Lessons Learned and the Fundamentals of Pyrolysis - Gas Chromatography/Mass Spectrometry (PY-GC/MS) for the Analysis of Microplastics in Water Media

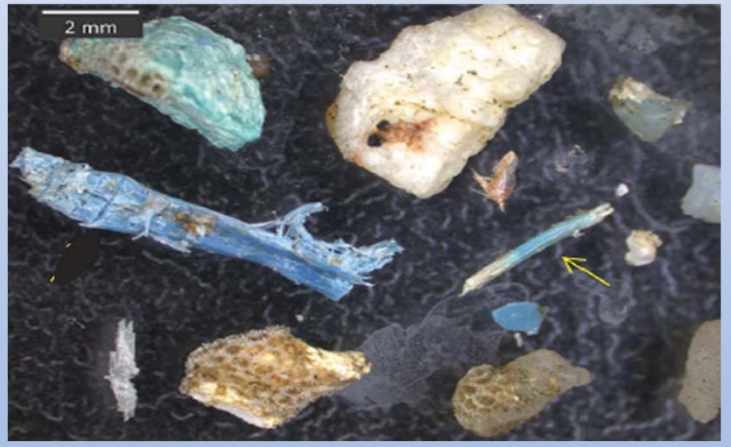
William Robberson, P.E. / Bill@OceanP3Systems.com

Analyzing Microplastics with Py-GC/MS

Measuring Microplastics: Building Best Practices & Methods for Collection, Preparation and Analysis

Harry L. Allen, EPA Region 9 On-Scene-Coordinator
Anna-Marie Cook, EPA Region 9 STL, ORD/CESER (Ret.)
Bill Robberson, P.E. - EPA Support / Ocean P3 Systems

Partners: California Department of Public Health
Amergent Techs
Pima County Water Resources
University of Arizona
Ocean P3 Systems
ASTM D19 Committee
Frontier Labs
Tohoku University



Disclaimer: *Although the U.S. EPA Office of Research and Development, EPA Region 9 and Frontier Laboratories funded the research described in this presentation, it does not necessarily reflect the Agency's nor Frontier's views. No official endorsement should be inferred. Additionally, neither EPA nor ASTM endorses the purchase or sale of any commercial products or services.*

ASTM Supporting Standards

1. D8332 - Collection of Water with high, medium or low suspended solids for the Identification and Quantification of Microplastic particles and fibers.
2. D8333 - Preparation of Water Samples with High, Medium or Low Suspended Solids for the Identification and Quantification of Microplastic Particles and Fibers using Raman Spectroscopy, IR Spectroscopy or Pyrolysis-GC/MS.
3. D5228-16 – Dissolving Polymer Materials

PY-GC/MS

Four technologies merge to form a unique system for analyzing solids

Pyrolysis	GC	MS	Software
Analysis of solids Thermal Degradation	Separation of Pyrolyzates	e- impact ionization	Identification quantitation Pyrolyzates

