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Application News

Microplastic Automatic Preparation Device MAP-100
Fourier Transform Infrared Spectrophotometer IRSpirit™-TX
Gas Chromatography Mass Spectrometer GCMS-QP2020 NX

Material Analysis of Microplastics in River Water
— FTIR and Pyrolysis-GC-MS Analysis—

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User Benefits

- Automated pretreatment of microplastics (MPs) reduces workload and enables highly reproducible pretreatment.
- Material analysis of MPs processed by the MAP-100 device can be easily performed by FTIR+ATR.
- Highly reproducible GC-MS analysis of MPs is possible by homogeneously pulverizing samples with Cryogenic Mill (IQ MILL-2070).
- Pyrolysis-GC-MS can measure the weight of multiple types of plastics even when they are mixed.

■ Introduction

Microplastics (MPs) are microscopic plastic particles measuring a few µm to 5 mm in size. They are feared to have an impact on ocean pollution and ecosystems. Against this backdrop, surveys and studies on MPs in surface waters such as oceans, rivers, lakes and marshes are being conducted worldwide. Fourier Transform Infrared Spectrophotometer (FTIR) is often used for material analysis of MPs. ASTM recently published the D8401-24 standard test method for the qualitative and quantitative determination of MPs in water that uses a pyrolysis gas chromatograph mass spectrometer (Py-GC-MS).

In this application news, a sample taken from a river was pretreated and analyzed for MPs using FTIR and Py-GC-MS.

■ Features of Each Analyzer

Table 1 shows the appearance and features of each instrument.

The FTIR instrument irradiates a sample with mid-infrared light and detects the degree of light absorption to perform qualitative and quantitative analysis. Non-destructive measurement is possible, so after FTIR measurement, a sample can be analyzed again using another instrument. The size of MPs that FTIR+ATR can measure is several hundred µm or more. A single plastic can be analyzed using a few 10-second measurements. Using Plastic Analyzer, a plastic analysis system that includes UV-Damaged and Thermal-Damaged Plastics Libraries, even those unfamiliar with analysis can easily measure and analyze MPs degraded in the environment.

Py-GC-MS is an instrument that thermally decomposes a sample instantaneously, separates the vaporized pyrolysis products by component on a column, and detects them by MS. Qualitative and quantitative analysis can be performed by detecting the thermal decomposition products specific to each plastic. Since the measured sample is thermally decomposed, it cannot be re-analyzed.

Py-GC-MS covers the analysis of very small MPs of less than 100 µm, and small sample volumes of several to tens of mg can be analyzed. Since the components are separated in a column, analysis is possible even if multiple plastics are mixed. However, it is necessary to make the sample uniform to obtain good reproducibility for a sample containing multiple plastics.

■ Flow of Material Analysis

An example of the flow of material analysis for MPs is shown in Fig. 1.

To accurately analyze MPs in environmental surface waters, it is necessary to perform pretreatment to remove environmental contaminants such as wood chips and sand. In this study, the samples were automatically pretreated using the MAP-100 to extract only MPs.

FTIR was used to analyze the extracted MPs as they were.

In Py-GC-MS, extracted MPs are homogenized by freeze grinding and analyzed.

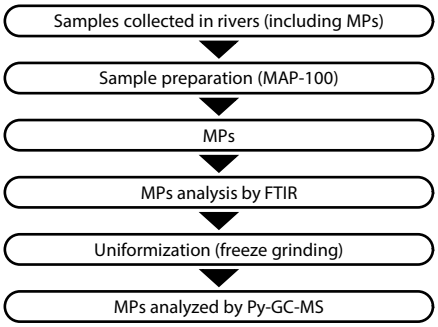

Fig. 1 Flow of Material Analysis

Table 1 Appearance and Feature Comparison of Instruments for MPs Analysis

	FTIR + ATR	Py-GC-MS
		
	IRSpirit™-TX + QATR™-S	EGA/PY-3030D + GCMS-QP2020 NX
Non-destructive and destructive	Non-destructive	Destructive
Size of MPs that can be measured	Several hundred µm or more	Up to 5 mm
Qualitative	✓✓ *1	✓✓✓ *2, *3
Quantitative	✓	✓✓✓
Advantages	• Non-destructive analysis method allows analysis with another instrument after FTIR analysis. • Qualification of environmentally degraded MPs is possible by using the UV-Damaged and Thermal-Damaged Plastics Libraries.	• Separation analysis is possible even when multiple types of plastics are mixed. • A small amount of sample, from several mg to several tens of mg, can be analyzed.

