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Application News

GC-MS GCMS-QP™2020NX

Analysis of Microplastics in Roadside Debris by Py-GC-MS

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User Benefits

- Pyrolysis-GC-MS and F-Search MPs 2.0 software enable qualitative and quantitative analysis of multiple microplastics in environmental samples individually.
- Reduces operator workload by eliminating tedious pretreatment to sort out only microplastics from environmental samples.

■ Introduction

Small plastic particles with diameters up to 5 mm are known as microplastics (MPs). There are now concerns about the impact of such MPs on environmental pollution and human health. In recent years, identification and quantitation using pyrolysis-GC-MS (Py-GC-MS) have been considered to evaluate the chemical properties of MPs.

Tire wear particles left on roads can cause marine pollution when they are carried by wind and rain into seas and air pollution when they float into the atmosphere. As a result, MPs are considered a major environmental pollutant. Because MPs are a mixture of multiple small particles, it is difficult to sort out only the MPs from environmental samples.

In this article using Py-GC-MS and F-Search MPs 2.0 mass spectral search software (from Frontier Laboratories Ltd.), qualitative and quantitative analysis of MPs present in sand, soil, and other material that accumulates on the road shoulders were performed individually without pretreatment. F-Search MPs 2.0 supports easy identification and quantitation of unknown MPs in the environment.

Fig. 1 Py-GC-MS

■ Preparation and Analytical Conditions

An MP calibration reference sample containing the 12 types of plastic with the highest global production quantities (MPs-$CaCO_3$ from Frontier Laboratories Ltd.) was used as a standard sample for qualitative and quantitative analysis. 0.4, 2.0, and 4.0 mg quantities of the MP calibration reference sample were placed in each sample cup, with quartz wool inserted to prevent scattering, and then analyzed.

Deposits on the road shoulder were prepared as a real sample (Fig. 2). The real sample was a mixture of sand, soil, and other matter. About 4.1 mg of the real sample was placed in a sample cup, 4 mg of $CaCO_3$ was added to the cup, quartz wool was inserted to prevent scattering, and then the sample was analyzed.

Analytical conditions are shown in Table 1. The twelve-types of plastic included in the MP calibration reference sample, the thermal decomposition products used for qualitative analysis, and the reference ions used for quantitative analysis are shown in Table 2.

Fig. 2 Roadside Debris

Table 1 Analytical Conditions

Pyrolyzer:	EGA/PY-3030D Multi-Shot Pyrolyzer (Frontier Laboratories Ltd.)
	AS-1020E Auto-Shot Sampler (Frontier Laboratories Ltd.)
GC-MS System:	GCMS-QP 2020 NX
Column:	UAMP column kit (Frontier Laboratories Ltd.)
[Pyrolyzer]	
Furnace Temp.:	600 °C
Interface Temp.:	300 °C
[GC]	
Sample Injection Unit Temp.:	300 °C
Carrier Gas:	He
Injection Mode:	Split
Split Ratio:	1:50
Control Mode:	Pressure (150 kPa)
Oven Temp.:	40 °C (2.0 min) – 20 °C/min – 280 °C (10 min) – 40 °C/min – 320 °C (15 min)
[MS]	
Ion Source Temp.:	230 °C
Interface Temp.:	300 °C
Ionization Method:	EI
Measurement Mode:	Scan (*m/z* 29 to 350)
Event Duration:	0.2 sec

Table 2 Twelve Types of Plastics Included in the MP Calibration Reference Sample, Thermal Decomposition Products Used for Qualitative analysis, and Quantitative Ions Used for Quantitative Analysis

No.	Plastic Type*1	Thermal Decomposition Product	Quantitative Ion (*m/z*)
1	PE	1,20-Heneicosadiene	82
2	PP	2,4-Dimethyl-1-heptene	126
3	PS	Styrene trimer	91
4	ABS	2-Phenethyl-4-phenylpent-4-enenitrile	170
5	SBR	4-Phenylcyclohexene	104
6	PMMA	Methyl methacrylate	100
7	PC	4-Isopropenylphenol	134
8	PVC	Naphthalene	128
9	PU	4,4'-Methylenedianiline	198
10	PET	Benzophenone	182
11	N-6	ε-Caprolactam	113
12	N-66	Cyclopentanone	84

*1 PE is polyethylene, PP is polypropylene, PS is polystyrene, ABS is an acrylonitrile-styrene-butadiene copolymer sheet, SBR is styrene-butadiene rubber, PMMA is poly(methyl methacrylate), PC is polycarbonate, PVC is poly(vinyl chloride), PU is polyurethane, PET is polyethylene terephthalate, N-6 is Nylon-6, and N-66 is Nylon-6,6.

