Identification of Microplastics in Water by Pyrolysis Gas Chromatography Mass Spectrometry

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From NEMC 2021:
How is MP Mass Balance Determined?

Mass Balance = Relative amounts of each polymer in MP sample

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

Today's Pyrolysis Focus

- Mass Balance of Microplastics by Pyrolysis is Established
- ASTM's D19 and ISO's TC147 groups have methods in draft
- To find mass balance, you have to find the polymer first
- Today the focus is on Polymer ID.

The end at the beginning

- Pyrolysis GC-MS is a great tool for the ID and measurment of Microplastics
- Advances in open source data analysis software make analysis more reliable
- The same advances make data work-up faster and largely automated
- The sample sizes are too small, resulting in more manual sample prep work

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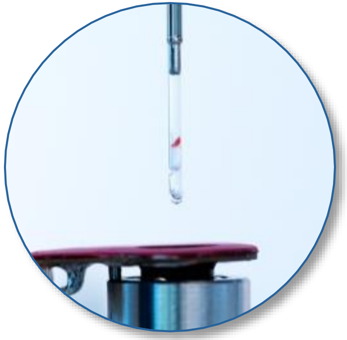
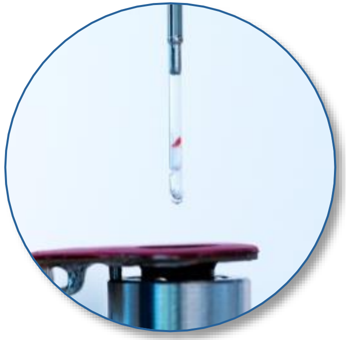
PYROLYSIS and Microplastics: How does pyrolysis GC-MS work?

- 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



PYROLYSIS and Microplastics: How does pyrolysis GC-MS work?



- 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

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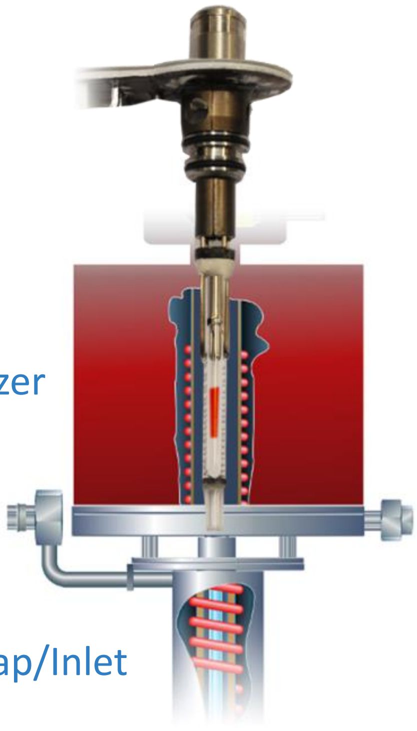
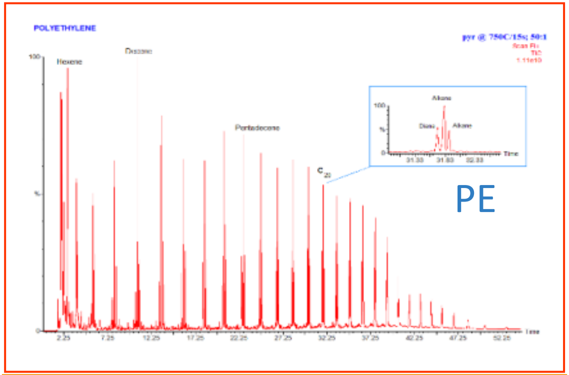
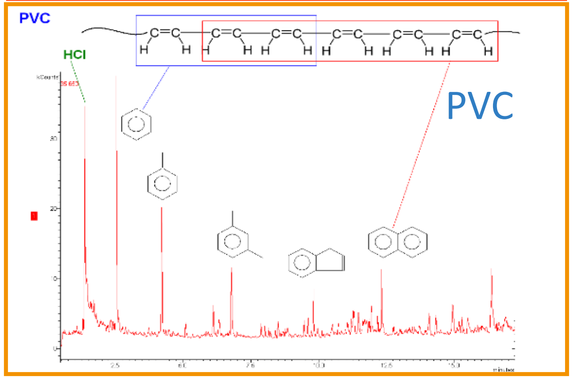
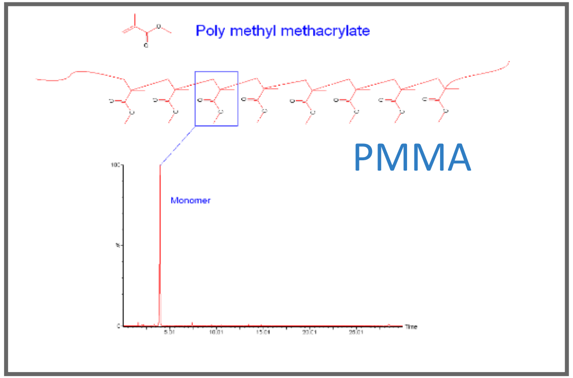






