Analysis of microplastics by using Pyrolysis-GC/MS/MS

Product used：Mass spectrometer(MS)

Introduction

Microplastics (MPs) have been studied internationally due to concern about their impact on marine ecosystems and human health. In general, MPs refers to plastics with a particle size of 5 mm or less. MPs have been analyzed for the type and number of polymers using microscopy and FT-IR. On the other hand, the type and amount of polymers are confirmed in recent years. For confirmation of polymer type and amount, GC/MS measurement coupled with pyrolysis equipment is suitable. It is guessed that polymer components contained in large amounts in environmental samples are confirmed by SCAN measurement, and polymer components contained in trace amounts are confirmed by SIM measurement. However, it has possibility that the SIM measurement is affected by pyrolysis components from polymer components and additive components contained in large amounts. Therefore, there is a concern that quantitative analysis by SIM measurement is difficult. On the other hand, the SRM measurement of GC/MS/MS use a combination of selected precursor ion and generated product ion from its selected precursor ion, so selectivity of detection ion and detection sensitivity will be improved. As a result, the influence of matrix components such as pyrolysis components can be reduced, and it is possible to detect components contained in material sample. In this application note, we report on the measurement result of a model sample of PP with four trace polymers using Pyrolysis-GC/MS/MS.

Method

The measurement was performed using Pyrolysis system (Frontier Laboratories Ltd.) with GC triple quadrupole mass spectrometer JMS-TQ4000GC UltraQuad™ TQ. In addition to the large producer of PP, PVC and PS in the world, PMMA and Nylon, which are used for cups and clothes were prepared as model sample for measurement. Regarding sampling, 4 μL (100 ng) of 25 ppm PS, PMMA, and PVC and 1 μL (100 ng) of 100 ppm Nylon6 were added to approximately 0.15 mg of a powdered sample of frozen and crushed PP plastic storage container. The measurement condition is shown in Table 1 and the SRM transition is shown in Table 2.

Table 1 Measurement condition

Pyrolysis condition	
Pyrolysis Temp.	600℃
GC condition	
Column	DB-5MS (30 m length, 0.25 mm i.d., 0.25 μm film thickness)
Inlet	Split/Splitless
Inlet Temp.	300℃
Flow	1 mL/min, Constant flow
Injection Mode	Split (50 :1)
Oven Program	50℃ (1 min) → 10℃/min → 300℃ (15min)
MS condition	
Ion Source Temp.	280℃
Interface Temp.	300℃
Ionization Mode	EI+, 70 eV
Measurement Mode	SCAN/SRM
Mass range	*m/z* 35-450
Collision Gas	N_2, 10%

Table 2 SRM transition

Polymer	Target component	Quantitative ion	Reference ion 1	Reference ion 2
PMMA	Methyl methacrylate	100->85 CE:5	100->69 CE:10	69->41 CE:5
PVC	Naphthalene	128->102 CE:25	128->127 CE:15	102->76 CE:15
	Biphenyl	154->153 CE:25	154->128 CE:25	154->115 CE:30
Nylon6	Caprolactam	113->56 CE:10	85->67 CE:10	113->85 CE:5
PS	Styrene dimer	208->193 CE:10	104->78 CE:15	130->115 CE:20
	Styrene trimer	207->129 CE:15	117->91 CE:25	207->91 CE:15

Red color: Quantitative component
Black color: Confirmation component

Result

- Confirmation of PP component in large amounts

TIICC, mass spectrum and the database search result using F-Search (Frontier Labs) are shown in Fig. 1. Many peaks were observed on the TICC, which are assumed to be mainly pyrolysis components of polymers. The mass spectrum showed fragment peaks at 14 u intervals, which are observed in the pyrolysis of PP. In addition, database search results indicated PP. As described above, the polymer component in large amounts can be confirmed by SCAN measurement and database search.