*1 Spectrum search using the library is possible. However, when multiple components are mixed, certain knowledge of spectrum analysis may be required.
*2 Pyrolysis products specific to each plastic must be selected.
*3 Even when multiple components are mixed, each component can be separated and detected because it is a separation instrument.

■ Sample Preparation

MAP-100 isolates microplastics contained in environmental surface water. The appearance of MAP-100 is shown in Fig. 2, and the pretreatment conditions are shown in Table 2. By using MAP-100, complicated decomposition, specific gravity separation and overflow (extraction) tasks can be automated. The size of microplastics that can be extracted by preparation by the MAP-100 is from 0.3 mm to 5mm. The collected MPs are shown in Fig. 3. For more information on MAP-100, see Application News No. 01-00522.

Fig.2 Appearance of the MAP-100

Table 2 Conditions for MPs Pretreatment Device

Device:	MAP-100
Digestion*1	
Digestion Time:	3 days
Stirring Speed:	200 rpm
Temperature:	60 °C *3
Density Separation*2	
Standing Time:	3 hours
Stirring Speed:	500 rpm
Overflow	
Number of Overflows:	3

*1 Oxidative decomposition of organic matter by 30 % hydrogen peroxide
*2 Specific gravity separation using 5.3 mol/L sodium iodide aqueous solution
*3 Set the solution temperature to approximately 55 °C.
Adjust the set temperature according to the ambient temperature.

Fig.3 Collected MPs placed on the sheet

■ FTIR Analysis Results

The extracted MPs were measured using FTIR+ATR. The FTIR analysis conditions are shown in Table 3.

Table 3 FTIR Analysis Conditions

Device:	IRSpirit-TX QATR™-S (Diamond)
Decomposition:	4 cm^{-1}
Accumulation Frequency:	45
Apodized Function:	SqrTriangle
Detector:	TGS

The results of the qualitative analysis, the number of each plastic, the ratio of the number (%), and the density per volume of filtered water (N/m^3) are shown in Table 4.

Polypropylene (PP), polyethylene (PE), and ethylene vinyl acetate (EVA) were detected in the 78 extracted MPs.

There were also 62 PP (79.5 %), 11 PE (14.1 %) and 5 EVA (6.4 %).

Table 4 FTIR Analysis Results

	Number/N	Number/N Ratio (%)	Density *1 (N/m^3)
PP	62	79.5	4.1
PE	11	14.1	0.7
EVA	5	6.4	0.3
Total	78	100	5.2

*1 Density was calculated based on the filtration volume of 15 m^3.

■ Freeze Grinding

The extracted MPs were freeze-ground before analysis by Py-GC-MS. Fig. 4 shows the appearance of Cryogenic Mill (IQ MILL-2070), and Table 5 shows the grinding conditions.

Amorphous silica powder (SiO_2) was added as a grinding aid to approximately 2.4 mg of MPs to make a total of approximately 200 mg, enabling the recovery of samples after grinding.

A spatula was used to collect pulverized samples from the pulverization container. The amount recovered after grinding was approximately 180 mg, and the recovery rate was approximately 90 %.

Fig. 4 Appearance of the IQ MILL-2070

Table 5 Cryogenic Mill Conditions

Device:	IQ MILL-2070 (Frontier Laboratories Ltd.)
Crushing Vessel:	Stainless Steel Sample Container L-SS (IQ1-2012)
Pulverizer:	Zirconia ball crusher 12 mmΦ (IQ1-ZR12)
Liquid Nitrogen Immersion Time:	10 times
Processing Speed:	3,000 rpm
Processing Time:	30 s
Number of Cycles:	1
Number of Times of Immersion in Liquid Nitrogen:	2

■ Py-GC-MS Analysis Results

The MPs Calibration Standard (MPCS) (MPs-SiO2, Frontier Laboratories Ltd.) containing 11 kinds of plastics was used for standards.

In addition to the components of the MPCS, EVA pellets with a vinyl acetate monomer content of 25 wt% were used.

Table 6 shows the 12 types of plastic, the pyrolysis products used in the analysis, and the quantitative ions.