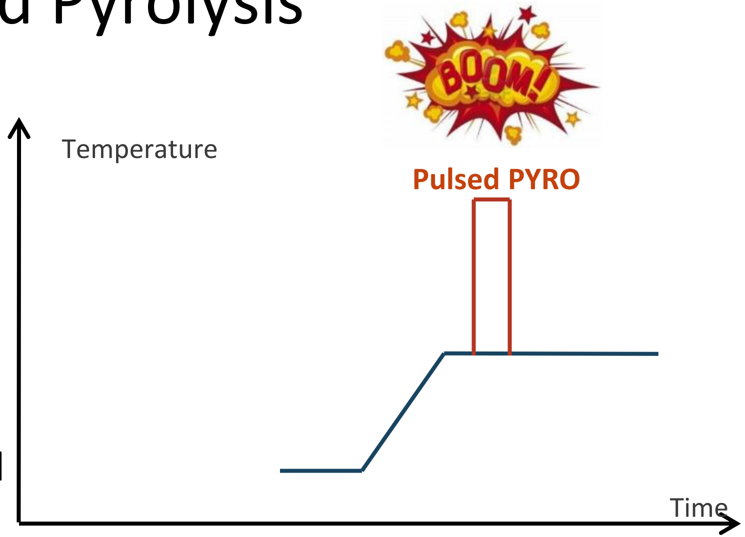


Sample weight:
~ 100 µg

In most cases, polymers give more than one GC peak per polymer analyte

Classic Standard Pulsed Pyrolysis

- Fast heating, fast pyrolysis
- Required if going direct to column without a focusing trap
- 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, pure samples
- Not suitable for complex unknown samples or complex mixtures (can't optimize temp)



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A newer alternative: Smart-Ramped Pyrolysis (SRP)

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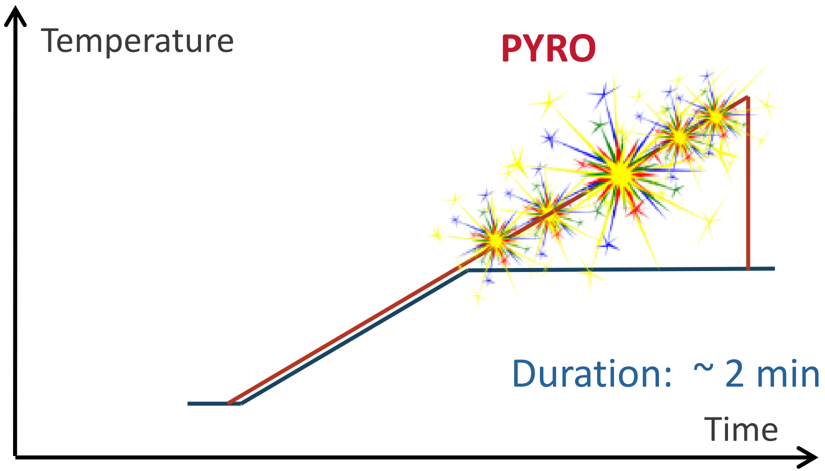
- Pyrolysis using a temperature ramp
- Trapping the pyrolysates is necessary before introduction to the column
- Polymers are pyrolyzed without overheating and secondary reactions are eliminated
- One combined GC/MS run follows with thermal pyrolysis AND thermal extraction data

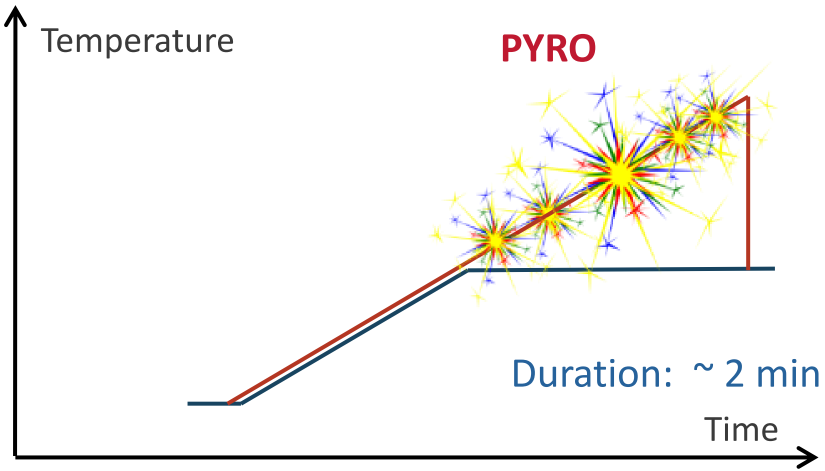


If you can do pulsed pyrolysis, you can also do ramped – the heating rate is a method parameter

Ramping does require trapping the pyrolysates on a focusing trap or the column head

Smart-Ramped Pyrolysis (SRP): 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 & additive information in one run



