Microplastics Analysis using Micro-Furnace Pyrolyzer and F-Search MPs Software

FRONTIER LAB

What are microplastics?

Microplastics (MPs) are tiny plastic particles that measure less than five millimeters across. They result from the breakdown of larger commercial plastic products. Some microplastics have formed by breaking away from larger plastics that have fragmented over time like debris from tire wear. Others have been made small intentionally, for example, cosmetic microbeads used in facial scrubs. The number of consumer and commercial products with intentionally added microplastics is massive: cosmetics, detergents, paints, medicines, diapers, pesticides – the list goes on. Over time, these tiny particles end up flooding into our environment.

As a pollutant, microplastics harm the environment and animal health. Microplastics are extremely persistent, meaning removing them from the environment where they accumulate is almost impossible. Due to their persistence nature and the chemicals they are composed of, studies suggest that they can be highly detrimental to the organisms that come into contact with them, leading to reduced feeding, poisoning, increasing mortality, and other harmful effects. They also tend to facilitate the transfer of contaminants along the food-chain, which can have a significant impact on human health. Microplastics can be found everywhere: in the ocean, mountains, and in our air, drinking water and bodies.

Microplastics analysis

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is a technique for obtaining qualitative and quantitative data on microplastic mixtures by selecting a set of characteristic pyrolyzates for each polymer. Recently, a new method for qualitatively analyzing twelve types of synthetic polymers has been developed, automated, and implemented in the search software (F-Search MPs) to propose a standardized procedure for data processing in Py-GC/MS analysis of plastics mixtures. The method improves the current literature and is based on generating summated mass spectra (SMS) for each polymer, obtained by extracting specific *m/z* and retention index coordinates corresponding to characteristic pyrolyzates.

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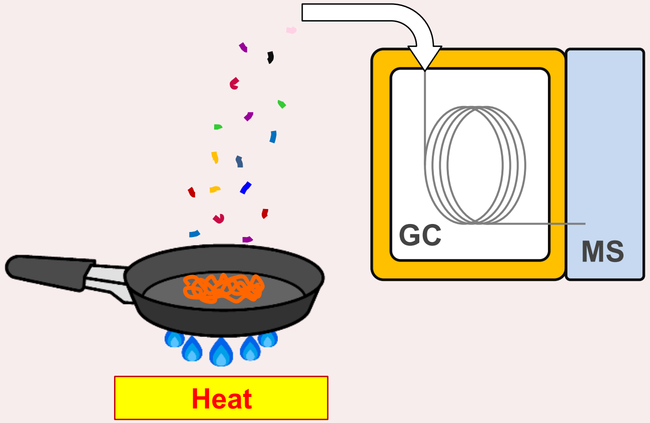
What is pyrolysis?

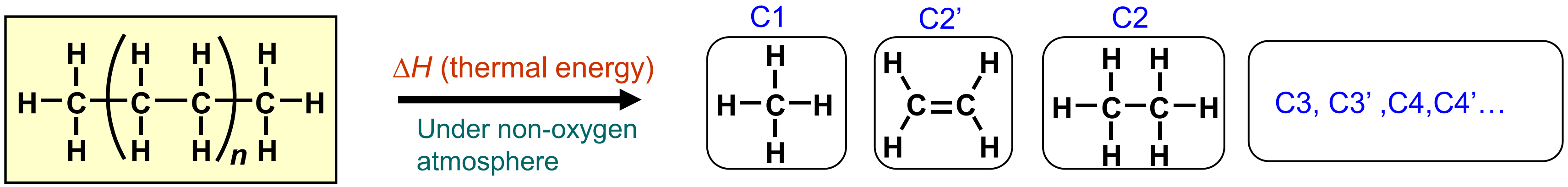
Pyrolysis decomposes a polymer into smaller molecules by heating at high temperatures. The image on the right may give you an idea of pyrolysis. However, in most analytical pyrolysis, this is done under inert atmosphere (no oxygen). Fission of molecular bonds and physical changes irreversibly take place. These smaller molecules obtained by fission in an inert atmosphere are called “Pyrolyzates”.

Here, analytical pyrolysis using ~~a~~ pyrolysis (Py)-GC/MS system is briefly described.

A polymer comprises repetitive atoms or molecules, each covalently bonded, forming a long molecular chain or macromolecule.

In analytical pyrolysis, these polymer molecular chains are broken up by rapidly heating to a high temperature usually at about 600 ºC, and the composition of the polymer is investigated by introducing the smaller molecules (pyrolyzates) into an analytical instrument such as GC/MS.





Polyethylene
(MW: 10,000 ～1,000,000)
n (number of repetitions of monomer)=300~30,000

Methane
(MW: 16)

Ethylene
(MW: 28)

Ethane
(MW: 30)

What is pyrolysis GC/MS technique?

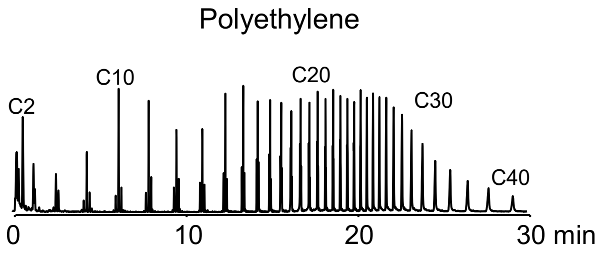
As described earlier, at high temperatures, covalent bonds break and the complex structure is degraded into smaller (stable and volatile) molecules which are referred to as pyrolyzates. The pyrolyzates formed and their relative intensities provide insight into the structure of the original material.

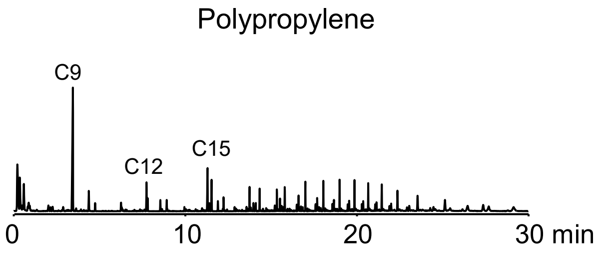
One of the most widely used analytical techniques is Pyrolysis-GC/MS (Py-GC/MS). Sub-milligram quantities are put in an inert sample cup. This technique is performed by the Multi-Mode Pyrolyzer with a vertical micro-furnace design. The Multi-Mode micro-furnace Pyrolyzer provides the users with multiple modes of operations and techniques. Evolved Gas Analysis (EGA) is another technique that can be performed as the rapid screening of evolved gases and identifying the optimal thermal desorption temperature zone(s) for thermal desorption technique (TD-GC/MS).

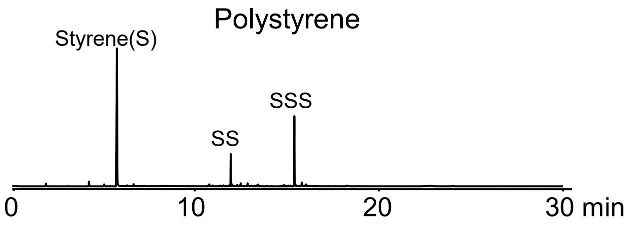
The Frontier Lab's Multi-Shot Pyrolyzer is interfaced directly to the GC inlet. The sample is placed in a small deactivated cup which is, in turn, positioned in the micro-furnace. The temperature of the sample is carefully controlled (±0.1ºC) to ensure that the sample-to-sample thermal profile is identical. Frontier's well-engineered technology ensures that the sample is maintained at ambient temperature, in an inert atmosphere, prior to pyrolysis; thus, eliminating evaporation, thermal degradation, and thermosetting before analysis.

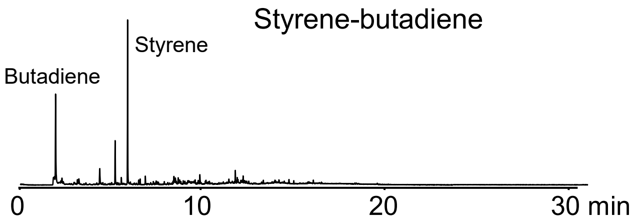
Shown below are pyrograms of some typical polymers, showing how different the pyrograms of each polymers are.

Pyrograms of typical polymers


Polyethylene


Polypropylene

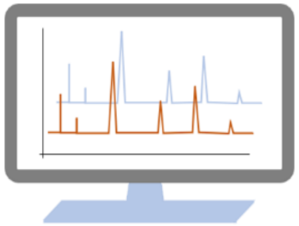

Polystyrene


Styrene-butadiene

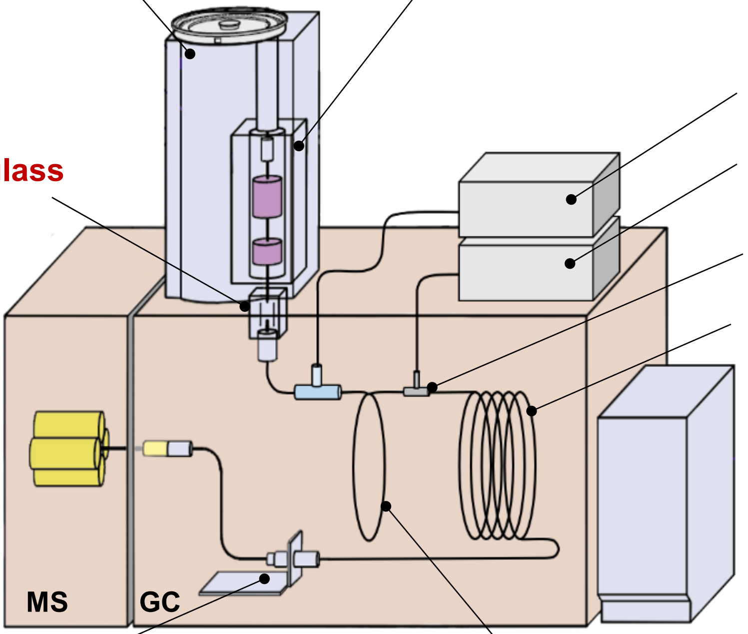
Micro-Furnace Pyrolysis-GC/MS configuration for microplastic analysis

Cryogenic mill*

F-Search MPs analysis software*



MP Calibration standard set*



Auto-Shot Sampler

Micro-Furnace Pyrolyzer*

MicroJet Cryo-Trap

Multi-Functional Splitless Sampler*

Packed GC glass insert*

Splitter

Separation column

Vent-free GC/MS adapter

Pre-column (UAMP column kit*)

*** Products required for MPs analysis**

* Micro-Jet Cryo-Trap needed when using Splitless pyrolysis-GC/MS

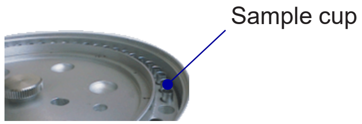
Micro-Furnace Pyrolysis-GC/MS configuration for microplastic analysis

Multi-Shot Pyrolyzer (EGA/PY-3030D)

A vertical micro-furnace pyrolyzer based on a ceramic heater is the most capable model and features high performance and ease of use. It is controlled by the control software installed on a PC. A sample is heated in the furnace to generate gaseous pyrolyzates, which are introduced into the GC. With optional accessory devices, it supports a wide variety of applications.

Auto-Shot Sampler (AS-2020E)

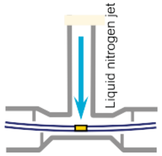
Up to 48 samples can be automatically analyzed using any of the analytical modes (e.g., Flash pyrolysis, Thermal desorption, Double-Shot, Heart-Cutting, etc.) with enhanced reliability.



Pyrolyzer is located in the housing of Auto-Shot Sampler.

MicroJet Cryo-Trap (MJT-2030E)

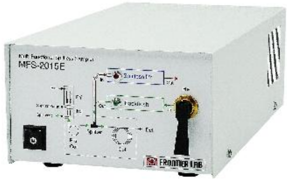
By blowing liquid nitrogen jet to the front of separation column, volatile compounds are cryo-trapped while maintaining the temperature at -196ºC using only one third of the amount of liquid nitrogen required for competitor's products. It supports automated analysis with the pyrolyzer’ control software.



Products specifically designed for microplastic analysis

These are peripheral accessories exclusively used with the Multi-Shot Micro-Furnace Pyrolyzer.

Multi-Functional Splitless Sampler (MFS-2015E)



The device allows "new splitless pyrolysis (F-Splitless pyrolysis)", "backflush", and improved separation. The splitless pyrolysis greatly improves the measurement sensitivity of pyrolyzates. The backflush shortens the run time and reduces system contamination.

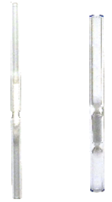
UAMP column kit

Designed for microplastics analysis, this kit consists of a separation column (UA5-30M-0.5F), a specially designed pre-column (UA^{+}-50), and a connector (UA Connector). Using this product improves the accuracy of analysis of a polymer mixture. Also, it reduces the contamination of the separation column.

MP Calibration standard set

This is used to identify and quantify 12 major polymers using Py-GC/MS. It allows the user to easily create calibration curves for quantification of MPs. Both SiO_2 (silicon dioxide) and $CaCO_3$ (calcium carbonate) are used as diluents for easy weighing on semi-microbalance and contain a few micro-grams of each of the 12 polymers. Standard set with lower concentrations (one-tenth of this product) is also available.

Packed GC glass insert



Packed GC Glass Insert is a GC glass insert with packing materials. Using this product improves a peak shape of pyrolyzates derived from microplastics.

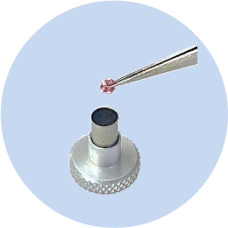
F-Search MPs 2.1 (JPN patent 6683335)

The unique search algorithm allows users with little experience in polymer analysis to obtain reliable microplastic identification and quantification results. The intelligent F-Search MP engine is competitive advantage. The search software allows you to create calibration curves for quantification of MPs for easy identification and quantification.

Cryogenic Mill (IQ MILL-2070)

This compact benchtop grinding mill has powerful and shear crushing capabilities and makes the sample grinding process into a simple pre-treatment operation. By using a special high elastic belt with excellent durability, efficient crushing is achieved in a short time by high-speed three-dimensional figure-8 motion.

