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Excellence in Science

Automated Py-GCMS Workflow for the Qualitative and Quantitative Analysis of Plastics of Diverse Sizes in Environmental Samples

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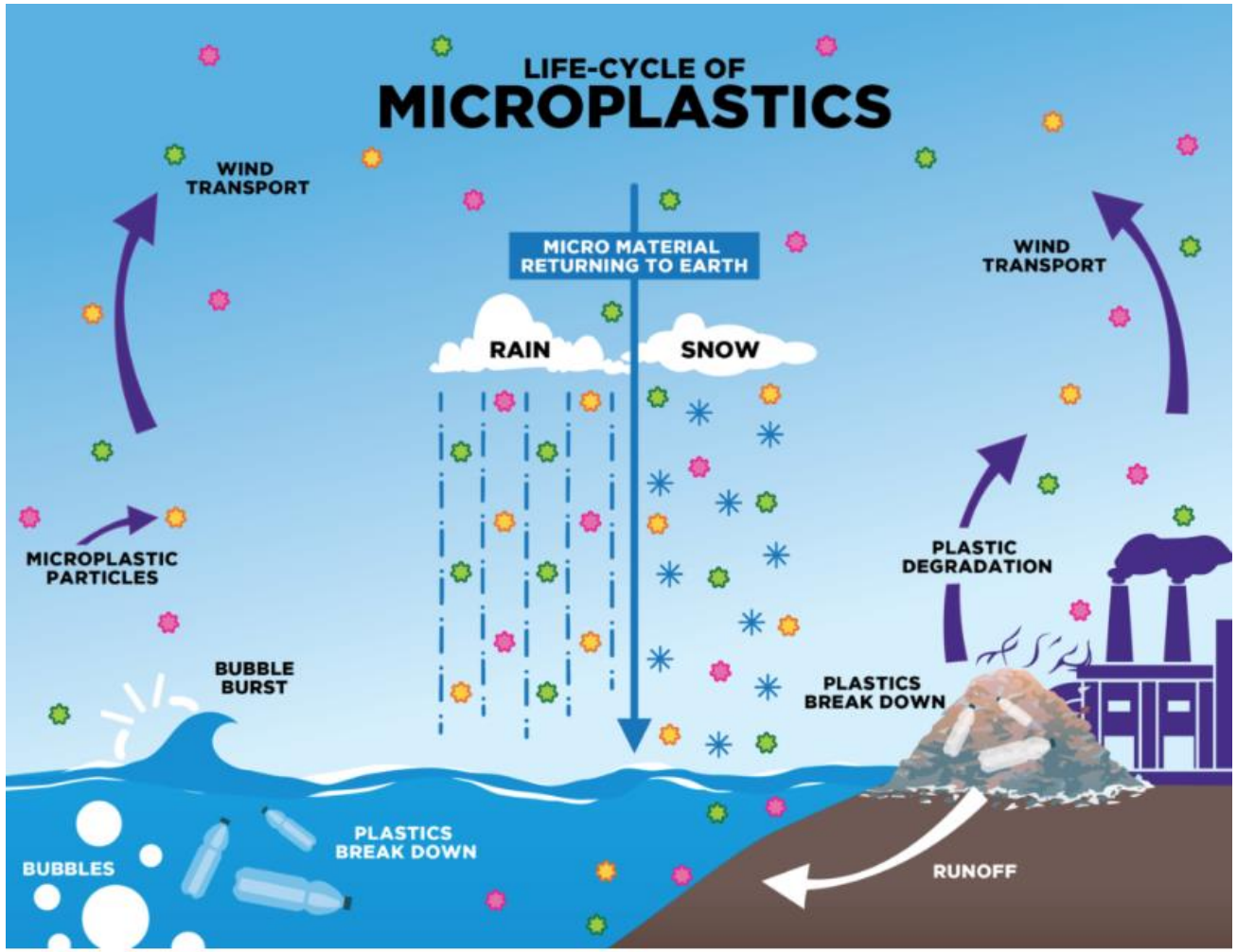
Life cycle of Plastics

- MP pollution is persistent and ubiquitous.
- MP life cycle involves the plastic break down, runoff into waterbodies, volatilization into the atmosphere, wind transport and atmospheric deposition.
- Some materials are not biodegradable and persist for along time

