

PY-GCMS analysis of microplastics in environmental samples using nitrogen as an alternative carrier gas

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1. Overview

The study represents a comprehensive microplastic Py-GC/MS GCMS method, using nitrogen as a carrier gas, that act as a guidance for other MP studies.

2. Introduction

The world produces million tons of plastic yearly. While many plastic products serve a good purpose in many industries, plastic waste can be detrimental to our global environment. The inherent properties of plastic materials prevent their degradation in the environment; hence the disposed products can persist for a long time.

Pyrolysis GCMS offers a quick workflow for analyses of microplastics (MP). Conventionally, helium has been used as a carrier gas for analysis. However, due to the low global supply of helium, many analytical laboratories demand the use of alternative gas to combat the helium gas shortage. This study explores the use of PY-GCMS for the measurement of microplastics in environmental samples using nitrogen as a carrier gas.

3. Method

A multi-shot Pyrolyzer (Py) was interfaced with a single quadrupole GCMS for quantitation (Figure 1). In evolved gas analysis (EGA) mode, an optimal temperature was determined for single shot analysis. The thermal zone for all polymers ranged in the study from 500 – 600 °C. Based on these results, a temperature of 600 °C was selected for single shot analysis. From subsequent single shot experiments, unique pyrolyzates were determined to characterize each analyte. A primary quantitative ion from each unique pyrolyzate was established for quantitative analysis while reference ions were determined for qualitative confirmation of each polymer.

A six-point calibration curve was prepared for most compounds, except for polystyrene that had five points, using a MPs-CaCO3 standard. Using an electronic semi-micro balance, calibration standards of 0.4, 0.8, 1.0, 2.0 and 4.0 mg were weighted in eco-sample cups in triplicates (n=3). Blank eco cups followed by samples were analyzed with the lowest concentrations first. Each sample cup was released into the pyrolyzer furnace resulting in thermochemical decomposition of the standard. Figure 2 illustrates the pyrogram of a 4 mg weight standard.



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

An optimized analytical method (Table 1.) and the results from the sample analysis is presented here.

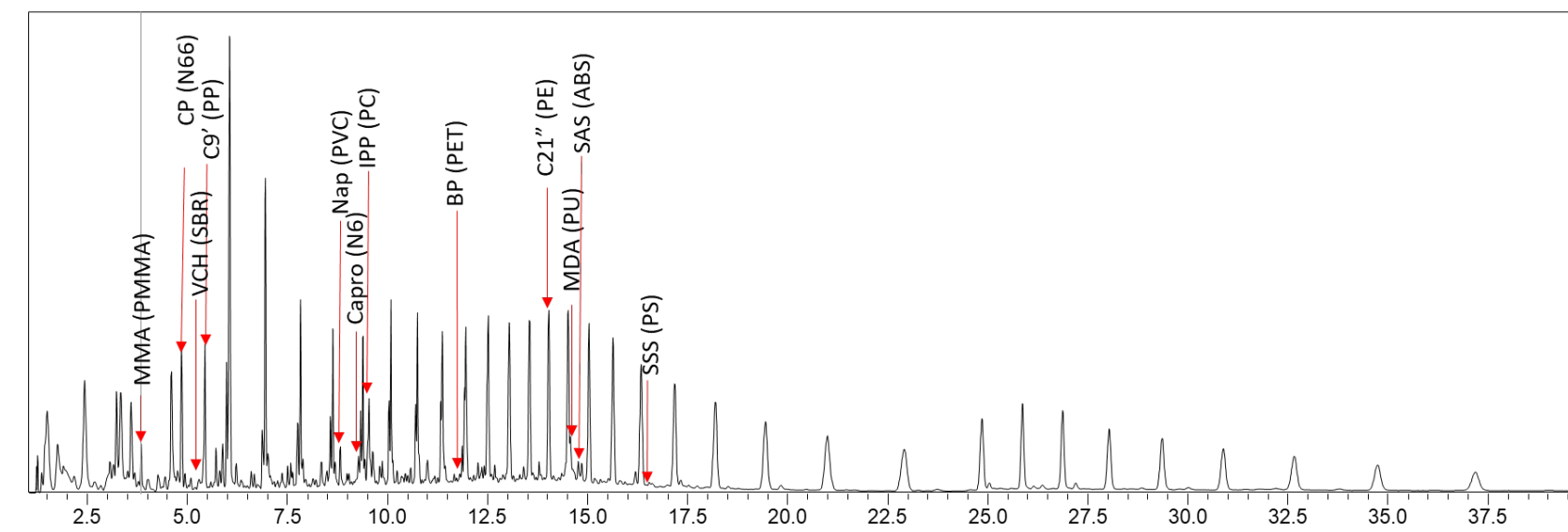


Figure 2. Pyrogram of 4 mg standard showing elution order of the 12 characteristic pyrolyzates