Workflow for Microplastics Analysis with Py-GC/MS System



Step 1 Sampling and pretreatment

Microplastics are extracted from environmental samples by appropriate pretreatment. The sample is then placed in a sample cup and weighed using a semi-micro balance.

Step 2 Setting sample cups on Auto-Shot Sampler

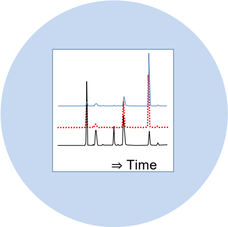
The sample cups are placed onto the Auto-Shot Sampler. Up to 48 cups can be loaded each time.

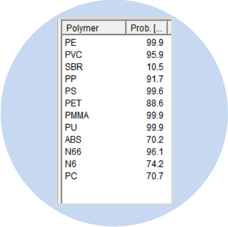
Step 3 Pyrolysis of samples

The sample is introduced into the micro-furnace Pyrolyzer by the Auto-Shot Sampler and is pyrolyzed. The plastics become pyrolysis products (pyrolyzates) and are introduced into the GC directly. On the other hand, the inorganics in the sample remain in the sample cup as residues.

Step 4 GC/MS analysis

Pyrolyzates are separated on a GC column and detected by a single Quadrupole mass spectrometer. The resulting pyrogram generally includes a peak for each pyrolyzate. The mass spectrum from each peak reflects the chemical structure of each pyrolyzate. Each polymer generates a unique set of pyrolyzates.





Polymer	Prob. [...
PE	99.9
PVC	95.9
SBR	10.5
PP	91.7
PS	99.6
PET	88.6
PMMA	99.9
PU	99.9
ABS	70.2
N66	96.1
N6	74.2
PC	70.7

Step 5 Data analysis

Reliable and quick Data analysis can be done using F-Search MPs 2.0. Calibration curves are created automatically based on the analytical results from the reference polymer mixture. Then F-Search MPs 2.1 performs quantitative calculation automatically and results are reported for each sample.

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A. Calibration standard for microplastic analysis

B. Road microplastics

C. Marine waste plastic debris

D. Marine sediment

A-1

Preparation and evaluation of calibration standard for microplastic (MP) analysis using SiO_2 as a diluent

Part 1: Investigation of inorganic diluents for MP analysis

- **BACKGROUND:** In recent years, demand for the analysis of microplastics (MPs) in the environment has increased. However, analytical methods and standard samples have not been established in this area. MPs in environmental samples generally contain multiple polymer species. Pyrolysis (Py)-GC/MS has the advantage of the ability of mass-based quantification for polymer mixtures in addition to qualitative analysis. Therefore, calibration standards were prepared for the analysis of environmental MPs by Py-GC/MS. An inorganic diluent in the calibration standard was used to reduce the weighing error of trace polymers, and the standard was prepared by homogeneous mixing of 12 types of polymers. In this report, six commonly used inorganic compounds were selected (to be used as diluents) in order to reduce weighing errors of trace polymers, and their effects on the pyrolysis of polymers were investigated.
- **EXPERIMENTAL:** To a sample cup containing 30 µg of polyurethane (PU), 2 mg of one of the six candidate inorganic compounds used as diluents (Fig. 2) was added and was subjected to Py-GC/MS measurement.
- **RESULTS:** Fig. 1 shows the hydrolysis reaction of 4,4'-diphenylmethane diisocyanate (MDI) to form 4,4'-methylene-dianiline (MDA), the major pyrolyzate of PU, and Fig. 2 shows the extracted ion chromatograms (EICs) for the ions of MDA and MDI. Without diluent, the MDI peak was clearly observed, and no MDA was detected. The MDI peak disappeared, and MDA was detected when α-Al_2O_3, γ-Al_2O_3, TiO_2, $CaCO_3$, or SiO_2 without deactivation treatment was present. These diluents seemed to adsorb and hydrolyze MDI. On the other hand, in the presence of deactivated SiO_2, the MDI peak was clearly visible as well as those without diluent, while no MDA was detected. It was also shown that deactivated SiO_2 had no effect on the pyrolysis of 11 polymers other than PU. In the next page, pyrograms of the MP calibration standard (MPs-SiO2) with deactivated SiO_2 used as a diluent are presented.

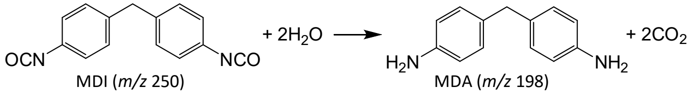

Fig. 1 Hydrolysis of MDI.

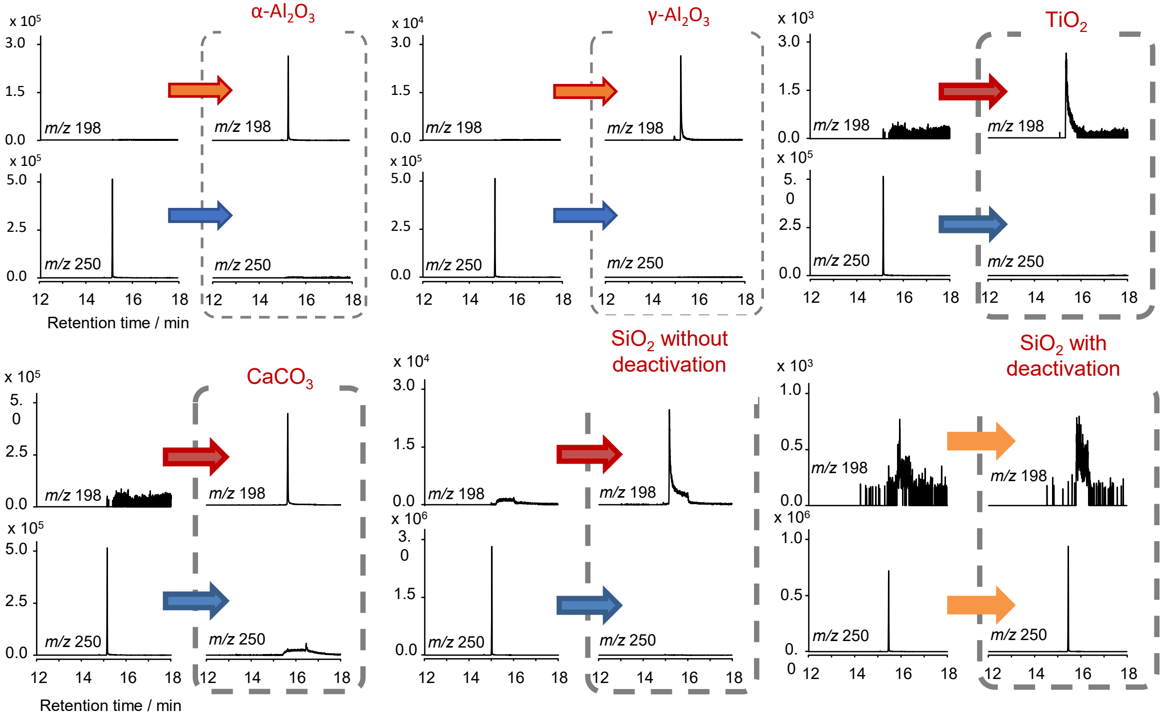

Fig. 2 EICs of mixtures of PU and inorganic compounds.

1) M. Matsueda *et al.*, *J. Anal. Appl. Pyrolysis* 154 (2021) 104993.

A-2

Preparation and evaluation of calibration standard for microplastic (MP) analysis using SiO_2 as a diluent

Part 2: Pyrogram of the calibration standard for MP analysis

- **BACKGROUND:** In the previous page, deactivated SiO_2 was selected as a diluent for the microplastic (MP) analysis of a mixed polymer sample. In this report, a pyrogram of the calibration standard (MPs-SiO2) containing 12 types of polymers is shown, where deactivated SiO_2 was used as a diluent.
- **EXPERIMENTAL:** The MP calibration standard MPs-SiO2 was prepared from a homogeneous mixture of deactivated SiO_2 and 12 polymers.1) The 12 polymers and their concentrations were determined considering the global production of plastics and their sensitivity in Py-GC/MS measurements. MPs-SiO2 was analyzed by a Py-GC/MS system shown in Fig. 1.
- **RESULTS:** A pyrogram of MPs-SiO2 and the characteristic pyrolyzate and the indicator ion for each polymer are shown in Fig. 2. Table 1 summarizes the characteristic pyrolyzates. When the calibration standard sample using deactivated SiO_2 as a diluent was used, MDI, a pyrolyzate of PU, reacted with pyrolyzates of PET and nylon, so the MDI peak was not observed. Analysis of PU can be accomplished using calibration standard (MPs-CaCO3) with $CaCO_3$ as a diluent (PYA1-146E ~ 148E). In the next page, calibration curves for each characteristic pyrolyzate are reported.

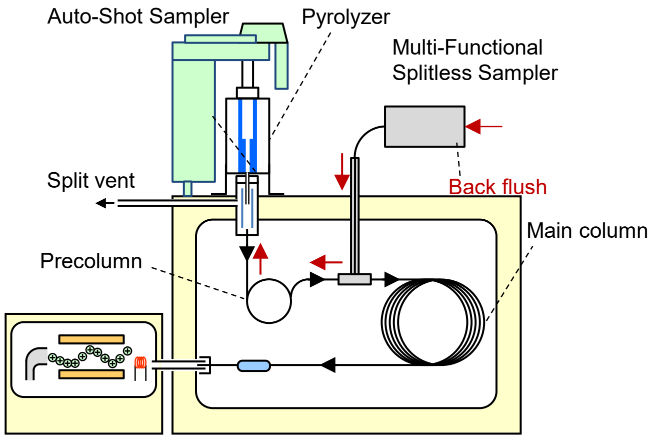

Fig.1 Analytical system for MPs analysis.

Table 1 Characteristic pyrolyzate of each polymer and its indicator ion (*m/z*).

Polymer	Abbr.	Characteristic pyrolyzates	*m/z*
PE	C21''	1,20-Heneicosadiene	82
PP	C9'	2,4-Dimethyl-1-heptene	126
PS	SSS	2,4,6-Triphenyl-1-hexene	91
ABS	SAS	2-Phenethyl-4-phenylpent-4-enenitrile	170
SBR	SB	4-Phenylcyclohexene	104
PMMA	MMA	Methyl methacrylate	100
PC	BPA	Bisphenol A	213
PVC	Nap	Naphthalene	128
PU	MDI	4,4'-Diphenylmethane diisocyanate	250
PET	BA	Benzoic acid	122
N6	Capro	Caprolactam	113
N66	CP	Cyclopentanone	84
PU	MDI	4,4'-diphenylmethane diisocyanate	250

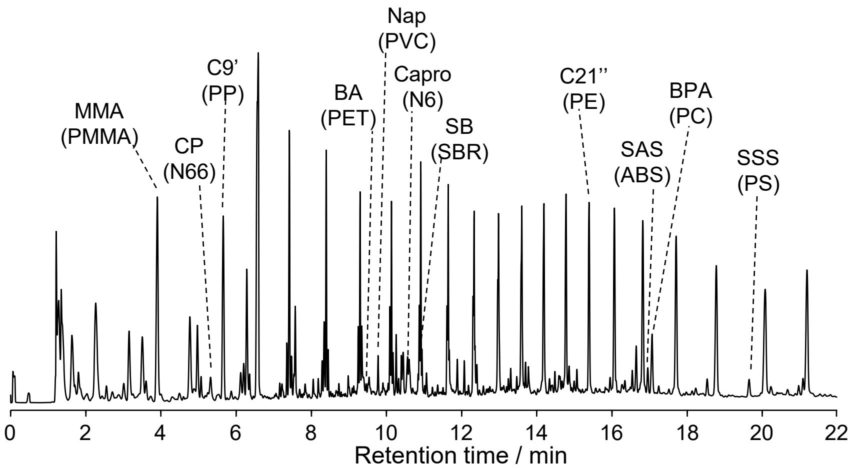

Fig. 2 Pyrogram of MPs-SiO2.

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1) M. Matsueda *et al.*, *J. Anal. Appl. Pyrolysis* 154 (2021) 104993.

A-3

Preparation and evaluation of calibration standard for microplastic (MP) analysis using SiO_2

Part 3: Calibration curves for polymers in MPs-SiO2 as a diluent

- **BACKGROUND:** In the previous page, a pyrogram of the MPs calibration standard (MPs-SiO2) were reported. In this report, calibration curves for the characteristic pyrolyzates of polymers in the calibration standard are described.
- **EXPERIMENTAL:** 0.4 mg, 2 mg, and 4 mg of MPs-SiO2 were placed in an Eco-Cup LF. Measurements were made by the method described previously, and the peak areas of the indicator ions (Table 1) in the extracted ion chromatograms were used to create calibration curves for the 11 polymers. The limit of detection (LOD = 3.3 *s*/*a*) determined from the slope of the calibration curve (*a*) and the standard deviation at the lowest concentration (*s*) is shown in Table 1. The GC was operated in a constant pressure mode (150 kPa) with a split ratio of 1/50. The mass spectrometer was operated in a scan mode.
- **RESULTS:** The calibration curves so created are shown in Fig. 1. The coefficients of determination R^2 for 10 polymers indicate a good linearity (>0.99) except PET. In the case of PET, use of MPs-CaCO3, in which $CaCO_3$ is used as a diluent, is recommended for the quantitative analysis as previously reported.

Table 1 Characteristic pyrolyzates and LODs for 11 polymers.

Polymer	Abbrev. of characteristic pyrolyzate*	*m/z*	LOD [µg]
PE	C21"	82	1.90
PP	C9'	126	0.56
PS	SSS	91	0.11
ABS	SAS	170	0.05
SBR	SB	104	0.15
PMMA	MMA	100	0.03
PC	BPA	213	0.24
PVC	Nap	128	0.38
PET	BA	122	0.94
N6	Capro	113	0.05
N66	CP	84	0.32

* See PYA1-144E for abbreviations.