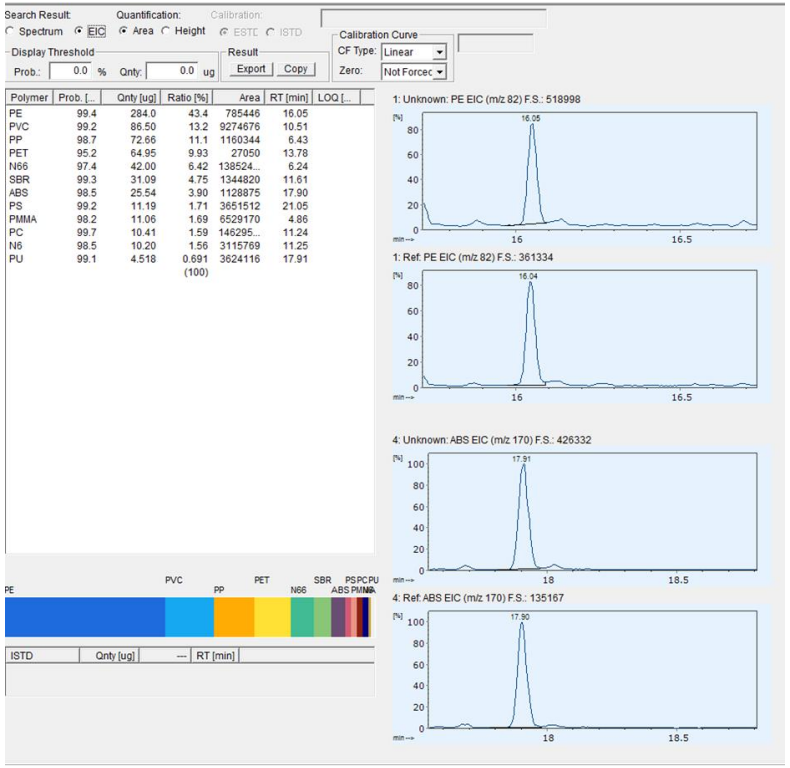


Goal of the Study

Automated Py-GCMS Workflow for the Qualitative and Quantitative Analysis of Plastics of Diverse Sizes in Environmental Samples

1. **Develop qualitative method for individual unknown polymers**
    1. Identify unique pyrolyzates of the polymers and their quant ions
    2. Analyze a mixed standard sample to ensure efficient separation and identification
2. **Perform quantitative analysis on mixed standard samples**
    1. Calibration curve creation with 5 levels
3. **Performance evaluation of the system and method**
    1. Demonstration of Precision
    2. Demonstration of Accuracy
    3. LOQs and IDLs

GCMS-QP2020NX with PY-3030D



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Microplastics Workflow

1. Polymer Preparation

- Solid polymers are sliced or ground
- Placed into an eco cup with quartz wool

2. EGA-MS Analysis

- Thermal zone established
- Optimum PY furnace temp determined for Single Shot

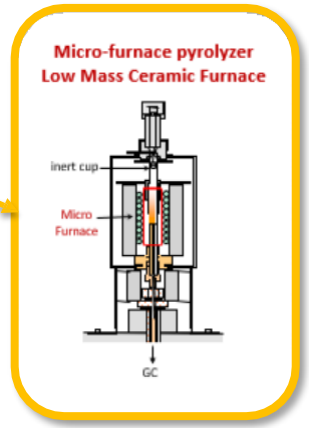
3. Single Shot GCMS

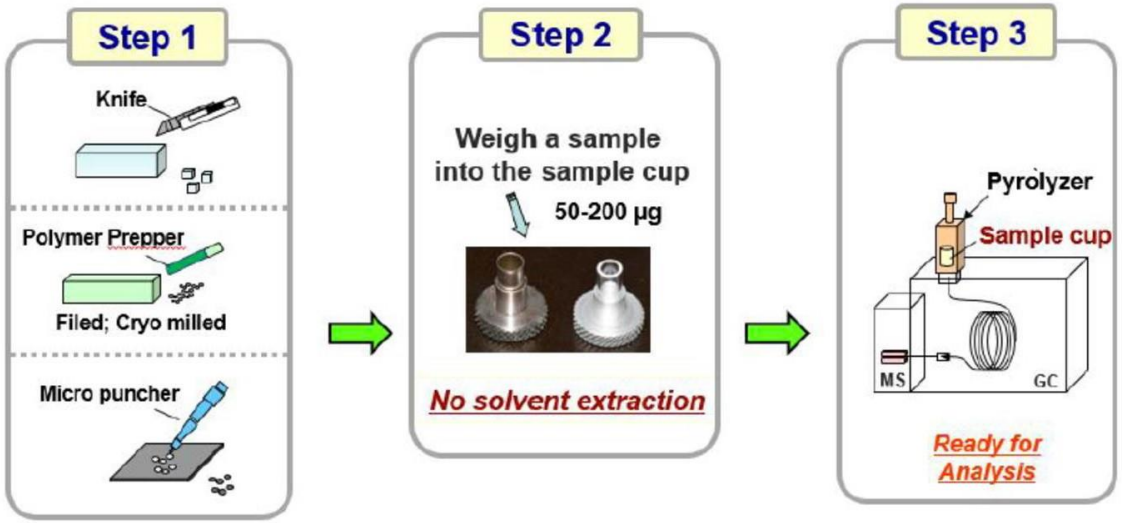
- Pyrolyzates formed by flash pyrolysis
- Pyrogram obtained

4. Data Analysis and Comparison

- All pyrolyzates identified via F-Search library
- Characteristic pyrolyzate determined via data comparison