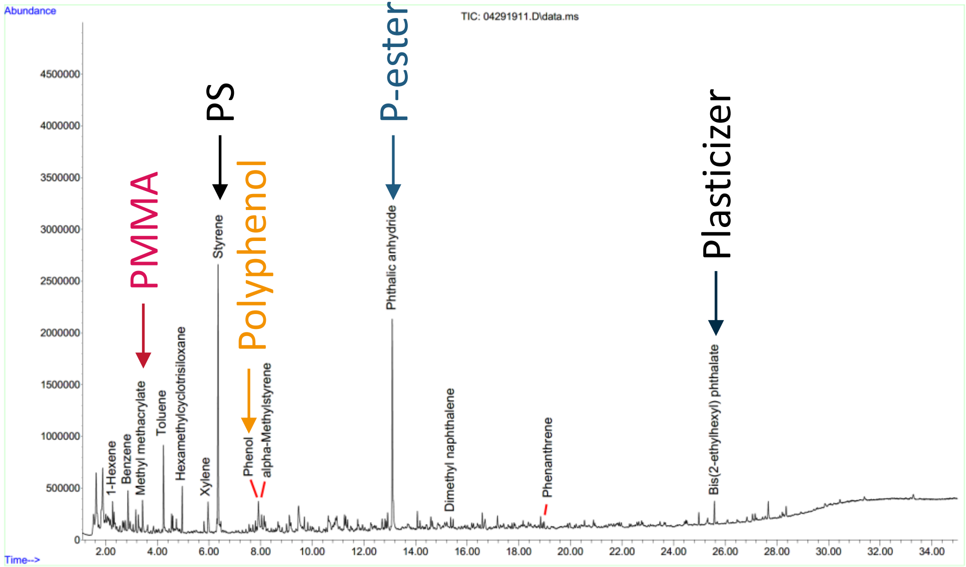
Lake Erie River Sediment: Smart-Ramped Pyrolysis

- 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)



Sample ER-60

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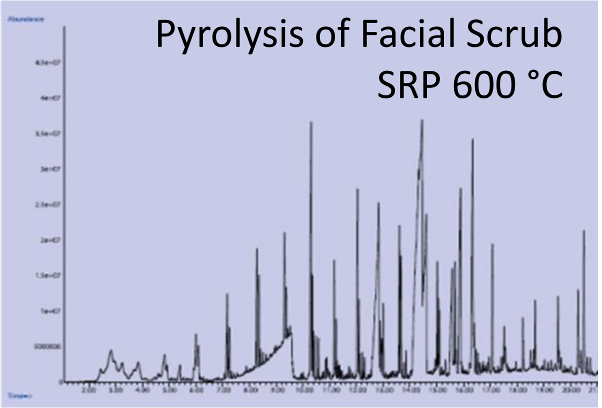
Alternatively, Fractionated Pyrolysis: Primary MP‘s in Facial Scrub

- 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

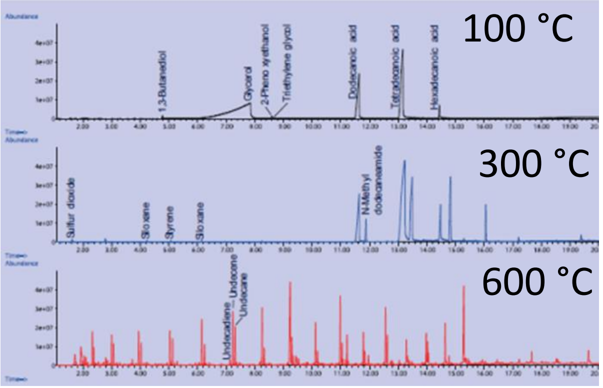
  A: 100 °C (VOCs)

  B: 300 °C (SVOCs, additives)

  C: 600 °C (Well defined pyrogram of MP polymer)

Thermal Extraction

Pyrolysis



- Fractionated pyrolysis is an easy way to get polymer and additive information from MP’s
- Interpretation is simplified, but data in 2-3 (or many more) files – dozens of ‘shots’ at a sample

Using Filters to Extract and Identify MP's: Practical Examples

- One Liter samples of local waters were run through a 10 um PTFE filter w/ vacuum
- All were allowed to dry overnight
- A 1.2 mm diameter punch was taken of each sample and pyrolyzed
- The Street Runoff did not give much signal, so a few milligrams were scraped off & run