Vertical µ-Furnace

Fused silica, cross-linked phases

Ion source design, vac

focused, in-house

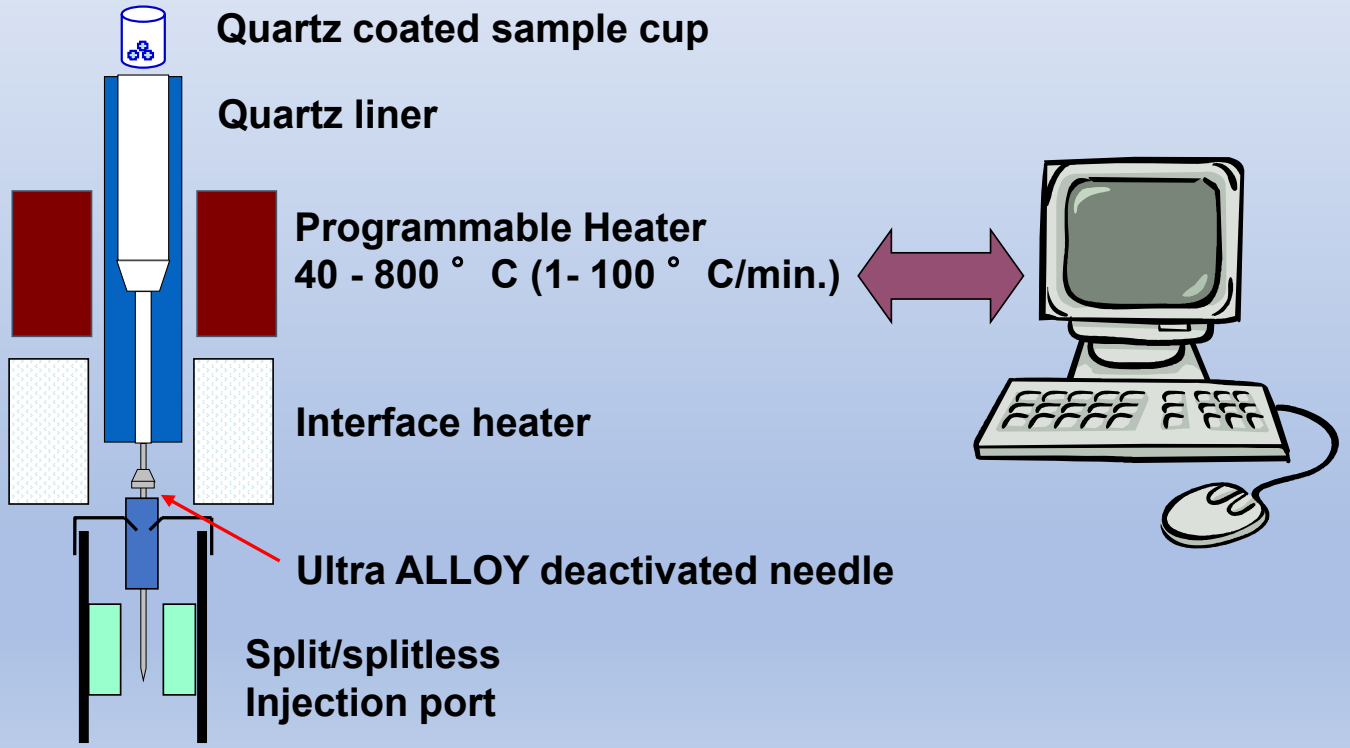
Analyzing Microplastics with Py-GC/MS

Preparing the sample for analysis

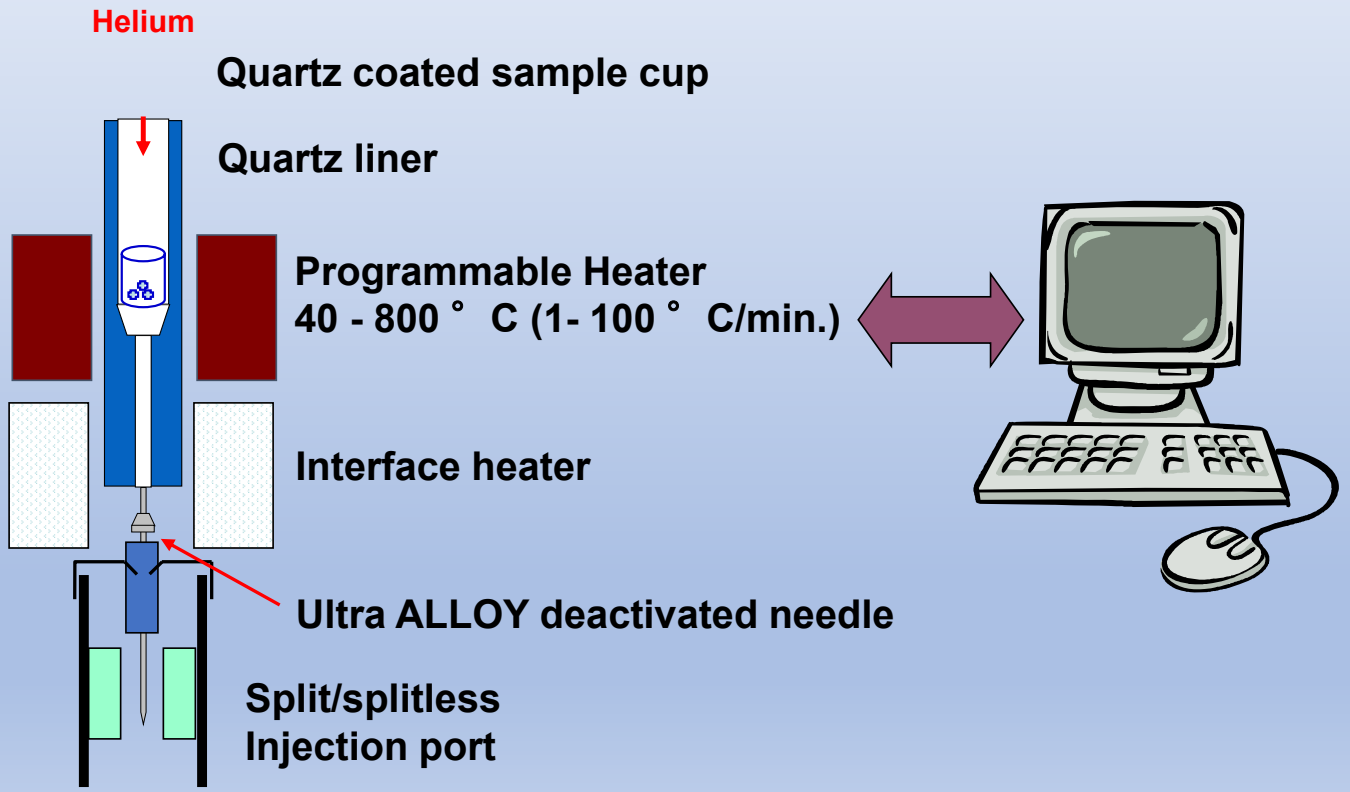
1. Prepare the sample: slices, chucks, small particles, solution, etc. → target compounds
2. Place a clean cup on a micro balance.
3. Tare the balance.
4. Place the sample in the cup.
5. Record the sample weight.

