Understanding the Need for Mass Balance Measurements in Microplastics and the Three GC/MS Techniques Used to Get Them

- A Short Overview -

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Today's Goal: Clarification!

- What is Mass Balance, and why care?
- How is it measured? (short answer: by some type of GC-MS)
- What are the three ways of measuring Mass Balance, and how are they different?

For what I want to measure related to Microplastics, what way is the best for me?

No “Catch-All” Analysis for MP’s

- Particle number
- Particle size
- Morphology
- State of degradation/oxidation
- Polymer ID(s)
- Mass Balance

Mass Balance (aka *Mass Fraction*) is the relative composition of the MP sample (such as 35% polyethylene, 40% polypropylene, etc.)

Additives don‘t contribute much to the overall mass, so they are not counted in mass balance (but can be used for other purposes)

Polymer ID, Mass Balance, and Additives together can potentially indentify the source of the MP

How is Mass Balance Determined?

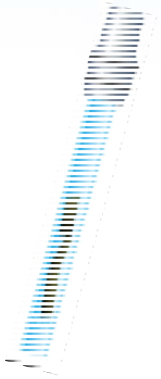
- Thermal Extraction GC-MS (TE GC-MS)
- Pyrolysis GC-MS (Py GC-MS)
- Thermal Extraction/Desorption GC-MS (TED GC-MS)

Note

- GERSTEL makes instruments for all three ways of determining mass balance by GC-MS
- Each way has advantages and disadvantages
- We do not endorse one over the other; you should choose a technique based on your needs

Method One : Thermal Extraction (TE)

- Heats a microplastic sample in an empty 3.5” L x ¼” OD tube to ~300 °C in the carrier-gas stream.
- Is a “special case” of Thermal Desorption GCMS (TD GC-MS)
- Extracts adsorbed/absorbed materials from the surface of the solid sample
- Results, if quantitated, are expressed as mass/mass (i.e. ng/mg)
- The sample is not consumed and only materials from the surface are released; most of the sample remains afterwards
- Sample size is typically 10-50 mg

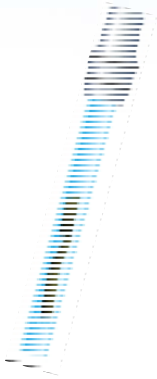


TE and Microplastics

- Instruments used for TD typically have a max temp of 350 to 450 ˚C. When a TD is used for TE, this is not high enough to decompose the MP polymer and ID/quantify it directly

- For some polymers, certain additives, such as antioxidants in PET, are always present at a known concentration

- The non-polymer species can serve as ‘marker compounds’ for the polymer itself, and quantitation of the polymer is possible by quantifying the non-polymer marker

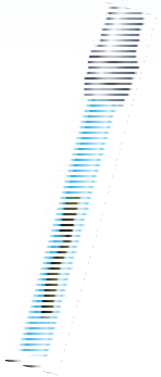


TE and Microplastics

- TE temperatures are high enough to also ‘extract’ out some other useful species, such as anti-oxidants, UV blockers, etc., but only if they are compatible with the TE and GCMS temperatures used

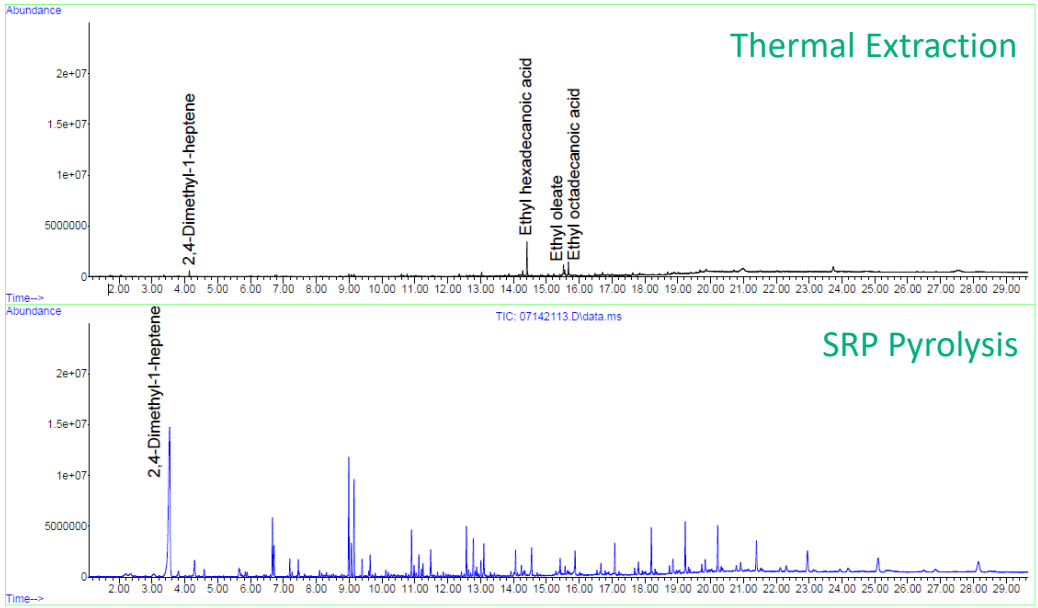
- The sample is NOT consumed in TE; the majority of it is left behind in the tube, and only ng to µg quantities are actually injected to the GCMS

- The tube allows for relatively large samples, including whole filtrate samples should they fit inside the tube