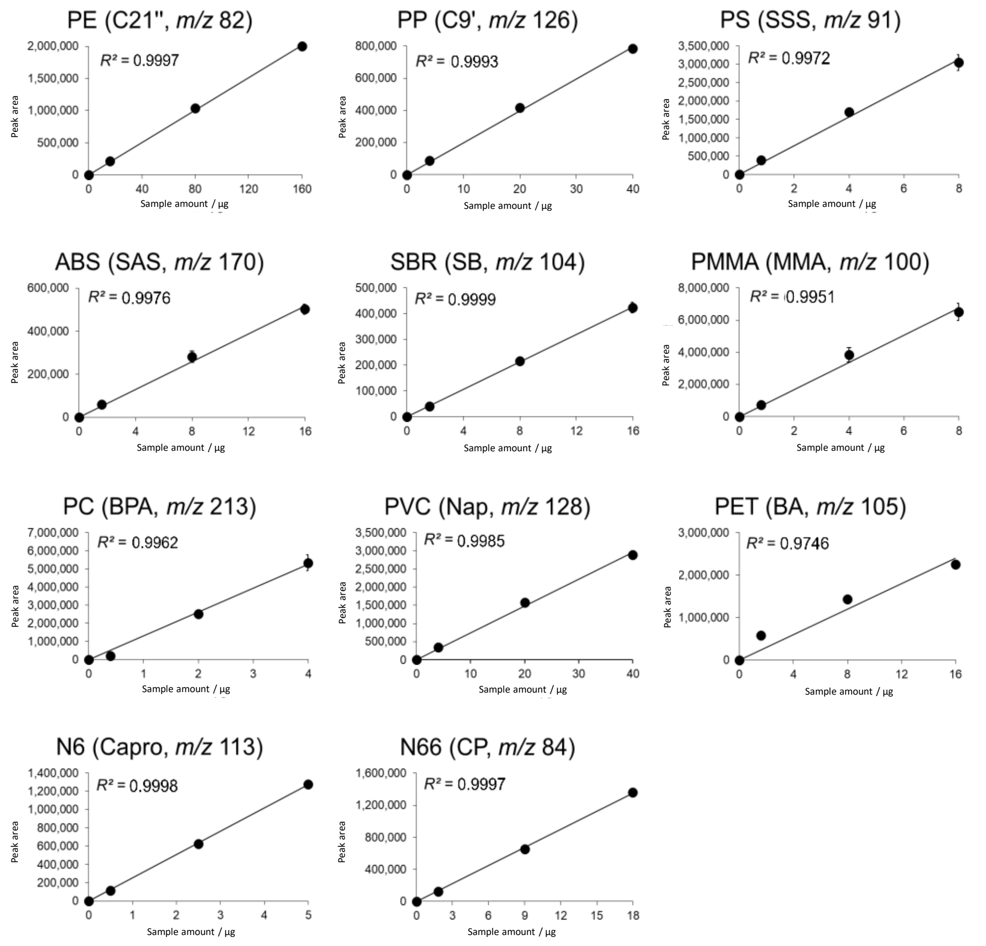

Fig. 1 Calibration curves for 11 polymers created using MPs-SiO2.

A-4

Preparation and evaluation of calibration standard for microplastic (MP) analysis using $CaCO_3$ as a diluent

Part 1: Reactions of polymer pyrolyzates in the presence of $CaCO_3$ as a catalyst

- **BACKGROUND:** The preceding pages described the characterization of a calibration standard for microplastic (MP) analysis. The standard is called MPs-SiO2 which is a homogeneous mixture composed of 12 types of polymers and diluent SiO_2 powders. However, with MPs-SiO2, MDI, a pyrolyzate of PU, reacts with pyrolyzates of PET and nylon, and this causes MDI peak to disappear. For stable detection of pyrolyzates of the 12 polymers including PU, the effect of $CaCO_3$ used as both a diluent and a catalyst on the reactions of pyrolyzates was investigated, and the MP analysis was examined by employing the MP calibration standard (MPs-CaCO3) by which reactive pyrolyzates are converted to stable compounds.[1,2] In this report, the reactions of pyrolyzates of PET, PC, and PU using $CaCO_3$ as a catalyst in the determination of characteristic pyrolyzates for the analysis of the MP calibration standard are described.

- **EXPERIMENTAL:** PET (16 µg), PC (2 µg), and PU (30 µg) with and without $CaCO_3$ (4 mg) were each put in a sample cup (Eco-Cup LF) and subjected to Py-GC/MS measurements.

- **RESULTS:** Fig. 1 shows pyrograms of PET, PC, and PU, and the reaction schemes for polymer pyrolysis and pyrolyzates catalyzed by $CaCO_3$. (a) PET: benzoic acid (BA) is converted to benzophenone (BP). (b) PC: the pyrolysis of bisphenol A (BPA), the main product, is accelerated and the amount of 4-isopropenylphenol (IPP) formed is increased. (c) PU: through the hydrolysis of 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-methylene-dianiline (MDA) is formed.

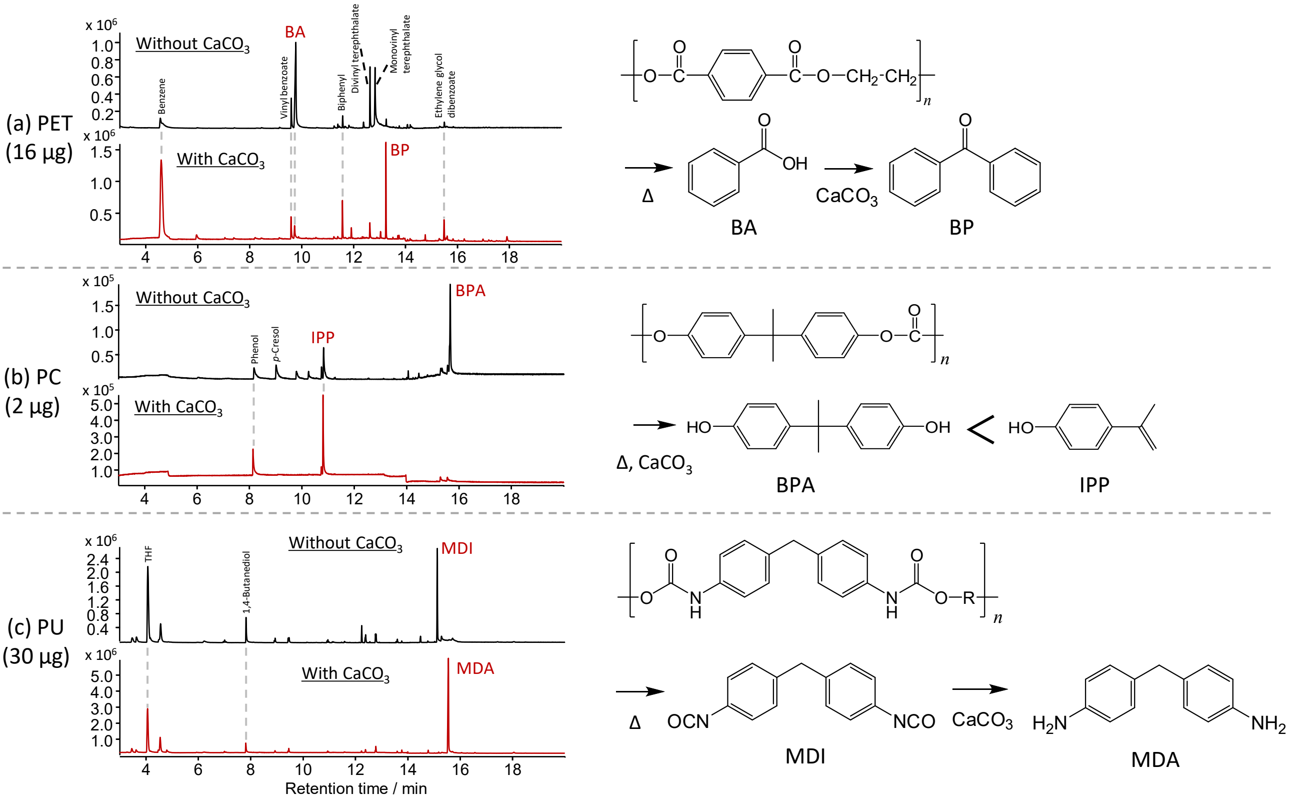

Fig. 1 Pyrograms of PET, PC, and PU (left) and reaction schemes of pyrolyzates catalyzed by $CaCO_3$ (right).

1) R. A. Hites and K. Biemann, *J. Am. Chem. Soc.* 94 (1972) 16, 5772–5777.
2) T. Ishimura *et al.*, *J. Anal. Appl. Pyrolysis* 157 (2021) 105188.

A-5

Preparation and evaluation of calibration standard for microplastic (MP) analysis using $CaCO_3$ as a diluent

Part 2: Pyrogram of MPs-CaCO3

- **BACKGROUND:** In the previous page, when $CaCO_3$ was used as a diluent and catalyst, conversion of pyrolyzates of PET, PC and PU due to catalytic reactions were observed. In this report, pyrograms of the MP calibration standard (MPs-CaCO3) using $CaCO_3$ as a diluent are described.
- **EXPERIMENTAL:** The MP calibration standard MPs-CaCO3 was prepared by homogeneously mixing $CaCO_3$ and 12 polymers.1) The 12 polymer species and their contents were chosen in consideration of the global plastic production and their sensitivity in Py-GC/MS. Pyrograms of MPs-CaCO3 were measured by the Py-GC/MS system shown in Fig. 1.
- **RESULTS:** A pyrogram of MPs-CaCO3 together with characteristic pyrolyzates for 12 polymers is shown in Fig. 2., Indicator ions for characteristic pyrolyzates are summarized in Table 1. While MDI, a pyrolyzate of PU, was not observable with MPs-SiO2, it can now be detectable as MDA. In the next page, calibration curves of characteristic pyrolyzates for 12 polymers are described.

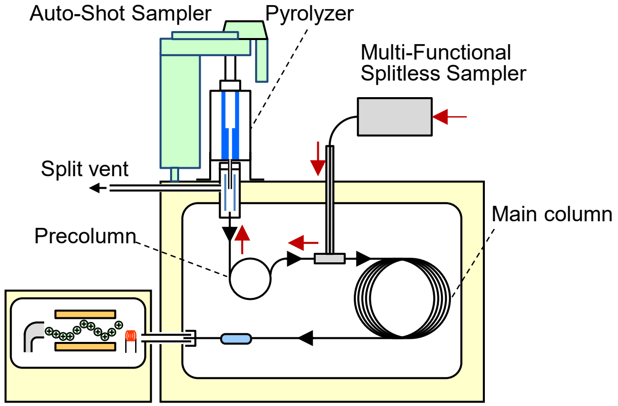

Fig. 1 Analytical system for MP analysis.

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SBR	SB	4-Phenylcyclohexene	104
PMMA	MMA	Methyl methacrylate	100
PC	IPP	4-Isopropenylphenol	134
PVC	Nap	Naphthalene	128
PU	MDA	4,4'-Methylenedianiline	198
PET	BP	Benzophenone	182
N6	Capro	Caprolactam	113
N66	CP	Cyclopentanone	84

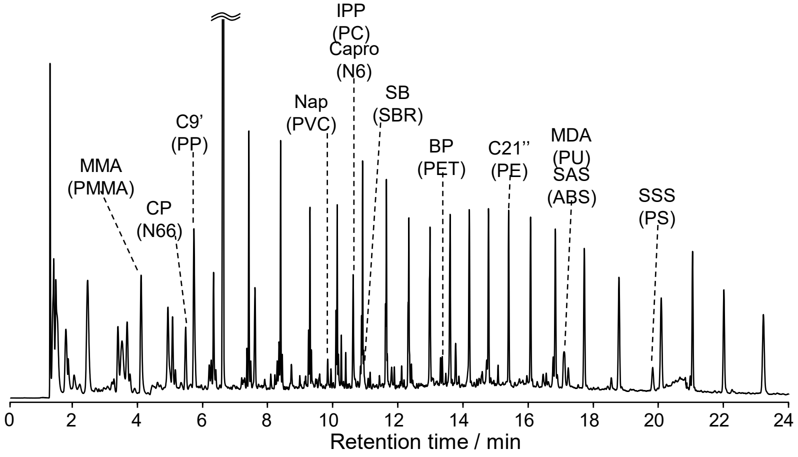

Fig. 2 Pyrogram of MPs-CaCO3.

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1) T. Ishimura *et al.*, *J. Anal. Appl. Pyrolysis* 157 (2021) 105188.

A-6

Preparation and evaluation of calibration standard for microplastic (MP) analysis using $CaCO_3$ as a diluent

Part 3: Calibration curves for polymers in MPs-$CaCO_3$

- **BACKGROUND:** Reported in the previous page is a pyrogram of MP calibration standard (MPs-CaCO3) and characteristic pyrolyzate of each of the 12 polymers. Here, calibration curves of the characteristic pyrolyzates and the limit of detection (LOD) for the 12 polymers are reported.
- **EXPERIMENTAL:** 0.4 mg, 2 mg, and 4 mg of MPs-CaCO3 were each placed in an Eco-Cup LF. Measurements were done by the method described in the previous page, and the peak areas of the extracted ion chromatograms (EICs) of the ions listed in Table 1 were used to create calibration curves for the 12 polymers. The detection limit (LOD=3.3 *s/a* ,*where a* is the slope of the linear calibration curve and *s* is the standard deviation at the lowest concentration) is summarized in Table 1 for each of 12 polymers. The GC injector pressure was 150 kPa (constant pressure mode) with a split ratio of 1/50. The mass spectrometer was operated in a scan mode.
- **RESULTS:** Fig. 1 shows the calibration curves for the 12 polymers in MPs-CaCO3, which showed good linearity with a determination coefficient R^2 >0.99, except for PS. The calibration curve for PS was found to be quadratic. For PET, which showed a poor linearity with MPs-SiO2, the linearity was improved by the conversion of benzoic acid, a pyrolyzate, to BP by the catalytic reaction with $CaCO_3$.

Table 1. Characteristic pyrolyzate for 12 polymers and LOD.

