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Determining microplastic content using a database software approach for identification:

A (quick) comparison of two different pyrolysis-GC/MS techniques

Kurt Thaxton
Product Manager, TD and Pyrolysis

Da Vinci
LABORATORY SOLUTIONS

What is a microplastic?

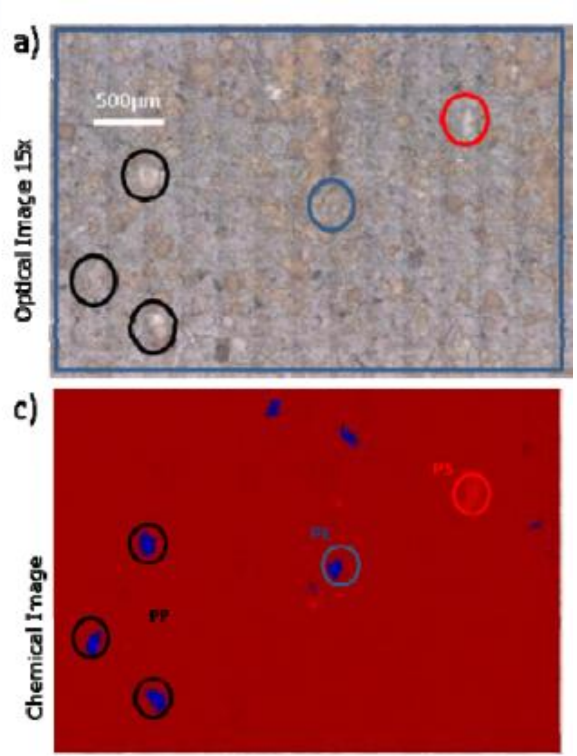
- No exact definition
- Regarding ISO/TR 21960: 1 µm to 1 mm
- Classification: Primary microplastics and secondary microplastics
- Including various polymers: thermoplastics, thermosets, but also elastomers

Analytical methods?

What information do we need ?

- Particle number
- Mass concentration
- Polymer types
- Particle size
- Morphology
- State of degradation?

Spectroscopic Analysis - Imaging (µ-FTIR or µ-Raman)



A.M. Elert, et al. Environmental Pollution 231 (2017) 1256

- Identification of plastic types possible
- Non-destructive
- Number of particles can be determined

But...

- Time-consuming with regard to measurement and Sample preparation
- Maximum semi-quantitative

Overview of techniques for microplastic analysis

Taken from ISO CD 24187

	Spectroscopic							Thermoanalytical			Chemical		
	µ Raman	µ FTIR (trans)	FPA FTIR (trans)	µ ATR-FTIR	ATR-FTIR / Raman	NIR	Hyper-spectral Imaging	Py-GC-MS	TED-GC-MS	DSC	SEC	LC-MS/MS	ICP-MS
Specimen mass	ng - µg	ng - µg	ng - µg	mg	mg	mg	mg	µg	mg	mg	mg	mg	mg
Measurable particles	10^3 -10^5	10^3 -10^5	10^3 -10^5	1	1	Un-defined	10^2-10^3	1	Un-defined	Un-defined	Un-defined	Un-defined	Un-defined
Measuring time	h - d	h - d	h -d	min	min	min	min	h	h	h	h	h	min
Detection level	1 - 10 µm	20 µm	20 µm	25 - 50 µm	500 µm	1 %	300 µm	<< 1 - 0,5 µg	0,5 – 2,5 µg			8-50 µg / kg	ppm
Sample preparation	On filter	On special filter	On special filter	Isolated particles	Isolated particles	On filter	On filter	Isolated particles	Filtrate or with filter	Filtrate	Filtrate	Filtrate	Filtrate
Type of Polymer	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Only PE, PP	Only PS, PET	Only PET, PC	Only tyre
State of degradation	Surface Oxid.	No	No	Surface Oxid.	Surface Oxid.	No	No	Oxid. Products	No	Mol. weight	Mol. weight	No	No
Particle size, number, morphology	Yes	Yes	Yes	Yes	Yes	No	Yes	No	No	No	No	No	No
Mass balances	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes

Pyrolysis-GC/MS – Close, but....

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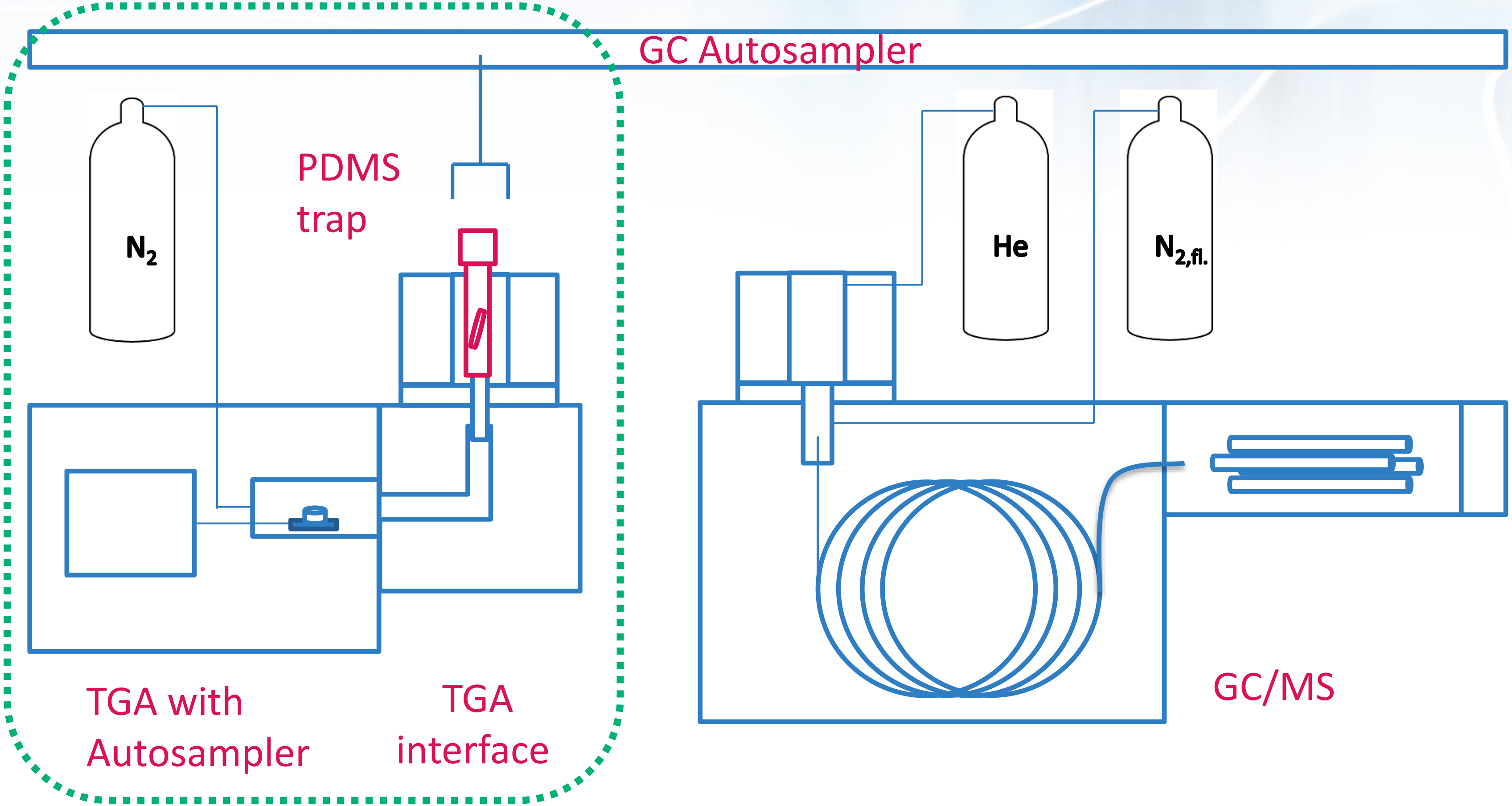
- Decomposition does yield markers unique to the polymer that cannot come from the overall sample (unlike phthalates, BHT, etc.)
- But samples are small in mass (0.1 - 10 mg)
- But samples small in size (≤ 1 mm^2)
- For filters, several punches must be taken