Synthetic Grey Water | Street Runoff | Pond Water | Bottled Water

Analysis Conditions

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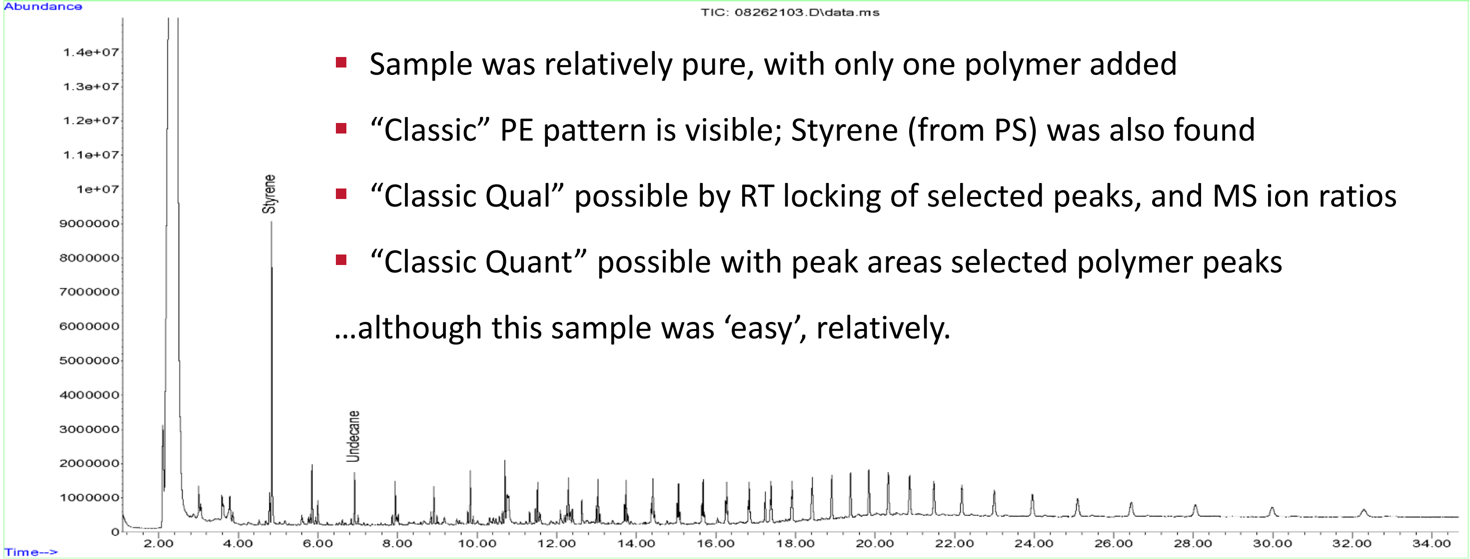
Column:	DB-5MS UI (Agilent) dia = 0.25 mm, d_f = 0.25µm, L = 30 m
Pneumatics:	Carrier = Helium Constant flow = 1.0 mL/min
GC:	Initial 40 °C (1.0 min) Ramp 15 °C/min to 320 °C (15 min) Detection = 5977 MSD

<u>Pyrolysis Conditions</u>

PYRO body	Splitless: 80 °C (0 min), 300 °C/min, 300 °C (2.17 min)
Trap:	Split 25:1 300 °C isothermal (not trapping)
Lead Time:	0.00 min
Follow up Time:	0.50 min
Initial Time:	0.00 min
PYRO Program:	SRP: Initial 300 °C (0 min), ramp 5.0 °C/s to 800 °C (0.0 min)

Synthetic Grey Water Filtrate Pyrogram

- A facial scrub was spiked with cryomilled PE
- The scrub was then added to pure water, shaken, and then analyzed

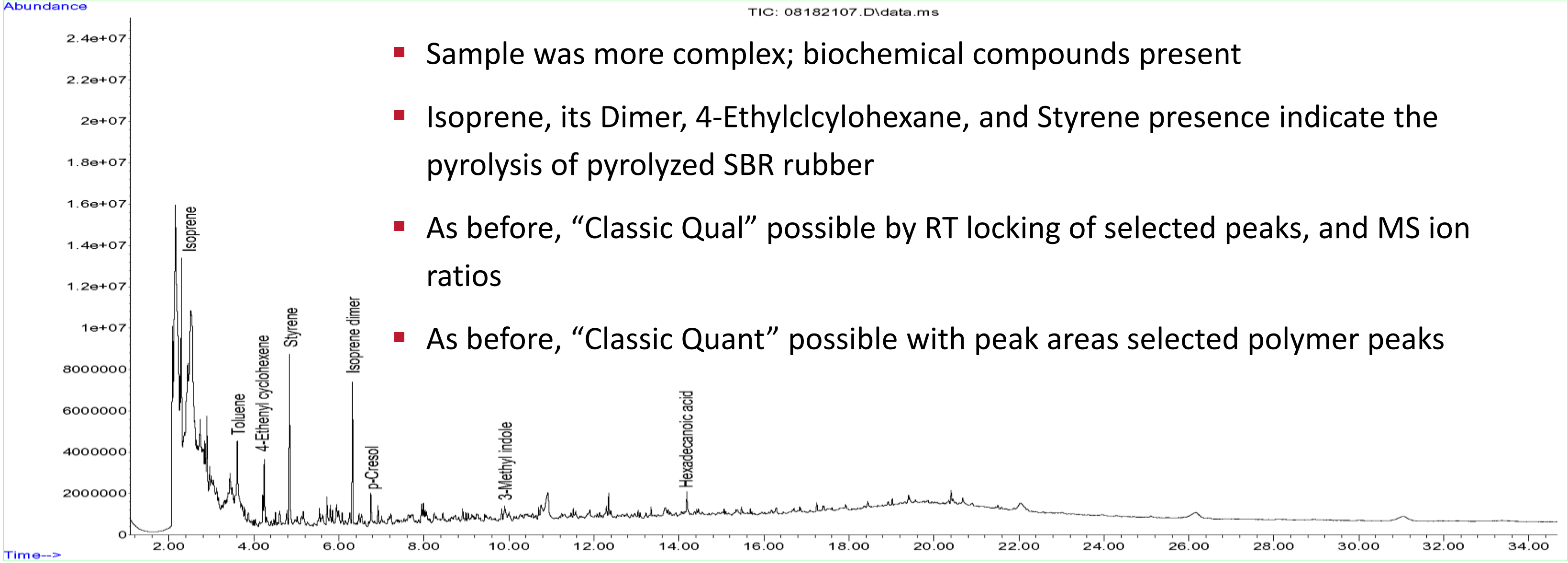


- Sample was relatively pure, with only one polymer added
- “Classic” PE pattern is visible; Styrene (from PS) was also found
- “Classic Qual” possible by RT locking of selected peaks, and MS ion ratios
- “Classic Quant” possible with peak areas selected polymer peaks

…although this sample was ‘easy’, relatively.