TE analysis of MP’s can be done on a Pyrolysis- or TED GC-MS system by heating the sample to only lower temps (such as 320 ˚C)

Thermal Extraction vs Pyrolysis: Lake Erie Microplastic Particle



- Thermal Extraction, 320 ˚C, 10 min
  - Some SVOC's that may or may not be related to the polymer
  - C_9 alkene is weak, but is a decomp product of one type of PP (but not all)
  - No library match to commercial libraries to any polymer
- Smart-Ramped Pyrolysis 300 - 800 ˚C
  - Polymer decomposition pattern for polypropylene clearly visible
  - Library match to PP: 93%
  - Multiple peaks can be used as markers

Themal Extraction GC-MS: Good, but…

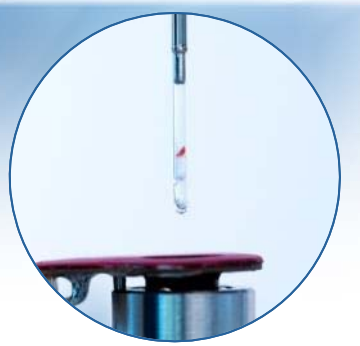
- Larger, representative sample sizes are possible (whole filter media)
- Additive information, although not used for mass balance, is readily accessible
- *Marker Compounds need to be SVOC additives or minor decomposition products that are unique to the polymer in the MP particle. ID and quantification is indirect, inferred.*
- The lower temperatures used in TD/TE instruments makes carry-over and contamination from difficult matrices more likely, for larger samples in particular

GERSTEL TD 3.5+

The utility for all common classes of common MP polymers (~10 or more) has yet to be demonstrated.

Method Two: PYROLYSIS and Microplastics

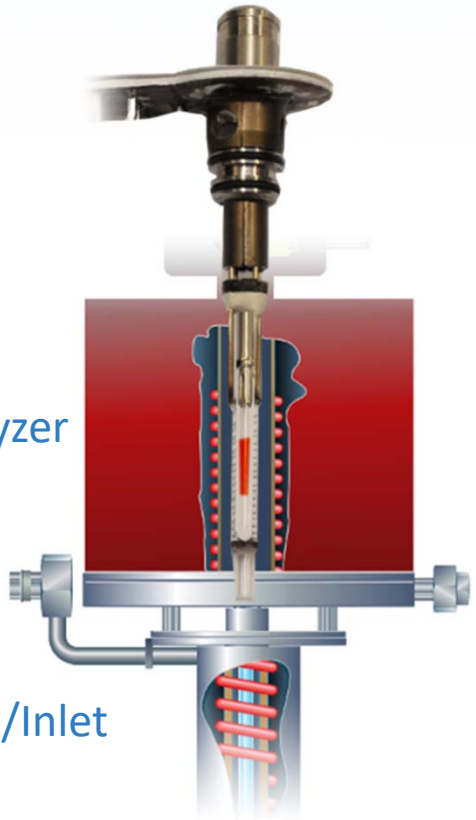
How does pyrolysis GC-MS work?

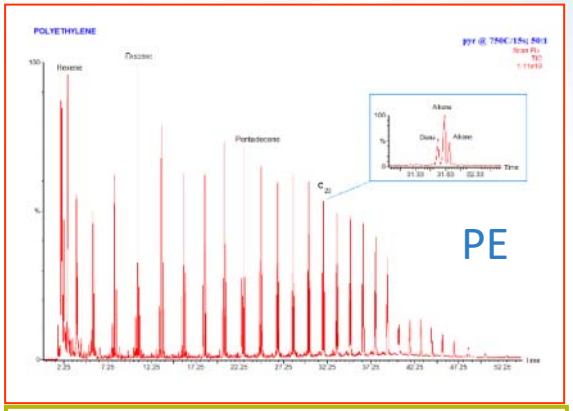


- Samples are placed in pyrolysis tubes
- Can be particles, punches of filter media, or cryo-milled sediment
- Pyrolysis occurs between 600 and 1000 ˚C
- Non-volatile sample material is decomposed
- The sample is fully consumed in the process
- 100% of the decomposition products are introduced to the GC/MS
  - A trap can optionally be used for trapping (focusing) and/or splitting of the sample
- Material(s) in the sample are identified by their pyrolysis fragments

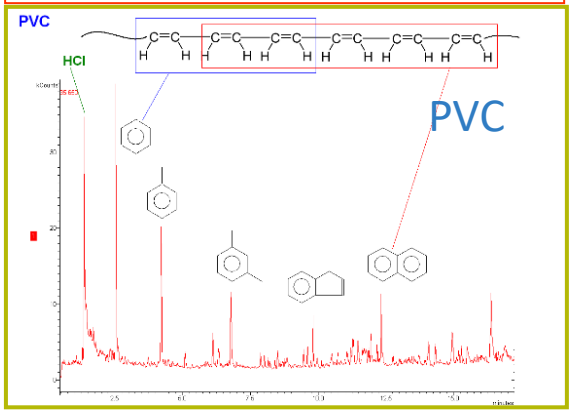
The resulting pyrograms show not what the sample *is*, but what it *became* when heated.