GERSTEL Pyrolyzer

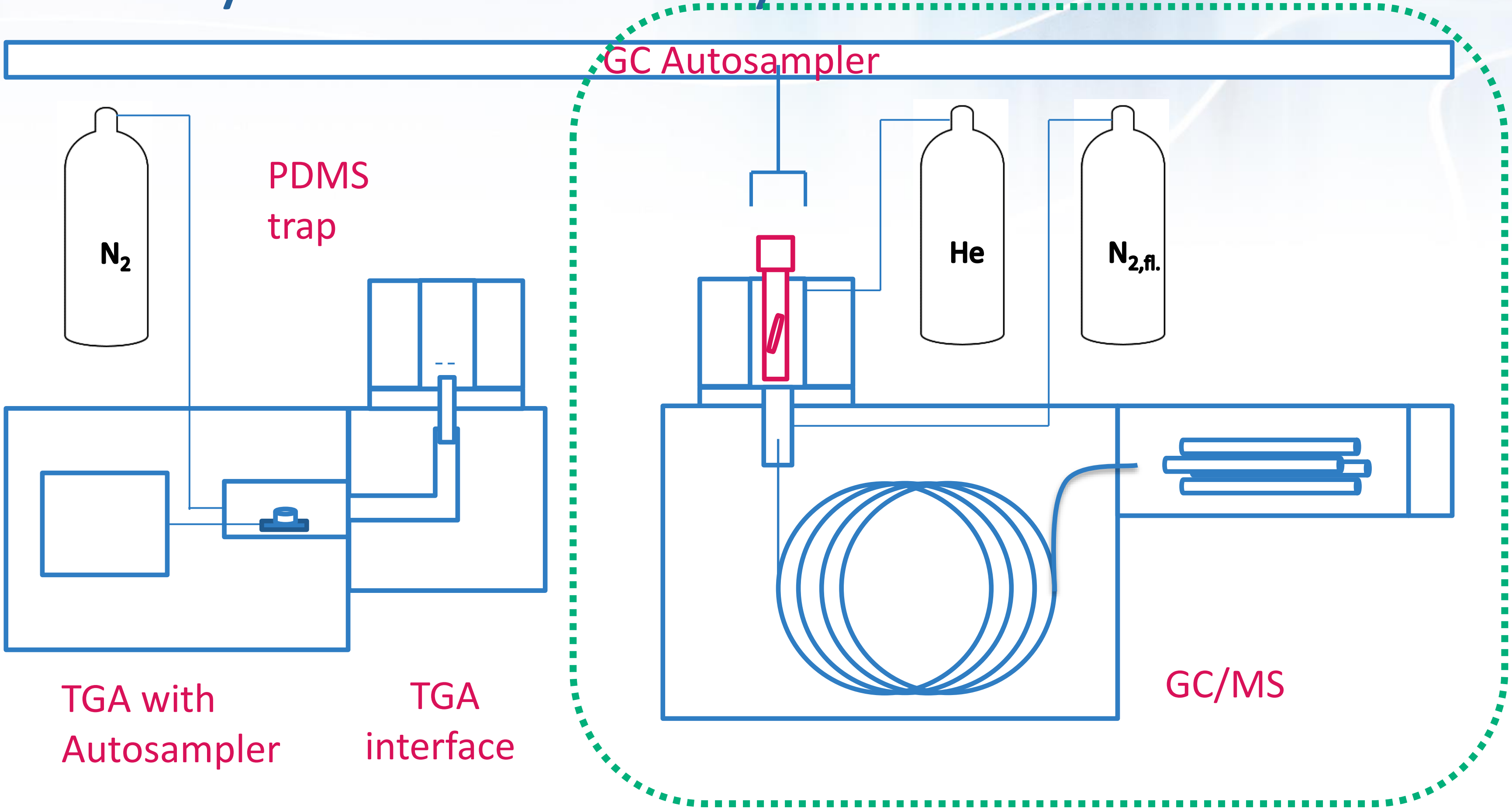
Many samples are needed for a representative result

Getting the most from one sample: Automated TED-GC-MS

TED: Decompose sample in TGA…



…analyze the markers by GCMS



What is Thermal Extraction/Desorption-GCMS?

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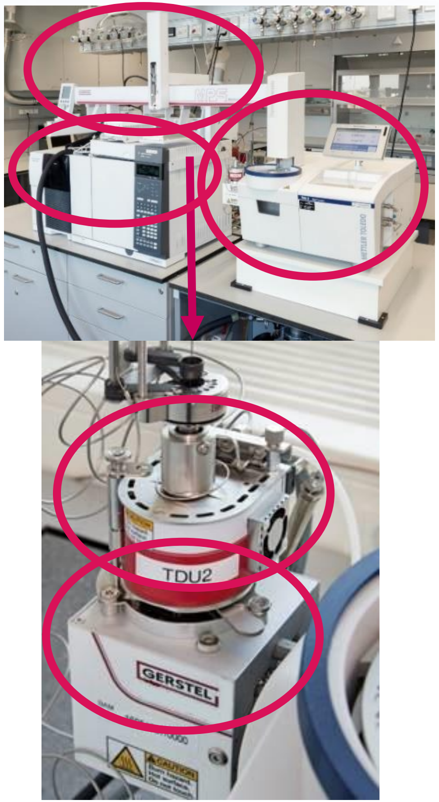


- Mettler Toledo TGA 2 Thermal Gravimetric Analyzer with A/S
- GERSTEL TED - TGA interface for TED (co-developed with BAM – the German Federal Office for Material Research and Testing)
- A GERSTEL TDU 2 / TD 3.5^+ that is placed on the TED – TGA interface
- GERSTEL Twisters (not shown)
- GERSTEL TDU 2 or TD 3.5^+ Thermal Desorber with Robotic A/S
- Agilent 8890 / 5977B GC-MSD
- All together, a TED system is: a TGA, a TD attached to the TGA with a custom interface, a rail system, a GERSTEL TD system, and a GCMS.

