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Application News

No. GCMS-2201

Gas Chromatography Mass Spectrometry

How to Kickstart Your Micro- and Nanoplastics PY-GC/MS Analysis

■ Abstract

Plastic pollution is a global concern impacting shorelines and freshwater bodies across the world. One of the analytical techniques used to analyze microplastics (MPs) is pyrolysis followed by gas chromatography mass spectrometry. In this study, we demonstrated the suitability of a Frontier Lab multi-shot pyrolyzer with a Shimadzu gas chromatograph/mass spectrometer (PY-GC/MS) for the sensitive identification of major polymeric components of MPs. Because many polymers have a similar chemical structure, in PY-GC/MS analysis, it is pivotal to determine a characteristic pyrolyzate that would be used for identification and measurement of a specific polymer.

Experiments were conducted to determine an optimal pyrolysis furnace temperature of 600 °C, which was used for single shot analyses in the second experimental step. A data comparison of pyrograms from these single shot studies determined that the following pyrolyzates are best for the identification and quantification of each polymer within a MP sample: 2-Phenethyl-4-phenylpent-4-enenitrile for acrylonitrile butadiene styrene copolymer (ABS), ε-caprolactam for Nylon-6 (N-6), cyclopentanone for Nylon-6,6 (N-66), benzophenone for polyethylene terephthalate (PET), 2,4-diemethyl-1-heptene for polypropylene (PP), styrene trimer for polystyrene (PS), and naphthalene for polyvinylchloride (PVC).

User Benefits

- Compared to other analytical techniques, PY-GC/MS analysis has less sample preparation (no need for solvent extraction), fewer interferences, less potential for analytical error, enables straightforward calibration [ii].
- Can be applied to complex matrices. Not affected by peak masking or florescent dyes.
- Ability to measure mix polymer sample. Not limited by particle size.

■ Introduction

With increasing use and disposal of plastic materials globally, plastic pollution has become a prevalent concern. Millions of tons of plastic from food packaging or other household and commercial products are disposed into landfills, or simply discarded without control; ultimately, these materials find their way into various water bodies and other environmental compartments. In the environment, plastics are not completely inert, and go through various mechanical and chemical decay to form microplastics (MP) and nanoplastics (NP). Additionally, discharges from plastics manufacturing facilities may contribute to the load of nurdles (plastic pellets of variable size) in the environment.

The implications of MP and NP pollution in our environment are currently not well understood[i]. Therefore, to understand the toxicological effects, calculate environmental mass-balances, and conduct any needed remediation actions, it is imperative to be able to identify and measure MP and NP in environmental samples.

There are several analytical techniques, such as infrared and Raman spectroscopy, which are used to identify individual polymers and count the number of particles. However, these techniques can be tedious and costly[ii]. PY-GC/MS, although a destructive technique, offers many advantages, such as its ability to create a fast workflow that quantifies the mass of contaminants, and is precise and accurate.

Due to the similar chemical properties that exist within many polymers, it becomes challenging to identify a targeted polymer in complex environmental matrices, i.e., the different polymers in samples interfere with the identification of each other if they present similar physicochemical properties. To provide guidance for minimizing these challenges when kickstarting the analysis of MP and NP by PY-GC/MS, two publications detailing the workflow for identifying and quantifying the targets of interest have been published.

The objective of this first document is to demonstrate how to qualitatively identify a characteristic pyrolyzate that can solely be used to distinguish a polymer within a complex microplastic sample by PY-GC/MS. This work uses evolved gas analysis (EGA) followed by flash pyrolysis to obtain pyrograms (a plot of detector response of analytical signal versus retention time) for several polymers that are important in environmental studies. The chromatographic separation of pyrolysis degradation products (pyrolyzates) achieved in the GC is essential for identifying the targeted compounds.

A characteristic pyrolyzate exclusively formed from the targeted polymer is selected for identification of that polymer, and its later quantification, in the environmental sample. The following section of this study describes the analysis of pure polymer standards to determine the exclusive pyrolyzate for each polymer of interest: polypropylene (PP), acrylonitrile-butadiene-styrene copolymer (ABS); nylon-6 (N-6); nylon-6,6 (N-66); polyvinylchloride (PVC), polyethylene terephthalate (PET) and polystyrene (PS).