Table 1. GCMS and Pyrolyzer operating conditions

Gas Chromatography	Nexis GC-2030
Injection port mode	Split mode; 35:1 split ratio
Injector pressure	94.1 kPa
Carrier gas	Nitrogen
Injection port temperature	300 °C
Column: Frontier Lab UAMP column	Restek Mxt-5 (20 m x 0.18 mmID x 0.40 µm)
Flow control mode	Linear velocity
Oven Temperature	40 °C (2 mins. hold), 20 °C /mins. to 280 °C (10 mins. hold), 40 °C /min to 320 °C (60 mins. Hold)
Mass Spectrometer	QP2020 NX
Interface Temperature	300 °C
Ion Source Temperature	230 °C
Detector Voltage	Relative to Tune 0 kV
Threshold	0
Acquisition mode	Scan/SIM
Scan Range	m/z 29 to 350; Event time 0.2 s
SIM ions	Listed in table 2
Pyrolyzer	EGA/PY-3030D
Single Shot Furnace Temp	600 °C
Interface Temp	300 °C
Auto sampler flushing gas	Nitrogen
Auto sampler Purge Time	10 sec

In the study a short-term repeatability test was conducted by analyzing ten replicates at the lower end and 10 replicates at the upper end of the calibration range. The accuracy or recovery of each standard was calculated using theoretical concentration for each component. The method LLOQ determined to be 0.4mg total standard mass. This is in accordance with MP studies currently being conducted by ASTM committee D19. A continuing calibration check standard, consisting of a mid-range calibration standard was analyzed to evaluate the validity of the initial calibration curve after a sequence of analysis.

4. Results

4-1. Evolved Gas and Single Shot Analysis

Based on results from prior evolved gas followed by single shot analysis, table 2 list the characteristic pyrolyzates as well as their quantitative and qualitative ions that are used to identify and measure the targeted microplastics that were analyzed in this study.

Table 2. Quantitative and Qualitative ions for characteristic pyrolyzates.

Microplastic polymer	Characteristic pyrolyzates	Quantitative Ion (m/z)	Reference ions
Polyethylene (PE)	1,20-Heneicosadiene	82	41,55,97
Polypropylene (PP)	2,4-Dimethyl-1-heptene	126	43,55,70
Polystyrene (PS)	Styrene trimer	91	117,207,312
Acrylonitrile-butadiene-styrene copolymer (ABS)	2-Phenethyl-4-phenylpent-enenitrile	170	91,115,118
Styrene-butadiene rubber (SBR)	4-Vinylcyclohexene	54	79,66,108
Poly (methyl methacrylate) PMMA	Methyl methacrylate	100	41,69,99
Polycarbonate (PC)	4-Isopropenylphenol	134	91,119
Polyvinylchloride (PVC)	Naphthalene	128	102
MDI-polyurethane (PU)	4,4'-Methylenediabiline	198	106,182,197
Polyethylene terephthalate (PET)	Benzophenone	182	51,77,105
Nylon-6 (N6)	ε-Caprolactam	113	30,55,85
Nylon-6,6 (N66)	Cyclopentanone	84	39,55,56

4-2. Calibration curve and linearity

Calibration results showed good coefficient of determination (r²) for all compounds. Figure 3 illustrates calibration curves for the targeted polymers. The r² for all 12 polymers was > 0.990 (Figure 3). The accuracy of each replicate calibrant was determined and mostly range between 80 -120 %. A few repeat calibrants were outside this range at 79 and 135%. Most polymers calibration curve was liner, except for PU, ABS and PS that had a quadratic fit.

