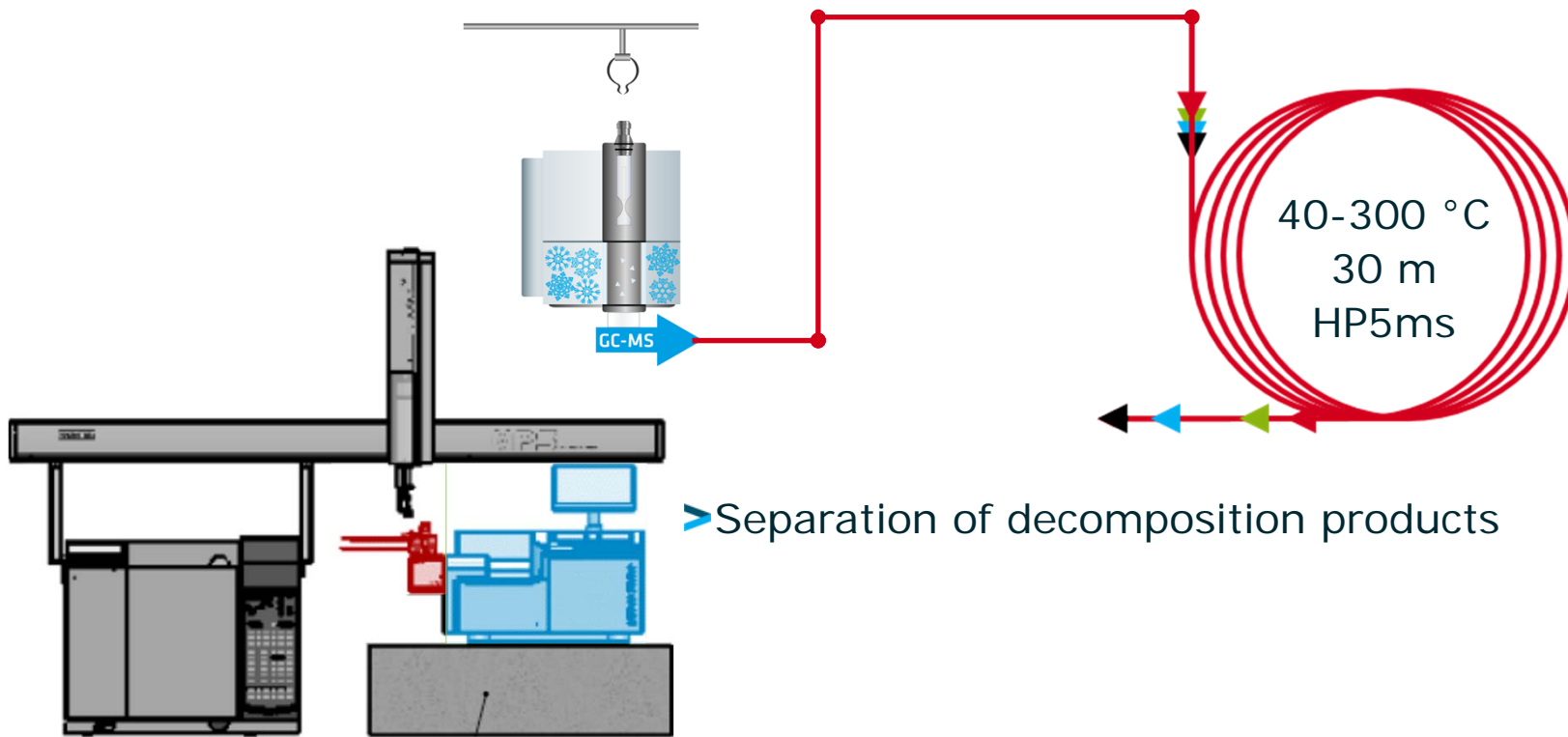
Working principle

-2st step: Desorption-GC/MS



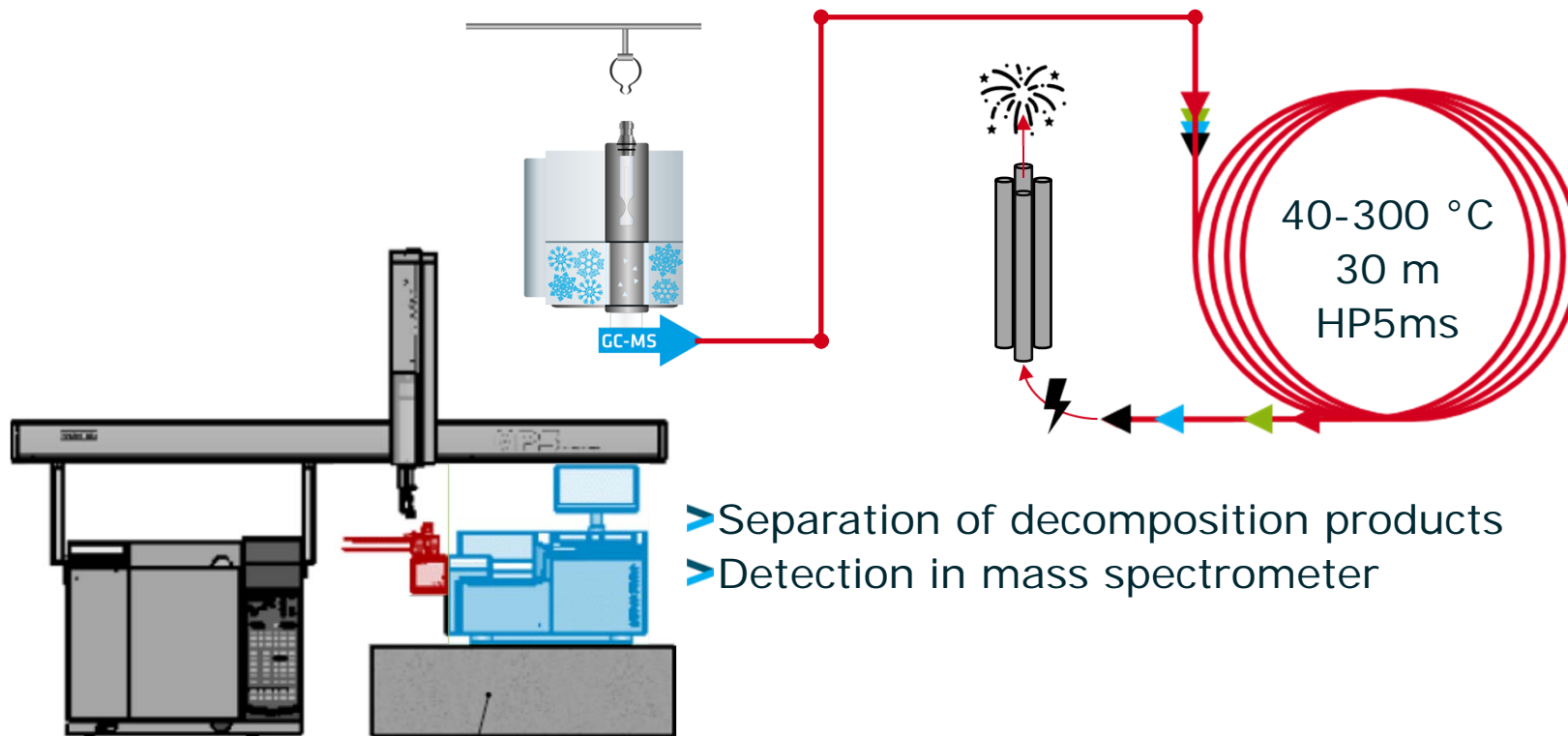
Working principle

-2st step: Desorption-GC/MS



Working principle