READY FOR ANALYSIS

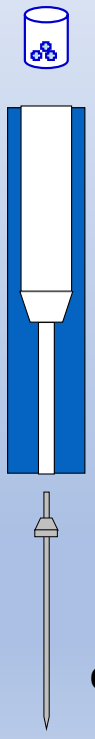
Analyzing Microplastics with Py-GC/MS



Analyzing Microplastics with Py-GC/MS

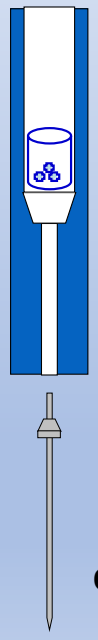


Analyzing Microplastics with Py-GC/MS



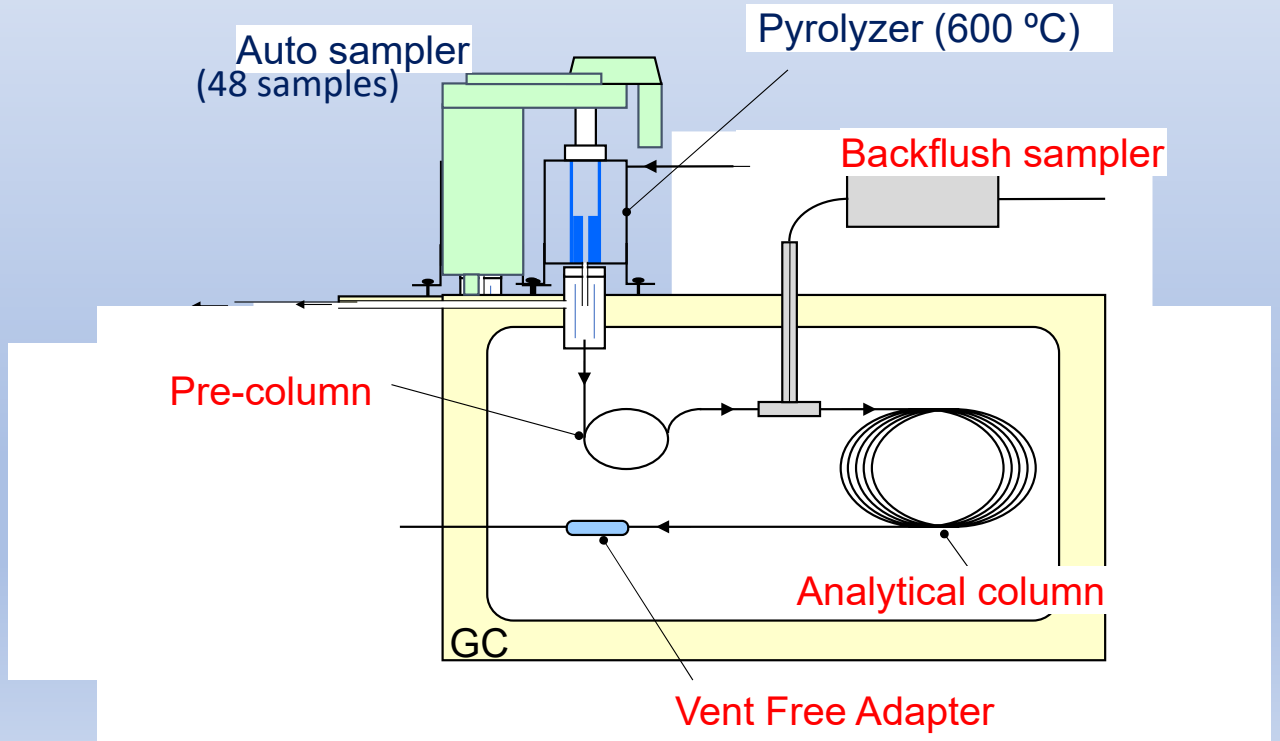
- Simple design
- Chemically inert surfaces
- No cold spots
- No dead volume
- Rapidly heated (<20msec drop time)
- Reproducible heat transfer

Analyzing Microplastics with Py-GC/MS



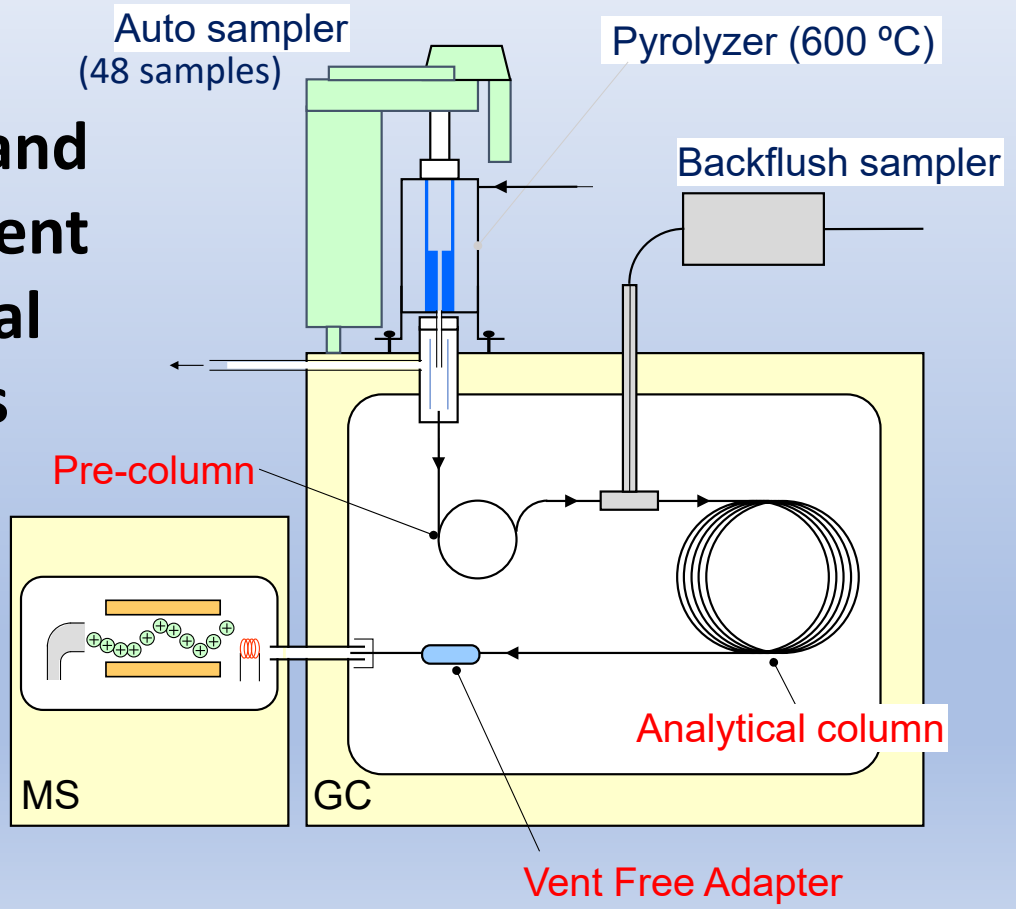
- Simple design
- Chemically inert surfaces
- No cold spots
- No dead volume
- Rapidly heated (<20msec drop time)
- Reproducible heat transfer