These characteristic pyrolyzates are essential for the proper quantification of micro- and nanoplastics. The MP quantitation workflow is published in application note GCMS-2202.

■ Experimental Approach

In the study, a Frontier Lab multi-shot pyrolyzer (PY), was interfaced with Shimadzu GC/MS (Figure 1).

The system configuration for this application consisted of a Shimadzu GC/MS, model QP2020 NX, a Frontier multi-shot pyrolyzer, model EGA/PY-3030D, an auto-shot sampler, model AS-1020E, an ultra-alloy metal capillary column, a short inert tube (EGA analysis), a vent-free GC/MS adapter, a F-Search search engine library and a computer.

Figure 1: Shimadzu GCMS-QP2020 NX and Frontier Multi-Shot Pyrolyzer EGA/PY-3030D.

Seven polymers were selected for this study based on their prevalence in environmental samples. These polymers are PP, ABS, N-6, N-66, PVC, PET, and PS (Figure 2). The polymer standards were obtained from a Hawaii Pacific University polymer kit. The solid standards were sliced into fine pieces and placed into a Frontier Lab PY eco-cup for analysis. A small amount of quartz wool was then placed into the cup.

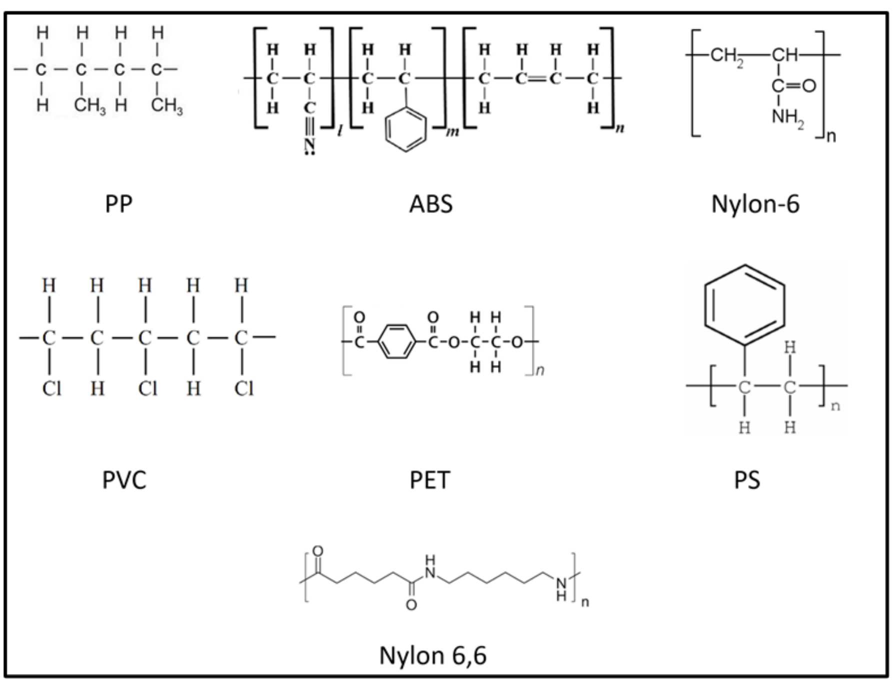

Figure 2: Targeted Polymer chemical structure

EGA mode

The PY-GC/MS was configured both in EGA and single shot modes. In EGA mode, the standard was heated from 100 to 700 °C and evolved gases were transferred to a short inert tube, in the absence of a traditional GC/MS column. A thermogram, which is a thermal profile of the sample, was generated. The thermal zone, the temperature region at the end of each thermogram, was determined from the thermogram and used to determine the optimum temperature for the PY furnace for single shot analysis.

Single shot analyses

In single shot (SS) analysis, an analytical column was used to generate a pyrogram. In this process, pyrolyzates were separated on a GC analytical column. From the pyrolyzates generated, the polymer physicochemical properties can be determined.