Pyrolysis – GC/MS: Polymer Preparation





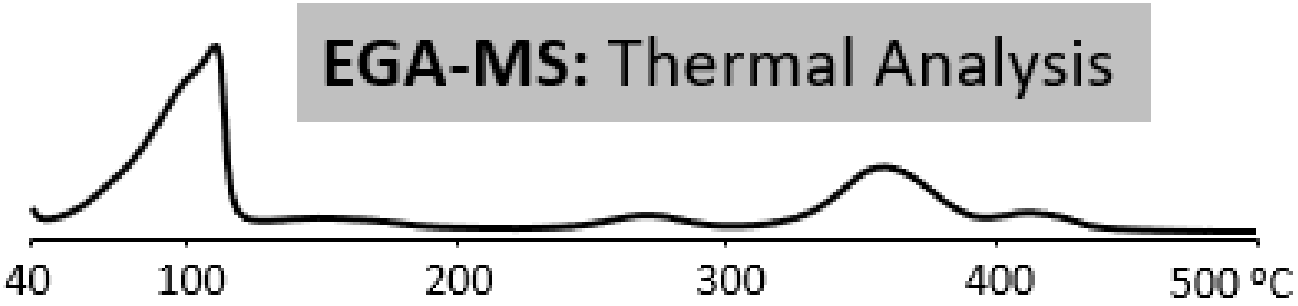
EGA/PY-3030D multi-shot pyrolyzer, AS-1020E auto-shot sampler (Frontier Laboratories Ltd.)