Polymer	Characteristic pyrolyzate*	*m/z*	LOD [µg]
PE	C21"	82	1.63
PP	C9'	126	0.54
PS	SSS	91	0.23
ABS	SAS	170	0.21
SBR	SB	104	0.38
PMMA	MMA	100	0.09
PC	IPP	134	0.06
PVC	Nap	128	0.51
PU	MDA	198	0.18
PET	BP	182	0.18
N6	Capro	113	0.10
N66	CP	84	0.35

* See previous page for abbreviation.

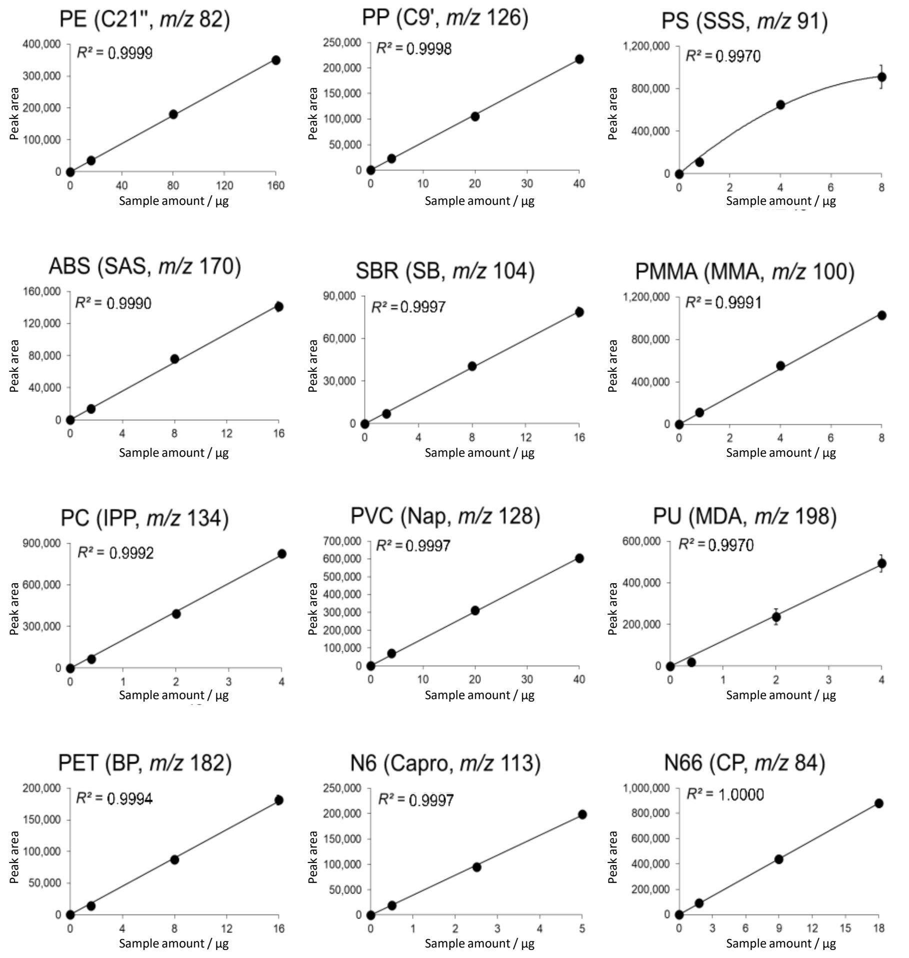


Fig. 1 Calibration curves for 12 polymers created using MPs-CaCO3.

High-sensitivity detection of polystyrene by F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

Part 1 Features of pyrograms obtained with different injection methods

- **BACKGROUND:** In pyrolysis (Py)-GC/MS, the split injection method is commonly employed. However, this method may lead to secondary reactions, such as accelerated decomposition, if pyrolyzates are not rapidly removed from the heated furnace. To address this issue, we developed a new F-Splitless injection method which involves the forced venting of the carrier gas and cryo-trapping of pyrolyzates. This report presents the pyrograms of polystyrene (PS) obtained through both the conventional split/splitless and the F-Splitless methods.
- **EXPERIMENTAL:** 1 mg of PS was dissolved in 10 mL of dichloromethane and subsequently diluted according to the split ratio so that 10 ng of PS is introduced into the separation column. The sample was put in a sample cup, followed by evaporation of the solvent. Py-GC/MS measurements were carried out at a furnace temperature of 550 ºC using the system shown in Fig. 1 with the total flow rate given in the caption of Fig. 2.

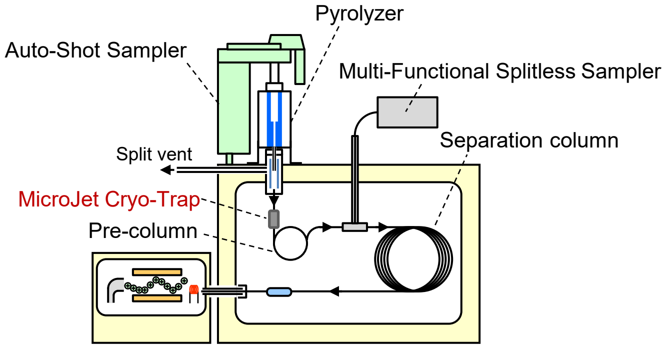


Fig. 1 System configuration of F-Splitless Py-GC/MS.

- **RESULTS:** The pyrograms of PS obtained by different injection methods are shown in Fig. 2. Styrene monomer (S), dimer (SS), and trimer (SSS) peaks are observed with variations in the peak area ratio of SSS/S. With the conventional splitless method, the low total carrier gas flow rate promotes the decomposition of SSS and results in the reduced peak areas and alters the pyrolysis behavior differed from that observed with the split method (split ratio: 1/13). On the other hand, the F-Splitless method suppresses the decomposition of SSS, resulting in a similar pyrolysis behavior to that of the split method. The next page will provide the comparison of SSS/S, an indicator of the secondary reaction in the pyrolysis of PS.

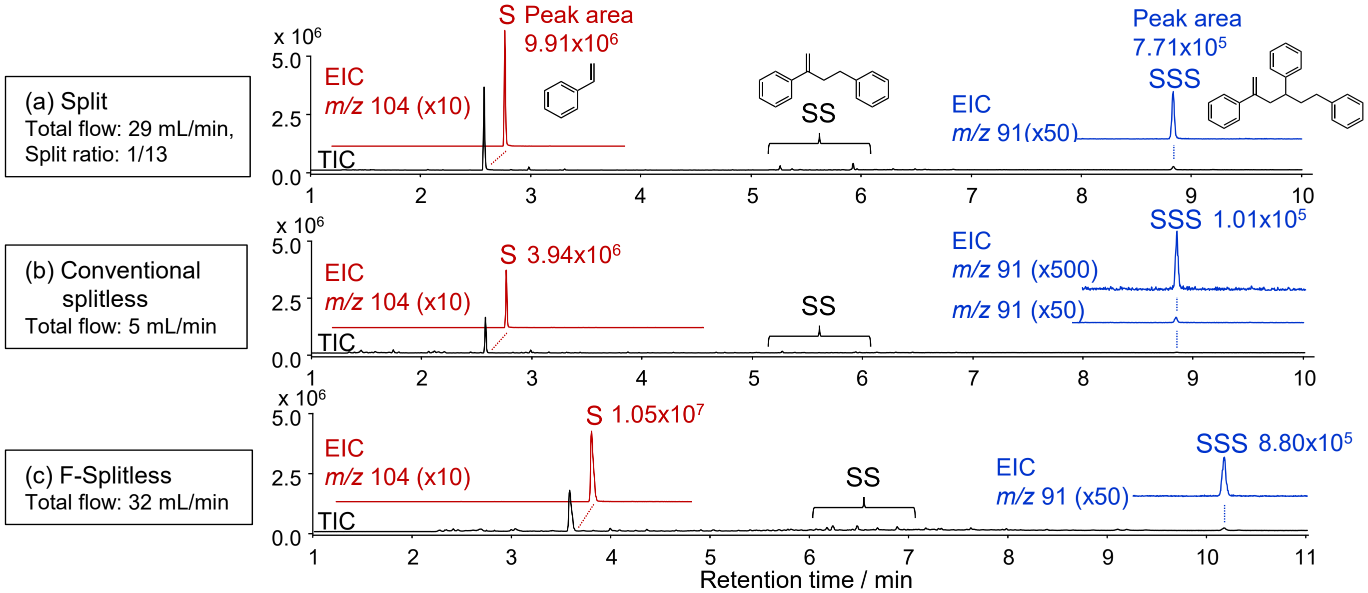


Fig. 2 Pyrograms of PS obtained by different injection methods.

Reference: K. Tei *et al.*, *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

A-8

High-sensitivity detection of polystyrene by F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

Part 2 Styrene trimer/monomer peak area ratios (SSS/S) and reproducibilities by injection methods

- **BACKGROUND:** In the previous page, the pyrograms obtained by different injection methods, i.e., the conventional split/splitless and new F-Splitless, were compared. Here, a comparison of the peak area ratios (SSS/S) of styrene trimer (SSS) to monomer (S) obtained using the different injection methods is reported. This serves as an indicator to evaluate the extent of secondary reactions that occur during the pyrolysis of polystyrene (PS).

- **EXPERIMENTAL:** Py-GC/MS of PS was carried out using the three injection methods described previously, and the peak areas were calculated based on the extracted ion chromatograms (EICs) for SSS (*m/z* 91) and S (*m/z* 104).

- **RESULTS:** Plots of the peak area ratio (SSS/S) against GC total flow rate for F-Splitless, conventional splitless, and split methods are shown in Fig. 1. In the split method (split ratio 1/5), SSS/S increases significantly as the total flow rate increased from 8 to 29 mL/min, and gradually increases up to 203 mL/min. This result indicates that in the split method, the transformation of SSS to S through the secondary reaction is suppressed as the total flow rate increases. In the conventional splitless method, due to the low total flow rate, the decomposition of SSS is promoted. In contrast, in the F-Splitless method, its SSS/S is comparable to that of the split method under the same total flow rate, indicating that the secondary reaction (accelerated decomposition) is suppressed. The reproducibilities of the peak area values for three injection methods are shown in Fig. 2. The peak areas of S and SSS obtained with the split method and the F-Splitless method at flow rates above 13 mL/min exhibited excellent reproducibilities compared to the SSS reproducibility obtained with the conventional splitless method. In conclusion, the newly developed F-Splitless method is an analytical technique that allows for the quantification of PS with good reproducibilities while suppressing the secondary reactions.

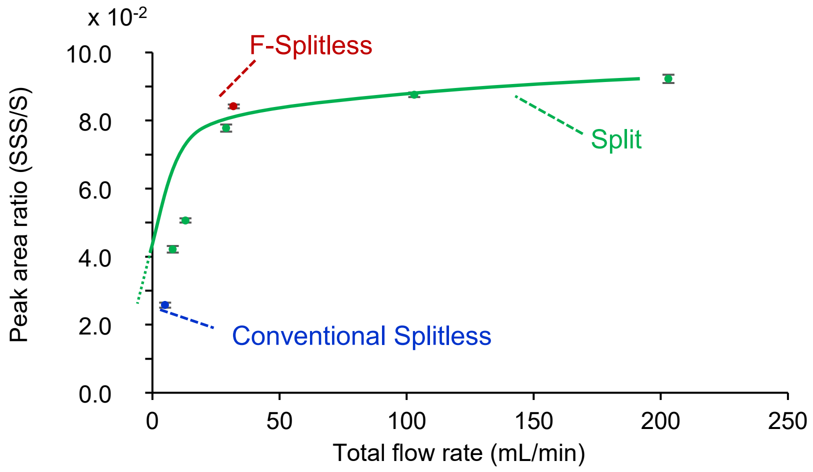


Fig. 1 Plots of peak area ratio (SSS/S) against total flow rate* of conventional split/splitless and F-Splitless methods.

* Total flow rate includes septum purge of 3 mL/min.

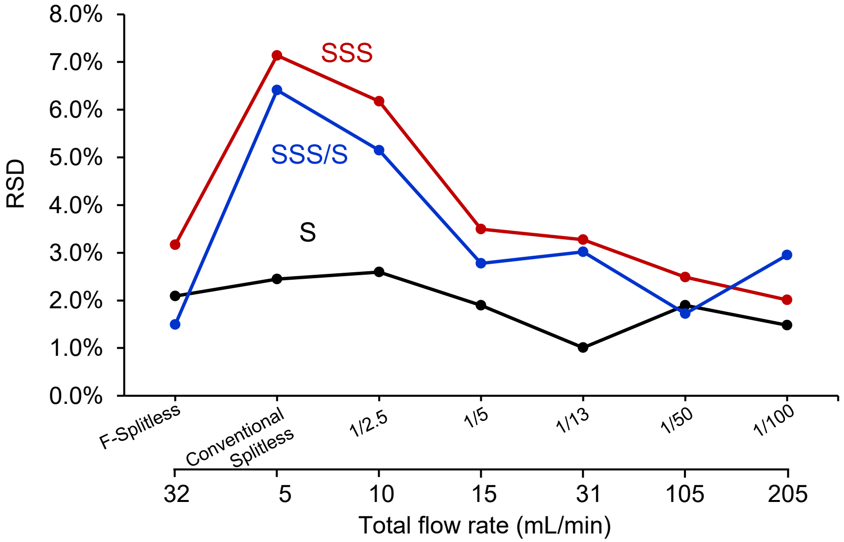


Fig. 2 Plots of RSD of S and SSS peak areas against total flow rate measured by the conventional split (split ratio 1/2.5 - 1/100)/splitless and F-Splitless methods (*n*=5).

Reference: K. Tei *et al.*, *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

A-9

High-sensitivity detection of polystyrene by F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

Part 3 Calibration curves for polystyrene pyrolyzates

- **BACKGROUND:** In the previous page, in the pyrolysis of PS, the peak area ratio of styrene trimer/monomer (SSS/S) obtained by different injection methods exhibited excellent reproducibilities while suppressing secondary reactions of pyrolyzates. Here, the linearity of calibration curves obtained by both split and splitless injection methods is presented.