The analytical steps in determining the unique pyrolyzate for each polymer is illustrated in Figure 3, while the experimental parameters for both GC/MS and PY systems when operated in single shot and EGA modes are listed in Table 1.

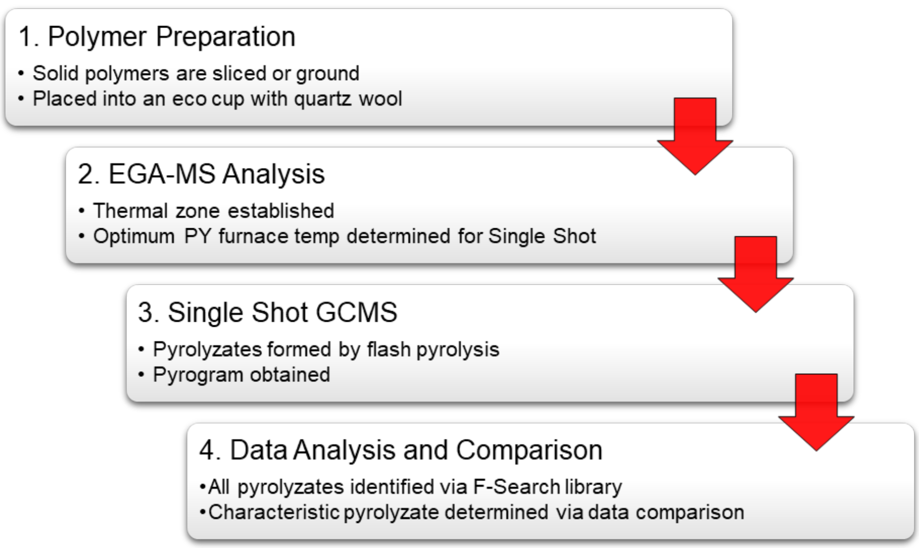

Figure 3: Typical steps in polymer characterization and characteristic pyrolyzate determination.

Table 1: GC/MS and Pyrolyzer operating conditions.

Gas Chromatography	**Nexis GC-2030**
Injection port mode	Split mode, 100:1 split ratio
Carrier gas	Helium
Injection port temperature (°C)	300
Column	Single Shot: SH-Rxi-5 MS, 30 m x 0.25 mmID x 0.25 µm; EGA: deactivated tube 2.5 m x 0.15mm
Flow control mode	Linear velocity, 36.1 cm/sec
Oven Temperature	Single Shot :40 °C (4.0 mins.), 20 °C /mins. to 280 °C (7mins); EGA: isothermal 300 °C
Mass Spectrometer	**GCMS-QP2020 NX**
Interface Temperature (°C)	280
Ion Source Temperature (°C)	230
Detector Voltage (kV)	Relative to Tune -0.03
Threshold	100
Scan Range	m/z 29 to 400 Scan Speed 1666
Pyrolyzer	**EGA/PY-3030D**
EGA Furnace Temperature	100 °C, 20 °C/mins. to 700 °C (Total mins 30)
Single Shot Furnace Temp (°C)	600
Interface Temp (°C)	300
Selective Sampler gas	Helium
Selective Sampler Pressure Stability Time	20 sec
Auto sampler Purge Time	10 sec

■ Results and Discussion

PY-GC/MS is one of the most powerful techniques for the analysis of MPs as it allows for the simultaneous identification and quantitation of polymers in environmental samples. However, for the successful operation of the analysis, it is crucial to determine unique polymer pyrolyzates used to accurately identify each individual polymer in a sample. In this study, a pyrogram data comparison of these targeted microplastic compounds was useful in selecting a characteristic pyrolyzate for each polymer.

EGA mode

In EGA mode, an optimal temperature was determined for single shot analyses. Figures 4 and 5 show EGA results of two selected polymers analyzed in this study. The thermal zone for all polymer ranged in the study from 500 – 600 °C (Table 2). Based on these thermal zones, a temperature of 600 °C was selected for single shot analysis.