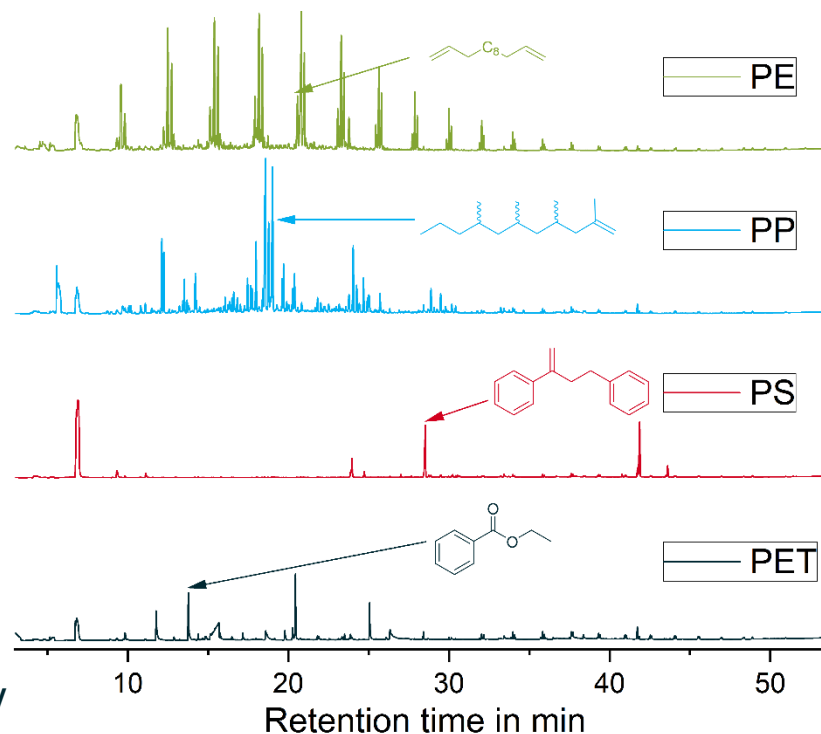
-2st step: Desorption-GC/MS



Working principle -Identification & LoD



- Specific decomposition products
- Specific ion fragments
- chromatographic patterns