- **EXPERIMENTAL:** Using the methods previously described, Py-GC/MS measurements of PS were conducted using the split and F-Splitless injection methods. The calibration curves were prepared using the peak areas of characteristic ions of S (*m/z* 104) and SSS (*m/z* 91) in scan mode. In the F-Splitless method, in addition to scan mode, measurements were done in the SIM mode, and calibration curves were constructed.

- **RESULTS:** The calibration curves obtained are shown in Fig. 1. Each calibration curve exhibits a fairly good linearity as indicated by the coefficient of determination (R^2) ranging from 0.994 to 0.999 for the split injection method and the F-Splitless injection method, covering sample amounts from 1 ng to 10 µg and 0.01 to 100 ng, respectively. Notably, in the F-Splitless method, both scan and SIM modes demonstrated good linearity in their calibration curves.

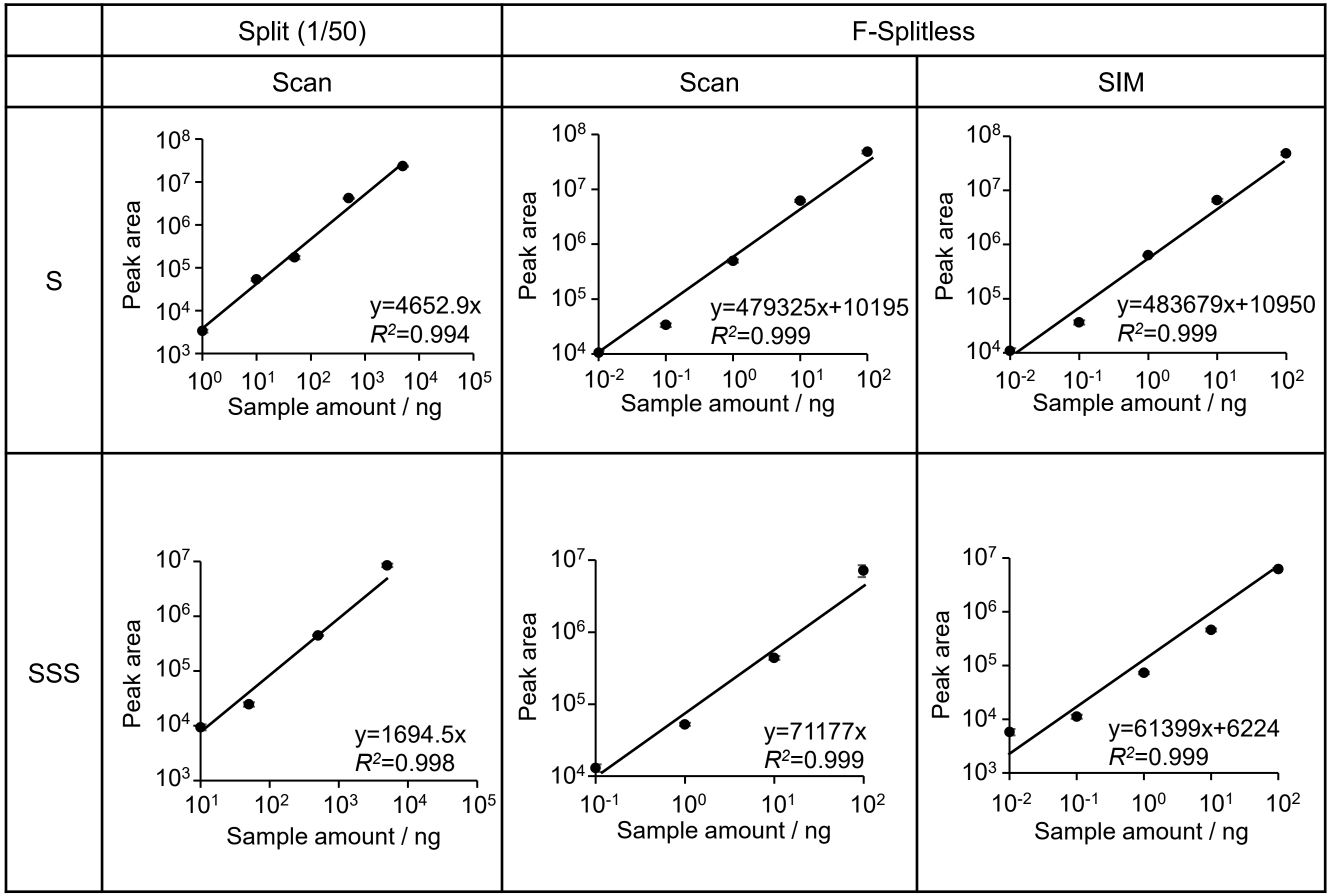


Fig. 1 Calibration curves for S and SSS obtained by Py-GC/MS of PS using split and F-Splitless injection methods.

PYA1-156E

Reference: K. Tei *et al.*, *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

A-10

High-sensitivity detection of polystyrene by F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

Part 4 LOD, LOQ, and S/N of polystyrene pyrolyzates

- **BACKGROUND:** In the previous report, the F-Splitless method was found to exhibit a fairly good linearity in the calibration curves. In this note, the detection limit (LOD=3σ/*a*), quantification limit (LOQ=10σ/*a*), and signal-to-noise ratio (S/N) were explored using the peak areas obtained from the extracted ion chromatograms (EICs) of styrene monomer (S; *m/z* 104) and trimer (SSS; *m/z* 91) found in the pyrolyzates of PS. LOD and LOQ were calculated from the slope (*a*) of the straight line of the calibration curve and the standard deviation (σ) at the lowest concentration.

- **EXPERIMENTAL:** Employing the previously described methods, PS was measured by Py-GC/MS using split and F-Splitless injection methods. Also, blank measurements were made by introducing an empty Eco-Cup into the furnace.

- **RESULTS:** EICs for S obtained by F-Splitless injection method in a scan mode are shown in Fig. 1. A trace peak of S was detected in the blank run. In addition, peaks of hexamethyl-cyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) were observed. Both D3 and D4 may originate from the septum, since the septum purge is turned off to prevent pyrolyzates from venting during the cryo-trapping of pyrolyzates in the F-Splitless injection method. The LOD and LOQ obtained from the slope and standard deviation of each calibration curve are summarized in Table 1. The F-Splitless injection method (scan mode) afforded an LOQ for SSS 32 times higher than that of the split method (split ratio: 1/50). In the case of the F-Splitless injection method (SIM mode), the LOD and LOQ of PS determined from the peak area of S were 17 pg and 56 pg, respectively, comparable to those obtained in the scan mode. The S/N values of S and SSS peaks in EICs are shown in Fig. 2. In the F-Splitless method, the S/N values of the S and SSS peaks were 570 and 22, respectively, in SIM mode with 100 pg of sample, which are 7 times larger than the S/N values in the scan mode. Based on the LOQ criterion of S/N=10, the F-Splitless injection method (SIM mode) allows the quantification of 1.8 pg of PS using the S peak. In contrast, pyrolysis of styrene-containing polymers such as ABS and SBR also forms S. To distinguish PS from other styrene-containing polymers, SSS can be an indicator compound. In Fig. 2, the S/N of the SSS peak formed by the pyrolysis of 100 pg of PS is 22, corresponding to a LOQ of 45 pg of PS. These results indicate that the F-Splitless injection method is capable of detecting pyrolyzates with high sensitivity.

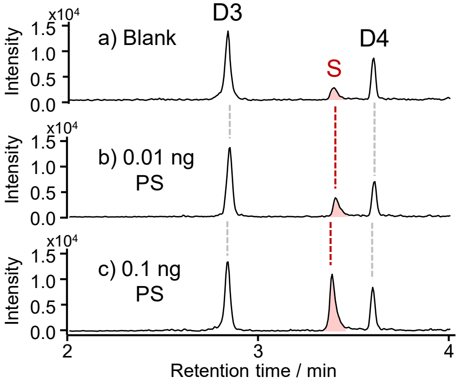


Fig. 1 EICs (*m/z* 104) for S obtained by F-Splitless injection method (scan mode).

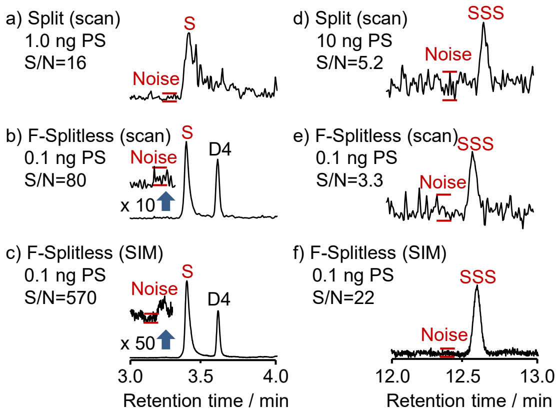


Fig. 2 EICs (S; *m/z* 104, SSS; *m/z* 91) of pyrograms obtained by Split and F-Splitless injection methods.

Table 1 LOD (LOD=3σ/*a*) and LOQ (LOQ=10σ/*a*) of PS based on Split and F-Splitless injection methods.

Injection method		LOD (ng)		LOQ (ng)	
		S	SSS	S	SSS
Split (Split ratio 1/50)	Scan (EIC)	1.75×10^{-1}	2.10	5.82×10^{-1}	6.99
F-Splitless	Scan (EIC)	1.76×10^{-2}	6.54×10^{-2}	5.88×10^{-2}	2.18×10^{-1}
	SIM	1.67×10^{-2}	3.36×10^{-2}	5.55×10^{-2}	1.12×10^{-1}

* Numerical values represent the peak areas of S and SSS and the data represents the averages of five repetitive measurements.

PYA1-157E

Reference: K. Tei *et al.*, *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

B-1

Quantification of tire wear particles in road dust

- **BACKGROUND:** The industrial production of plastics over the past decades has created a variety of environmental impacts, due to inappropriate disposal of plastic waste. In accordance with the increased waste plastics, the amount of microplastics (MPs) in the environment has been increasing, posing a threat to human health and marine ecosystems. One of the major contributors of MPs is the wearing of automobile tire treads, i.e., tire and road wear microparticles (TRWMPs), accumulated in road dust (RD). Here, the quantification of TRWMPs in RD samples using pyrolysis (Py)-GC/MS is reported.
- **EXPERIMENTAL:** RD samples were collected by the vacuum sweep method from industrial and residential areas of Seoul. The RD samples were dried in an oven at 120 ºC, and then sieved to obtain particles with sizes less than 75 µm in diameter. The raw materials of tire components, i.e., natural rubber (NR) and styrene–butadiene rubber (SBR 1502, styrene content: 23.5 %) were cryo-milled and used as standard materials. For EGA-MS and Py-GC/MS measurements, a Py-GC/MS system equipped with a Multi-Shot Pyrolyzer (EGA/PY-3030D, Frontier Lab.) directly interfaced to the GC injector was used. In EGA-MS analysis, 20 mg of RD and tire tread in sand was put in a sample cup and heated from 100 ºC to 800 ºC in the pyrolyzer furnace under a helium gas stream of 100 mL/min. Evolved gases were introduced to a mass detector through a deactivated metal tube installed in the GC oven. In flash pyrolysis, 20 mg of a RD sample in a sample cup was introduced into the pyrolyzer furnace heated at 670 ºC, and pyrolyzates were separated and detected by GC/MS with a separation column. Quantification of TRWMPs was done according to ISO/TS 20539 method.
- **RESULTS:** An EGA-MS thermogram of the RD sample is shown in Fig. 1. The presence of SBR, BR, and NR in the RD sample is indicated by the observation of typical ions (m/z 69, 91, 93, 105, etc.) as their pyrolyzates. The pyrogram obtained from the Py-GC/MS analysis of the RD sample at 670 ºC is shown in Fig. 2. A variety of gases such as CO2, butadiene, isoprene, and aromatic hydrocarbons such as benzene, toluene, 4-vinylcyclohexene, styrene, methylstyrene are generated through the thermal decomposition of rubbers and intramolecular cyclization. The typical pyrolyzates of BR (butadiene, 4-vinylcyclohexene), SBR (butadiene, styrene), and NR (isoprene, dipentene) showed high intensity peaks. Hence, SBR 1502 was used as the standard for the quantification of BR and SBR. Dipentene (isoprene dimer) was used as the indicator ion of NR for its quantification. It was found that the average concentration of TRWMPs was 22,581 µg/g in the industrial area and 9,818 µg/g in the residential area of Seoul, indicating that the industrial area has 2.5 times higher TRWMPs concentration.

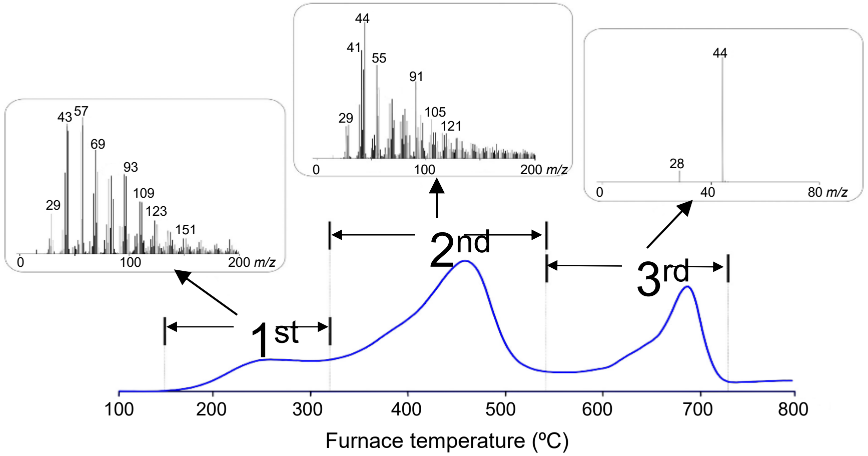


Fig. 1 Thermogram of an RD sample obtained by EGA-MS. (Heating rate: 20 ºC/min)

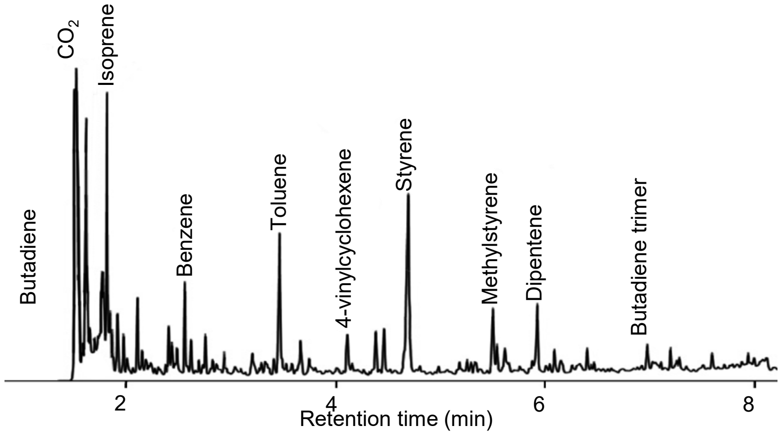


Fig. 2 Chromatogram of an RD sample obtained by Py-GC/MS at 670 ºC.