Separation of pyrolyzates: GC



Analyzing Microplastics with Py-GC/MS

Detection and Measurement of individual pyrolyzates



Analyzing Microplastics with Py-GC/MS

Figure 2. Specific set points for the analytical method

Pyrolyzer (Micro furnace type)
Automatic solid Sampler
Backflush System

- Furnace: 600 °C
- ITF: 300 °C
- Backflush time: 13 min

GC /MS

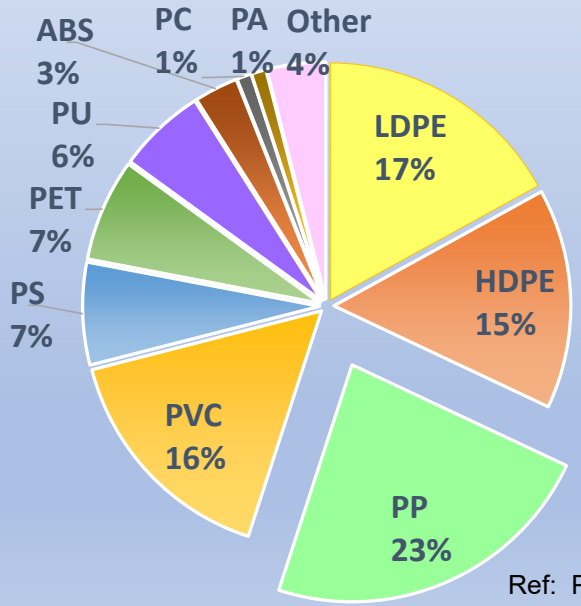
- Injector: split/splitless injector
- Insert tube: filled with deactivated packing [Ref. 2.2.5]
- Injection port temperature: 300 °C
- Oven: 40 (2min) - 20 ° C/min → 280 ° C (11 min hold)
- Pre-column: (50% diphenyl 50% dimethylpolysiloxane, 2 m, 0.25 mm i.d., 1.0 µm)
- Column: (5% diphenyl) dimethylpolysiloxane
- (30 m, 0.25 mm i.d., 0.5 µm)
- Carrier gas (He): Column flow: 1.0 mL/min,
- Total flow: 50 mL/min,
- Split ratio: 1/50
- Vent-free GC/MS adaptor
- MS interface: 300 °C
- Scan range: *m/z* 29 - 400
- Scan speed: 4 scans/s
- Threshold: 150 counts

Analytical semi-micro balance

Analyzing Microplastics with Py-GC/MS

Homogeneity of polymer samples

- Soluble polymers -> As solution
- Insoluble polymers -> As micro-powder



Ref: Plastics Europe（PEMRG） ［Marine plastic waste and microplastic, 1st vol］,Asahi research center Ltd.(**2017**).

Quantitation

Analyzing Microplastics with Py-GC/MS

How to spike STD polymers in the sample cup?

- Typical way to analyze polymer samples for Py-GC/MS
  → Ultra Micro balance is utilized. Weigh Solid samples (0.01~0.5 mg)

- For Micro Plastic analysis, we need to weigh 12 polymers separately for the quantitation.
  → It takes time and lot of work!