➤ LoDs depend on decomposition chemistry

	PE	PP	PS	PET	PA6	SBR	NR	PMMA	PLA	PBAT
LoD in µg	2.2	0.14	0.08	0.24	0.24	0.06	0.03	0.12	0.39	0.42

Working principle -Quantification

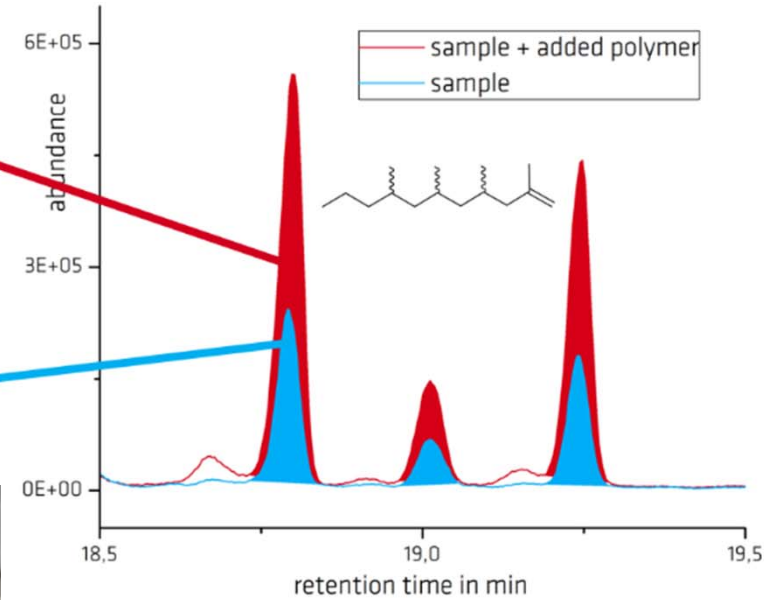
- Standard addition
BAM-reference materials available, R_f partly transferable



$$\Delta A \sim m_{\text{dot}}$$

$\updownarrow V_{\text{gl}}$

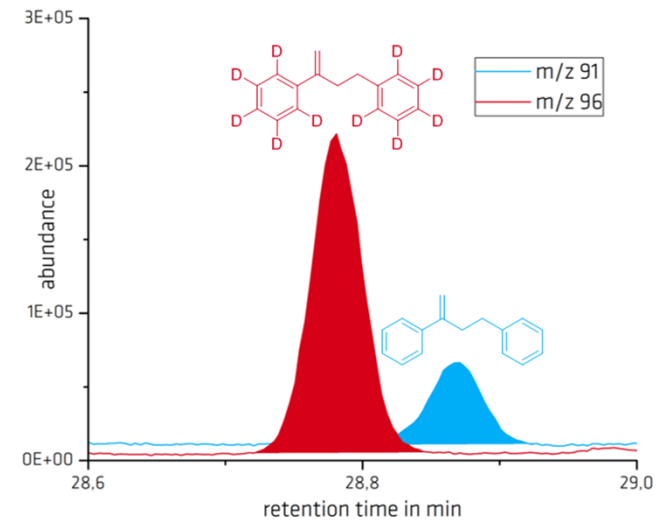
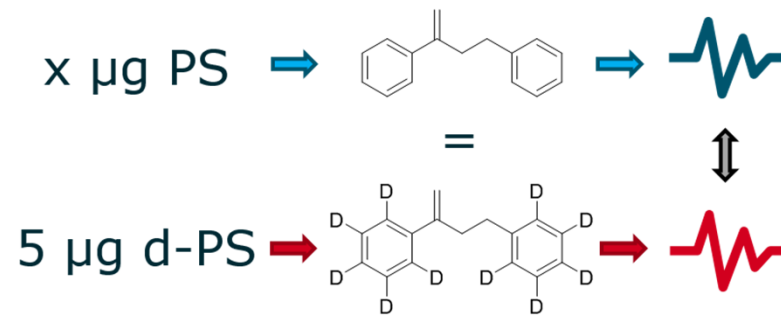
$$A_0 \sim m_0$$



Working principle -Quantification

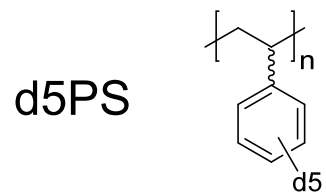


- Internal standard
- Stable isotope labeled polymers
- D-PS, $^{13}\text{C}_6$ -PS
- Limited to few available polymers