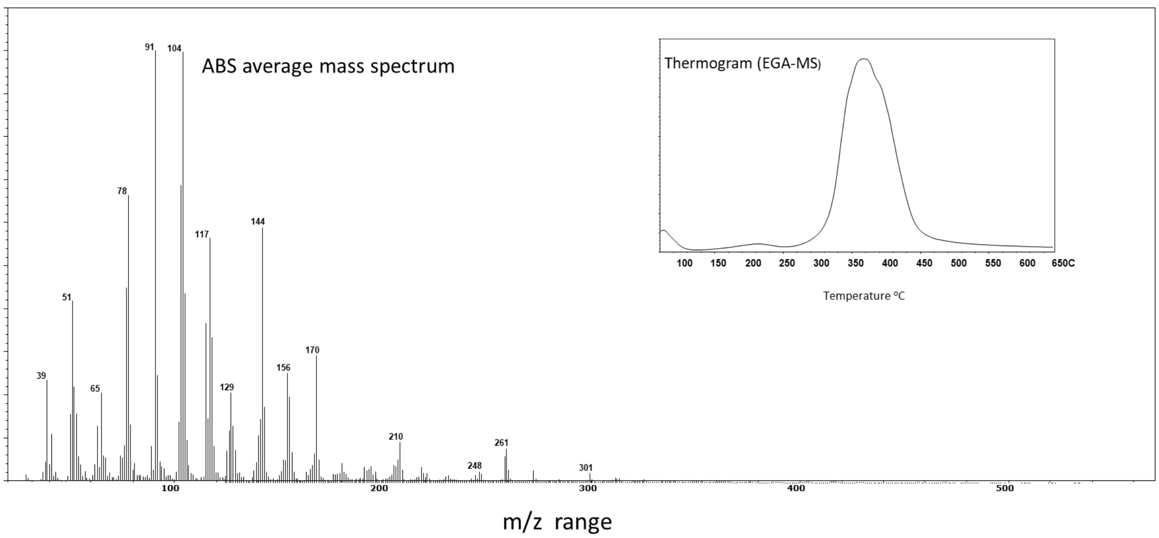

Figure 4: ABS average mass spectrum and EGA thermogram.

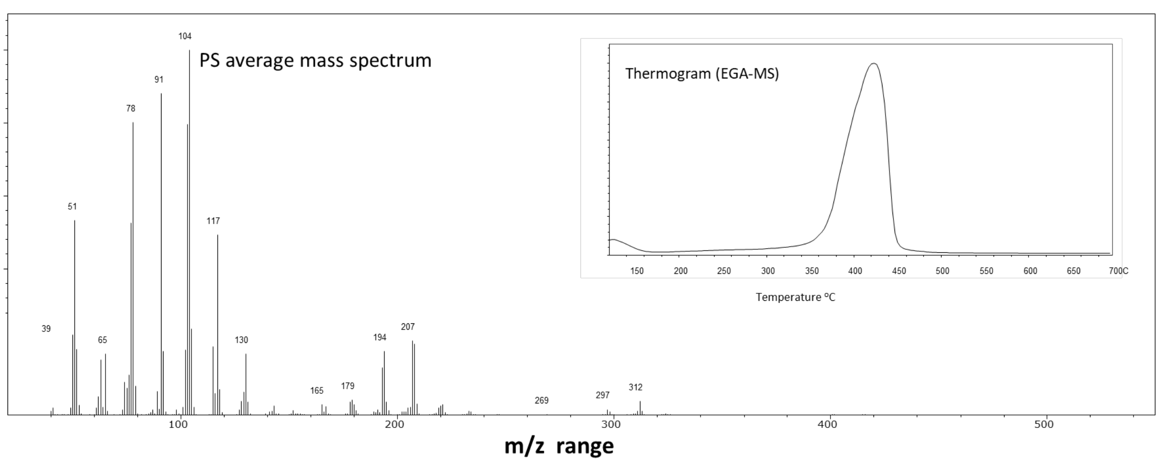

Figure 5: PS average mass spectrum and EGA thermogram.