Contents extracted from J-S Youn, Y-M Kim, M. Z. Siddiqui, A. Watanabe, S. Han, S. Jeong, Y-W Jung, K-J Jeon, *Sci. Total Environ.* 784 (2021) 147177.

C-1

Analysis of microplastics using pyrolysis (Py)-GC/MS

Part 1: Identification of white marine microplastics

❖ **BACKGROUND:** Plastic wastes that flow into ocean are degraded by various mechanical and chemical forces, such as ocean waves and photo-oxidation by sunlight, and they are transformed into small fragments and the fragments less than 5 mm in size are called as microplastics (MPs). Environmental pollutions by MPs have attracted great global concern due to possible risks to ecosystems and human health. This report describes the Py-GC/MS analysis of MPs present in sea surface water at Osaka Bay and demonstrates the usefulness of Py-GC/MS for the identification of environmental MPs.

❖ **EXPERIMENTAL:** A Py-GC/MS system in which a Multi-Shot Pyrolyzer (EGA/PY-3030D) was directly interfaced to a GC injector was used for the measurements. Three different (based on appearance) white MP samples collected from the surface water at Osaka Bay were cut into ca. 1 mm squares and placed in an Eco-Cup LF (volume 80 µL). The cup was placed in the stand-by-position and then dropped into the pyrolyzer furnace pre-heated at 600 ºC. The degradation products (pyrolyzates) were separated on a UA$^+$-5 column and detected by a quadrupole mass spectrometer.

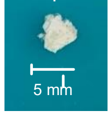
❖ **RESULTS:** Pyrograms of the MP samples obtained by Py-GC/MS are shown in Fig. 1. The library search by F-Search revealed that Samples A, B, and C are polystyrene, polyethylene, and polypropylene, respectively.

All samples courtesy of Prof. S. Tanaka of Kyoto University.

Sample A

Sample B

Sample C



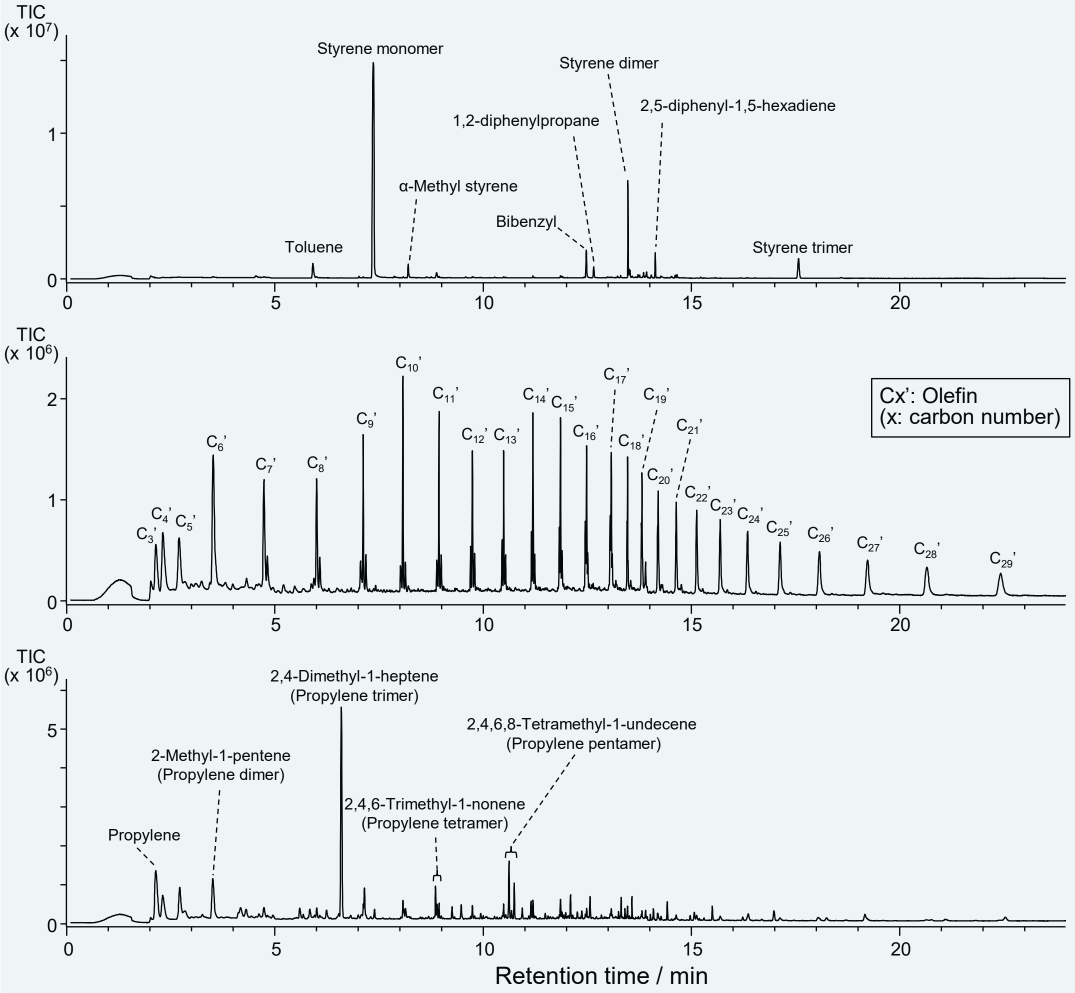


Fig. 1 Pyrogram of MP samples.

C-2

Analysis of microplastics using pyrolysis (Py)-GC/MS

Part 2: Identification of colored marine microplastics

- **BACKGROUND:** In the previous page, white micro-plastic (MP) samples were identified using Py-GC/MS. In this report, Py-GC/MS analysis of colored MP samples is described.

- **EXPERIMENTAL:** A Py-GC/MS system in which a Multi-Shot Pyrolyzer (EGA/PY-3030D) was directly interfaced to a GC injector was used for measurements. Six different colored MP samples (Sample A: green, Sample B: black, Sample C: yellow, Sample D: red, Sample E: green, and Sample F: blue) collected from the surface water at Osaka Bay were cut into ca. 1 mm squares with a cutting knife. Each piece was placed in an Eco-Cup LF (volume 80 µL) and introduced into the pyrolyzer furnace pre-heated at 600 ºC for flash pyrolysis.

- **RESULTS:** The pyrograms of the six different MP samples obtained by Py-GC/MS are shown in Fig. 1. Through the library search with F-Search, Sample A was identified as polyethylene, and Samples C to F show almost the same pyrogram and were identified as polypropylene. From FT-IR measurements, Sample B was identified as ethylene propylene rubber based on the library search. However, Sample B shows peaks ascribed to isoprene, styrene, and butadiene in its pyrogram (Fig. 1), suggesting that Sample B will be a rubber composed of natural rubber (or isoprene rubber) and styrene-butadiene rubber.

All samples courtesy of Prof. S. Tanaka of Kyoto University.

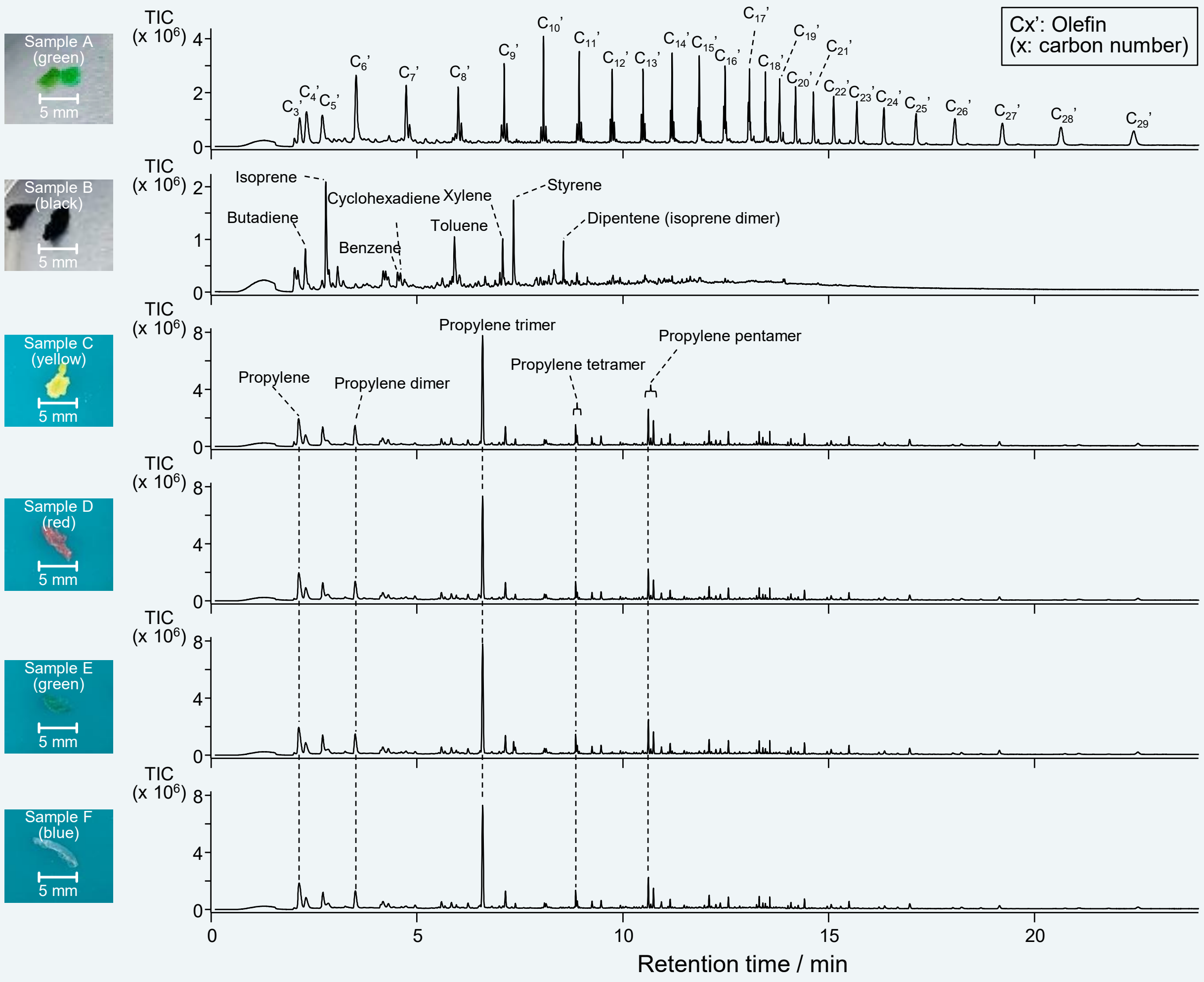


Fig. 1 Pyrograms of MP samples.

C-3

Analysis of Beach Plastic Wastes using Pyrolysis (Py)-GC/MS

- **BACKGROUND:** Ocean debris constitutes 80% of plastic wastes that have created a global concern in terms of aquatic and marine life, human and environmental health. This report describes the Py-GC/MS analysis of beach plastic wastes of 19 samples collected from seashore, Chennai (Fig. 1).

Fig. 1. Collected beach waste plastics with codes

- **EXPERIMENTAL:** The beach plastic wastes were washed with water and dried at 60 °C overnight. The dried samples were coded (Fig. 1) and cut into small pieces. 240 ± 20 μg of the sample in an Eco-Cup was placed onto a double-shot sampler and loaded into the pyrolyzer. The Eco-Cup was then dropped into the pyrolyzer furnace. First, thermal desorption (TD-GC/MS) was carried out (100 °C - 320 °C at 10 °C/min, 2 min hold), followed by flash pyrolysis (Py-GC/MS) at 600 °C. A micro-furnace pyrolyzer (EGA/Py-3030D, Frontier Laboratory) interfaced directly to a GC/MS system was used in double-shot mode. Thermally desorbed vapors and pyrolyzates were separated using a UA$^+$-5 column and detected by a quadrupole mass spectrometer. Finally, mass spectra were compared against NIST 20 library to identify the compounds.