Street Runoff Filtrate Pyrogram

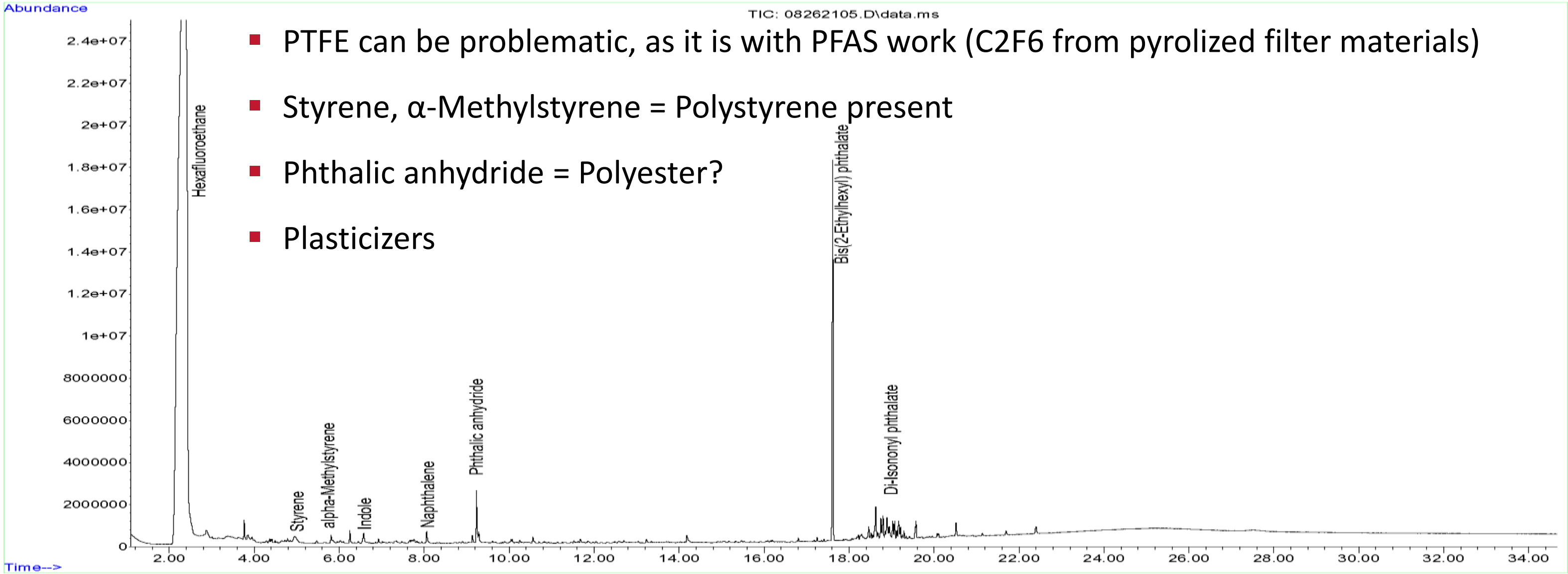
- A punch of the filter did not yield much signal
- Several milligrams of filtrate were scraped off and a 1-2 mg sample of that was run



- Sample was more complex; biochemical compounds present
- Isoprene, its Dimer, 4-Ethylclcylohexane, and Styrene presence indicate the pyrolysis of pyrolyzed SBR rubber
- As before, “Classic Qual” possible by RT locking of selected peaks, and MS ion ratios
- As before, “Classic Quant” possible with peak areas selected polymer peaks

Pond Water Filtrate Pyrogram

- A 1.2 mm diameter punch produced sufficient signal
- Several polymers and plasticizers present



- PTFE can be problematic, as it is with PFAS work (C_2F_6 from pyrolized filter materials)
- Styrene, α-Methylstyrene = Polystyrene present
- Phthalic anhydride = Polyester?
- Plasticizers

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Problems with the "Classical Approach"

- Polymers usually have more than one GC peak / polymer; we are ignoring information ("Qualifier Peaks" aka Marker Compounds)
- A polymer should also have the right NUMBER of GC peaks, and at RT's that are known
- The library used should then have both GC and MS information in it, and not MS information alone

