Automated PY-GCMS Workflow for the Qualitative and Quantitative Analysis of Microplastics in Environmental Samples

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1. Introduction

Millions of tons of plastic from food packaging or other household and commercial products are dumped into landfills, or simply thrown out to find their way into various water bodies. The implications of MP pollution in our environment are currently not well understood. In this study, we demonstrated the suitability of a Frontier Lab multi-shot pyrolyzer with a Shimadzu gas chromatography/mass spectrometer (Py-GC/MS) for identification and quantitative measurement of major polymeric components of microplastics. Evolved gas analysis (EGA) analysis followed by flash pyrolysis is used to qualitatively identify these polymers. A quantitative method is also used to determine the number of analytes in the sample.

2. Experimental

The configuration consisted of a Shimadzu GCMS, model QP2020 NX, a Frontier Lab multi-shot pyrolyzer, model EGA/PY-3030D, an auto-shot sampler (Shown in figure 1). The PY-GCMS was configured both in EGA and single shot modes. In EGA mode, evolved gases from the polymer appear from heating the sample and were injected into a short inert tube, in the absence of a traditional GCMS column. The temperature program range was from 100 to 700 ° C. Leading to a thermogram, a plot of detector response of analytical signal versus furnace temperature, being generated.

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

3a. Analytical Method

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 : 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	**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

Table 1. Analytical conditions of PY-GCMS

3b. Sample Prep

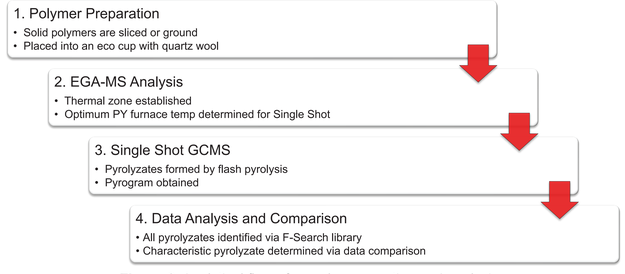

Figure 2. Analytical flow of sample preparation and analysis

For qualitative analysis, seven polymers including: acrylonitrile-butadiene-styrene copolymer (ABS); Polycaproamide (Nylon-6); Polyhexamethylene adipamide (Nylon-6,6); Polyethylene terephthalate (PET); Polypropylene (PP); Polystyrene (PS) and Polyvinyl chloride (PVC) were selected. The solid samples were sliced into fine particles (< 200 ug); samples were then placed in a PY eco sample cup for analysis.

Regarding quantitative analysis, twelve solid polymers in CaCO3 were obtained using Frontier MP kit. The homogeneous mixture of the polymers with the CaCO3 diluent made weighing easier as well as prevent reaction within the PY micro furnace. Standards were weighed in the range 0.20 – 4.0 mg. The mass of each polymer in the 4mg of the standard range from 2.10 – 145.8 µg.

4. Results

Qualitative Analysis

Figure 2. shows EGA results of the two selected polymers analyzed in this study. EGA was used for identifying a thermal zones

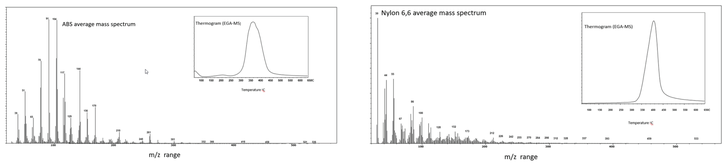

Figure 3. Average Mass spectrum and EGA thermogram for ABS and Nylon 6,6.

From the thermal zone, a single shot temperature of 600 °C was determined to use for all analytes. Figure 3 shows pyrogram of 2 selected polymers analyzed by single shot analysis. Table 2 lists the pyrolyzates found in the two selected standards shown in figure 3.

5. Results

From the thermal zone, a single shot temperature of 600 °C was determined to use for all analytes. Figure 3 shows pyrogram of 2 selected polymers analyzed by single shot analysis. Table 2 lists the pyrolyzates found in ABS shown in figure 4.

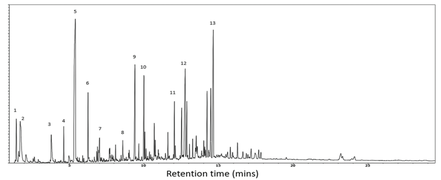

Figure 4. ABS Pyrogram at 600 °C

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 2. ABS pyrolyzates-MS library F-search results

Quantitative Analysis

A five-point calibration curve was prepared using MPs-CaCO3. Using an electronic semi-balance, 0.2, 0.4, 0.8, 2.0 and 4.0 mg of standard were weighted in quadruplets. The average of the quadruplet analyses was determined and used to plot the calibration curve. Figure 5 illustrates the pyrogram of a 4 mg sample weight standard used in this study.

For a precision test, eight cups were analyzed in a straight order within the sequence, i.e. injection 1 through 8. Percent RSD for the various polymers ranged from 2.634-13.672 (Table 4).

For full calibration curve plots and additional chromatograms, please refer to Shimadzu published application notes.

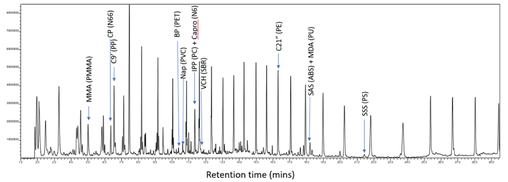

Figure 5. Pyrogram of the seven targeted polymers

Microplastic polymer	Characteristic pyrolyzates	Linear range (µg)	Linearity r²	Inter day precision test (3 mg standard weight, n=8) %RSD	Retention Times (mins)	LOQ
PE	1,20-Heneicosadiene	7.29-145.8	0.9999	4.6171	16.204	6.02
PP	2,4-Dimethyl-1-heptene	1.79-35.7	0.9999	3.4314	6.555	3.63
PS	Styrene trimer	0.26-5.2	0.9947	13.6718	21.341	0.73
ABS	2-Phenethyl-4-phenylpent-enenitrile	0.60-12.1	0.9999	3.4278	18.112	1.06
SBR	4-Vinylcyclohexene	0.75-15.0	0.9997	2.6343	11.731	1.24
PMMA	Methyl methacrylate	0.27-5.3	0.9985	2.6684	5.009	0.50
PC	4-Isopropenylphenol	0.26-5.1	0.9999	2.9668	11.357	0.52
PVC	Naphthalene	2.12-42.4	0.9997	5.5736	10.633	4.12
PU	4,4'-Methylenediabiline	0.11-2.1	0.9972	6.1670	18.116	0.08
PET	Benzophenone	1.43-28.6	0.9995	3.9091	14.090	1.10
N6	ε-Caprolactam	0.25-4.9	0.9998	3.3403	11.367	0.46
N66	Cyclopentanone	1.03-20.7	1.0000	3.2528	6.359	1.96

Table 3. Summary of method performance

6. Conclusion

The study demonstrated the satisfactory performance of the Shimadzu GCMS-QP2020NX coupled to a Frontier PY-3030D pyrolizer in quantitation of selected plastics. In this application a fast, robust, and precise workflow was developed for quantitation of twelve polymers. Calibration curve results showed linearity for all compounds, coefficient of determination (r2) ranging from 0.9947-0.9999. Using 8 replicates of standards at 3 mg sample weight, a precision experiment was conducted. Percent RSD results for the targeted compound ranged from 2.634-13.6718.