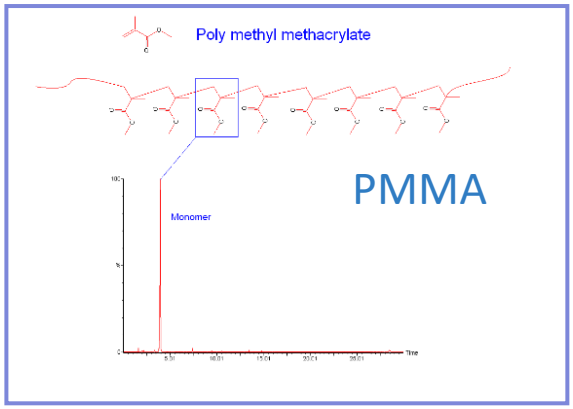
Pyrolysis Examples of Common Plastics





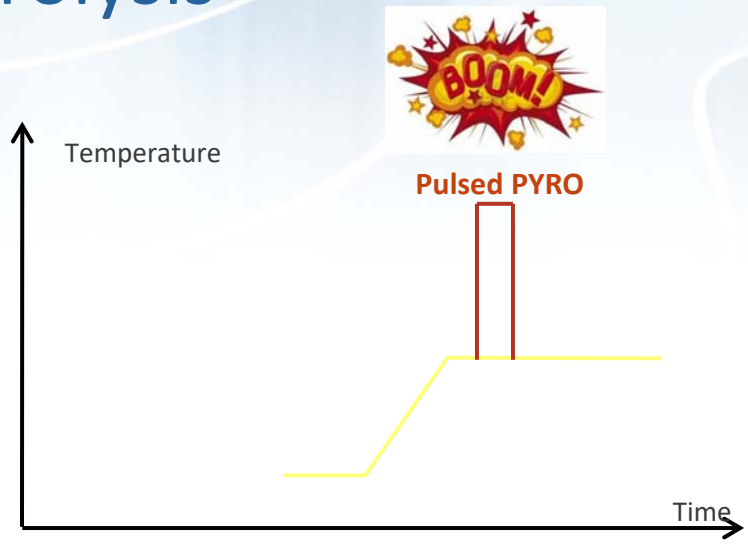
Sample weight:
~ 100 µg





Classic Standard Pulsed Pyrolysis

- Fast heating, fast pyrolysis
- Required if going direct to column
- Same temperature used for ALL polymers in the sample
  - The pulse temp is a compromise
  - Secondary reactions due to overheating add complexity
- Requires method development
  - Works best for known samples
- Not suitable for complex unknown samples (can't optimize temp)

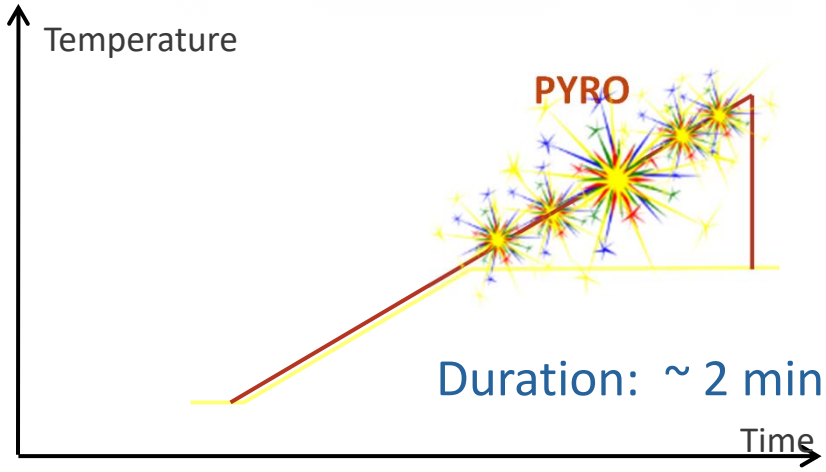


A newer alternative: Smart-Ramped Pyrolysis (SRP)

- Pyrolysis using a temperature ramp
- Trapping the pyrolysates is necessary before introduction to the column
- Polymers are pyrolyzed without overheating and secondary reactions are eliminated
- One combined GC/MS run follows

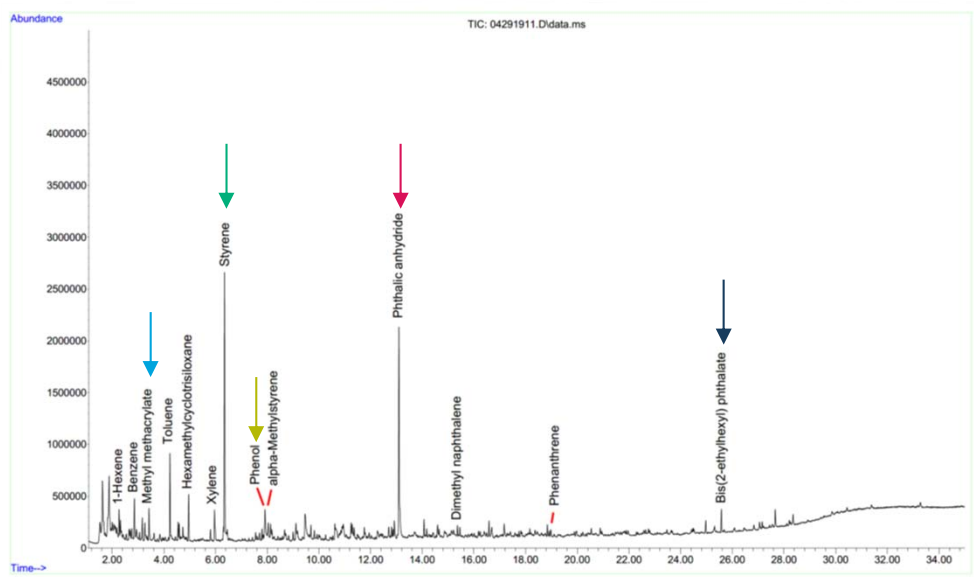
Improvements over Pulsed Pyrolysis

- Better signal and less noise
- Don't have to choose a single pyro temp
- Even unknown samples can be analyzed
- Polymer and additive information in one run are possible