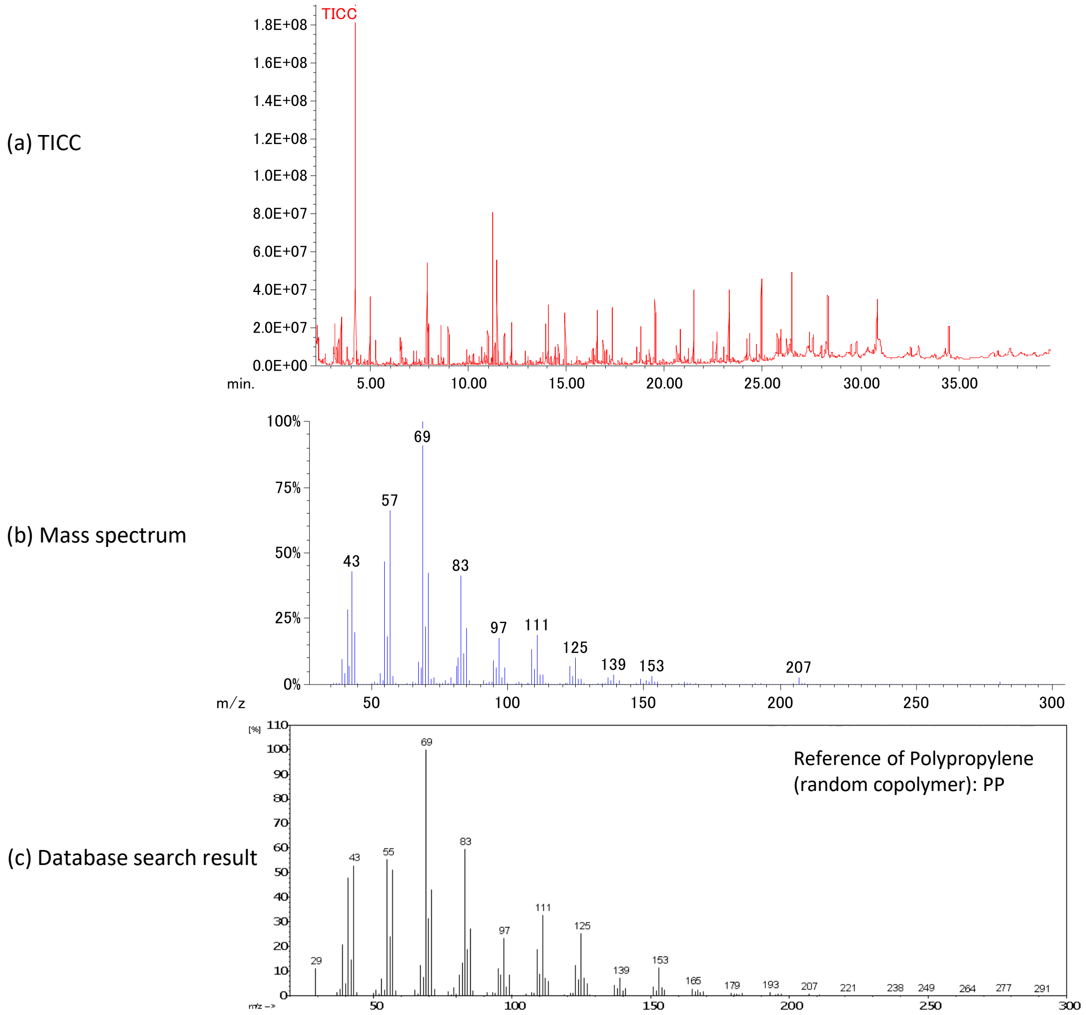

Fig. 1 TICC (a), mass spectrum (b) and database search result (c)

- Confirmation of PMMA, PVC, Nylon6 and PS components in trace amounts

The chromatogram peaks of Methyl methacrylate (PMMA), Naphthalene (PVC), Biphenyl (PVC), Caprolactam (Nylon6), Styrene dimer (PS) and Styrene trimer (PS) obtained by SRM measurements are shown in Fig. 2. The observed peaks can be confirmed to originate from the target component based on the relationship between precursor ion and product ion.