Advances in open-source software has solved these problems

Openchrom & ChromIdent: ID and Quant of Pyrolysis Products

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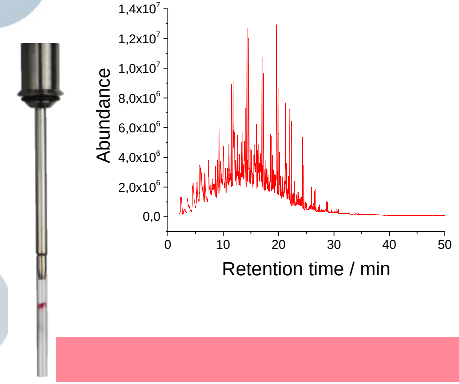
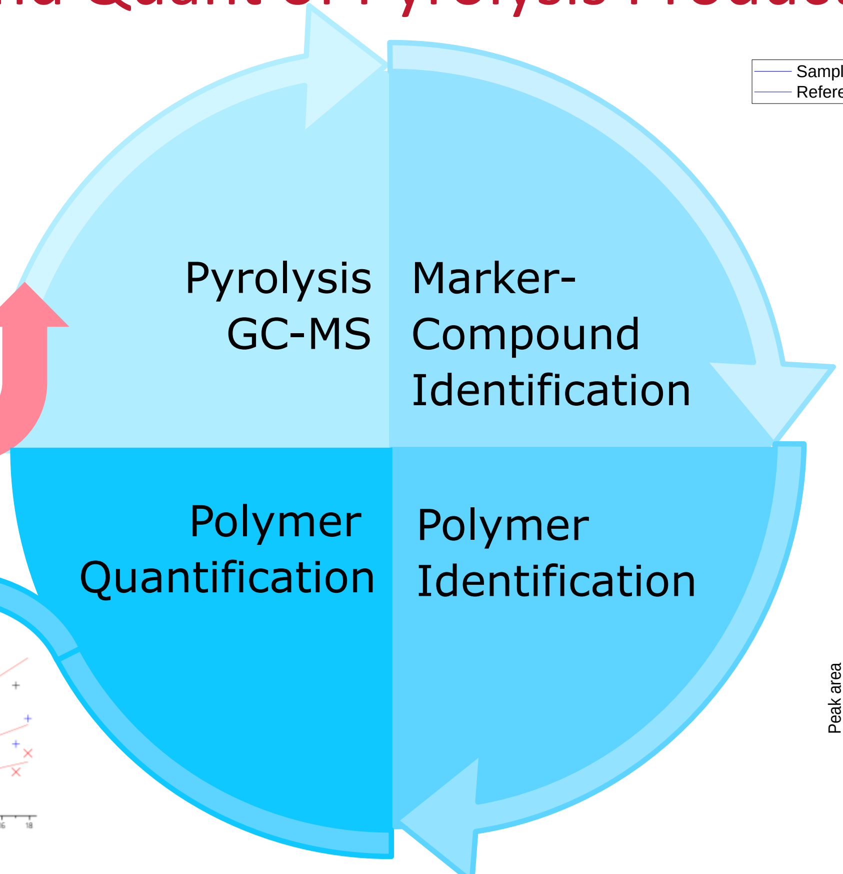
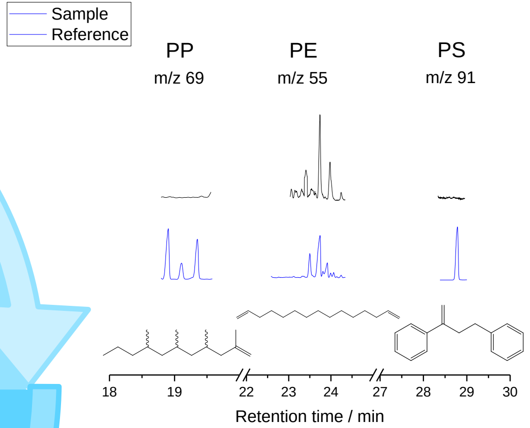
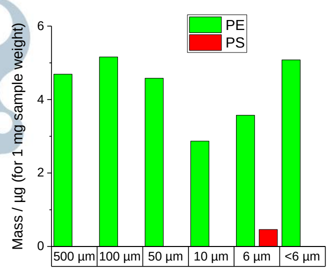
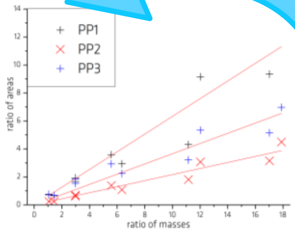
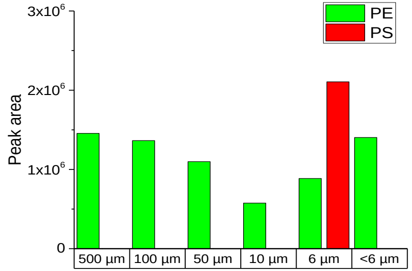