- 12 Polymer powder mix was created experimentally
  → Poor repeatability due to inhomogeneity of powder mix

- **10 polymers are soluble in the solvents. Polymer mix solution is spiked in the cup. (Easy, quick and homogeneous sample mix)**
- **2 polymers (PE and PP) are not soluble. These polymers are added as fine powder.**

Analyzing Microplastics with Py-GC/MS

Polymer Standard Mix: 3 solutions one powder

Step 1) Put 8 µL each of solution A, Solution B and Solution C into Eco-cup LF

Solution A	Solvents	Concentration (µg/µL)	Wt. (µg in 8 µL)
PVC	Tetrahydrofuran (THF)	5.0	40.0
PU		1.25	10.0

Solution B	Solvents	Concentration (µg/µL)	Wt. (µg in 8 µL)
PS	Dichloromethane (DCM)	1.0	8.0
ABS		2.0	16.0
SBR		2.0	16.0
PMMA		1.0	8.0
PC		0.50	4.0
Reference (Methyl Eicosanoate)		0.25	2.0

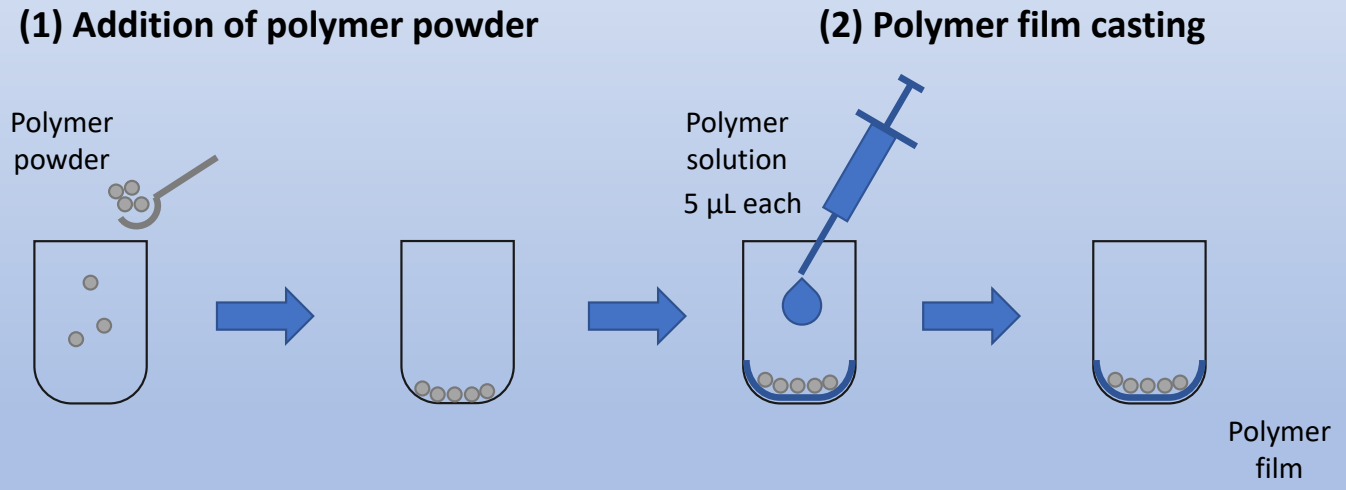
Solution C	Solvents	Concentration (µg/µL)	Wt. (µg in 8 µL)
PET	Hexafluoroisopropanol (HFIP)	2.0	16.0
N-6		0.625	5.0
N-66		2.25	18.0

Step 2) Dry above polymer sample mixture in Eco-cup at room temperature for 20 minutes.
Step 3) Put 4 mg of Powder mixture into above Eco-cup in Step 2)

Powder (homogeneous mixture)	Wt. (µg in 4 mg)
PE	160
PP	40
$CaCO_3$	3,800

Analyzing Microplastics with Py-GC/MS

Preparation of Polymer Calibration Standard



Analyzing Microplastics with Py-GC/MS

Polymer Standard Mix (One example)

12 MP reference samples (Vial #1 -7; MP-1-7)						
Sample name	Polymers		Glass vial (6 mL)		Concentration	
MP1	Powder	PE/ PP/ CaCO3 (4/1/45 wt ratio)	1 gram	x1	100%	
MP2	Powder	PE/ PP/ CaCO3 (2/0.5/45)	1 gram	x1	50%	
MP3	Powder	PE/ PP/ CaCO3 (0.4/0.1/45)	1 gram	x1	10%	
MP4	Solution A	PS	Film mixture in 6mL Vial (Put 5 mL of DCM in use)	x1	8 µg	in 10 µL of DCM
		ABS			16 µg	
		PMMA			8 µg	
		PC			2 µg	
		C20 Me-ester			2 µg	
MP5	Solution B	PVC	Film mixture in 6mL Vial (Put 5 mL of THF in use)	x1	40 µg	in 10 µL of THF
		PU			30 µg	
MP6	Solution C	PET	Film mixture in 6mL Vial (Put 5 mL of HFIP in use)	x1	16 µg	in 8 µL of HFIP
		Nylon-6			2.8 µg	
		Nylon-66			18 µg	
MP7	Pellet	PS	20 pellets	x1		