GCMS-QP™2020 NX

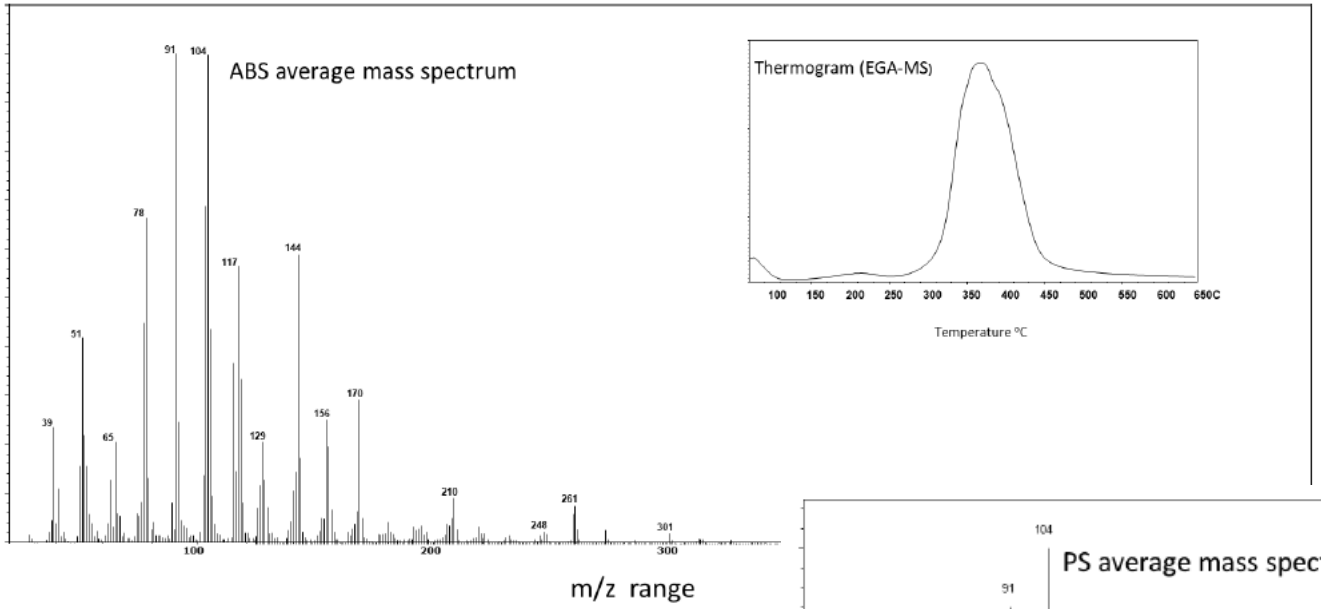
EGA Analysis

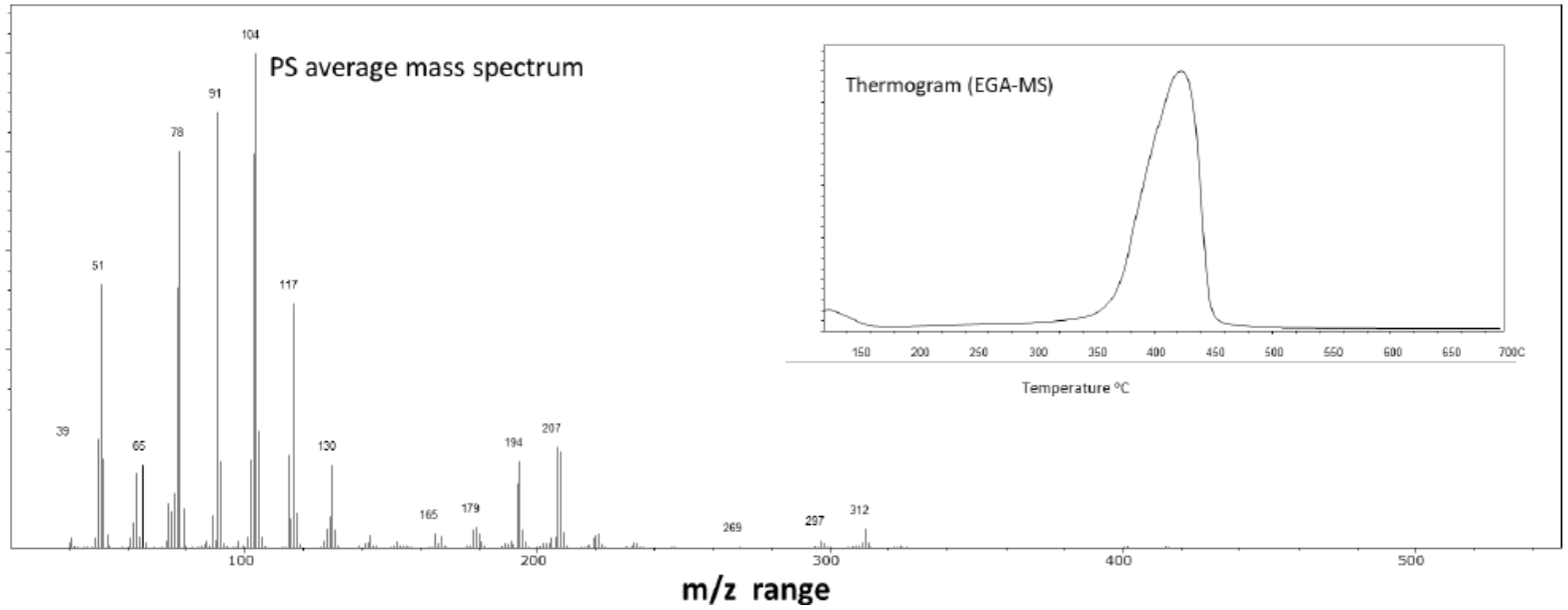
- **Imperative to understand the thermal zones of the polymers in question**
- **Initial spectral information for specific polymers**
  - Average mass spectrum can be matched against libraries
  - Thermograms can be complex requiring additional analysis
- **Major m/z could be prevalent for multiple polymers**

