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Application News

No. M298

Gas Chromatography Mass Spectrometry

Analysis of Mixed Polymer Sample as Microplastics using Pyrolysis GC/MS

Fine plastic particles with sizes of several µm to about 5 mm are called microplastics (MPs), and their effect on pollution and ecosystems in marine environments is a serious concern. It has been pointed out that bioaccumulation may occur by a process of adsorption of harmful substances on MPs, and ingestion of those MPs by marine organisms in marine environments. Due to that, many surveys of the actual condition of MPs and evaluation of their toxicity are being conducted.

As analytical instruments, the Fourier transform infrared spectrometer (FTIR) is used in qualitative analysis of comparatively large MPs, while the FTIR microscope employing an infrared microscope is mainly used for fine MPs which cannot be analyzed by the attenuated total reflectance (ATR) method of FTIR. The FTIR microscope enables highly sensitive analysis of fine MPs with a size of approximately 10 µm. However, in cases where it is difficult to distinguish the MPs containing multiple types of fine particles, it has been reported that the pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) method is effective.

Using Py-GC/MS method, qualitative analysis of individual polymers contained in mixed samples is possible by highly sensitive detection of the distinctive pyrolysis products of each polymer. This article reports the results of a qualitative analysis of a sample, prepared by mixing multiple polymers to simulate MPs, using Py-GC/MS method.

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Fig. 1 Appearance of Py-GC/MS System

Sample and Analysis Conditions

Fig. 1 shows the Py-GC/MS system (GCMS-QP2020 NX and EGA/PY-3030D pyrolyzer) used in the analysis.

Approximately 0.05 mg each of fragments of four types of commercially-available standard polymer sample materials (polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC)) were introduced into a sample cup, and about 1 mg of wool was placed in the cup to prevent scattering. This sample was then set in the auto-shot sampler of the pyrolyzer.

Table 1 shows the instruments and the analytical conditions. According to References (1) and (2), the contents of the polymers were judged by detecting the pyrolysis products shown in Table 2 (however, some of these compounds were selected independently).

Table 2 Pyrolysis Products and Analytical Conditions Used in Detection of Polymers

Polymer	Pyrolysis product	Retention time (min)	SIM monitoring ion
PE	C20, alkane	20.937	99, 85
	C20, α-alkene	20.879	97, 83
	C20, α, ω-alkene	20.817	95, 82
PP	2,4-dimethylhept-1-ene	5.231	126, 70
	2,4,6,8-tetramethyl-1-undecene	12.908	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.027	111, 69
	2,4,6,8-tetramethyl-1-undecene	13.145	111, 69
PS	Styrene	6.17	104, 78
	3-butene-1,3-diyldibenzene	18.136	208, 91
	5-hexene-1,3,5-triyltribenzene	25.032	312, 207
PVC	Benzene	2.498	78, 51
	1-Chloroindan	8.874	116, 115
	Dihydronaphthalene	10.835	130, 115
	Azulene	11.145	128, 102

Table 1 Analytical Conditions

Instruments
Pyrolyzer : EGA/PY-3030D multi-shot pyrolyzer, AS-1020E auto-shot sampler (Frontier Laboratories Ltd.)
GC-MS : GCMS-QP™2020 NX
Column : UA-5 (MS/HT)-30M-0.25 (Length 30 m, I.D. 0.25 mm, df = 0.25 µm) (Frontier Laboratories Ltd.)

Pyrolyzer conditions
Pyrolyzer furnace temp. : 600 °C
Interface temp. : 300 °C (manual)

GC conditions
Vaporizing chamber temp. : 300 °C
Column oven temp. : 40 °C (2 min) → 10 °C/min → 320 °C (16 min)
Carrier gas : Helium
Control mode : Constant linear velocity
Injection mode : Split (1 : 50)
Linear velocity : 36.1 cm/min
Purge flow rate : 3 mL/min

MS conditions
Interface temp. : 300 °C
Ion source temp. : 230 °C
Ionization method : EI
Measurement mode : Scan/SIM (*m/z* 29 - 700)
Scan event time : 0.3 s
SIM event time : 0.15 s

Simultaneous Analysis of Polymers in Mixed Polymer Sample

Fig. 2 shows the total ion current chromatogram (TIC chromatogram) obtained by analyzing the mixed sample containing multiple polymers. Since the result of this analysis takes the form of a complex chromatogram in which the pyrolysis products of the respective polymers are intermixed, it was difficult to specify the individual polymers contained in the sample from this chromatogram alone.