Note: The “connection” between the GCMS and TGA through the Robotic rail system is not strictly required.

The TED-TGA and TD-GCMS can be operated separately, even in separate rooms. Connecting them together fully automates the process.

TED-GC-MS
1st step: Pyrolysis in TGA

Environmental sample:
Sediment, Soil, Sand, Filter
= Matrix + Microplastics

NOTE THE SIZE
Sample size up to 200 mg

TED-GC-MS

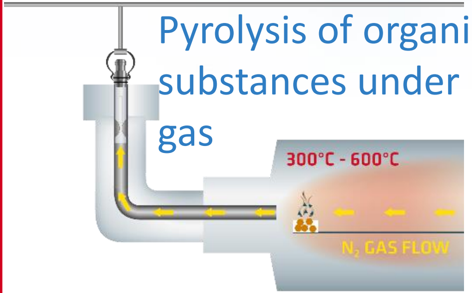
1st step: Pyrolysis in TGA

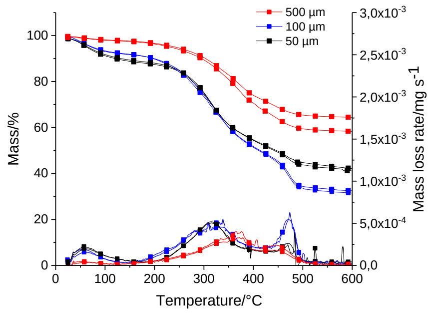
Environmental sample:
Sediment, Soil, Sand, Filter
= Matrix + Microplastics

NOTE THE SIZE

Sample size up to 200 mg

Pyrolysis of organic substances under inert gas





Thermogravimetric Analysis (TGA) System

TED-GC-MS

1st step: Pyrolysis in TGA

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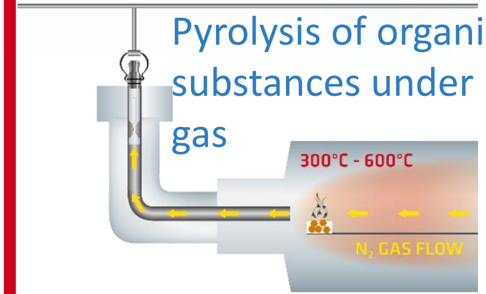
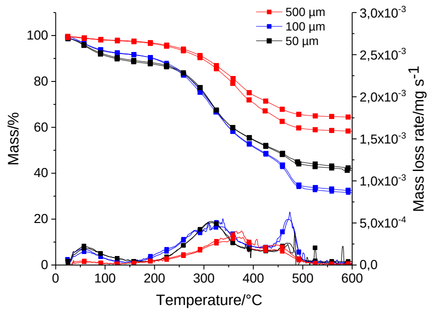
Environmental sample:
Sediment, Soil, Sand, Filter
= Matrix + Microplastics

<u>NOTE THE SIZE</u>

Sample size up to 200 mg



Pyrolysis of organic substances under inert gas



Thermogravimetric Analysis (TGA) System

Collection of pyrolysis products on Polydimethylsiloxane (PDMS) using a GERSTEL Twister

Alternate Sample Intro to TGA: Filter Crucibles

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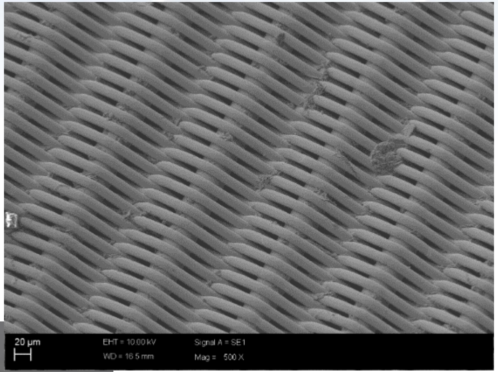
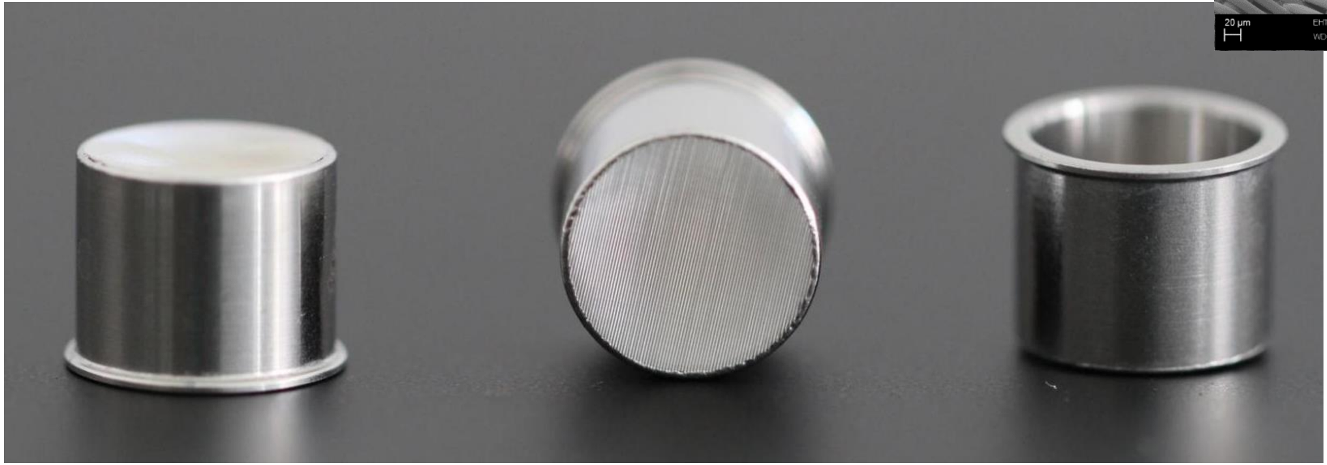
Material:
stainless steel, stable to 600°C, ~ 500 µl.

Use:
water media with low suspended solids (drinking water, etc).