Table 2: Polymer EGA-MS library similarity search and thermal zone results for targeted compounds.

Compound name	Thermal zone, °C
ABS	550
Nylon 6	550
Nylon 6,6	550
PET	600
PP	600
PS	500
PVC	600

Single shot analyses

Single shot analyses were conducted at an optimal PY isothermal temperature of 600 °C, determined during the EGA experiment and described above. Figures 6 and 7 show pyrograms of two selected polymers (ABS and Nylon 6,6, respectively) analyzed by single shot analysis. Tables 3 and 4 list key pyrolyzates found in these two polymers. Similar results were obtained for the other polymers studied in this work.

These pyrolyzates were compared against theoretical data from a PY-GC/MS data book of synthetic polymers[iii]. All pyrolyzates in the seven standards matched those listed in the PY-GC/MS data book. Thus, each polymer standard was accurately confirmed by this process.

Table 5 shows the selected characteristic pyrolyzate for the seven targeted standards. Each characteristic pyrolyzate is unique to a specific polymer because this product only forms from the thermochemical decomposition of that polymer. Therefore, the challenges for the identification of each polymer in complex matrices are minimized. In reference to ABS and PS, both compounds contain styrene. Thus, because of the overlap of styrene among both compounds, this would lead to selectivity issues in identifying both compounds, if existing in the same matrix. The above explains the importance of determining a characteristic pyrolyzate for each polymer that would aid in the identification of many polymers in a complex matrix.

After determining the characteristic pyrolyzate for each polymer, a single shot analysis was conducted on a homogenous mix standard containing the seven polymers. Figure 8 shows characteristic pyrolyzates in this mixed standard.

Table 3: ABS polymer pyrolyzate-MS library F-search results.

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)

Table 4: PS polymer pyrolyzate-MS library F-search results.

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

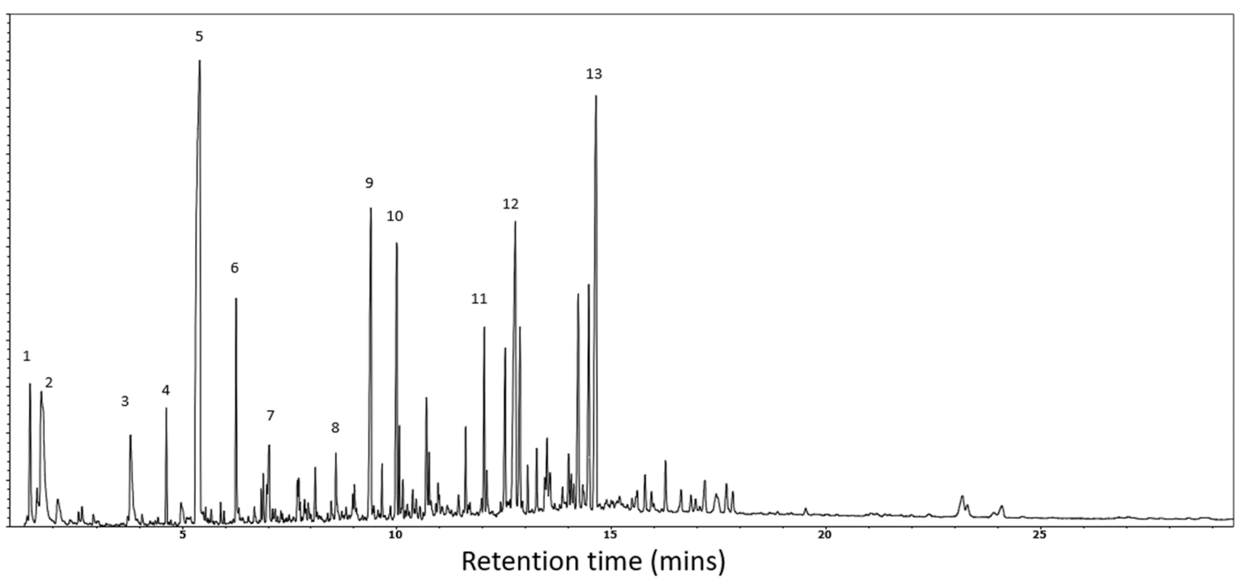

Figure 6: ABS pyrogram at 600 °C.