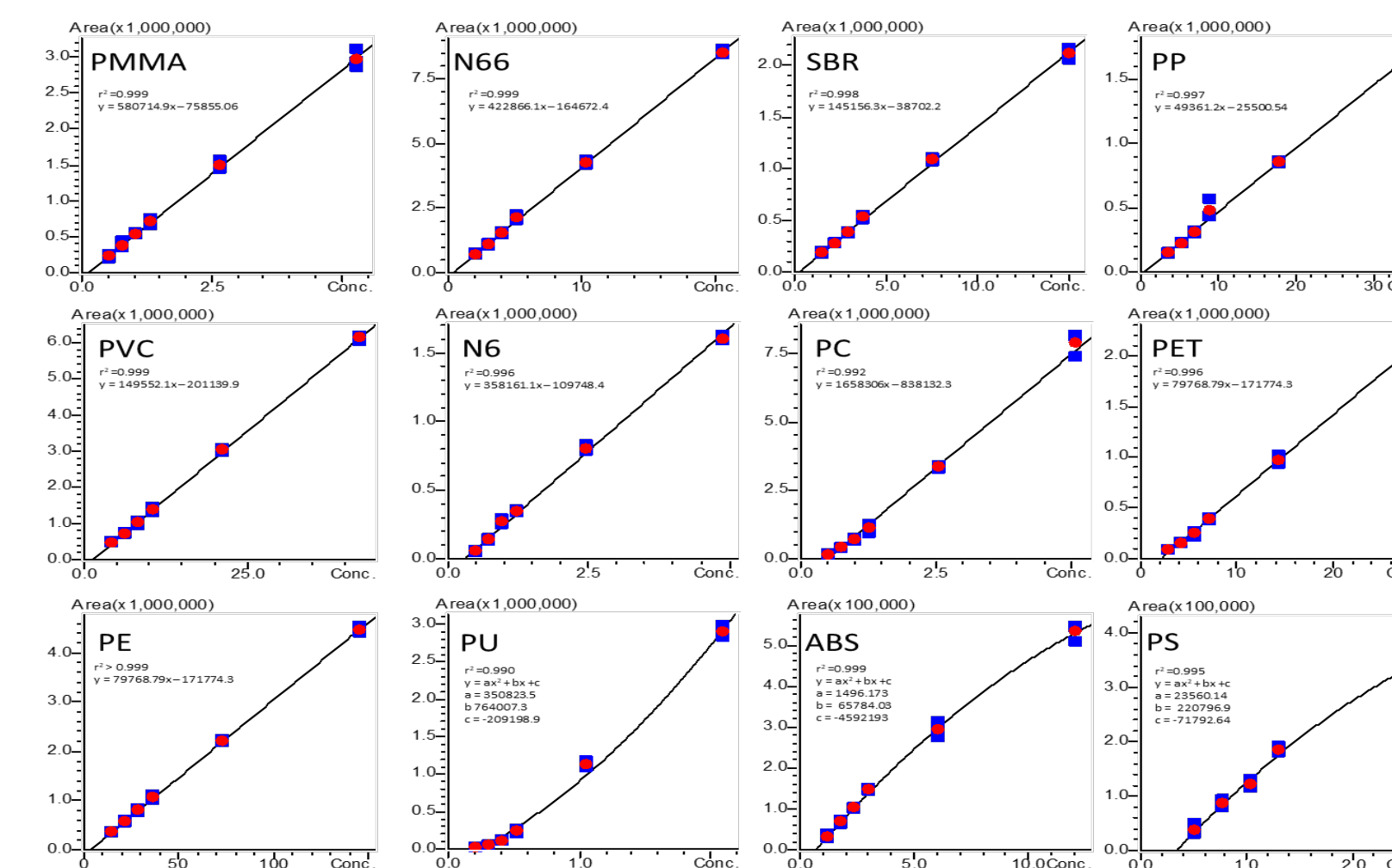


Figure 3. Calibration curves for the targeted polymers.

4-3 Precision

A repeatability test was done on the lower and upper end of the calibration curve. Both 0.4 and 3 mg of MPs-CaCO3 standard mass were placed into ten individual cups and analyzed in order within the sequence, i.e., injection 1 through 10. The concentration of each analyte in each replicate was calculated using the initial calibration curve.

Percent RSD for the ten polymer replicates at 0.4 mg and 3 mg standard weights respectively ranged from 0.8 to 6.6 and 2.0 to 8.4 (Figure 4). All compounds were within an RSD of 10 %. There was no results for polystyrene at 3mg because this mass was outside the calibration curve range. In future experiments the precision at the upper concentration end for this compound will be determined.