■ Calibration Curves

F-Search MPs 2.0 was used to create a calibration curve for each type of plastic included in the MP calibration reference sample. All calibration curves had good linearity, with an R^2 value of 0.995 or higher for all twelve types of plastic. For example, Fig. 3 shows overlaid mass chromatograms for PE in 0.4, 2.0, and 4.0 mg quantities of the MP calibration reference, and Fig. 4 shows the calibration curve for PE.

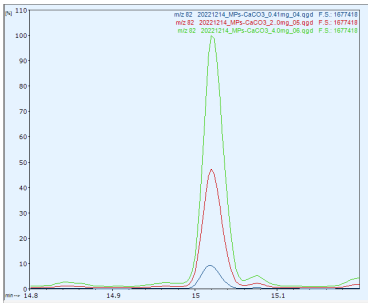


Fig. 3 Chromatogram Overlay from 0.4, 2.0, and 4.0 mg of MP Calibration Reference Sample (PE, *m/z* 82)

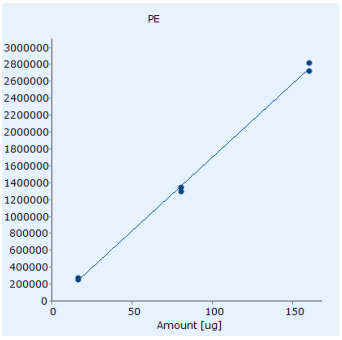


Fig. 4 Calibration Curve for PE (*m/z* 82, n = 2)

■ Real Sample Results

Real sample was measured, and similarity search for the detected peaks were performed. The results showed a 90 % or over similarity to 6 types of plastic, PMMA, N66, SBR, PET, PE, and PS. For the plastics with a 90 % or over similarity, quantitation values and their percent content were calculated based on the calibration curves created (Table 3). PE is the highest percent rate. It is assumed originated from container packaging materials, agricultural films, and other materials based. SBR is second, and used in the tire tread (the part in direct contact with the ground), and presumably derive from tire wear.

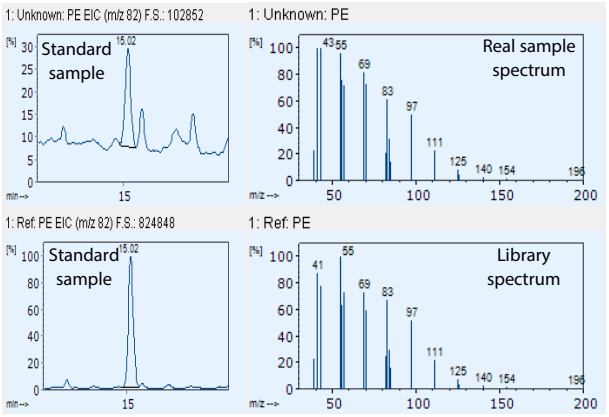
For example, Fig. 5 compares SIM chromatograms and corresponding mass spectra for PE and SBR in the real sample and standard sample (2.0 mg MP calibration reference sample).

Table 3 Qualitative and Quantitative Analysis Results

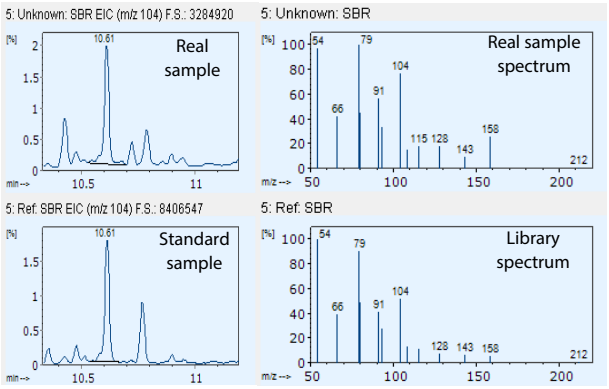
Plastic	Retention Time (min)	Quantitated Value*2 (µg)	Rate*3 (%)	Similarity (%)
PMMA	3.77	(0.062)	0.66	98.3
N66	5.18	(0.47)	5.0	99.8
SBR	10.61	3.5	37	95.4
PET	12.82	(1.0)	11	90.8
PE	15.02	(4.2)	44	98.6
PS	19.05	(0.25)	2.6	97.9

*2 Values indicated in parentheses were calculated by extrapolation of calibration curve.

*3 Calculated assuming the total sum of quantitation values for all plastics with a 90 % or over similarity is equal to 100 %.



PE Analysis Results



SBR Analysis Results

Fig. 5 Comparison of SIM Chromatograms and Mass Spectra for Real and Standard Samples
(Left: SIM Chromatograms Right: Mass Spectra)

■ Conclusion

This article described qualitative and quantitative analysis of MPs accumulated on the road shoulders using Py-GC-MS. The calibration curves created from the MP calibration reference sample provided good results. Py-GC-MS and F-Search MPs 2.0 software enable qualitative and quantitative analysis of multiple MPs in environmental samples individually. This method improves the simplicity and efficiency of analysis without pretreatment steps.

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