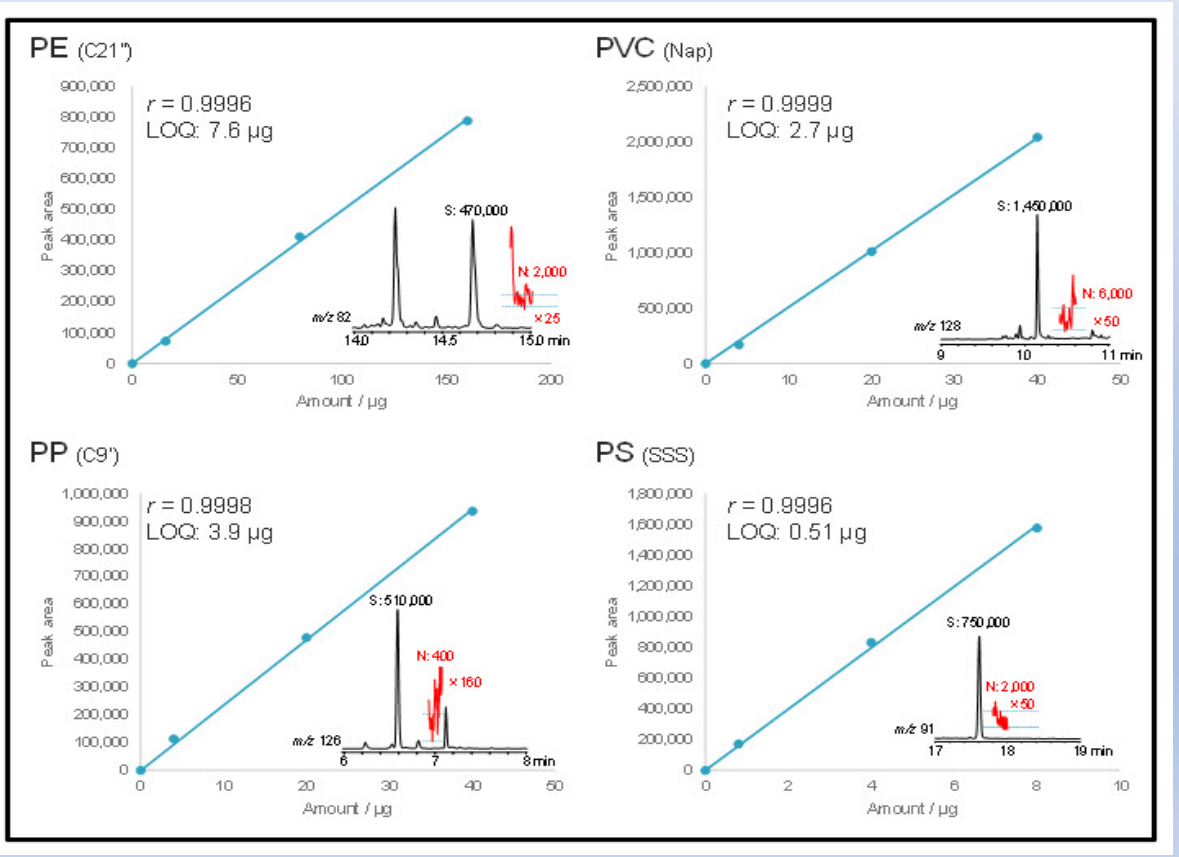
Analyzing Microplastics with Py-GC/MS

Target and Reference Ions

Polymers		Target compound		*m/z*			R.T.
Name	Abbr.	Name	Abbr.	Measure	Other ions	M.W.	(min.)
Polyethylene	PE	1,20-Heneicosadiene	C21"	82	41, 55,97	208	14.67
Polypropylene	PP	2,4-Dimethyl-1-heptene	C9'	126	43,55,70	126	6.62
Polyvinylchloride	PVC	Naphthalene	Naph	128	102	128	10.17
Polycarbonate	PC	4-Isopropenylphenol	IPP	134	91,119	134	10.83
Polyethylene terephthalate	PET	Benzophenone	BP	182	51,77, 105	182	13.26
Polymethyl methacrylate	PMMA	Methyl methacrylate	MMA	100	69,41,99	100	5.17
Nylon-6	N-6	ε-Caprolactam	Capro	113	30,55, 85	113	10.76
Polystyrene	PS	Styrene trimer	SSS	91	117, 207,312	312	17.63
Acrylonitrile butadiene styrene copolymer	ABS	2-Phenethyl-4-phenylpent-4- enenitrile	SAS	170	91,115,118	261	15.68
Styrene-butadiene rubber	SBR	4-Vinylcyclohexene	VCH	54	79, 66, 108	108	6.68
Nylon-6,6	N-66	Cyclopentanone	CP	84	39, 55, 56	84	6.38
Polyurethane	PU	4,4'-Methylenedianiline	MDA	198	106,182,197	198	15.58
Reference	Ref	Methyl eicosanoate	Me-Eic	326	74, 143	326	16.01