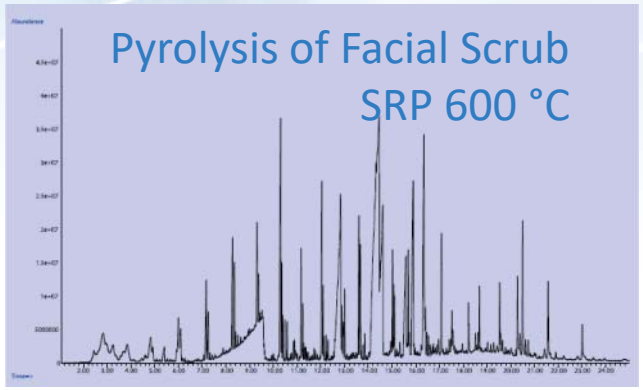
Lake Erie River Sediment: Smart-Ramped Pyrolysis

- Several polymers present:
  - Methyl Methacrylate / PMMA
  - Styrene (PS)
  - Phenol (Polyphenol)
  - Phthalic Anhydride (Polyester)
- Monomers can be used as “marker compounds”
- Markers can be used for ID and for quantitation.
- Note the presence of some additives as well (Bis(2-ethylhexyl)phthalate)

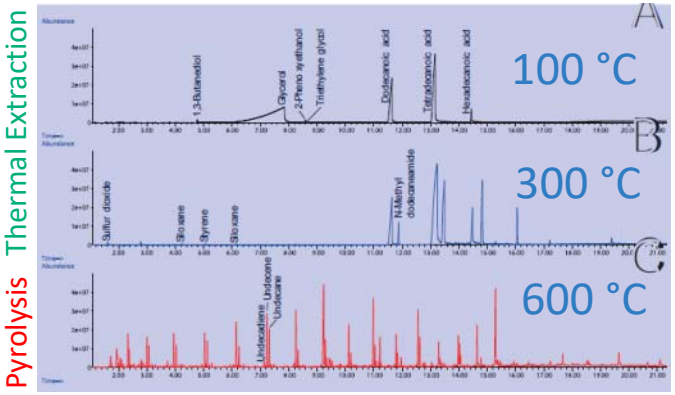


Fractionated Pyrolysis: Primary MP‘s in Facial Scrub

- Direct SRP Pyrogram up to 600 °C
  - Very complex but the use of marker compounds allows the MP polymers to be ‘pulled out’ (more later)



- Fractionated Pyrolysis: TE followed by Pyrolysis
  - A: 100 °C (VOCs)
  - B: 300 °C (SVOCs, additives)
  - C: 600 °C (Well defined pyrogram of MP polymer)



- Fractionated pyrolysis is an easy way to get polymer and additive information from MP’s
- Interpretation is simplified, but data in 2-3 files

PYRO and Microplastics

Publications

- Microplastics (MPs) by Pyrolysis GC-MS (AppNote 212)
  - MPs in Filtered Great Lakes Water and Sediment
  - MPs in Body Care Product (Facial Scrub)
- Microplastics from fish stomach content, Texas Gulf Coast …
  - E. Hendrickson et al., Mar. Pollut. Bull., 2018, 137, 91-95
- Microplastics from Western Lake Superior …
  - E. Hendrickson et al., Environ. Sci. Technol., 2018, 52, 1787-1796
- Simultaneous Determination of Plastic Particle Identity and Adsorbed Organic Compounds by TD-Pyrolysis GC-MS
  - Molecules 2020, 25, 4985; doi:10.3390/molecules25214985

Pyrolysis GC-MS: Good, but….

- Samples are small in mass (0.1 - 1 mg, ideally)
- Samples small in size (few square mm^2)
- For filters, several punches must be taken

GERSTEL Pyrolyzer

- Pyrolyzing the whole filter risks overloading the GCMS (pyrolyzers are connected directly to the GCMS)

Thus many smaller samples from a single filtrate need to be run to get a representative sample, or sample must be cryomilled

Method Three: Automated TED-GC-MS

Thermal Extraction and Pyrolysis of Larger Samples, Offline in a TGA, followed by Mass Balance Determination via Evolved Gas Analysis – TD GC-MS

Example: Water Sample on a Filter Crucible

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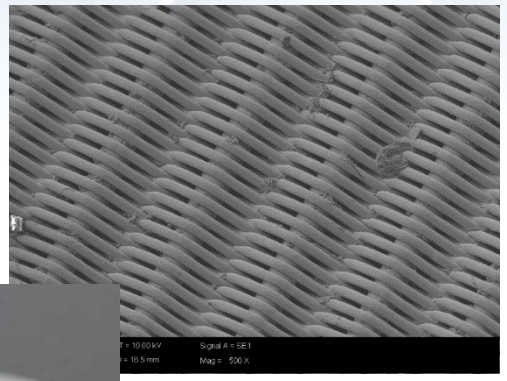
Large enough for a representative sample