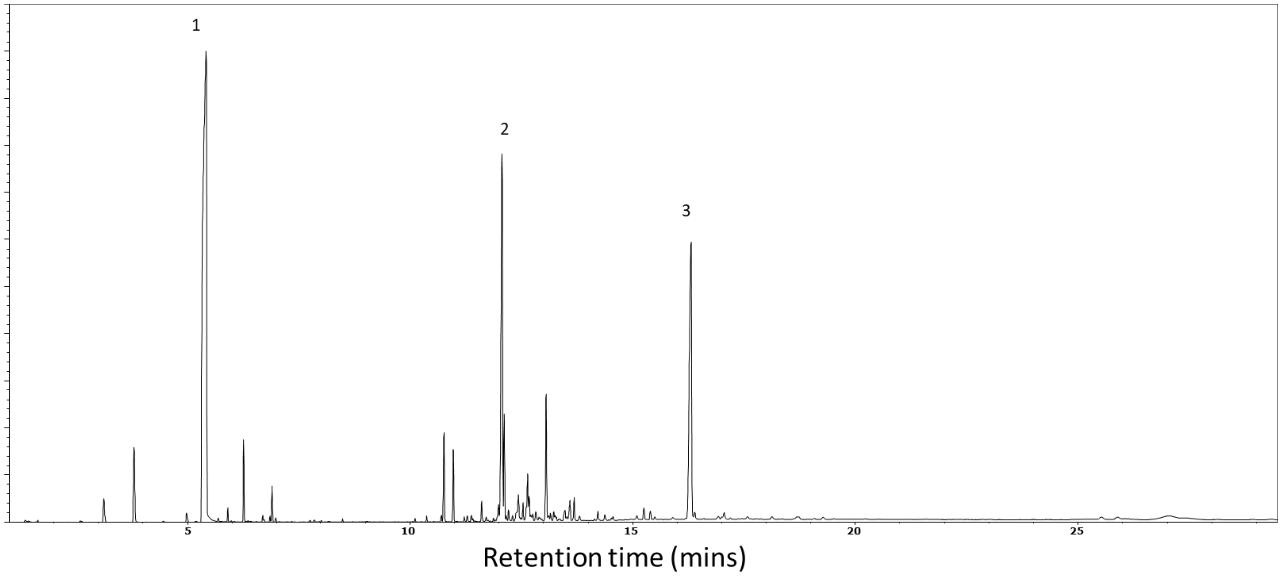

Figure 7: PS pyrogram at 600 ºC.

Table 5: Characteristic pyrolyzate for targeted polymers.