Analyzing Microplastics with Py-GC/MS

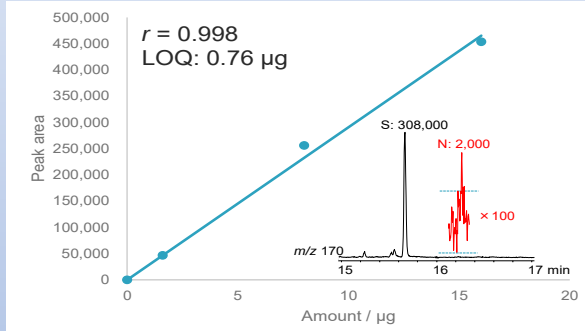
Calibration curve (ESTD)-1



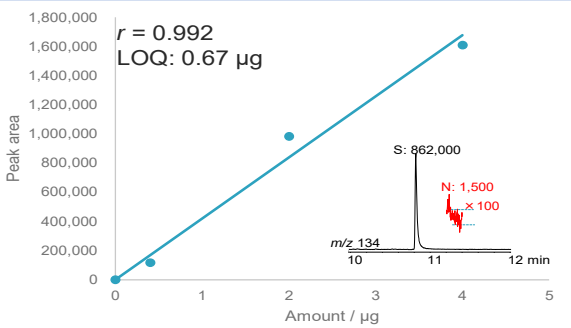
Analyzing Microplastics with Py-GC/MS

Calibration curve (ESTD)-2

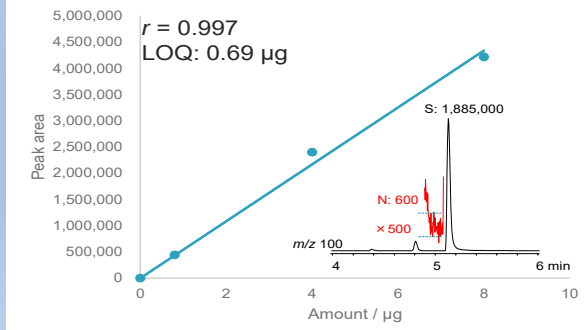
ABS (SAS)



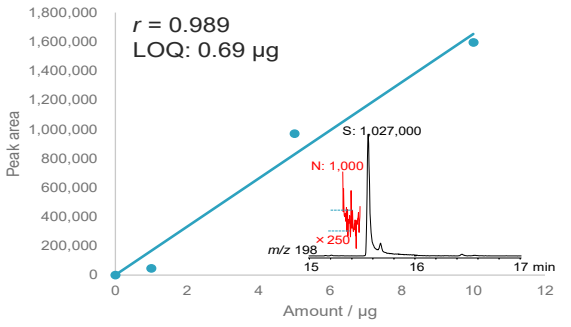
PC (IPP)



PMMA (MMA)

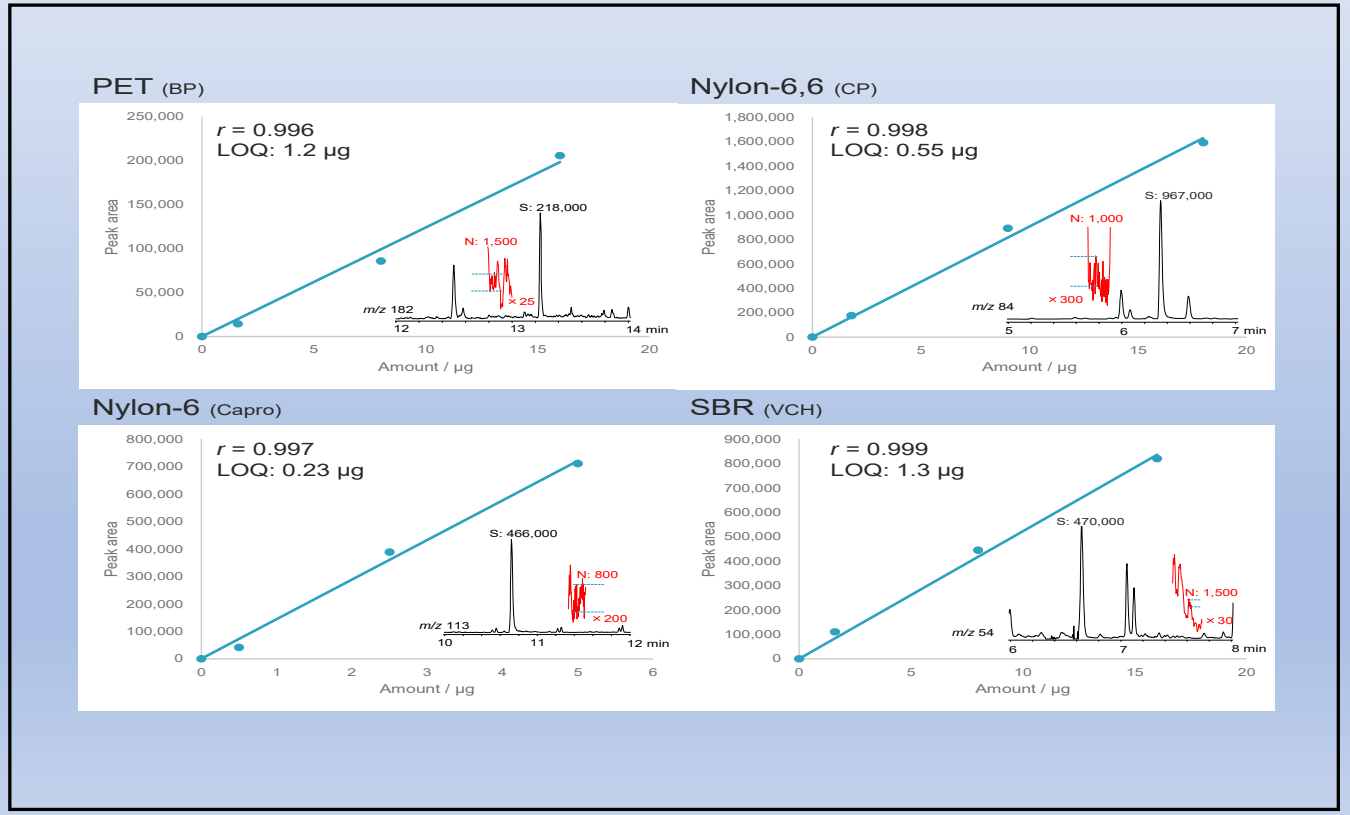


PU (MDA)