No punching or cutting of paper filters

No other filter media needed

mesh size 5-6 µm



RUSEKU GKD

Example: Water Sample on a Filter Crucible

Analysis of Microplastics in drinking Water and beverages with limited matrix load

- Filtration set-up
- For aqueous samples with low matrix load
- When filtration is complete, the crucible placed directly in TED system for analysis

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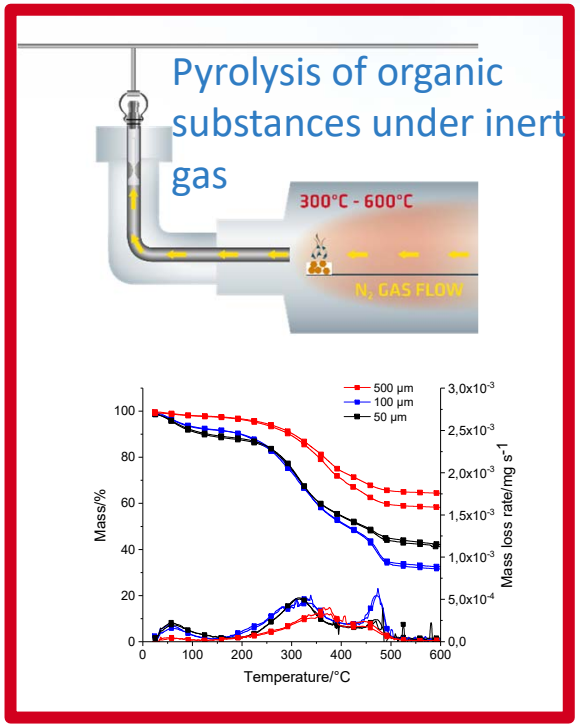
TED-GC-MS
1st step: Thermal Extraction in TGA

Environmental sample:
Water Filtrate or
Sediment, Soil, Filter Paper
= Matrix + Microplastics

NOTE THE SIZE
Sample size up to 100 mg



Thermogravimetric Analysis (TGA) System

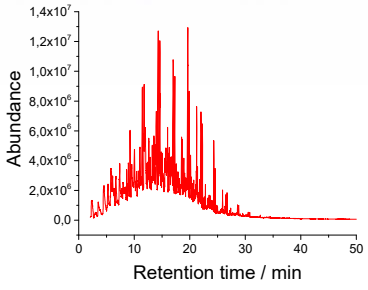
Collection of pyrolysis products on Polydimethylsiloxane (PDMS) using a GERSTEL Twister or similar

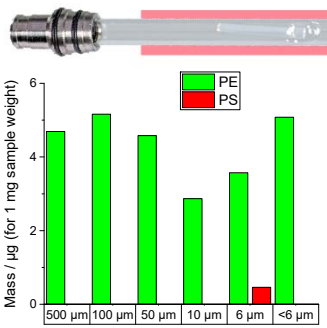
Off-line to GC-MS:

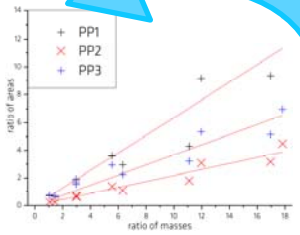
Autosampler moves the Twister to a TD GC-MS for analysis