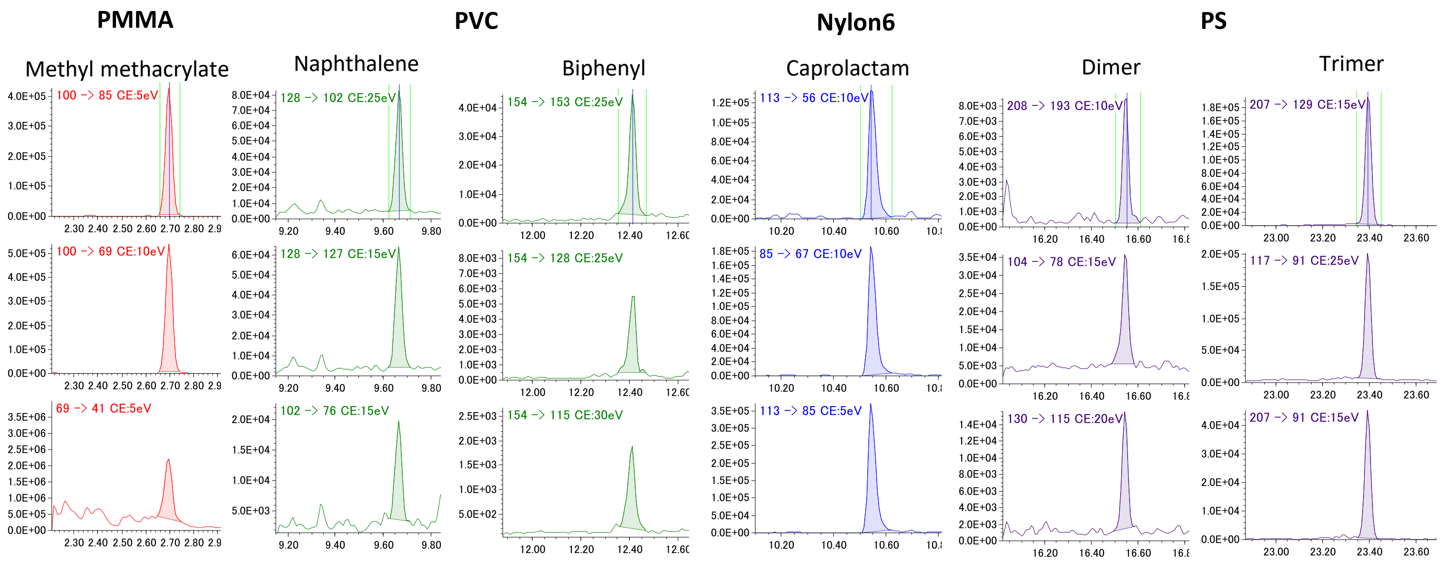

Fig. 2 SRM chromatogram peaks of each target component

- Quantitative results of PMMA, PVC, Nylon6 and PS components in trace amounts

SRM chromatogram peaks of each quantitative component are shown in Fig. 3. Also, quantitative value, recovery percentage and coefficient of variation (CV) are shown in Table 3. The observed peak area values for each target component were used to calculate quantitative value from single-point calibration curve that prepared from each standard sample. The recovery percentage was 92% to 122%, and CV was 1.7% to 6.1%. Thus, the obtained results was showed a high reproducibility.

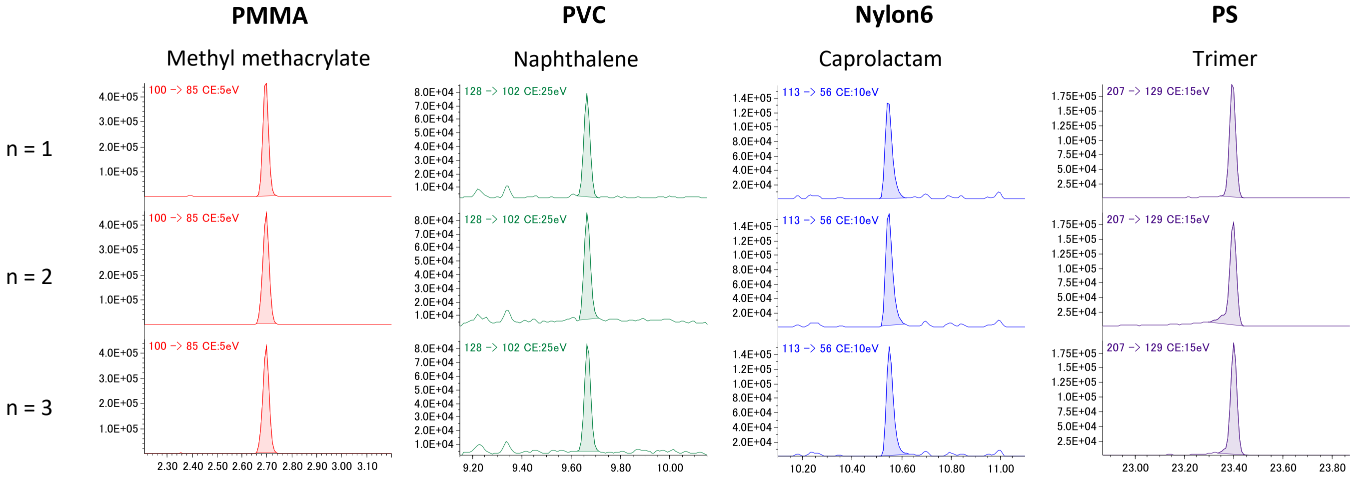

Fig. 3 SRM chromatogram peaks of each quantitative component

Table 3 Quantitative value, recovery percentage and CV of each quantitative component

Component	Quantitative value(ppm) n = 1	n = 2	n = 3	Average	Recovery percentage by average (%)	STDEV	CV (%)
Methyl methacrylate	30.0	31.6	29.9	30.5	122.0	1.0	3.2
Naphthalene	23.2	24.3	24.4	24.0	95.9	0.7	2.8
Caprolactam	98.9	111.8	105.0	105.2	105.2	6.4	6.1
Styrene trimer	23.3	22.6	23.1	23.0	92.0	0.4	1.7

Conclusion

For the analysis of MPs, the SCAN/SRM measurement of pyrolysis GC/MS/MS is an effective measurement method. The SRM measurement use a combination of selected precursor ion and generated product ion from its selected precursor ion, so selectivity of detection ion and detection sensitivity are improved. As a result, the influence of matrix components can be reduced, and it is possible to detect components contained in trace amounts.