- **Heated from 100°C → 700 ° C**
- **2.5 M EGA tube**



EGA Analysis

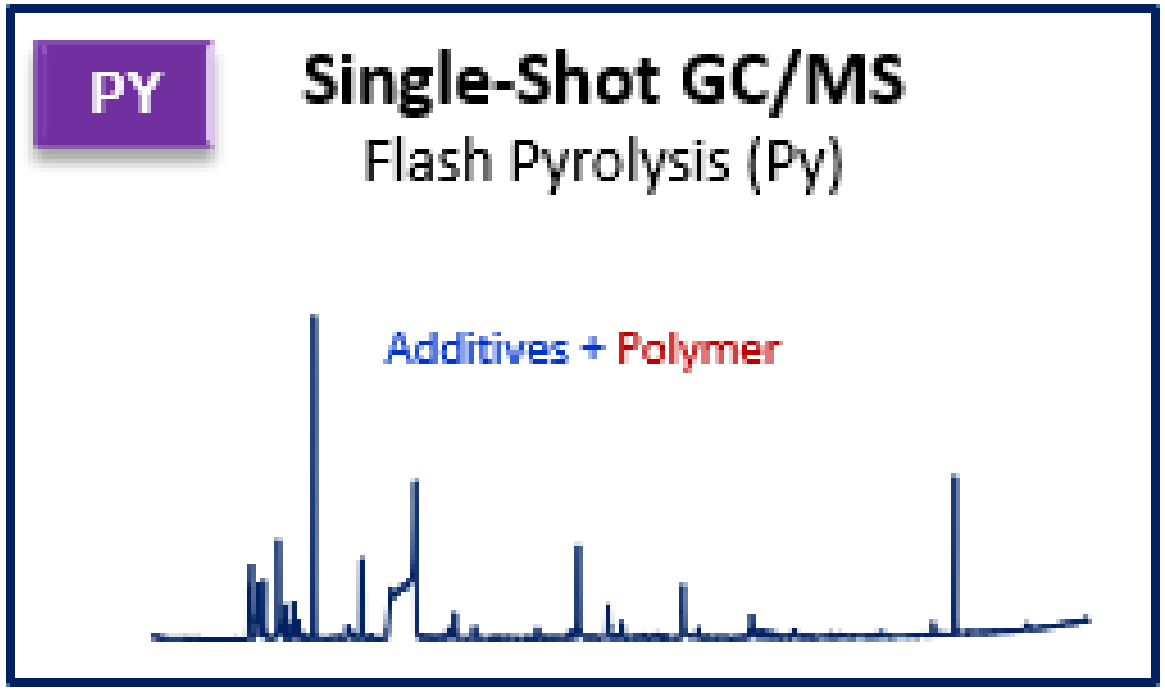




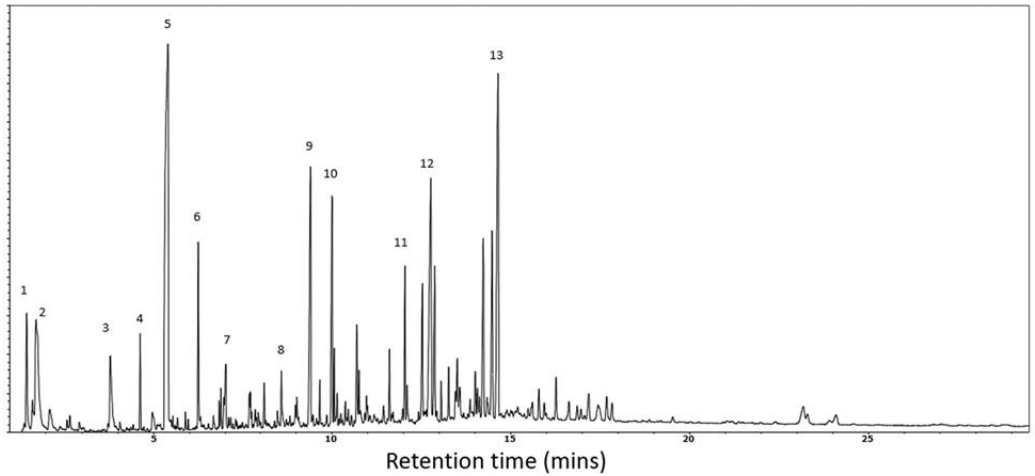
Single Shot Analysis

- Flash pyrolysis temperature determined from EGA analysis
- Identify compounds unique to each individual polymer (pyrolyzates)
- Plastics analysis creates complications due to the fact several major components are shared amongst polymers

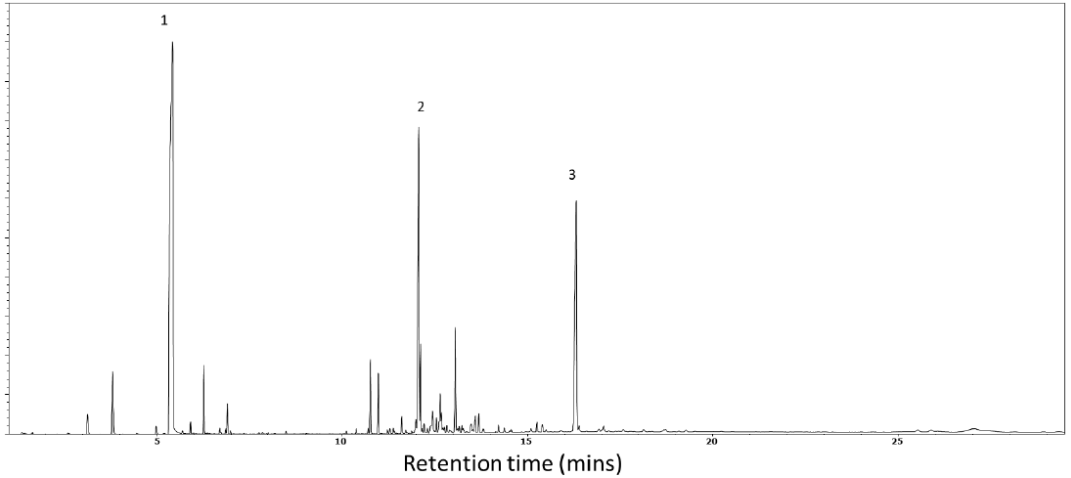
- Flash Pyrolysis temperature was set to 600 °C
- UAMP Column 30 M with 2 M pre column