TED GC-MS

2nd Step: analysis of the pyrolysis products





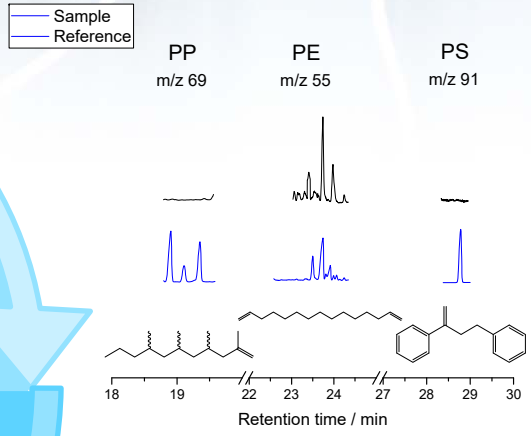


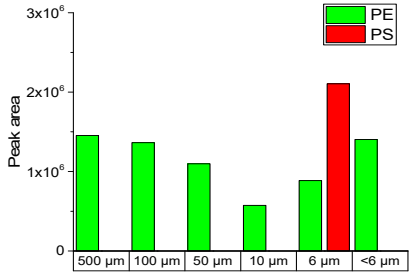
Thermal Desorption GC-MS

Marker-Compounds Identification

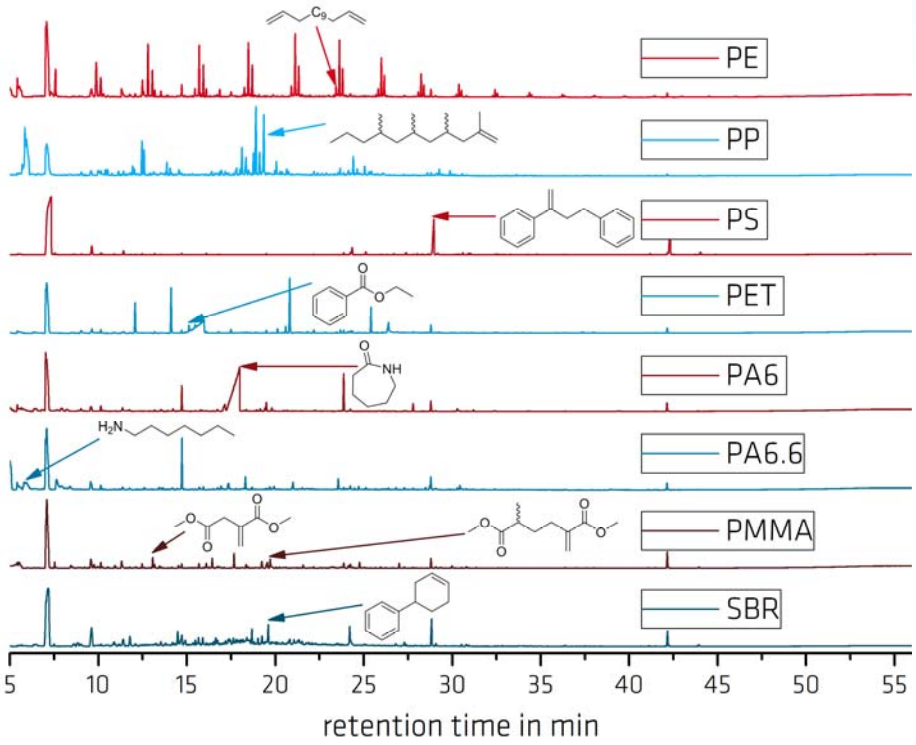
Polymer Quantification

Polymer Identification



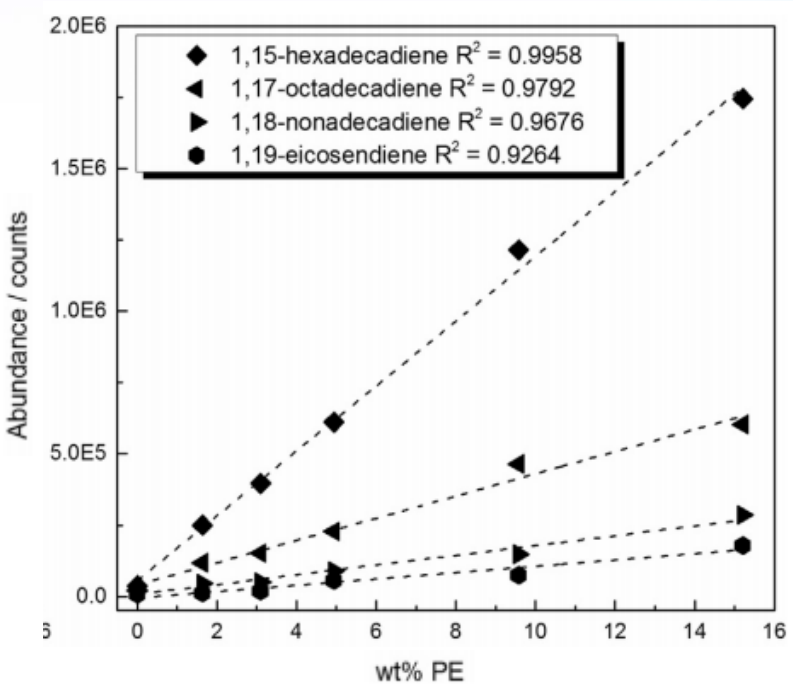


Eight example polymer pyrolysis products and example marker compounds



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

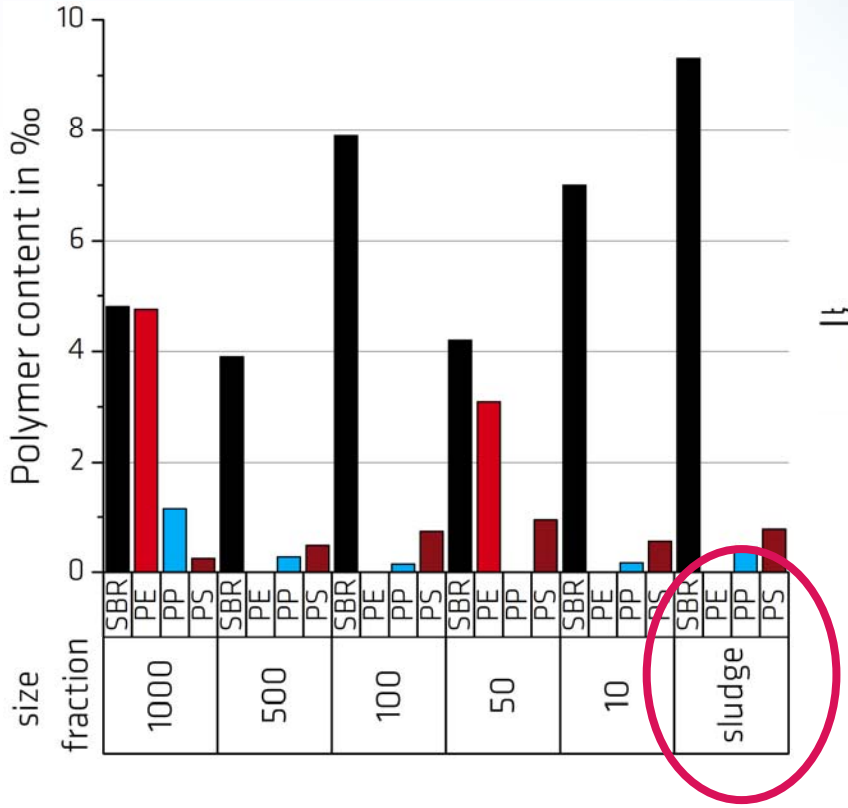
Example Calibration for PE samples



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

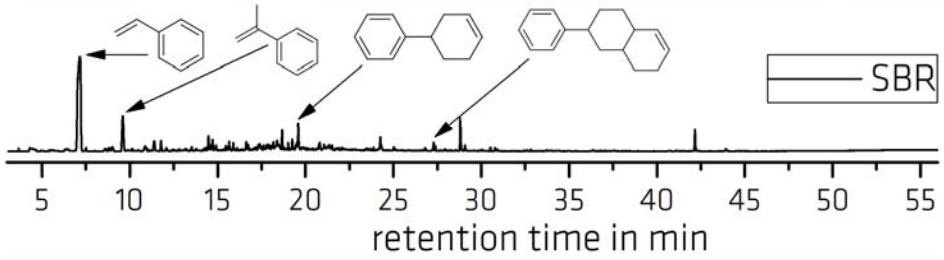