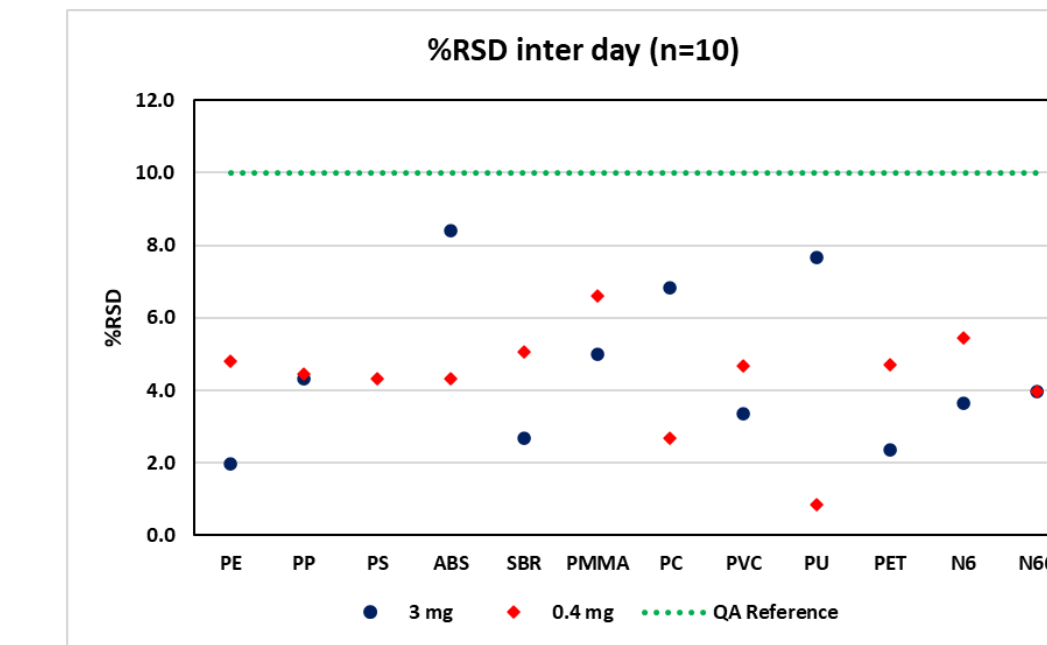


Figure 4. Precision test %RSD (n=10).

4-4 Lower Limit of Quantification (LLOQ)

The LLOQ was arbitrarily defined as the lowest calibration point and, in this study, determined as 0.4 mg standard weight of the mix polymer. LLOQ for all polymers ranged from 0.21 to 14.58 (Figure 5). Noise calculation was determined by Peak-to-Peak calculation.