Single Shot Analysis

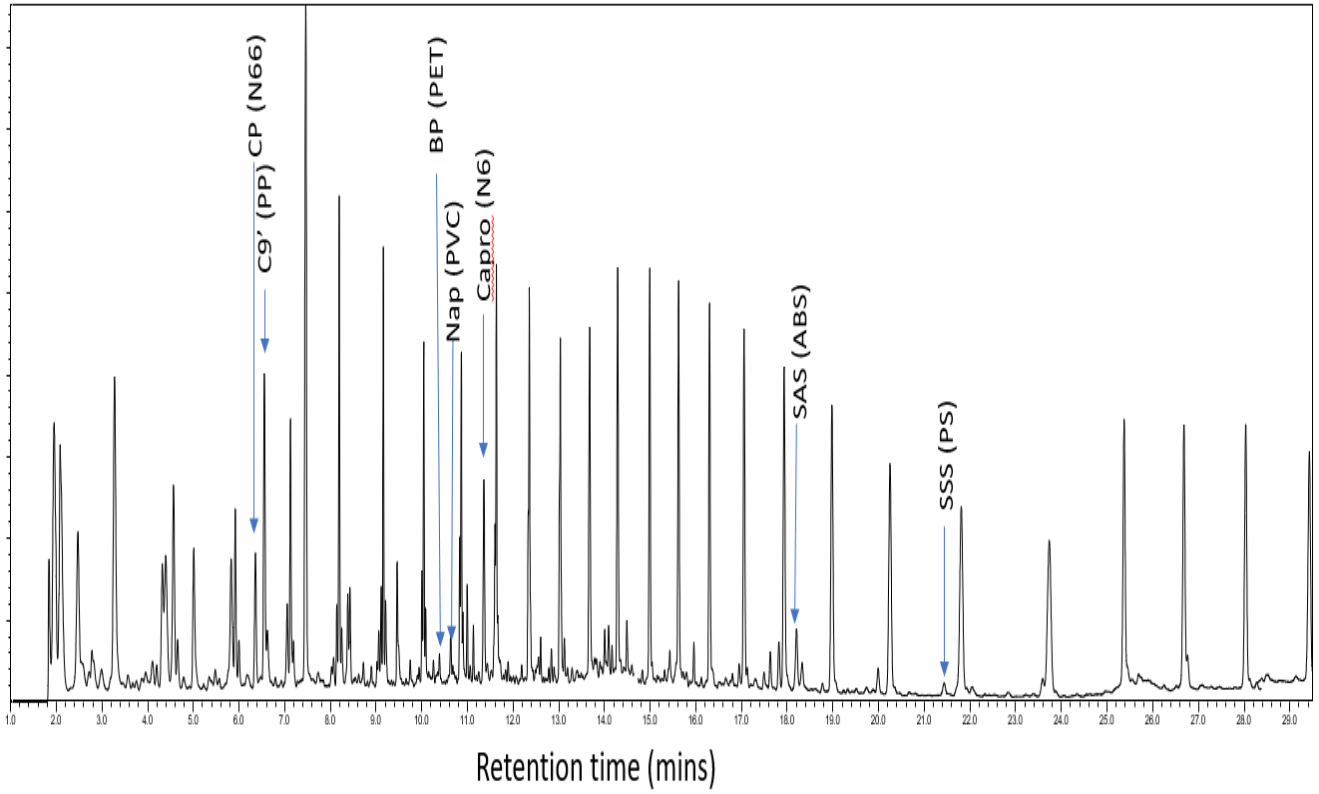


Peak # ABS	F-Search Result
1	1,3-Butadiene
2	Acrylonitrile
3	Toluene
4	4-Vinylcyclohexane
5	Styrene
6	Alpha-Methylstyrene
7	2-Methylenepentanedinitrile (A dimer)
8	2-Methylene-4-phenylbutanenitrile (hybrid dimer)
9	4-Phenylbutanenitrile
10	4-Phenylpent-4-enenitrile (hybrid dimer)
11	3-Butene-1,3-diyldibenzene (styrene dimer)
12	2-Methylene-4-phenylheptanedinitrile (hybrid trimer)
13	2-Phenethyl-4-phenylpent-4-enenitrile (hybrid trimer)



Peak # PS	F-Search Result
1	Styrene
2	3-Butene-1,3-diyldibenzene (styrene dimer)
3	5-Hexene-1,3,5-triyltribenzene (styrene trimer)