Working principle

-Stable isotope labeled polymer



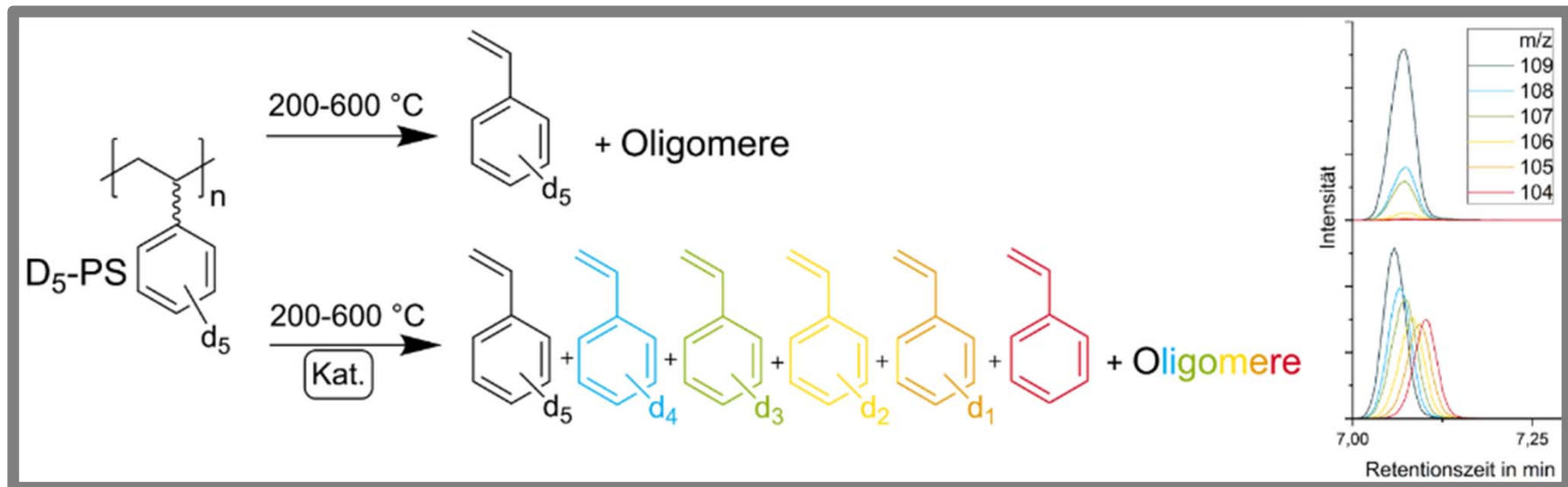
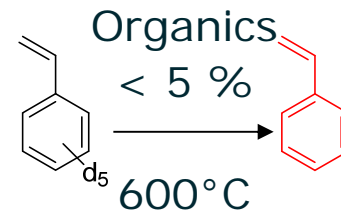
- 250 US-\$/g
- 4 µg/run
- 250.000 runs
- 0,1 US-cent/run
- easy to solve & dose