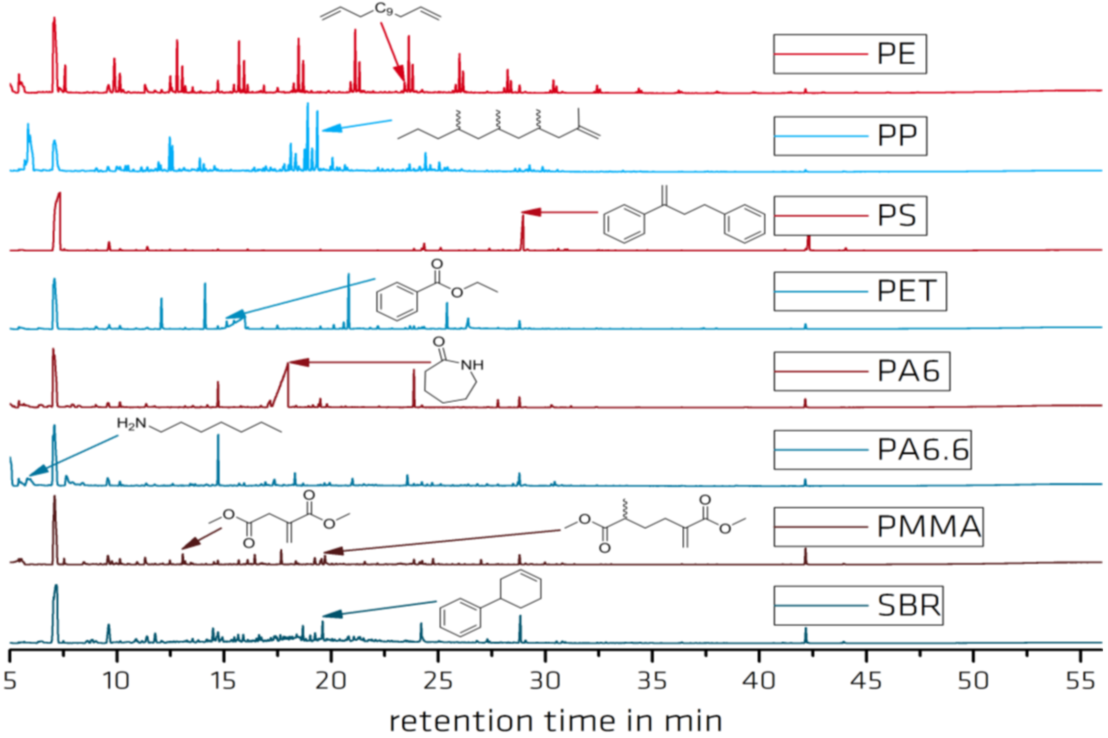






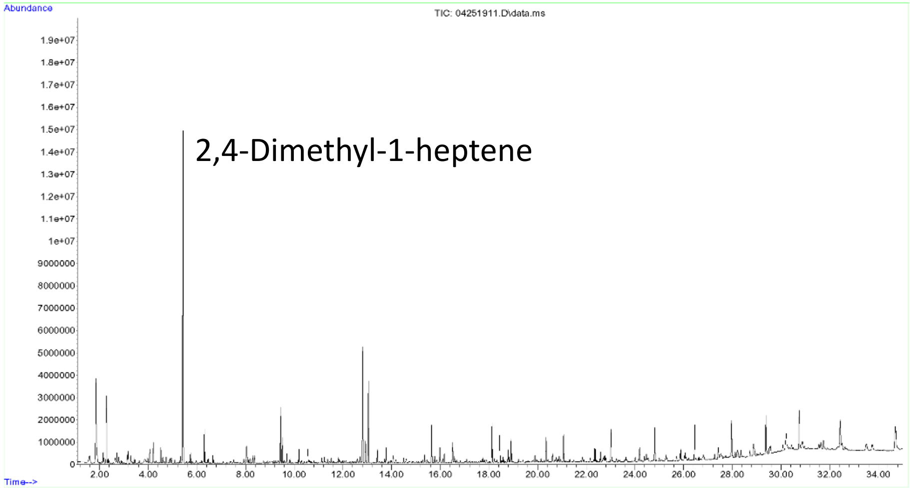


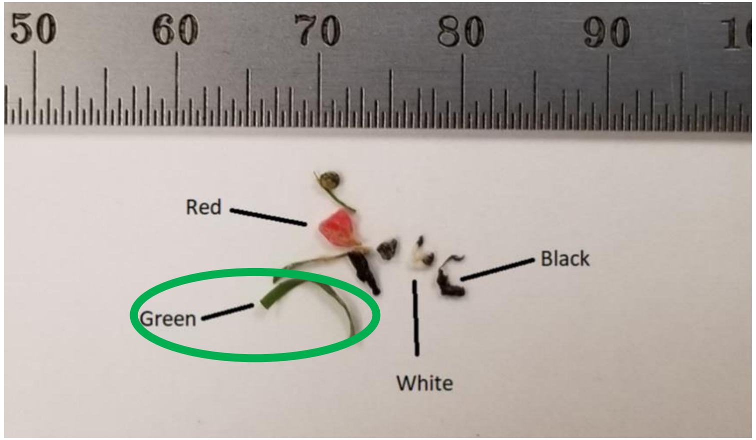
Eight example Microplastic targets and example marker compounds