Mixed Polymer Standard

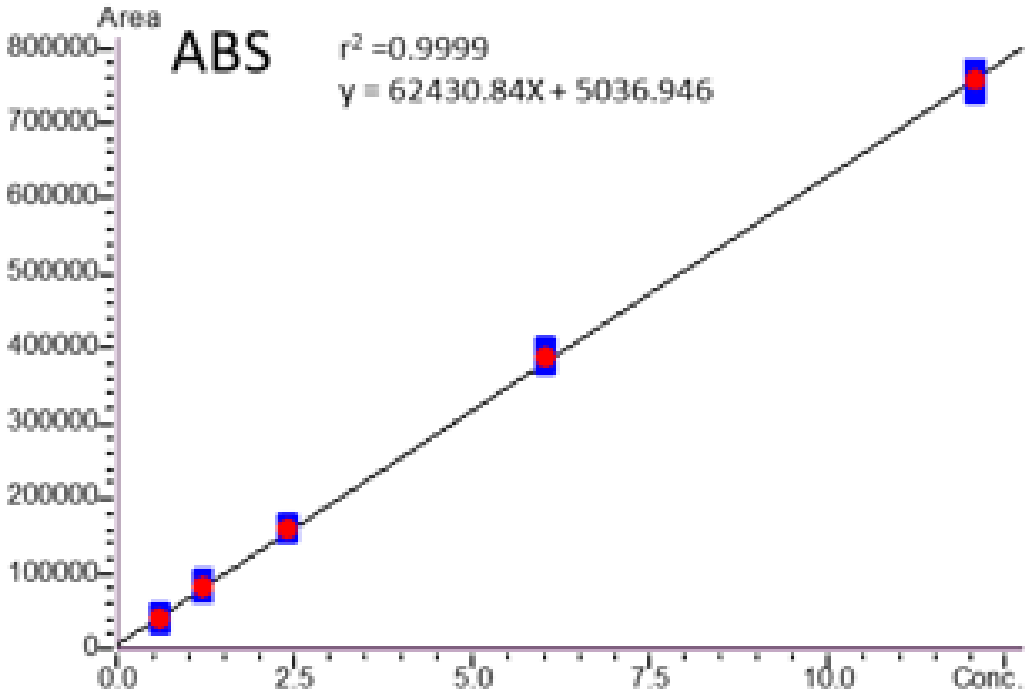


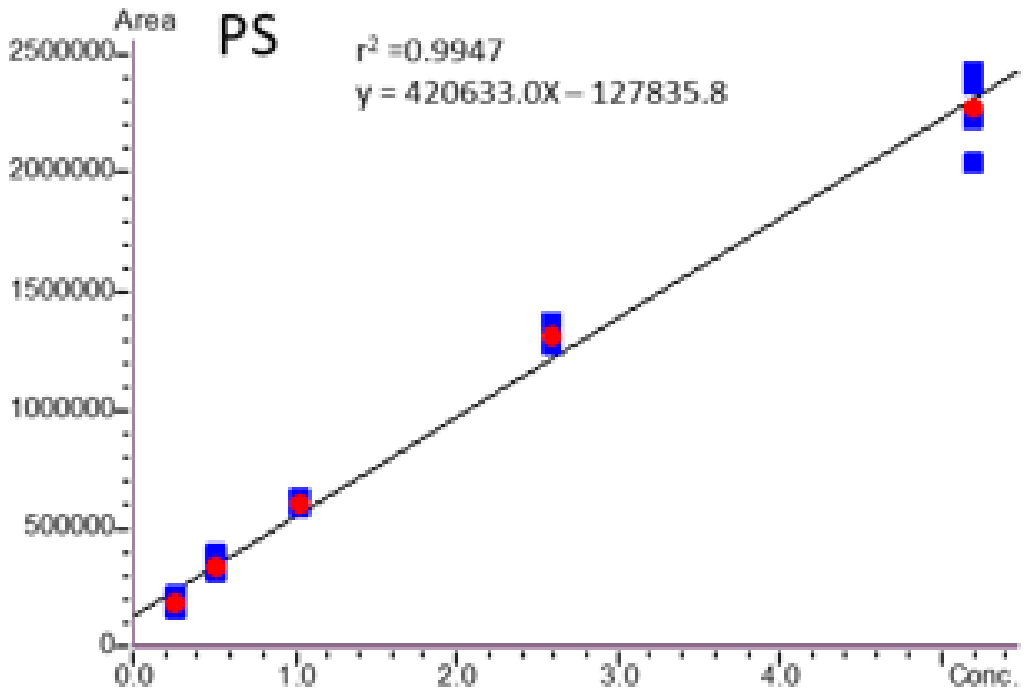
Compound name	Characteristic pyrolyzate	Quant ion	Qual ion
ABS	2-Penyl-4-phenylpent-4-enenitrile (SAS)	170	91,115,118
Nylon 6	ε -Caprolactam (Capro)	113	30,55,85
Nylon 6,6	Cyclopentanone (CP)	84	39,55,56
PET	Benzophenone (BP)	182	51,77,105
PP	2,4-Diemethyl-1-heptene (C9')	126	43,55,70
PS	Styrene trimer (SSS)	91	117,207,312
PVC	Naphthalene (Nap)	128	102

Quantitative Analysis

- **Imperative to understand the thermal zones of the polymers in question**
- **Initial spectral information for specific polymers**
  - Average mass spectrum can be matched against libraries
  - Thermograms can be complex requiring additional analysis
- **Major m/z could be prevalent for multiple polymers**
- **Calibration curve consisted of five points: 0.2, 0.4, 0.8, 2.0 and 4.0 mg of a Frontier MPs-$CaCO_3$ standard**
- **2 mg of quartz wool was used to prevent contamination**

Calibration Results





Statistical Analysis of Calibration Curves

Microplastic polymer	Characteristic Pyrolyzates	Linear range (µg)	Linearity (r^2)	Polymer mass in 4mg sample weight
PE	1,20-Heneicosadiene	7.29 -145.8	0.9999	145.8
PP	2,4-Dimethyl-1-heptene	1.79-35.7	0.9999	35.7
PS	Styrene trimer	0.26-5.2	0.9947	5.2
ABS	2-Phenethyl-4-phenylpent-enenitrile	0.60-12.1	0.9999	12.1
SBR	4-Vinylcyclohexene	0.75-15.0	0.9997	15.0
PMMA	Methyl methacrylate	0.27-5.3	0.9985	5.3
PC	4-Isopropenylphenol	0.26-5.1	0.9999	5.1
PVC	Naphthalene	2.12-42.4	0.9997	42.4
PU	4,4'-Methylenediabiline	0.11-2.1	0.9972	2.1
PET	Benzophenone	1.43-28.6	0.9995	28.6
N6	ε-Caprolactam	0.25-4.9	0.9998	4.9
N66	Cyclopentanone	1.03-20.7	1.0000	20.7