Working principle

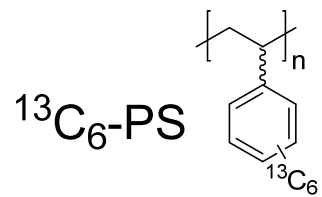
-Stable(?!) isotope labeled polymer

> H/D-exchange
w/ certain samples



Working principle

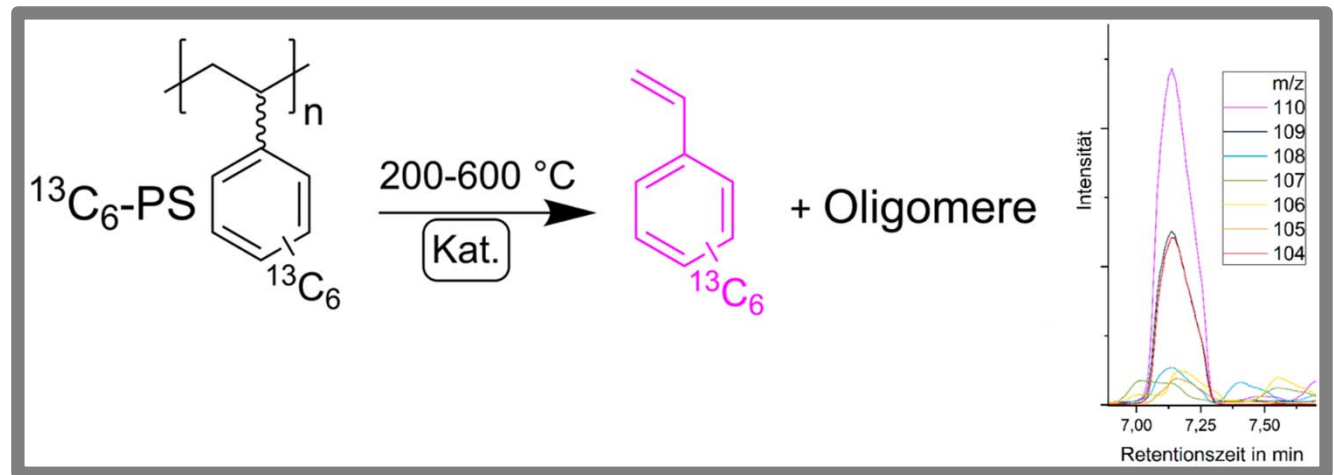
-Stable(?!) isotope labeled polymer



> 8600 €/g

> 4 µg/run

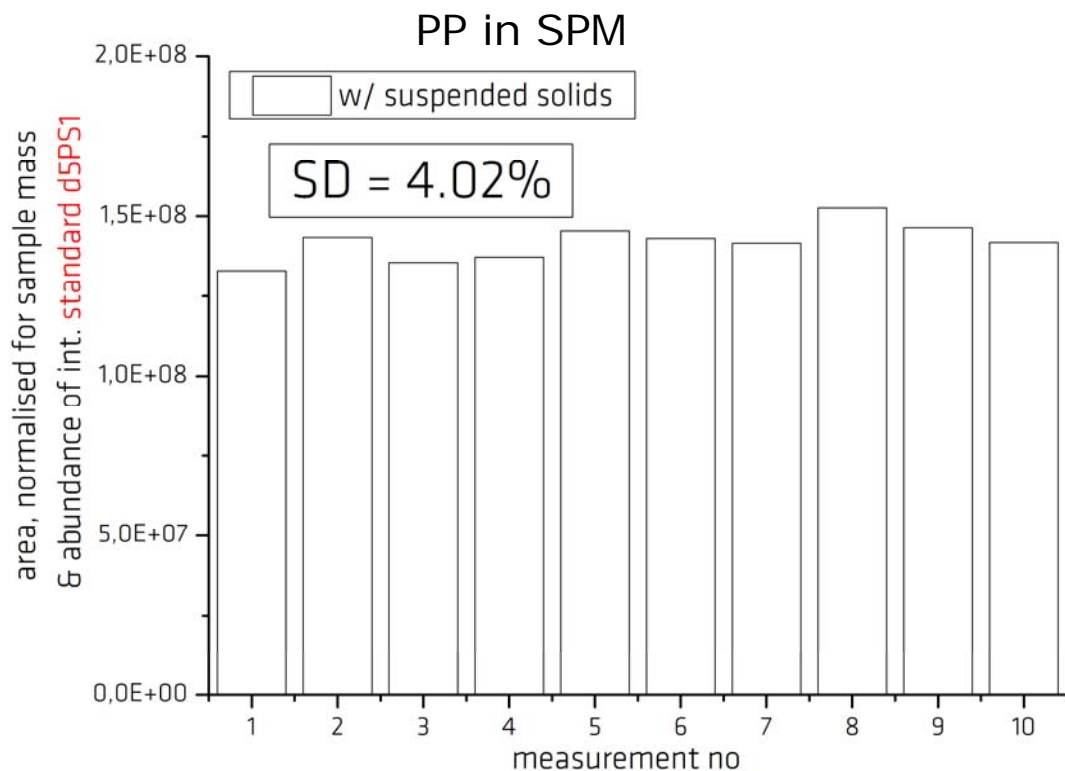
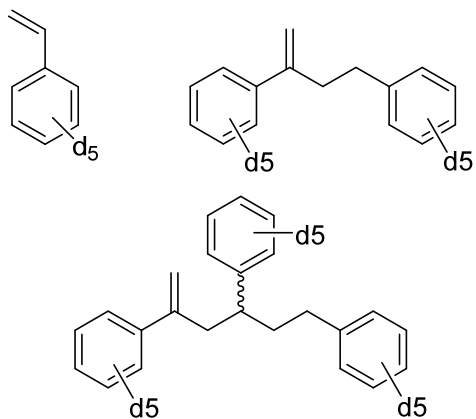
> 4 €-Cent/run
(solid phase 2€)



Working principle -Reproducibility



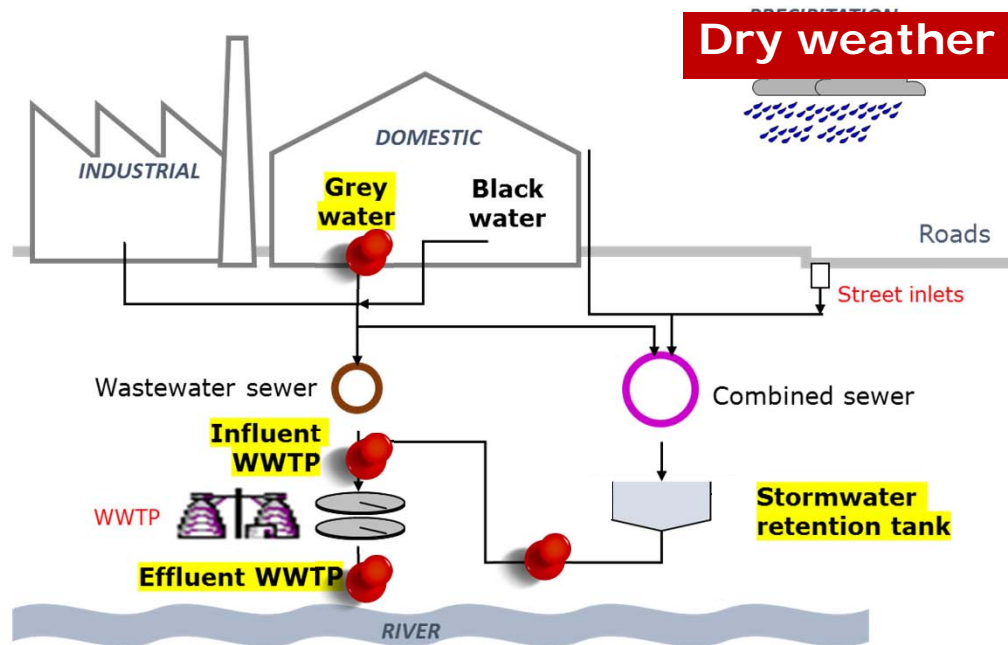
- Start: 31 % rSD
- New system: 30 % rSD
- + Int. Standard: 17 % rSD
- w/ Matrix: 13 % rSD
- > New dec.prod.: 4 % rSD
- Solid phase mass: 3 % rSD*