Filters adapted to direct use in TED-GC/MS; no other filter media needed

mesh size 5-6 µm



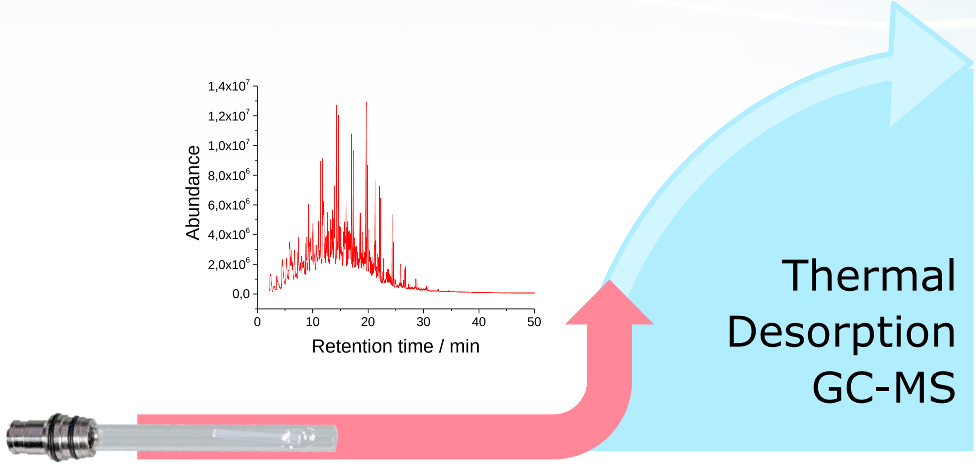


RUSEKU

GKD

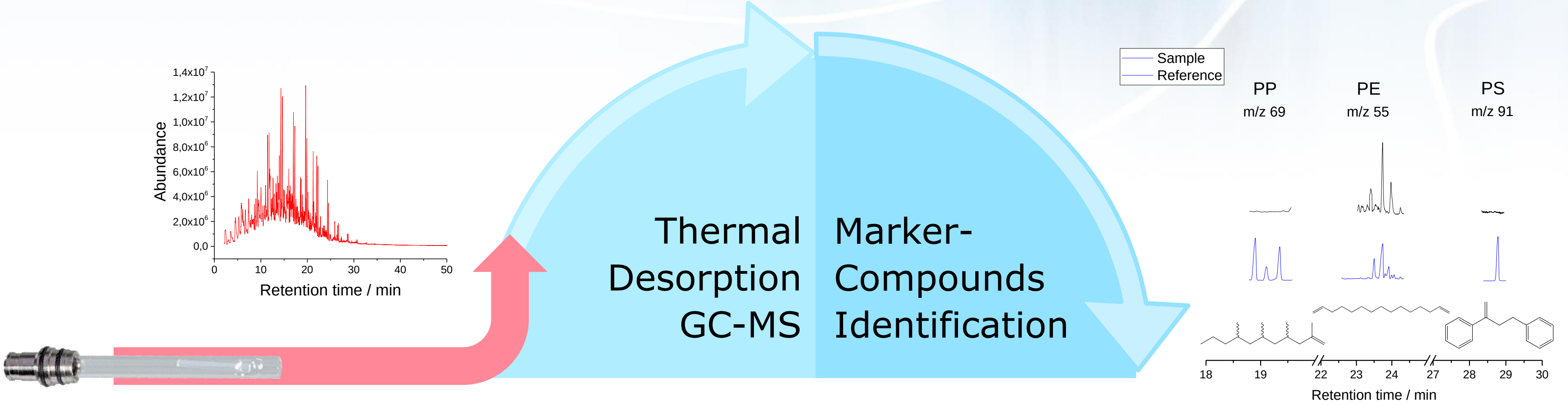
TED-GC-MS

2nd Step: analysis of the marker compounds