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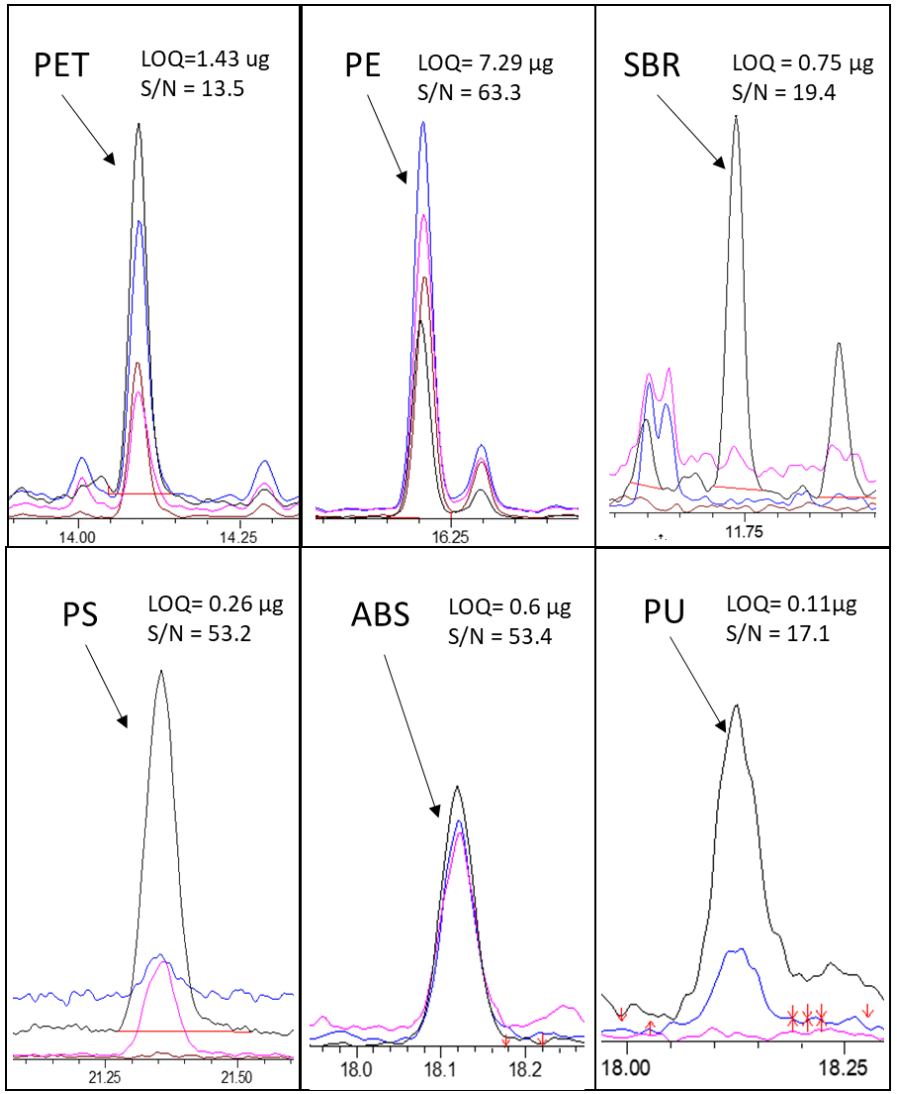
Precision Test

Polymer	Inter day precision test RSD (%) (n=7)		Recovery % (n=7)		Retention Time (min)	LOQ (µg)	% Drift (0.8mg)
	3 mg	0.2 mg	3 mg	0.2 mg			
PE	3.6	9.7	99.0	99.9	16.2	7.3	-16.6
PP	2.5	9.2	99.6	111.2	6.6	1.8	-7.3
PS	12.1	23.6	92.2	66.4	21.3	0.3	-4.1
ABS	3.3	7.8	92.9	107.3	18.1	0.6	-18.1
SBR	2.3	6.8	96.0	121.8	11.7	0.8	-10.3
PMMA	2.5	8.5	102.8	103.6	5.0	0.3	-3.5
PC	2.8	7.1	97.2	123.0	11.4	0.3	-11.0
PVC	5.9	9.3	97.5	114.1	10.6	2.1	-11.6
PU	5.9	3.6	94.9	145.1	18.1	0.1	-20.5
PET	4.0	12.7	95.0	126.7	14.1	1.4	-20.4
N6	2.9	10.9	100.1	112.0	11.4	0.3	-10.0
N66	2.5	8.1	100.8	121.5	6.4	1.0	-7.4

Limits of Quantitation

- **Lowest calibration point of 0.2mg was used for LOQ**
- **Goal of s/n of 10 or greater required**
- **LOQs ranged from 0.1 – 7.29ug**



Where Do We Go From Here?

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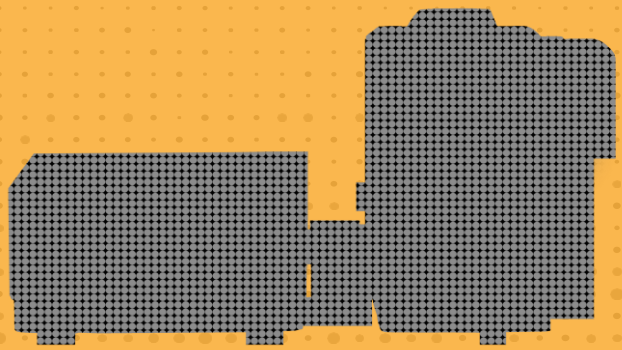
AIM-9000 Infrared Microscope
with IRXross FTIR Spectrometer

PY-3030D with
GCMS-QP2020NX

Sign-up to join the launch of the new instrument that will magnify your workflows for plastic analysis!



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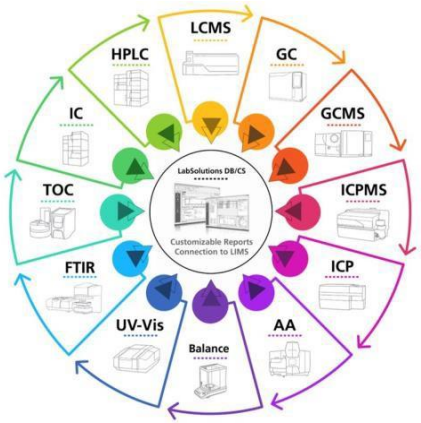

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