- Good correlation between spiked mass of polyethylene and the peak area of typical PE marker substances
- Note the use of four unique marker compounds to make data more reliable
- Marker compounds are created during pyrolysis, and don‘t exist “naturally” in the sample
- Unlikely to have false positives

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.

Polymer particle mixture with Py-GC/MS and TED-GC/MS

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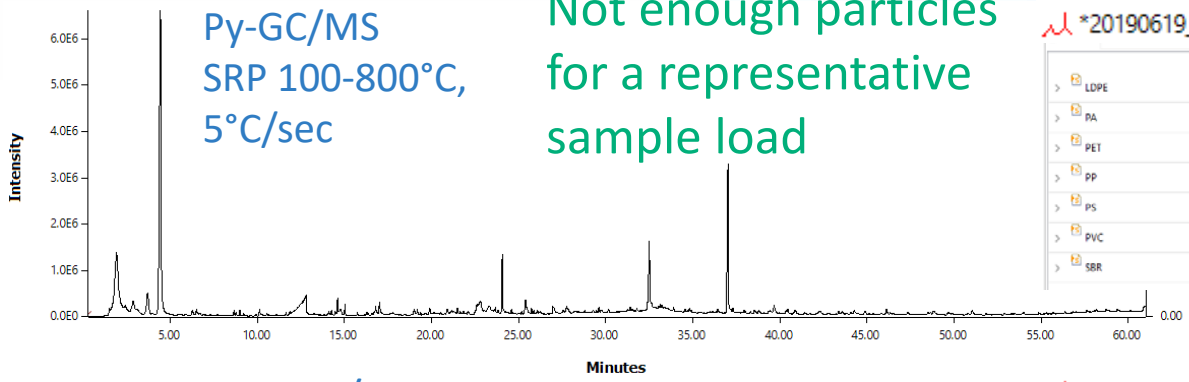
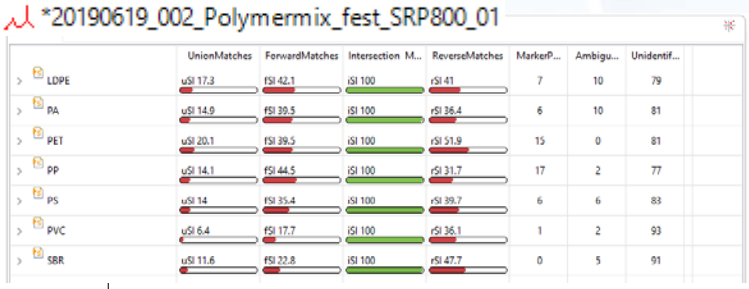
Py-GC/MS
SRP 100-800°C,
5°C/sec

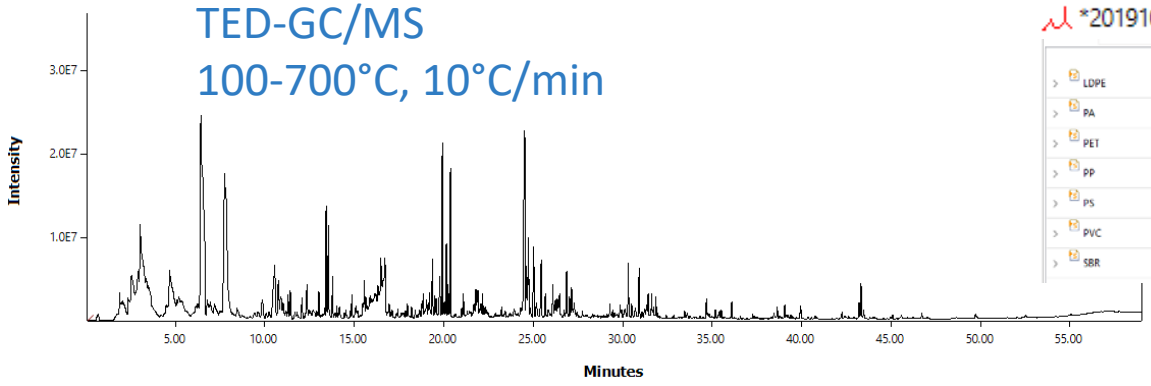
Not enough particles for a representative sample load