Fig.6 Type of Plastic and Pyrolysis Products, Quantitative Ions

#	Plastic Type *1	Pyrolysis Products	Quantitative Ions (*m/z*)
1	PE	1,20-Heneicosadiene	82
2	PP	2,4-Dimethyl-1-heptene	126
3	PS	Styrene trimer	91
4	ABS	Styrene-acrylonitrile-styrene hybrid trimer	170
5	SBR	4-Phenylcyclohexene	104
6	PMMA	Methyl methacrylate	100
7	PC	Bisphenol A	213
8	PVC	Naphthalene	128
9	PET	Benzoic acid	105
10	N-6	ε-Caprolactam	113
11	N-66	Cyclopentanone	84
12	EVA	Acetic acid	60

*1 PE (polyethylene), PP (polypropylene), PS (polystyrene), ABS (acrylonitrile-styrene-butadiene copolymer plate), SBR (styrene-butadiene rubber), PMMA (poly(methyl methacrylate)), PC (polycarbonate), PVC (poly(vinyl chloride)), PET (polyethylene terephthalate), N-6 (Nylon-6), N-66 (Nylon-6,6), EVA (ethylene-vinyl acetate)

To build calibration curves, 0.40, 1.00, 2.00, and 4.00 mg of MPCS and an internal standard (IS *2) were placed in a sample cup and analyzed with quartz wool to prevent scattering. For EVA, pellets were cut into 2.8, 5.6 and 13.6 µg pieces with a cutter knife and placed in sample cups with IS for analysis. The analysis conditions for Py-GC-MS are shown in Table 7.

Calibration curves were prepared for 11 types of plastic in MPCS using the F-Search MPs*3 (Frontier Laboratories Ltd.) mass spectrum search software. EVA was separately analyzed using GCMSsolution™ for qualitative analysis and calibration curves.

*2 As IS, 5 µL chryserin d-12 (0.10 mg/mL) dichloromethane solution was added.
*3 F-Search MPs can automatically generate calibration curves for each plastic registered in the library from the analysis results of standards and simultaneously perform qualitative analysis.

Table 7 Py-GC-MS Analysis Conditions

Pyrolyzer:	EGA/PY-3030D Multi-Shot Pyrolyzer AS-1020E Auto-Shot Sampler MFS-2015E Multi-Functional Splitless MS402280 Vent-free GC/MS Adapter (Frontier Laboratories Ltd.)
GC-MS:	GCMS-QP2020 NX
Column:	UAMP column kit UAMP-K01*4 (Frontier Laboratories Ltd.)
[Detailed Conditions]	
Pyrolyzer	
Furnace Temp.:	600 °C
Interface Temp.:	300 °C
Back Flush:	22-50 min
GC	
Sample Injection Unit Temp.:	300 °C
Carrier Gas:	He
Injection Mode:	Split
Split Ration:	50
Control Mode:	Pressure (75 kPa)
Oven Temp.:	40 °C (2 min) - 20 °C/min - 280 °C (10 min) - 20 °C/min - 300 °C (25 min)
MS	
Ion Source Temp.:	230 °C
Interface Temp.:	300 °C
Ionization Method:	EI
Measurement Mode:	Scan (*m/z* 29-350)
Event Duration:	0.2 sec

*4 Precolumn: Smart COL (inactivation tube 1 m, 0.25 mm i.d.) + Ultra ALLOY+-50 (50 % diphenyl-50 % dimethylpolysiloxane, 1 m, 0.25 mm i.d., 1.0 µm)
Separation column: Ultra ALLOY+-5 (5 % diphenyl-95 % dimethylpolysiloxane, 30 m, 0.25 mm i.d., 0.5 µm)

The limit of quantification (LOQ) and limit of detection (LOD) of PE, PP, and PS contained in MPCS were calculated using the following calculation method.

LOQ and LOD Calculation Methods

LOQ = 10σ / slope	Slope: Slope of the calibration curve
LOD = 3σ / slope	σ: Standard deviation at 0.40 mg

Table 8 shows the calculated LOQ and LOD for each MP. For more information on Py-GC-MS analysis of MPCS, refer to Application News No. GCMS-2202.

Table 8 LOQ and LOD for PE, PP, and PS

	PE	PP	PS
LOQ (µg)	4.26	1.28	0.64
LOD (µg)	1.28	0.38	0.19

■ Py-GC-MS Analysis Results (MPs in River Water Water)

In the analysis of samples, approximately 10 mg of freeze-ground samples (MPs+SiO_2) and IS were placed in a sample cup and quartz wool was inserted to prevent scattering.

PE, PP, PS and EVA were detected from the MPs collected. The mass chromatograms and mass spectra of PE, PP and PS pyrolysis products output from F-Search MPs are shown in Figs. 5 to 7. It was confirmed that the elution time and mass spectra of the pyrolysis products of each plastic were consistent between the standards and the samples and that they were correctly characterized.