Fig. 3 shows the SIM chromatograms of the pyrolysis products of the respective polymers. By tracing the distinctive pyrolysis products of the respective polymers, the contents of the polymers could be specified accurately, even multiple polymers were intermixed in a sample.

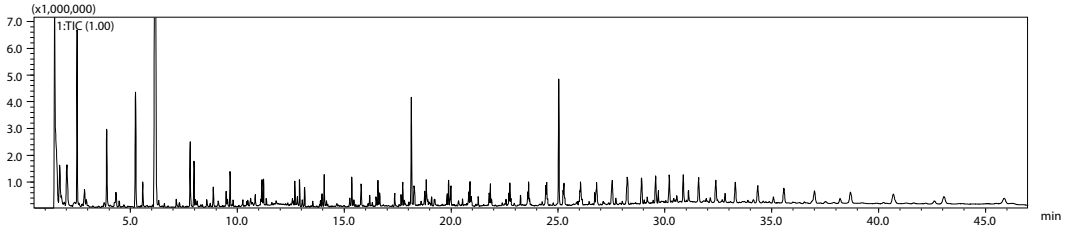

Fig. 2 TIC Chromatogram Obtained by Analysis of Mixed Polymer Sample by Py-GC/MS Method

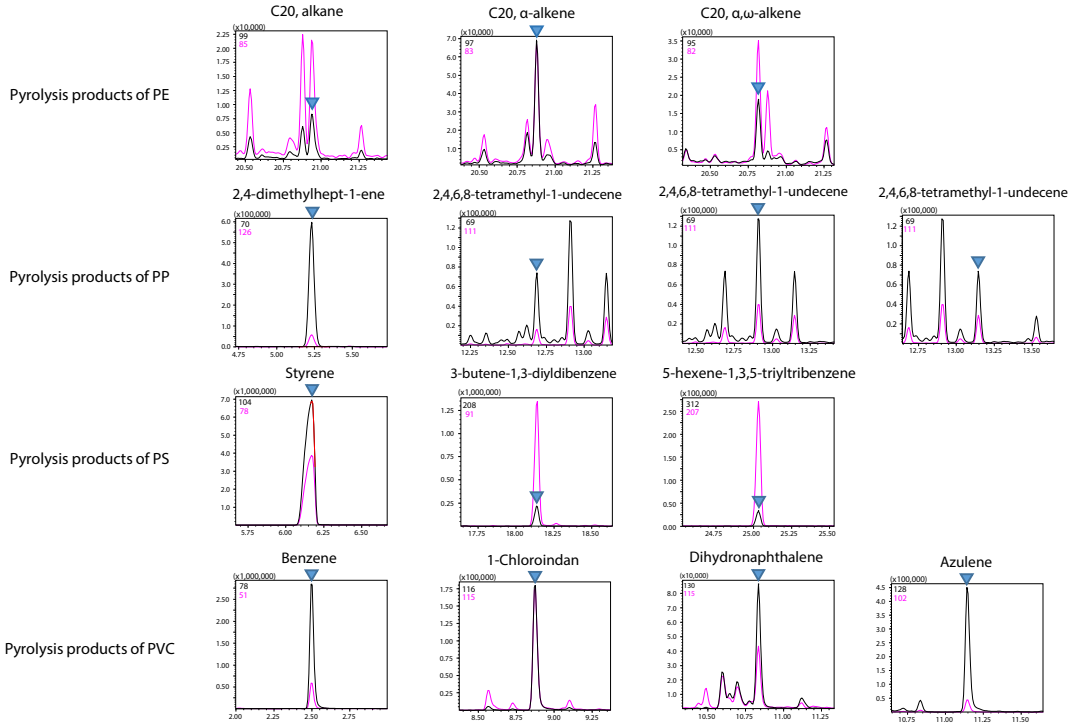

Fig. 3 SIM Chromatograms of Pyrolysis Products of Polymers in Mixed Polymer Sample

Conclusion

In this experiment, it was found that qualitative analysis of various polymers is possible, even the sample contains multiple polymers, by monitoring the pyrolysis products of the respective polymers using the Py-GC/MS method. Although the object of analysis in this experiment consisted of four substances (polymers), it is thought that this technique is also applicable to larger numbers of polymers. Thus, this technique is expected as a new analysis method of MPs.

<References>

(1) M. Fisher and B. M. Scholz-Böttcher, Environ. Sci. Technol., 51,5052-5060 (2017)
(2) S. Tsuge, H. Ohtani, C. Watanabe: Pyrolysis-GC/MS Data Book of Synthetic Polymers -Pyrograms, Thermorgams and MS of Pyrolyzers-,1st Edition, Elsevier, 420 (2011)

First Edition: Jun. 2020

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