Selected results



Urban Sewage System



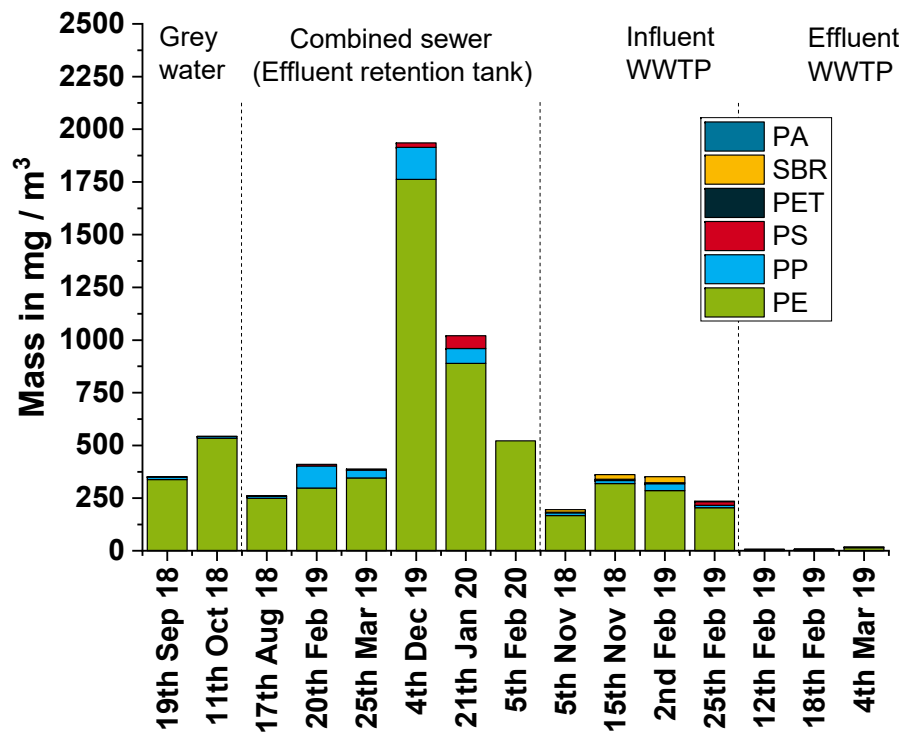
● Sampling location

- > Grey water
- > Stormwater retention tank (dry weather flow)
- > Influent waste water treatment plant (WWTP)
- > Effluent WWTP

● Sampling method

- > Fractional filtration
- > Mesh sizes of sieves: 500, 100, 50 and 5 μm
- > Filtered volumes: 18 – 1000L

Urban Sewage System



- > Mainly PE
- > Additional PP, PS, SBR
- > Mass: Influent WWTP >> effluent WWTP
- > Highest masses found in combined sewer
- > Daily high fluctuations
- > Retention WWTP ~ 96%

Beverage

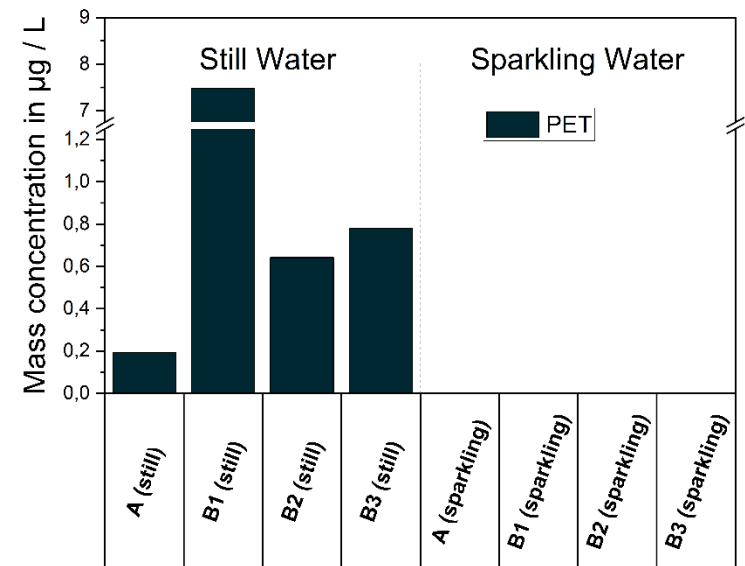


Measuring filter crucible for TED-GC/MS

(DE 10 2019 135 311.4)



- Filter and measuring crucible in one
- Temperature stable up to 600 °C, reusable
- For water with very low masses concentrations
- Reduced mass losses and contamination



- PET only in still water

Washing machine



	Men's shirt	T-shirt
Fibres	65% CO, 35% PET	55% CO, 45% PA
Fabric construction	Woven	Knitwear
Colour	Dark grey	Dark blue
Sizes	39,5/41/42/ 43/44,5	M, L, XL, XXL