TED-GC-MS

2nd Step: analysis of the marker compounds



TED-GC-MS

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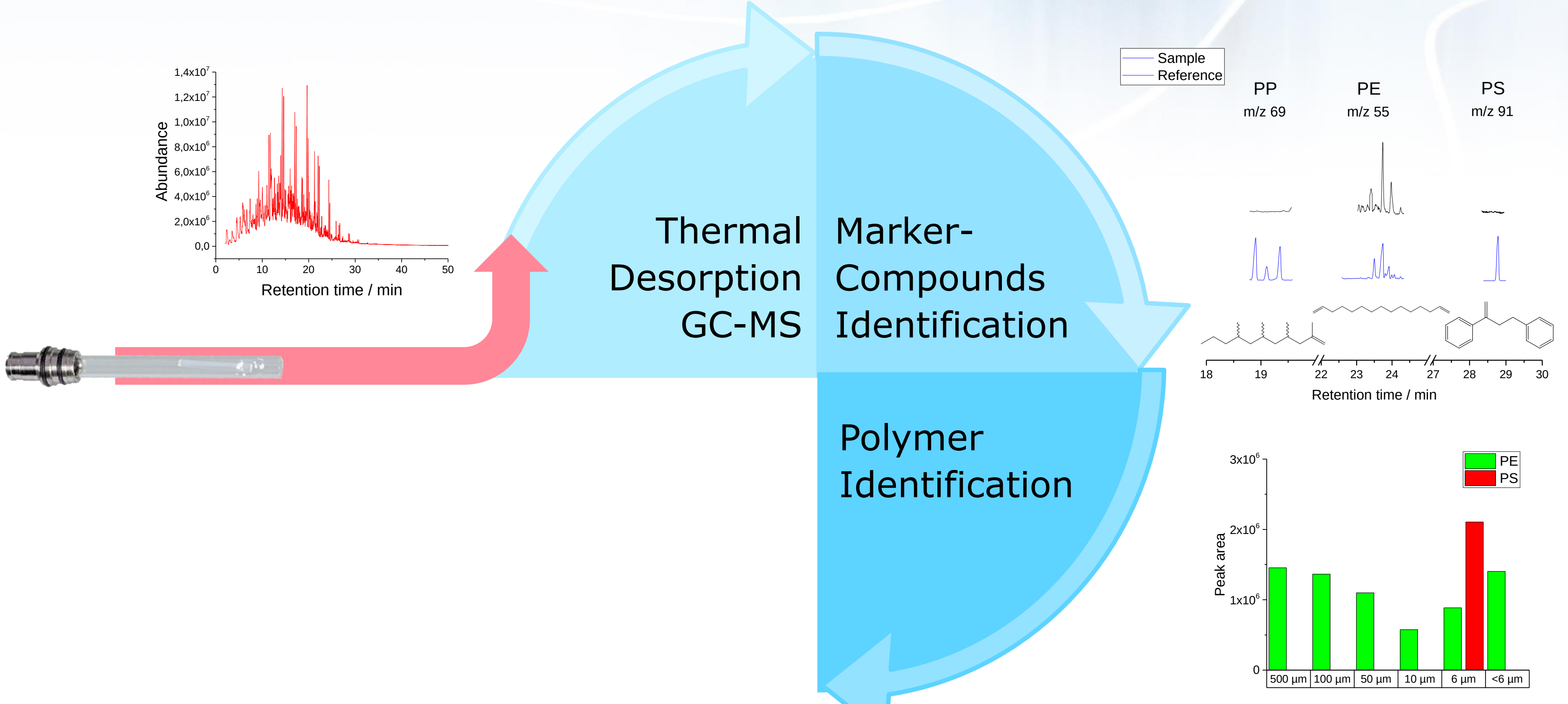
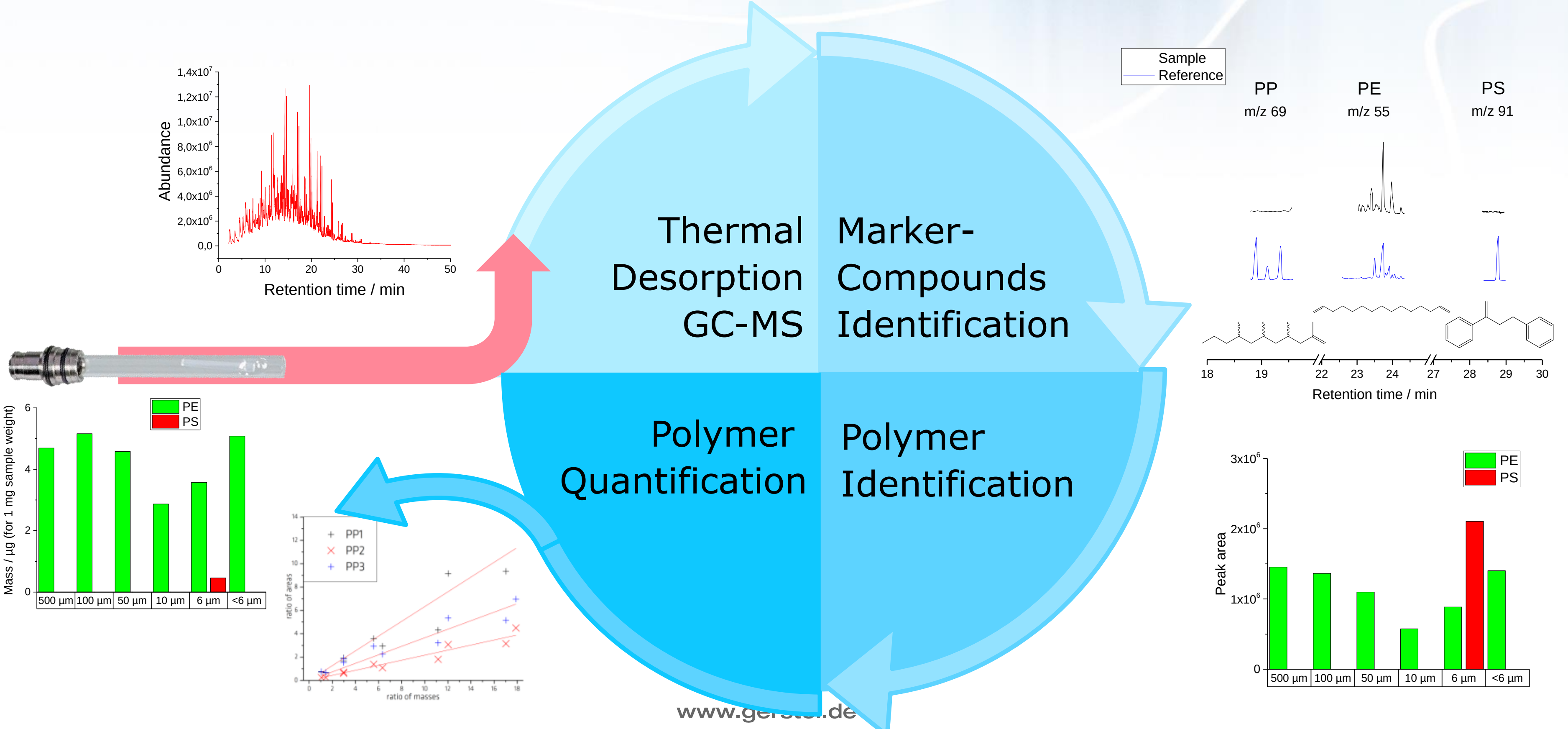
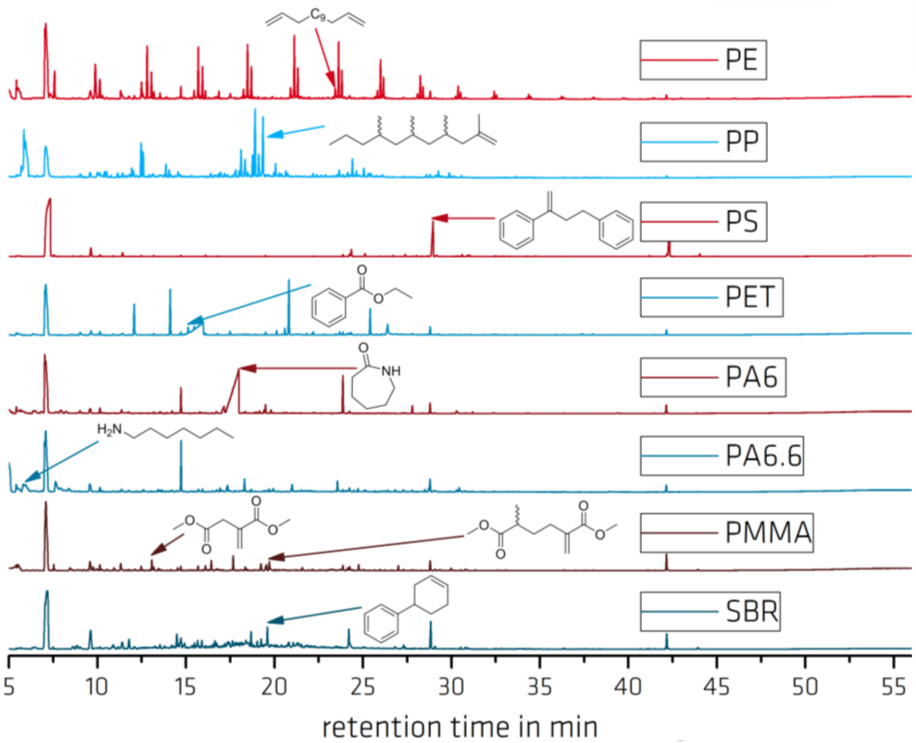