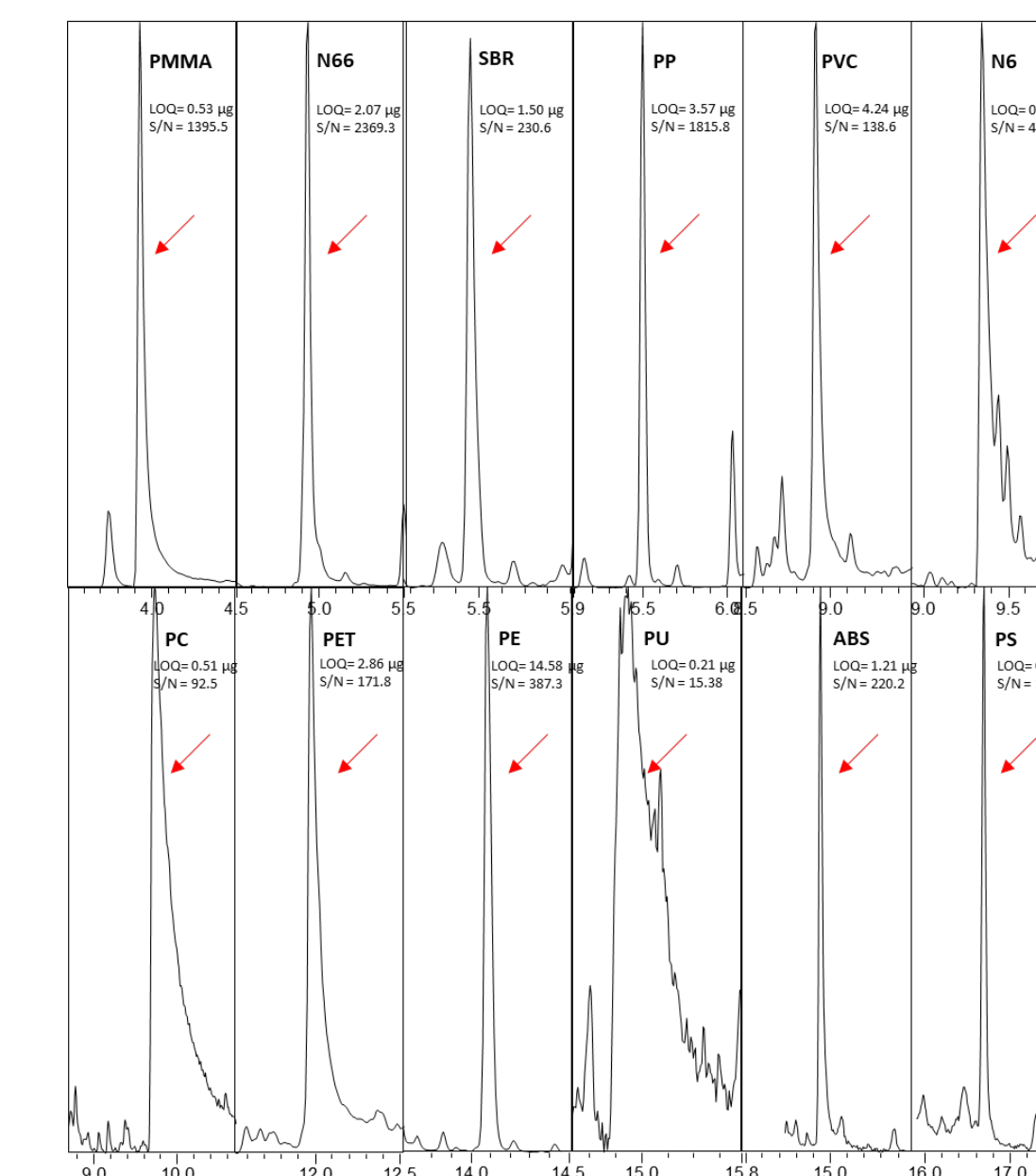


Figure 5. Limit of quantitation for the targeted polymers in this study.

4-4 Accuracy

The mean concentration of each analyte in all replicates from the repeatability test was determined. This average concentration and the theoretical concentration were used to calculate the percent recovery at 0.4 and 3mg standard mass (Table 3). The 0.4 mg standard mass had percent recoveries of each polymer that ranged from 102.6 to 133.8 and at 3 mg recoveries ranged from 101.3 to 109.2. There was no calculated recovery for PS at 3 mg because this mass was outside the calibration range.

Table 3. Summary of method performance.

Polymer	Recovery % (n=10)		Retention Time (min)	LOQ (µg)	Linearity (r ²)	% Drift (0.8mg)
	3 mg	0.4 mg				
PE	109.2	112.8	14.0	14.58	0.999	23.3
PP	103.8	109.2	5.6	3.57	0.993	12.7
PS	N/A	103.7	16.8	0.52	0.997 ^a	-5.5
ABS	108.1	104.9	15.0	1.21	0.999 ^a	9.0
SBR	106.7	116.6	5.6	1.5	0.998	13.3
PMMA	105.1	115.3	4.0	0.53	0.999	22.6
PC	107.9	122.0	9.7	0.51	0.992	23.0
PVC	101.3	114.8	9.0	4.24	0.999	16.3
PU	102.1	125.0	14.8	0.21	0.995 ^a	12.7
PET	103.1	133.8	12.0	2.86	0.996	23.3
N6	104.2	102.6	9.4	0.49	0.996	31.0
N66	104.5	111.1	5.0	2.07	0.999	19.9

^a Quadratic fit
^a Quadratic fit; 1/c weighted regression

5. Conclusion

The study demonstrated the satisfactory performance of the Shimadzu GCMS-QP2020NX coupled to a Frontier Py-3030D pyrolyzer for quantitation of selected plastics. The method validation results in this application note acts as a Py-GC/MS method condition guidance for ongoing MPs studies. In this application, a fast and precise workflow was developed for quantitation of twelve polymers. Calibration results showed linearity for all compounds, coefficient of determination (r²) > 0.990 were obtained. Percent RSD for the polymer replicates at 0.4 mg and 3 mg respectively ranged from 0.8 to 6.6 and 2.0 to 8.4. An accuracy evaluation showed that the 0.4 mg standard mass had percent recoveries of each polymer that ranged from 102.6 to 133.8 and at 3 mg recoveries ranged from 101.3 to 109.2. The LLOQ for all polymers ranged from 0.2 to 14.6 (0.4 mg standard weight). A CCC test was conducted. After 42 injections, the percent drift for all compounds was less than 31 %.