> Realistic laundry setup

- + Standard dirt
- + Standard washing powder

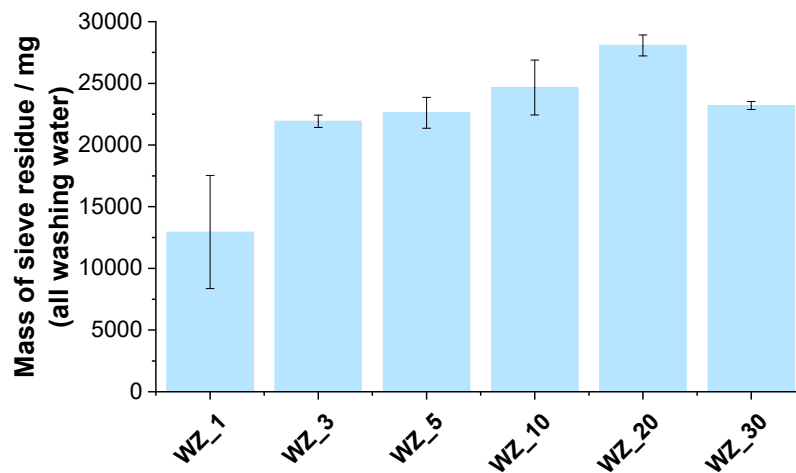


- Washing parameter:
- > Easy care
 - > Temperature: 40°C
 - > Max. Speed: 1200 rpm
 - > Load quantity: 4 kg