TED-GC-MS

2nd Step: analysis of the marker compounds

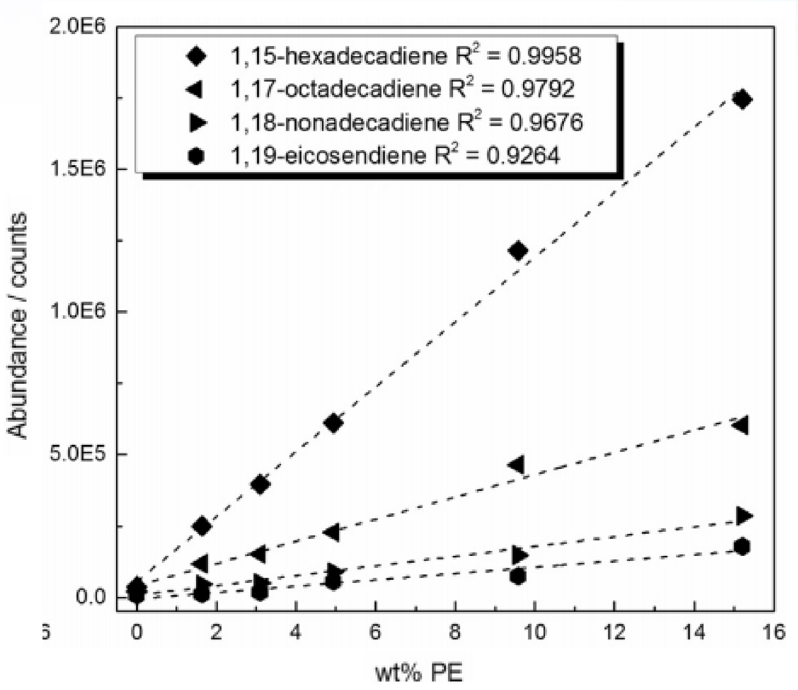


Eight polymer pyrolysis products and example marker compounds



Polymer	LOD in µg
PE	2,2
PP	0,14
PS	0,08
PET	0,24
PA6	0,24
PA 6.6	3,4
PMMA	0,12
SBR	0,06

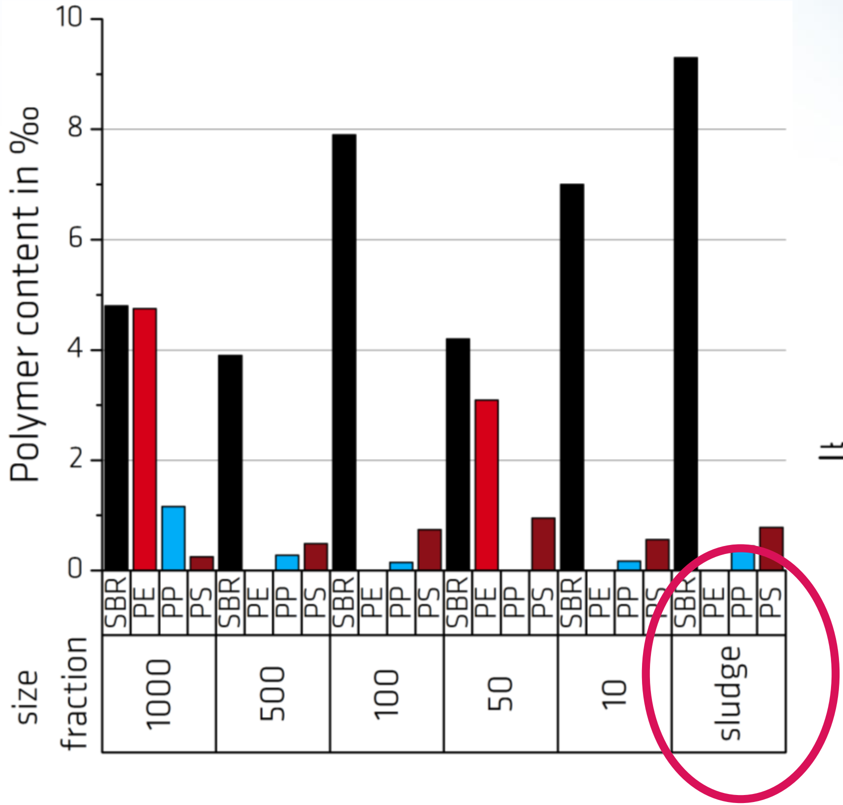
Example Calibration for PE samples



E. Dümichen, et al. Water Research 85 (2015) 451

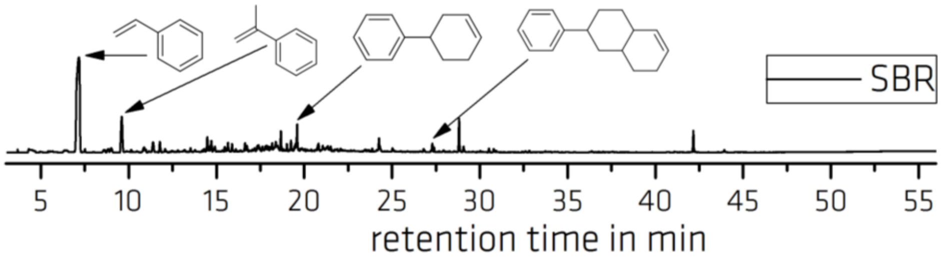
- Good correlation between spiked mass of polyethylene and the peak area of typical PE marker substances
- Note the use of four unique marker compounds to make data more reliable, eliminate false positives
- Marker compounds are created during pyrolysis, and don‘t exist “naturally” in the sample, making it unlikely to have a false positive
- In other words, you won’t find 1,15-hexadecadiene from anything but PE)

Application example: street drainage



Styrene-Butadiene rubber (SBR)

from tire wear ≈ 4-10 % by mass



P. Eisentraut , E. Dümichen, A. S. Ruhl, M. Jekel, M. Albrecht, M. Gehde, U. Braun, *Emviron. Sci. Technol. Lett.*, 2018, 5, 10 608-613.