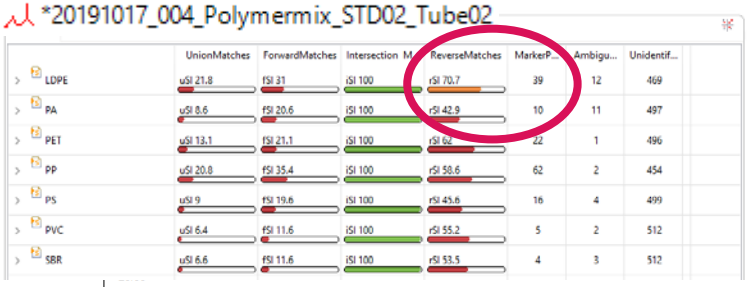


Marker Compounds from ChromIdent Software



TED-GC/MS
100-700°C, 10°C/min





70.7% match with larger sample;
39 marker peaks found

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

Contents lists available at ScienceDirect

Journal of Chromatography A

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

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

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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

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Environmental Pollution xxx (2017) 1–9

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

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Chemosphere 174 (2017) 572–584

Contents lists available at ScienceDirect

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

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Environmental Science & Technology Letters

Letter

Cite This: Environ. Sci. Technol. Lett. XXXX, XXX, XXX–XXX

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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

Microplastic Analysis using TED-GC-MS

So what does it all mean?

The Short Answers

- All three techniques can determine the mass balance of MP samples on filter media; all three can determine the ID of polymers AND additives
- Thermal Extraction GC-MS analyzes larger representative samples but is indirect: polymers must have unique marker additives and samples should be relatively clean (e.g., PET MP's in drinking water); MP analysis range is limited / undetermined
- Pyrolysis GC-MS offers direct MP ID and analysis of a wide range of polymers, can also do additives if needed, and can handle a wider range of matrices; sample sizes are smaller & multiple reps required for representative sampling
- TED GC-MS can do a wide range of polymers, additives runs, larger representative samples, and being off-line to the GC-MS makes it the most robust; more investment (two instruments and training) are needed

Thermal Desorber used as a Thermal Extractor

Pyrolyzer

Thermal Extraction/Desorption (TED-GCMS) System

Instrumentation Comparison

	Thermal Extraction (~315 °C)	Pyrolysis (600 to 1000 °C)	TED (600 to 1000 °C)
Sample Intro	On-line to GCMS	On-line to GCMS	Off-line from GCMS
Process	Thermally extract to trap, then to column (through valve / transfer line or direct to column)	Pyrolyze direct to GCMS (direct to column, or optional trapping step before column)	Extraction/Pyrolysis in TGA; trap on PDMS and transfer to TD-GCMS (PDMS trap is desorbed in TD; re-trapping before column recommended)
Bake-out	Up to 450 °C, N_2 or He	Up to 1000 °C, N_2 or He	Up to 1000 °C, in N_2, He, O_2
Sample Size	Typically 10-50 mg	0.1 - 10 mg (0.1 – 1 mg typically; all goes to inlet)	Typically 10-50 mg
Representative Sample	One Run	Multiple Runs	One Run
Type of Data	Mass Spectral	Mass Spectral	MS and TGA both

Analytical Comparison

	Thermal Extraction (~310 °C)	Pyrolysis (600 to 1000 °C)	TED (600 to 1000 °C)
Sample Prep (filter media)	Dry, solvent rinse of filter, dry again, analyze	Dry, punch out correct sized samples, analyze (multiple punches very likely needed)	Dry, punch out correct sized samples, analyze (one, larger punch is typically sufficient)
Polymer ID	Yes, Indirect / Inferred (marker additives)	Direct (un-zipped monomer or targeted degradant markers)	Direct (un-zipped monomer or targeted degradant markers)
Range of Polymers	Limited to uniqueness of additives (typ. PET)	Eight or more common MP polymers (PET, PE, PP, PS, …)	Eight or more common MP polymers (PET, PE, PP, PS, …)
Mass Balance	Yes, Indirect / Inferred quant through additives	Yes, direct quant through monomers / degradants	Yes, direct quant through monomers / degradants
Additives (note: not needed for mass balance)	Yes, Direct, one step	Yes, Direct, one or two steps (300 °C and then 600 to 1000 °C), if two steps needed	Yes, Direct, one or two steps (300 °C and then 600 to 1000 °C), if two steps needed

Cost and Complexity

	Thermal Extraction (~310 'C)	Pyrolysis (600 to 1000 'C)	TED (600 to 1000 'C)
Instruments	Three (TD, GC, and MS)	Three (PYRO, GC, and MS)	Four (TGA, TD, GC, and MS)
Cost	$$	$$	$$$
Support	One Provider	One Provider	Two Providers (TGA and TD-GCMS)
Whole Filtrate in One Run	Possible	No	Possible
Carry-over Risk (sludge, tissue, …)	Highest (TE only = lowest temp technique)	High (PYRO only less risky) or Higher if TE step used	High (or Moderate with O_2 cleaning step)

Thanks to:

BAM
Bundesanstalt für Materialforschung und -prüfung

GERSTEL

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Ulrike Braun
Erik Dümichen
Paul Eisentraut
et al.

Eike Kleine-Benne
Huan-Xiao Zhou,
Jackie Whitecavage,
John R. Stuff