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

Netted Polymer Sample – Lake Erie: Section of Green Portion Only, ~ 0.9 mg



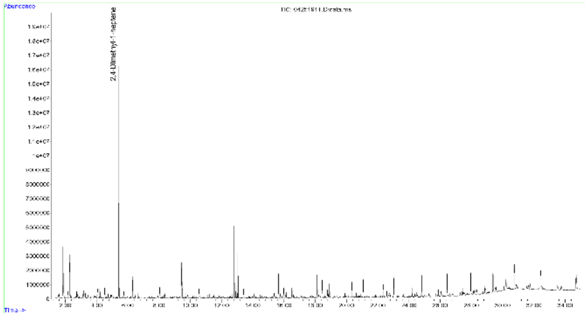


Sample GL 13-3

Library Entry	Polymer	Forward Match	Reverse Match	Marker Peaks	Ambiguous Peaks	Unidentified Peaks
P-0001	PP	82.1	81.4	1	55	73
P-0024	PP	89.9	83.8	0	58	71
P-0046	PP	84.1	63.5	14	79	36

How ChromIdent "Does It"

- Look for entries with a high number of marker peaks (entry #46 had 14)
- A high Forward match indicates a pure material (84% in this case – relatively pure)
- A low Forward match and high number of unidentified peaks points to a mixed material
- A low Forward match and high number of unidentified peaks but a good Reverse match are an indication that the polymer is present in the mix.



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Non-targeted via ChromIdent

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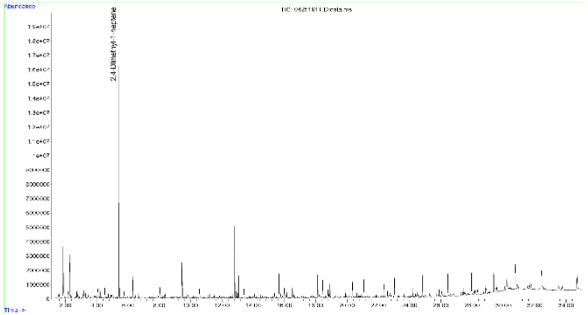
- Look further at the marker peaks and Compare the mass spectra of the marker peaks with the library
- Verify a match by direct comparison of the database entry and sample
- Finally, if more than one entry for a polymer appears in the results list look at results with high numbers of ambiguous peaks
- If no Marker peaks are identified, go through the ambiguous peak identifications to possibly identify the polymer.



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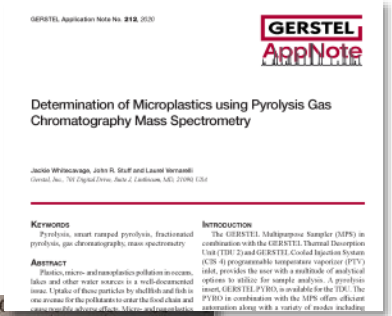
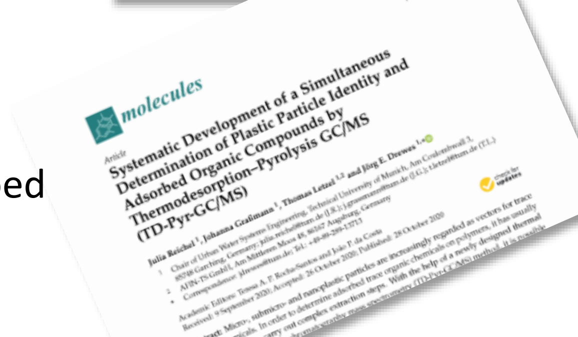
P-0046	PP	84.1	63.5	14	79	36

Selected PYRO & Microplastics References

- Microplastics (MPs) by Pyrolysis GC-MS (AppNote 212)
  - MPs in Filtered Great Lakes Water and Sediment
  - MPs in Body Care Product (Facial Scrub)
- Identification of Microplastics in Water by Pyrolysis Gas Chromatography Mass Spectrometry (AppNote 232)
  - Grey Water, Pond Water, Street Runoff, Bottled Water
- 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





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

GERSTEL Pyrolyzer

Thus many smaller samples from a single filtrate need to be run together to get a representative sample

Or, the sample must be cryomilled to make it homogeneous

So what does it all mean?

The Short Answers

- Thermal Extraction GC-MS analyzes larger representative samples but is indirect: polymers must have unique additives and samples should be relatively clean (e.g., PET MP‘s in drinking water); <u>MP analysis range is limited / undetermined</u>

- 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 and/ or cryomilling required for representative sampling

- TED GC-MS can do a wide range of polymers, additives runs, larger representative samples without cyromilling, and being off-line to the GC-MS makes it the most robust; more investment (two instruments and training) are needed

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GERSTEL TD 3.5^+ used as a Thermal Extractor

GERSTEL PYRO

Thermal Extraction/Desorption (TED-GCMS) System

The end at the end

- Pyrolysis GC-MS is a great tool for the ID and measurment of Microplastics
- Advances in open source data analysis software make analysis more reliable
- The same advances make data work-up faster and largely automated
- The sample sizes are too small, resulting in more manual sample prep work

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Advantec 47 mm PTFE Filters

- Large filters are great for large samples!
- "PYRO-Sized" samples are 1.2 mm diameter punches
- One sample alone could 'miss' analytes
- Best answer is cryomilling, but it's labor intensive
- Also, TEFLON is a BAD IDEA

~ 1 mm punch visualization

Synthetic Grey Water | Street Runoff | Pond Water | Bottled Water

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Jackie Whitecavage,
John R. Stuff,
Nicole Kfoury

Reference Material

Instrumentation Comparison

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	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

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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)