Comparison Py-GCMS vs. TED-GCMS

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Py-GC/MS

- Single Instrument
- Limited sample capacity (<1mg) → more runs necessary
- Higher risk of GCMS contamination (sewage sludge…)

Comparison Py-GCMS vs. TED-GCMS

GERSTEL

Py-GC/MS

- Single Instrument
- Limited sample capacity (<1mg) → more runs necessary
- Higher risk of GCMS contamination (sewage sludge…)

TED-GC/MS

- TGA and GCMS needed (coupled or indiviually)
- High sample capacity 20mg (up to 200mg) → representative sample
- Pyrolysis is off-line to GCMS (in TGA), making process cleaner & more reliable

Polymer particle mixture with Py-GC/MS not as representative as TED-GC/MS

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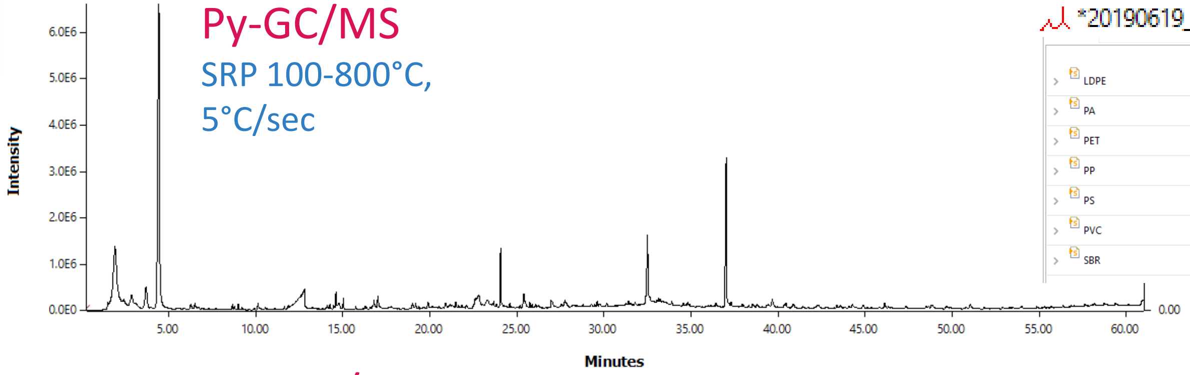
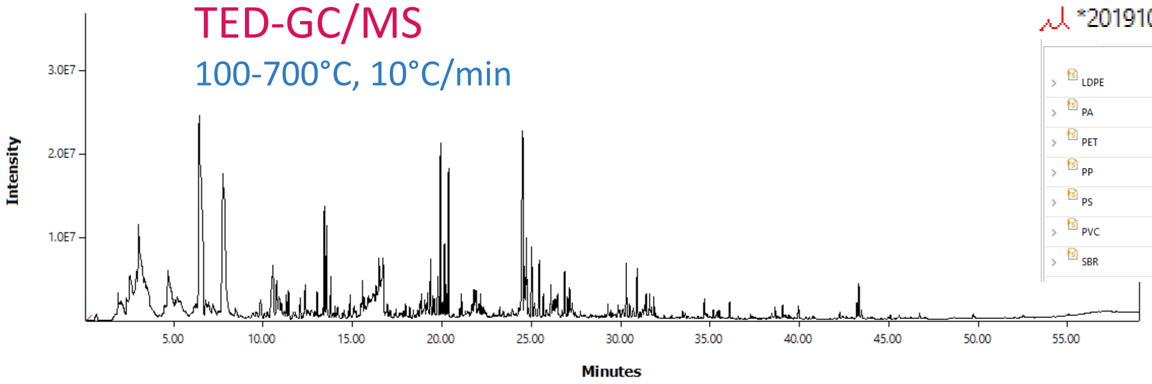
MARKER PEAKS ↓



*20190619_002_Polymermix_fest_SRP800_01

	UnionMatches	ForwardMatches	Intersection M...	ReverseMatches	MarkerP...	Ambigu...	Unidentif...
LDPE	uSI 17.3	fSI 42.1	iSI 100	rSI 41	7	10	79
PA	uSI 14.9	fSI 39.5	iSI 100	rSI 36.4	6	10	81
PET	uSI 20.1	fSI 39.5	iSI 100	rSI 51.9	15	0	81
PP	uSI 14.1	fSI 44.5	iSI 100	rSI 31.7	17	2	77
PS	uSI 14	fSI 35.4	iSI 100	rSI 39.7	6	6	83
PVC	uSI 6.4	fSI 17.7	iSI 100	rSI 36.1	1	2	93
SBR	uSI 11.6	fSI 22.8	iSI 100	rSI 47.7	0	5	91



*20191017_004_Polymermix_STD02_Tube02

	UnionMatches	ForwardMatches	Intersection M...	ReverseMatches	MarkerP...	Ambigu...	Unidentif...
LDPE	uSI 21.8	fSI 31	iSI 100	rSI 70.7	39	12	469
PA	uSI 8.6	fSI 20.6	iSI 100	rSI 42.9	10	11	497
PET	uSI 13.1	fSI 21.1	iSI 100	rSI 62	22	1	496
PP	uSI 20.8	fSI 35.4	iSI 100	rSI 58.6	62	2	454
PS	uSI 9	fSI 19.6	iSI 100	rSI 45.6	16	4	499
PVC	uSI 6.4	fSI 11.6	iSI 100	rSI 55.2	5	2	512
SBR	uSI 6.6	fSI 11.6	iSI 100	rSI 53.5	4	3	512

Polymer particle mixture with Py-GC/MS not as representative as TED-GC/MS

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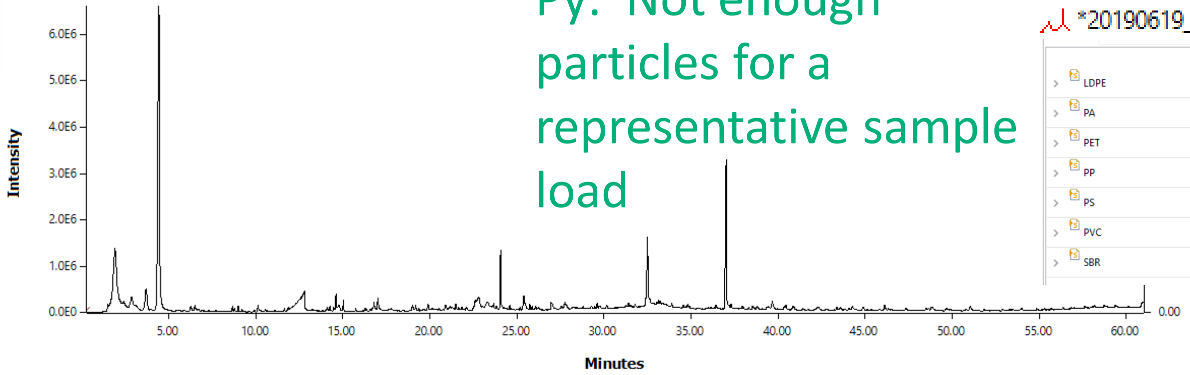
MARKER PEAKS ↓