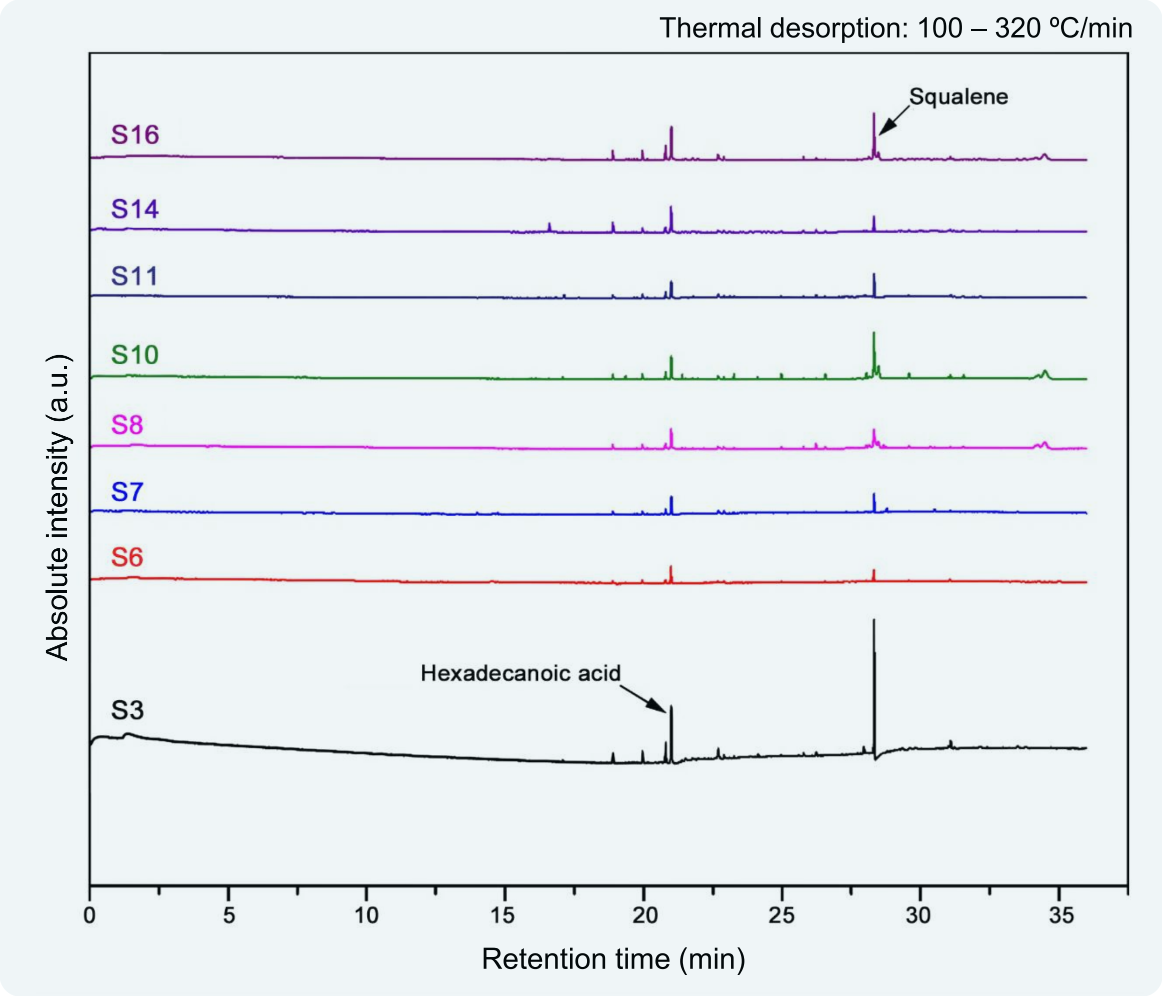


Fig. 2. Chromatograms of waste plastics (PE) obtained by TD-GC/MS (100-320 ºC, 10 ºC/min).

This work was done by [1]Subhan Kumar Pal, Dr. R. Vinu[1*], Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India
[1*]Corresponding Author E-mail: vinu@iitm.ac.in, Phone: +91-44-22574187.

C-3

Analysis of Beach Plastic Wastes using Pyrolysis (Py)-GC/MS

(continued from the previous page)

- **RESULTS:** Thermograms and pyrograms of beach plastic wastes obtained are shown in Figs. 2 ~ 3, respectively. Thermal desorption indicated the presence of long-chain fatty acids and plasticizers such as dimethyl and diethyl phthalates. As majority of plastics was PE, detailed analysis and quantification was carried out to investigate the recovery potential for basic chemical feedstock.

- **Analytical conditions:**

Pyrolysis temp.: 600 ºC, GC inj. temp.: 300 ºC, GC oven temp.: 40 ºC (2 min hold) - 300 ºC (10 ºC /min, 10 min hold), Split ratio: 1/100, Separation column: UA$^+$-5 (5 % diphenyl 95 % dimethylpolysiloxane), *L*=30 m, id=0.25 mm, df=0.5 µm, Column flow rate: 1.50 mL/min (He), Scan range: *m/z* 19 – 500.

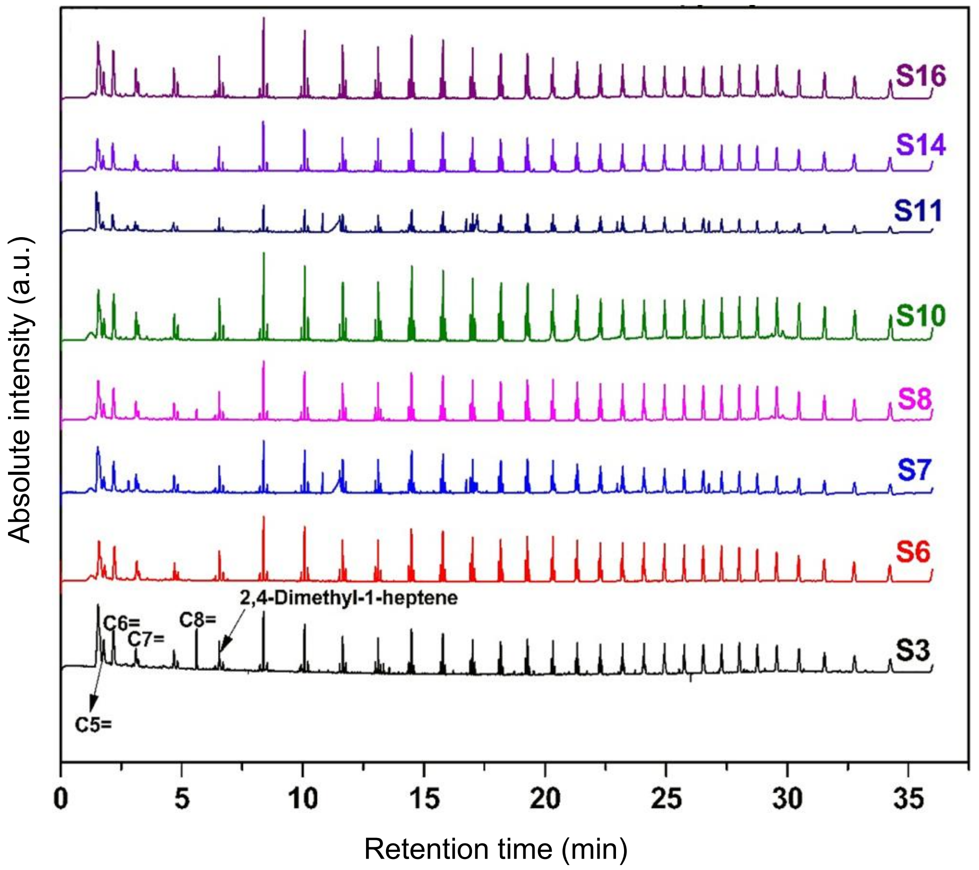


Fig. 3. Pyrograms of waste plastics obtained by PY-GC/MS (600 ºC, 30 s).

This work was done by [1]Subhan Kumar Pal, Dr. R. Vinu[1*], Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India [1*]Corresponding Author E-mail: vinu@iitm.ac.in, Phone: +91-44-22574187.

C-4

Characterization of Multi-layered Packaging (MLP) based Plastic Wastes using TD-GC/MS

- **BACKGROUND:** Multilayer packaging (MLP) based waste plastic constitutes a significant fraction of municipal solid waste. Around 40% of the total plastic produced is used in MLP manufacturing. For the protection of goods from water/moisture, light and air, MLP is typically made up of 4 to 7 layers of different polymers. Typically, polyesters, polyamides, polyethylene and ethylene vinyl alcohol are used in MLP. This report demonstrates the TD-GC/MS analysis of MLP used for variety of food materials packaging, viz., juice, dairy products, potato chips and other beverages.

- **EXPERIMENTAL:** Analytical pyrolysis experiments were carried out using a micro-furnace pyrolyzer (EGA/Py-3030D, Frontier Laboratory, Japan) in double-shot mode hyphenated with gas chromatography and mass spectrometry (GC/MS). The first-shot (thermal desorption, TD-GC/MS) was carried out by increasing the temperature of the sample from 100 ºC to 320 ºC at 10 ºC/min, and finally holding at 320 ºC for 2 min. Non-catalytic fast pyrolysis (CFP) of MLPs were carried out at various temperatures of 450, 550, 650, 750 and 850 ºC. Thermally desorbed and pyrolytic vapors were separated through UA$^+$-5 column, detected by quadrupole mass spectrometer and finally compounds were compared with NIST 20 library to identify molecular structure of the compound. (To be continued on the next page.)

Fig. 1. Images of all collected MLP-based waste plastics.

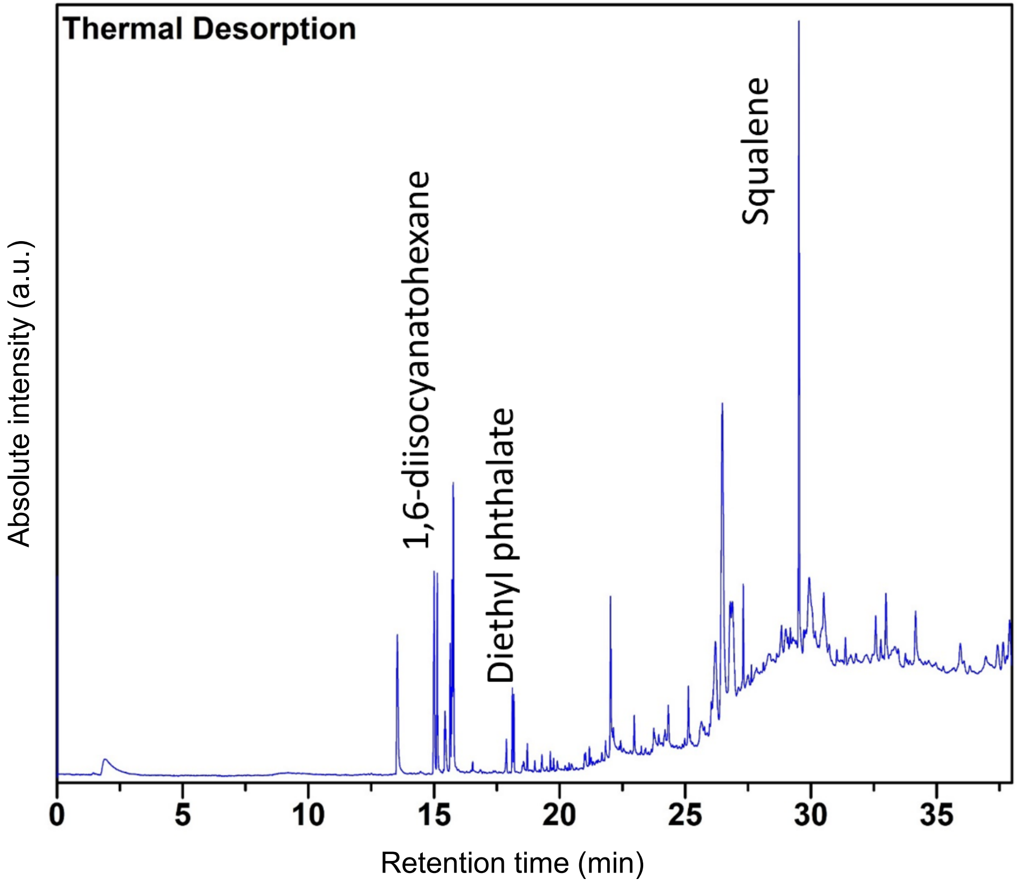


Fig. 2. Chromatogram of MLP obtained by TD-GC/MS.

This work was done by [1]Subhan Kumar Pal, Dr. R. Vinu[1*], Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India
[1*]Corresponding Author E-mail: vinu@iitm.ac.in, Phone: +91-44-22574187.

C-4

Characterization of Multi-layered Packaging (MLP) based Plastic Wastes using TD-GC/MS - continued

- **EXPERIMENTAL** (continued from the previous page)**:**
  The collected MLP wastes were remnants of packaging materials. All the samples were thoroughly washed with surfactant water and dried in an oven at 60 ºC overnight. The dried samples were stored in Ziploc bags and each coded with a sample name. The samples were not powdered but cut into small pieces.
  The sample of mass 330 ±10 μg was taken in a deactivated stainless-steel Eco-Cup. An Eco-Stick was used to hold the sample cup upright and was attached to a double-shot sampler. Finally, the whole assembly was connected to the head of the pyrolyzer. The Eco-Cup was then dropped into the quartz tube located in the pyrolyzer.

- **RESULTS:** Non-catalytic pyrolysis of MLP produced wide range of products of mixtures of aliphatic hydrocarbons (alkanes, alkenes and alkadienes) with trace amounts of MAHs.
  Thermal desorption analysis showed the presence of plasticizers such as diethyl phthalate along with other additives like 1,6-diisocyanato-hexane in MLPs.

- **Analytical conditions:**
  Thermal desorption temp.: 100 ºC – 320 ºC, (10 ºC/min, 2 min hold)
  Pyrolysis temp.:450 ºC, 550 ºC, 650 ºC, 750 ºC, 850 ºC
  GC Inj. temp.: 300 ºC, GC oven temp.: 45 (2 min hold) - 300 ºC (5 ºC/min, 10 min hold),
  Split ratio: 1/100 Separation column: UA^+-5 (5 % diphenyl 95 % dimethyl-polysiloxane), *L*=30 m, id=0.25 mm, df=0.5 µm, Column flow rate: 1.50 mL/min (He),
  Scan range: *m/z* 35 – 500.