Analyzing Microplastics with Py-GC/MS

Calibration curve (ESTD)-3



Analyzing Microplastics with Py-GC/MS

Calibration curve Correlation Coefficient and LOQ

Polymer	PE	PP	PVC	PS	ABS	PMMA	PC	PU	PET	N-6	N-6,6	SBR
Correlation coefficient	0.9996	0.9998	0.9999	0.9996	0.998	0.997	0.992	0.989	0.996	0.997	0.9998	0.999
LOQ (μg)	7.6	3.9	2.7	0.51	0.76	0.69	0.67	0.69	1.2	0.23	0.55	1.3

Repeatability

Analyzing Microplastics with Py-GC/MS

Repeatability (n = 7)

File No.		PE	PP	PVC	PS	ABS	PMMA	PC	PU	PET	N6	N66	SBR	Ref.	Powder mix (µg)
	µg	160	40	40	8	16	8	4	10	16	5	18	16	2	
	target	C21"	C9'	Nap	SSS	SAS	MMA	IPP	MDA	BP	Capro	CP	VCH	Me-Eic	
	R.T. min	14.67	6.62	10.17	17.63	15.68	5.17	10.83	15.58	13.26	10.76	6.38	6.68	16.01	
	m/z	82	126	128	91	170	100	134	198	182	113	84	54	326	
TIAR 20080423	Area /Ref.	1.44	1.66	3.49	2.74	0.795	7.28	2.98	2.57	0.343	1.12	2.71	1.42	1	4,090
TIAR 20080424		1.34	1.54	3.41	2.60	0.764	6.98	2.95	2.61	0.333	1.22	2.64	1.34	1	3,920
TIAR 20080425		1.30	1.49	3.23	2.29	0.697	6.68	2.53	2.46	0.325	1.15	2.53	1.30	1	3,960
TIAR 20080426		1.32	1.57	3.39	2.80	0.748	6.87	2.62	2.74	0.326	1.17	2.66	1.37	1	4,100
TIAR 20080427		1.19	1.50	3.31	2.46	0.726	6.86	2.54	2.46	0.319	1.15	2.56	1.32	1	3,900
TIAR 20080428		1.30	1.57	3.33	2.47	0.738	6.96	2.47	2.77	0.354	1.14	2.55	1.32	1	4,060
TIAR 20080429		1.14	1.39	3.22	2.67	0.719	6.57	2.34	2.61	0.349	1.17	2.55	1.31	1	3,950
Ave		1.29	1.53	3.34	2.57	0.741	6.88	2.63	2.60	0.336	1.16	2.60	1.34	1	
SD		0.091	0.077	0.090	0.165	0.030	0.211	0.225	0.113	0.013	0.027	0.063	0.039	0	
RSD % (n=7)		7.0	5.0	2.7	6.4	4.0	3.1	8.5	4.3	3.7	2.4	2.4	2.9	0.0	

(CaCO3: 3,800 µg)

Analyzing Microplastics with Py-GC/MS

63-day Testing Table

			RSD (%)												
Date	GC/MS	N=	PE	PP	PS	ABS	SBR	PMMA	PC	PVC	PU	PET	N6	N66	Ref.
7/7/2020	Vendor A	5	2.9	3.2	1.7	2.7	1.9	1.8	3.8	1.0	12.0	8.8	2.2	2.0	1.5
7/10/2020	Vendor A	5	2.4	1.8	3.6	0.5	1.1	0.6	3.6	1.2	10.0	1.6	3.5	0.6	1.0
7/22/2020	Vendor A	7	3.2	2.7	4.4	1.5	0.7	0.6	2.0	1.8	4.6	3.1	1.6	1.0	0.9
7/22/2020	Vendor B	7	2.1	2.8	2.5	6.4	2.2	2.0	2.8	1.2	4.6	3.1	4.3	1.7	1.2
8/4/2020	Vendor A	7	3.9	2.6	6.6	2.5	2.9	2.5	4.2	2.6	6.7	6.8	5.7	3.2	5.0
8/12/2020	Vendor A	5	3.5	2.3	3.2	1.2	0.6	1.2	6.3	1.0	12.1	4.5	1.8	1.7	1.1
8/17/2020	Vendor A	5	3.3	3.1	7.1	1.7	2.2	1.8	2.5	1.3	2.8	4.2	1.9	1.1	2.6
8/24/2020	Vendor A	5	1.2	1.3	2.6	1.7	1.0	1.4	2.8	1.8	7.1	2.8	1.7	1.0	1.4
Average	Average		2.8	2.5	4.0	2.3	1.6	1.5	3.5	1.5	7.5	4.4	2.8	1.5	1.8

Analyzing Microplastics with Py-GC/MS

SUMMARY

- The combination of Py-GC/MS and application software written specifically to deconvolute pyrograms of multi-polymer mixtures is a powerful tool for the determination of micro-polymers in water.

- Twelve common polymers are validated using the sample prep and analytical protocols described in the method. Repeatability for all 12 polymers is consistently <5%RSD.

- The method has demonstrated comparability with a number of commercially available GC/MS systems.

Analyzing Microplastics with Py-GC/MS