Py: Not enough particles for a representative sample load

*20190619_002_Polymermix_fest_SRP800_01

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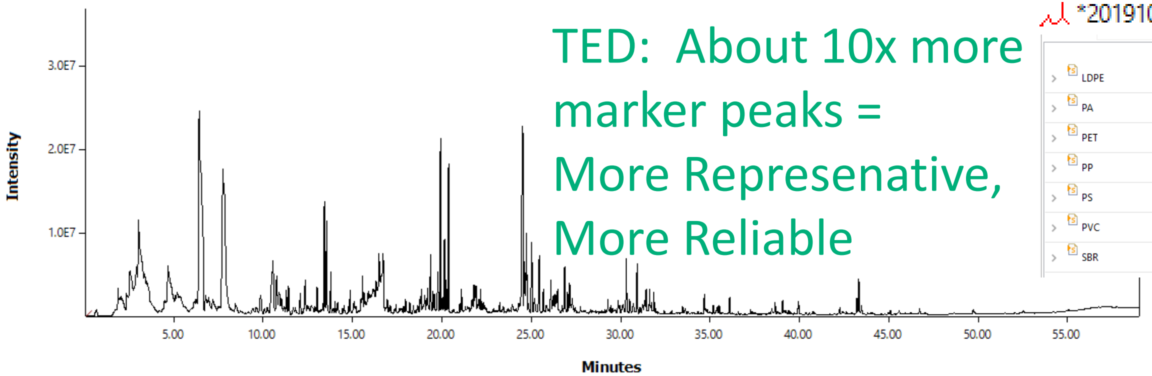
SBR	uSI 11.6	fSI 22.8	iSI 100	rSI 47.7	0	5	91



TED: About 10x more marker peaks = More Represenative, More Reliable

*20191017_004_Polymermix_STD02_Tube02

	UnionMatches	ForwardMatches	Intersection M...	ReverseMatches	MarkerP...	Ambigu...	Unidentif...
LDPE	uSI 21.8	fSI 31	iSI 100	rSI 70.7	39	12	469
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SBR	uSI 6.6	fSI 11.6	iSI 100	rSI 53.5	4	3	512

PP in Sewage Sludge by TED-GC/MS

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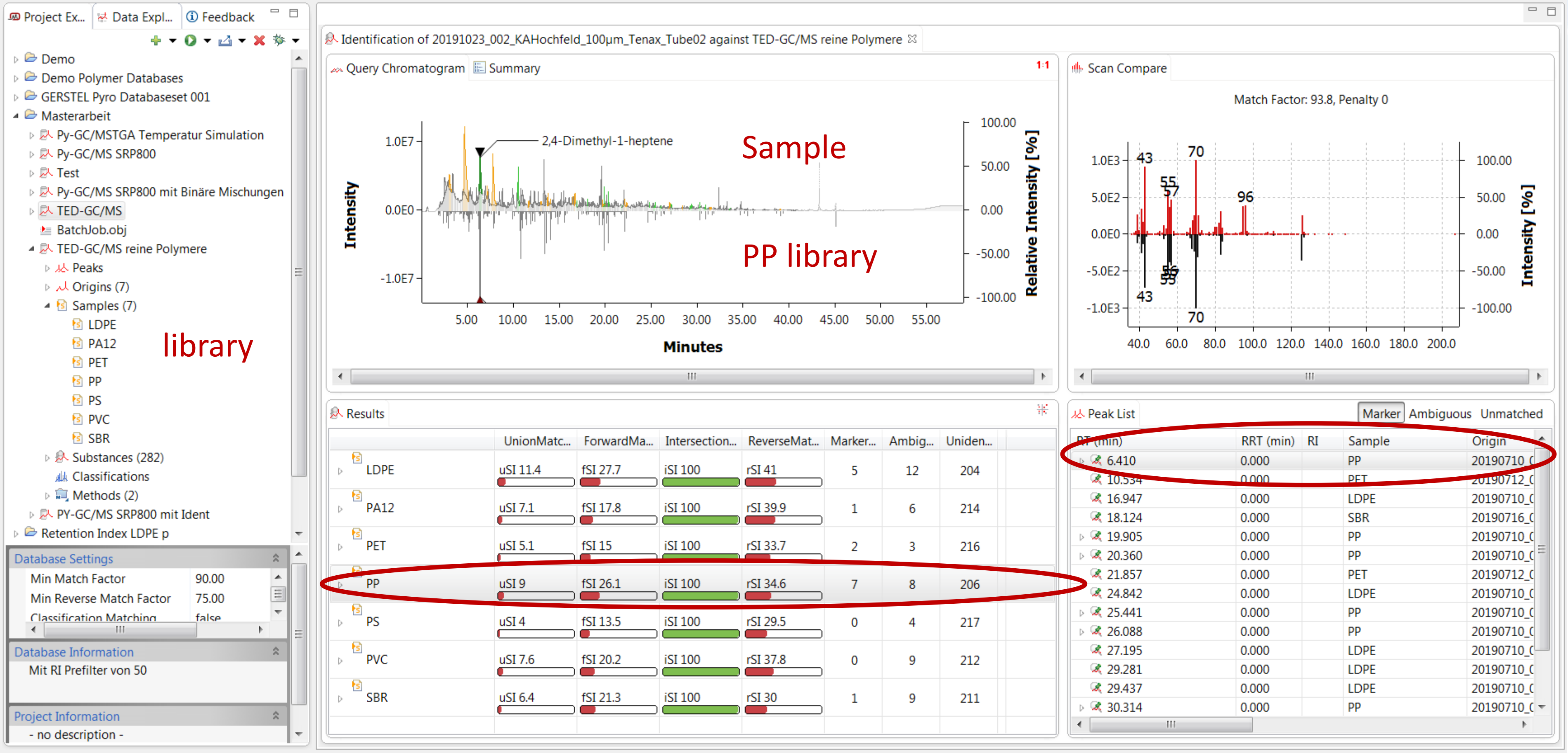

Journal of Chromatography A, xxx (2018) xxx–xxx

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Journal of Chromatography A

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Automated thermal extraction-desorption gas chromatography mass spectrometry: A multifunctional tool for comprehensive characterization of polymers and their degradation products

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Chemosphere 174 (2017) 572–584

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Fast identification of microplastics in complex environmental samples by a thermal degradation method

CrossMark

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Water Research 85 (2015) 451–457

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Analysis of polyethylene microplastics in environmental samples, using a thermal decomposition method

CrossMark

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Letter

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Two Birds with One Stone—Fast and Simultaneous Analysis of Microplastics: Microparticles Derived from Thermoplastics and Tire Wear

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Supporting Information

ABSTRACT: Analysis of microplastic particles in environmental samples needs sophisticated techniques and is time intensive due to sample preparation and detection. Alternatives to the most common (micro-) spectroscopic

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Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Comparison of different methods for MP detection: What can we learn from them, and why asking the right question before measurements matters?☆

Anna M. Elert*, Roland Becker, Erik Duemichen, Paul Eisentraut, Jana Falkenhagen, Heinz Sturm, Ulrike Braun

Federal Institute for Material Research and Testing (BAM), Unter den Eichen 87, 12205 Berlin, Germany

GERSTEL

Thank you!

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Eike Kleine-Benne
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