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

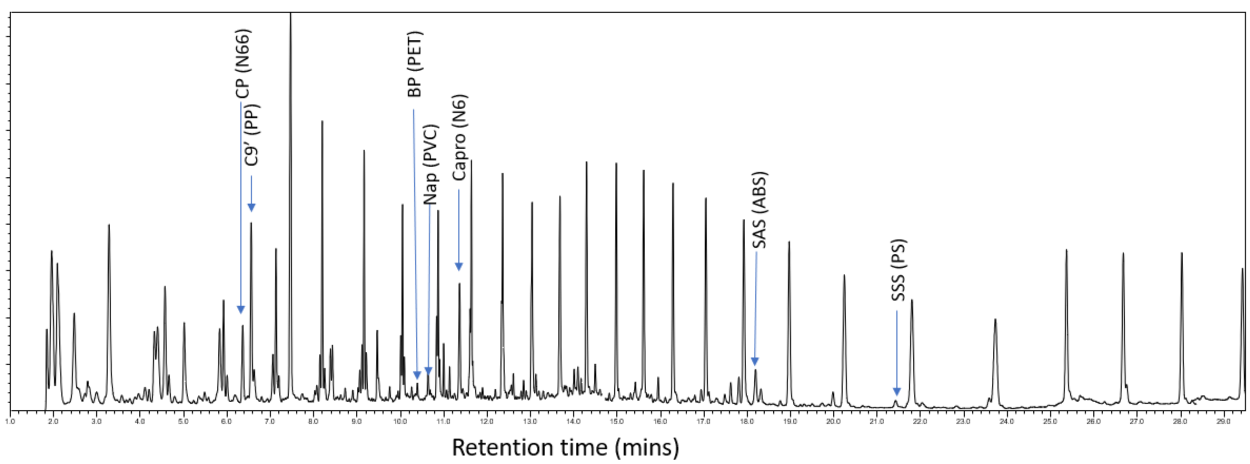

Figure 8: Pyrogram of the seven target polymers and their characteristic pyrolyzate.

■ Conclusion

This study demonstrates the use of a Frontier Lab pyrolyzer in tandem with a Shimadzu GCMS-QP2020 NX to determine a characteristic pyrolyzate that can be used to identify and measure MPs. Unlike other analytical techniques used to analyze MPs in the environment, PY-GC/MS has several advantages:

- Less sample preparation (no need for solvent extraction, fewer interferences, less potential for analytical error, enables straightforward calibration[ii])
- Can be applied to complex matrices. Not affected by peak masking or florescent dyes.
- Ability to measure mix polymer samples. Not limited by particle size.

EGA followed by single shot analysis was conducted to determine a characteristic pyrolyzate. The EGA results showed a thermal zone for each polymer ranging from 500 – 600 °C. Based on these results, a PY furnace temperature of 600 °C for a single shot analysis was determined. Single shot analyses were conducted in the second experimental step.

An analysis of the pyrogram from this study determined that the following pyrolyzates are best for the identification and quantification of each polymer within a microplastic sample: 2-penyl-4-phenylpent-4-enenitrile for ABS, ε-caprolactam for Nylon 6, cyclopentanone for Nylon 6, 6, benzophenone for PET, 2,4-Diemethyl-1-heptene for PP, styrene trimer for PS, and naphthalene for PVC. Results from this study establish the method conditions for the unequivocal quantification of MPs in environmental samples.

■ References

I. Ishimura, T.; Iwai, I.; Matsui, K.; Mattonai, M.; Watanabe, A.; Robberson, W.; Cook, A.; Allen, H.L.; Pipkin, W.; Teramae, N.; Ohtani, H.; Watanabe, C. Qualitative and quantitative analysis of mixture of microplastics in the presence of calcium carbonate by pyrolysis-GC/MS. Journal of Analytical and Applied Pyrolysis, **2021** (157): 105188.

II. Pipkin, W.; Belganeh, R.; Robberson, W.; Allen, H.L.; Cook, A.; Watanabe, A. Identification of Microplastics in Environmental Monitoring Using Pyrolysis-GC-MS Analysis. LCGC North America. **2021** April 01; 39(4):179-186.

III. Tsuge, S.; Ohtani, H.; Watanabe, C. Pyrolysis-GC/MS Data Book of Synthetic Polymers: Pyrograms, Thermograms and MS of Pyrolyzates. **2011** August 02.

■ Consumables

Part Number	Item Name	Item Description
221-75940-30	Capillary Column	SH-I-Rxi-5MS, 30m x 0.25mmID x 0.25 µmm
220-90784-00	Split Inlet Liner	General purpose split liner with wool
220-90906-00	Eco-Cup LF	PY-2020 Eco-Cup LF
220-94824-18	Quartz PY Tube	Pyrolysis tube, 120MM PY
220-90418-15	Ferrule: GVF-005	Capillary MS ferrule for 0.32 mm ID columns
220-90418-14	Ferrule: GVF-004	Capillary MS ferrule for 0.25mm id columns
220-94824-14	Needle Set	Syringe, deactivated needle
221-49662-91	O-ring	O-ring for sealing glass liners when using a pyrolyzer
220-94792-00	Septa	Septa for pyrolysis
CMDR Polymer Kit 1.0	Polymer kit 1.0	Hawai'i pacific polymer kit 1.0
220-94792-03	Quartz wool	Phthalate-free quartz wool

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