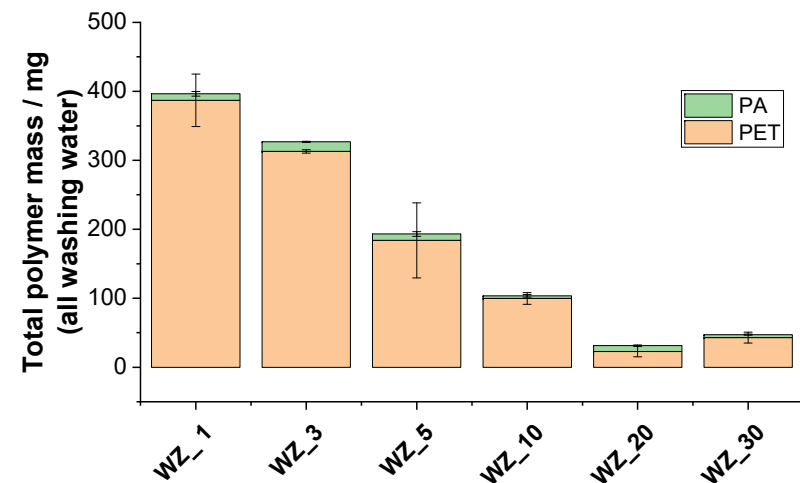
Washing machine



Sieve residue



Polymer mass

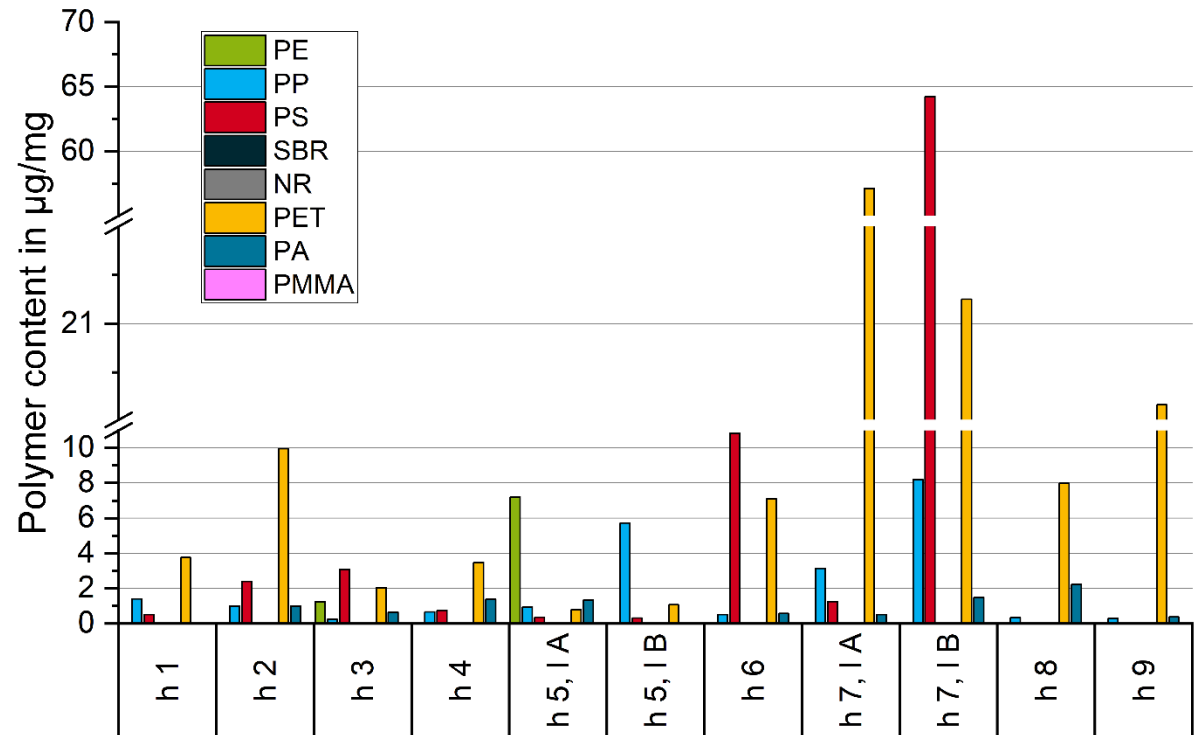


- Synthetic polymer fiber release regarding sieve residue is 0.7%.
- Sieve residue mainly consist of cotton fibers as well as residues of dirt and washing powder.
- Polymer fiber release from knitwear (endless thread of PA) is very low compared to fabric (PET).

Dust



- Samples from BAM employee households
- Indoor dust dominated by fiber polymers
PET, PA, PP



Reference Material



MP Reference Material



Application:

- > Method validation
- > Risk assessment

Properties:

- > Polymer type
- > Particle size
- > Aged/Non-aged
- > Shape



Challenges:

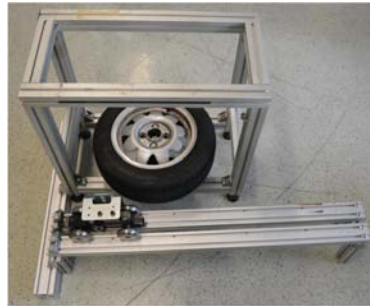
- > Diverse requirements, e.g. particle size from 1 mm to 1 nm
- > Should be applicable to diff. non-harmonized methods
- > Homogeneous suspension
- > Very low particle number/mass needed

Production of (close-to-realistic) MP reference material

Weathering
w/ UV/T



Mechanic abrasion
of tire tread



Granulate/Foils



Fragmentation of the material
by cryomilling into particles



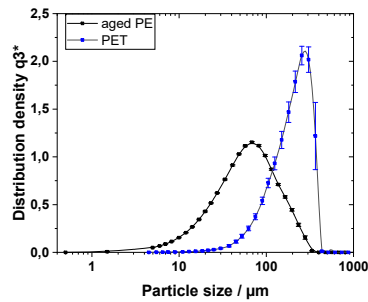
Characterization of the reference material



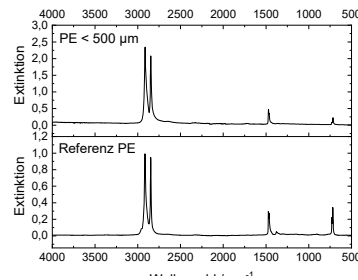
Non-aged polymers	Artificially aged polymers
PE (LD-PE) (< 500 μm)	PE (HD-PE) (< 500 μm)
PP (< 500 μm)	PS (< 500 μm)
PS (< 500 μm)	PA (< 500 μm)
PET (< 500 μm), PET (1-200 μm)	



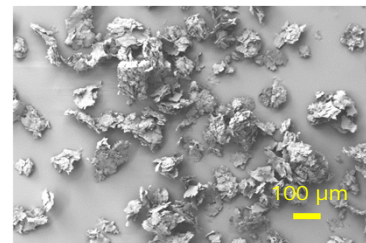
Particle size distribution



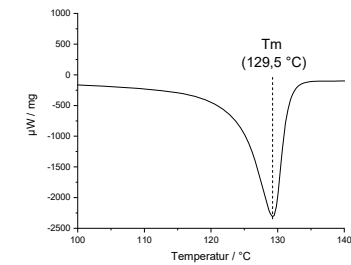
FTIR



SEM



DSC



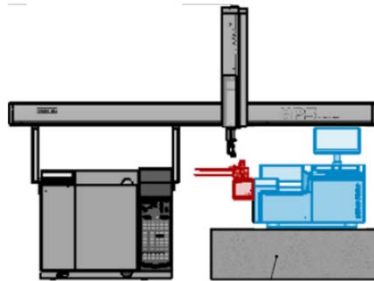
Summary



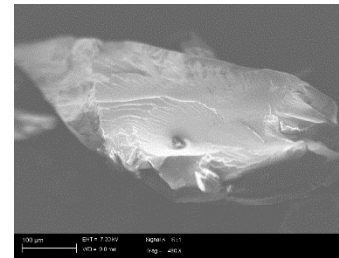
> Motivation



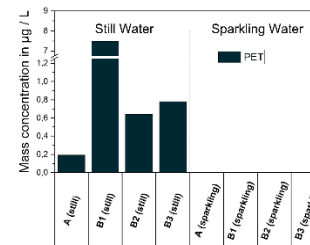
> TED-GC/MS



> Reference Material



> Microplastic



> Selected results

Acknowledgments

Bundesanstalt für Materialforschung und –prüfung (BAM)

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**Thank you for
your attention.**



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Volker Wachtendorf
Jana Falkenhagen
Heinz Sturm**

**Umwelt
Bundesamt**



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