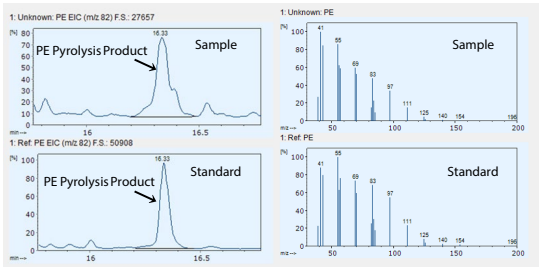

Fig. 5 Pyrolysis Products of PE
Mass Chromatogram (Left) and Mass Spectrum (Right)

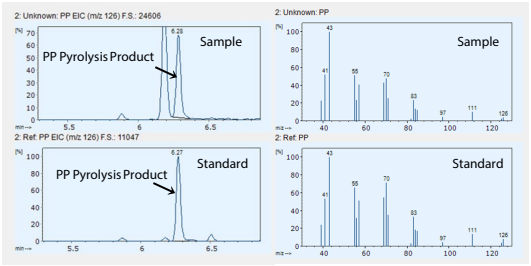

Fig. 6 Pyrolysis Product of PP
Mass Chromatogram (Left) and Mass Spectrum (Right)

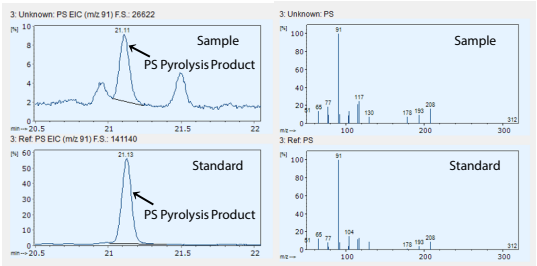

Fig. 7 Pyrolysis Product of PS
Mass Chromatogram (Left) and Mass Spectrum (Right)

Table 9 shows the results of the quantitative analysis of each type of plastic from the calibration curves.

Table 9 Results of Py-GC-MS Analysis *1

#	amount of sample (mg)	quantitative value (µg) PE	PP	PS	EVA	Total
1	10.000	57.8	37.3	0.136	2.70	97.9
2	9.998	58.1	35.3	0.126	2.20	95.7
3	10.007	60.1	36.1	0.123	2.36	98.7
4	9.997	59.5	36.6	0.123	2.24	98.5
5	9.991	58.4	34.9	0.122	1.99	95.4
Average	9.999	58.8	36.0	0.126 *2	2.30	97.2
%RSD	0.06	1.7	2.7	4.6	11.4	1.6

*1 PE, PP, and PS have more than 80 % match rate in F-Search MPs
*2 The quantitative value of PS was below the LOD.

The relative standard deviation (%RSD) of the quantitative value (µg) of each plastic in the sample was 1.7 to 11.4 %, indicating that the plastics were pulverized uniformly. The total quantitative value of MPs in approximately 10 mg of the sample (MPs+SiO2) was 97.2 µg, indicating that approximately 1.9 mg of MPs was contained in approximately 200 mg of the sample. This study used approximately 2.4 mg of MPs, and the recovery rate was calculated to be approximately 82 %.

■ Conclusion

Samples collected from river water were automatically pretreated using MAP-100, and the MPs materials were then analyzed by FTIR and Py-GC-MS. PP, PE and EVA were detected in both instruments, indicating that PP and PE are the main components (Fig. 8).

Using an FTIR, individual qualitative results can be obtained easily, and the number ratios and densities can be calculated. Py-GC-MS also provides a more accurate mass to material ratio (%).

The system supports screening methods that take advantage of the features of each instrument, from preparation to analysis of MPs.

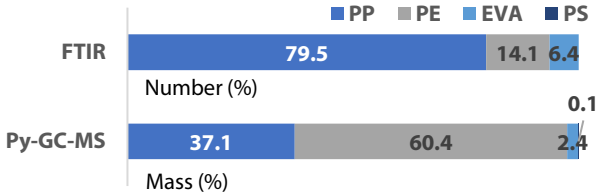

Fig. 8 Comparison of Quantitative Results of MPs in Each Instrument *1

*1 Since the size of MPs is not evaluated for both instruments, there is a difference between the number (%) and mass (%).

<Related Applications>

1. Analysis of Microplastics in Environmental Water Using Microplastic Automatic Preparation Device MAP-100 and FTIR Application News No. 01-00522
2. An Automated Workflow for Quantitative Analysis of Microplastics in Environmental Samples via Pyrolysis-GC/MS Application News No. GCMS-2202

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