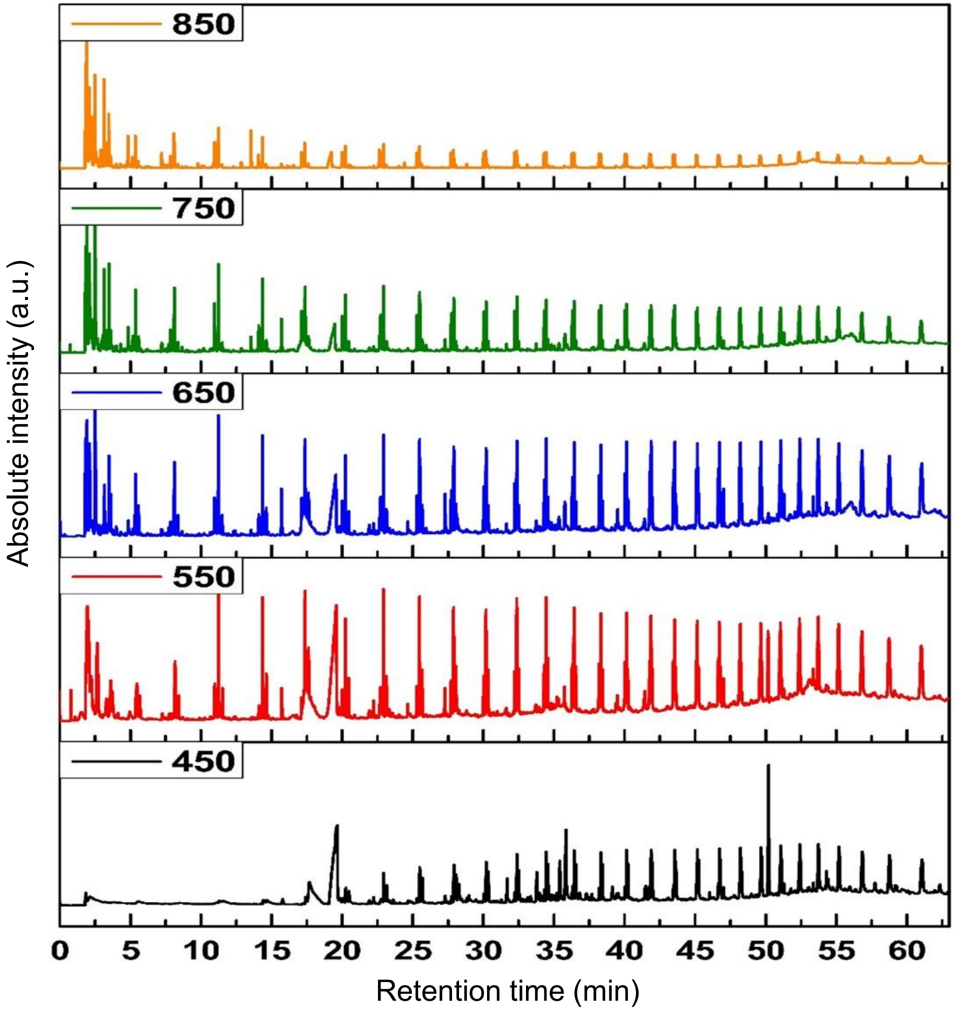


Fig. 3. Non-CFP pyrograms of MLPs obtained at various temperatures.

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C-5

Catalytic pyrolysis of MLPs based waste plastics using Pyrolysis (Py)-GC/MS

- **BACKGROUND:** Owing to the complex composition and difficulties in separating layers of MLPs, mechanical and solvothermal recycling of MLP is challenging. This report demonstrates the Py-GC/MS analysis of MLPs used for variety of food materials packaging. In the context of circular economy, the MLPs were subjected to catalytic pyrolysis employing zeolite catalysts.

- **EXPERIMENTAL:** 330±10 μg of MLP sample was placed in an Eco-Cup. Then, appropriate amount of catalyst was added to the cup for catalytic fast pyrolysis (CFP) measurements. The MLP to catalyst mass ratios were 1:5, 1:15 and 1:25 wt/wt. Measurements were carried out using a micro-furnace pyrolyzer (EGA/PY-3030D, Frontier Laboratory, Japan) in single-shot mode hyphenated with a GC/MS system. The pyrolyzates were separated through UA$^+$-5 column, detected by quadrupole mass spectrometer and finally compounds were compared with NIST 20 library to identify molecular structure of the compound.

- **RESULTS:** The catalytic pyrolysis of MLPs were performed using various zeolites, including HZSM-5, Zeolite-Y, Zeolite β and Zeolite Mordenite, and it demonstrated that the waste MLP can be a potential feedstock to produce value-added monoaromatic hydrocarbons (MAHs) such as, benzene, toluene, ethyl benzene and xylene (BTEX). The use of catalyst not only reduced the pyrolysis temperature of the MLP, but also yielded BTEX with high yield at optimized process conditions.

- **Analytical conditions:**

Pyrolysis temp.: 650 ºC,
GC inj. temp.: 300 ºC, GC oven temp.: 45 ºC (2 min hold) - 300 ºC (5 ºC /min, 10 min hold),
Split ratio: 1/100, Separation column: UA$^+$-5 (5 % diphenyl 95 % dimethyl-polysiloxane), *L*=30 m, id=0.25 mm, df=0.5 μm,
Column flow rate: 1.50 mL/min (He), Scan range: *m/z* 35 – 500.

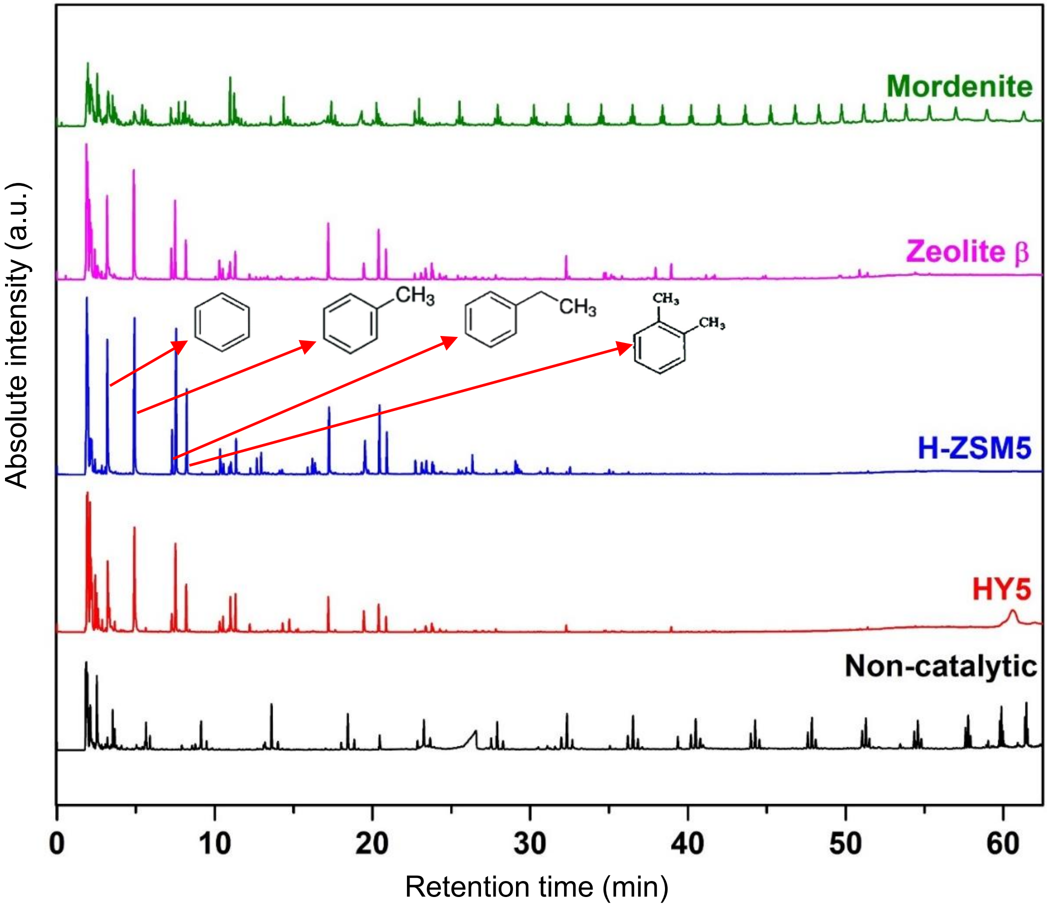

Fig. 1. Pyrograms of MLP waste plastics obtained by catalytic Py-GC/MS.

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D-1

Analysis of trace microplastics (MPs) in sediment samples

Part 1: F-Splitless Py-GC/MS using Multi-Functional Splitless Sampler

- **BACKGROUND:** In the analysis of microplastics (MPs) using pyrolysis (Py)-GC/MS , the F-Splitless Py-GC/MS method (F-Splitless method), which uses a Multi-Functional Splitless Sampler, can be used to boost the measurement sensitivity1). In this report, the F-Splitless method was used for the analysis of microplastics in sediment samples collected in environment and its validity was investigated2).

- **EXPERIMENTAL:** Sediment samples were provided by Dr. Scholz-Böttcher, ICBM, University of Oldenburg and were collected from the seafloor surface off the Bay of Biscay in the North Atlantic Ocean. The samples were pretreated with acid digestion and density separation. About 4 mg of the sediment was placed in an Eco-Cup LF, covered with quartz wool, and measured by the Split or F-Splitless method at a pyrolysis temperature of 600 ºC using the analytical system shown in Fig. 1.
- **RESULTS:** The pyrograms obtained by the Split and F-Splitless methods are shown in Fig. 2. As clearly seen, the use of the F-Splitless method allows peak intensities to be significantly increased. As an example, the peak area of 1-tridecene, one of the pyrolyzates of polyethylene, increased about 48-fold compared to that by the split method. From the above, it was demonstrated that the F-Splitless method increased the sensitivity of the measurement. In the next page, the identification and quantitation of MPs in the sample by F-Search MPs are presented.

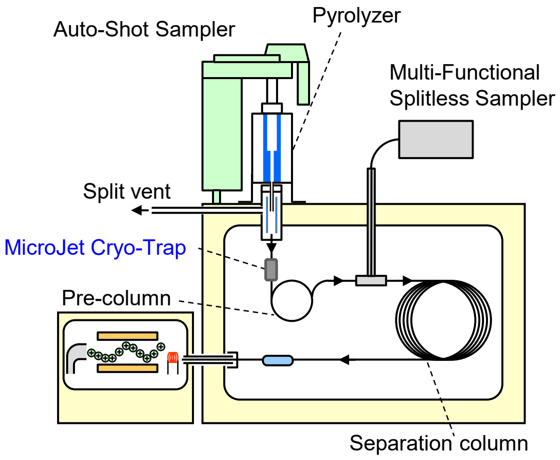

Fig.1 Analytical system for MPs analysis

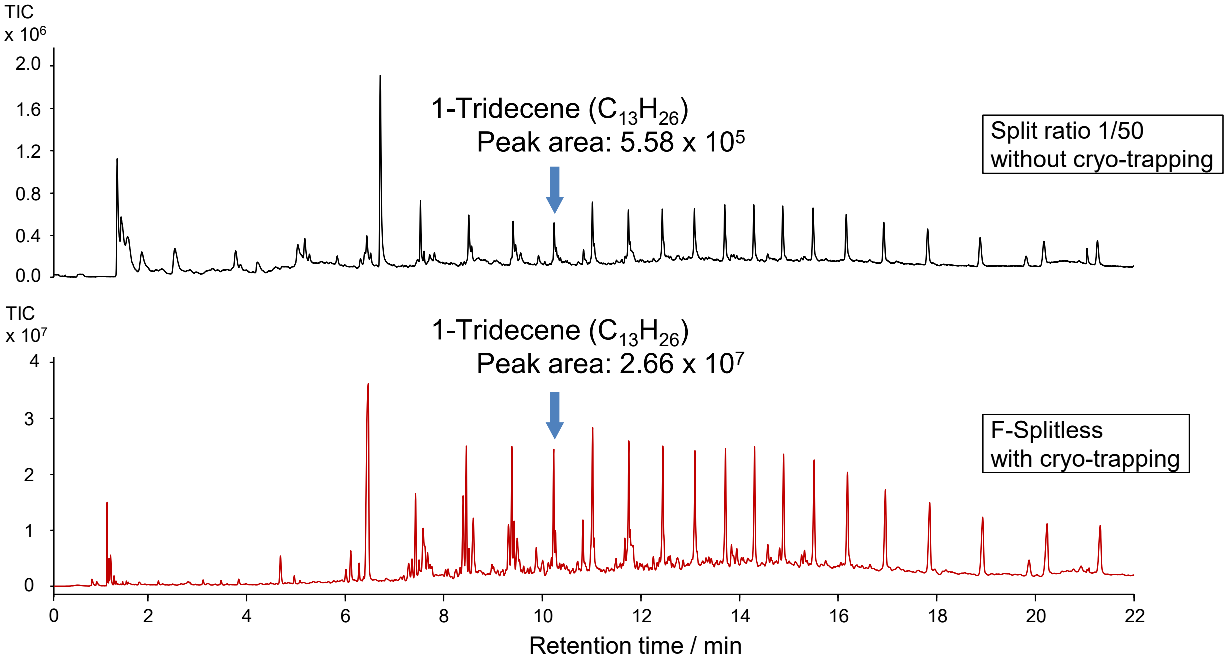

Fig. 2 Pyrograms of sediment samples (Top: Split method, Bottom: F-Splitless method)

1) K. Tei *et al.*, *J. Anal. Appl. Pyrolysis* 168 (2022) 105707.

D-2

Analysis of trace microplastics (MPs) in sediment samples

Part 2: Pyrogram and qualitative/quantitative results of sediment sample

- **BACKGROUND:** In the previous page, sediment samples collected offshore were measured by the F-Splitless Py-GC/MS (F-Splitless method) and it was found that the F-Splitless method was able to detect MPs with a higher sensitivity than the split method. In this report, qualitative and quantitative analysis of MPs in sediment samples are carried out using the F-Splitless method.
- **EXPERIMENTAL:** Sediment samples were provided by Dr. Scholz-Böttcher, ICBM, University of Oldenburg, and pretreated before measurements, as described in the previous page. About 4 mg of the sediment sample was placed in an Eco-Cup LF and covered with quartz wool, then Py-GC/MS measurements were done by the F-Splitless method at a pyrolysis temperature of 600 ºC using the analytical system and experimental conditions described in the previous page. Further, MP calibration standard1), which is a polymer-silica mixture with known polymer contents, was used to make calibration curves of polymers. Qualitative and quantitative analysis of MPs were done using the F-Search MPs software2).
- **RESULTS:** A pyrogram of a sediment sample is shown in Fig. 1, where styrene monomer and linear hydrocarbons were mainly detected. The results of qualitative and quantitative analysis by F-Search MPs are shown in Table 1, where PE was the most abundant polymer. Other polymers such as PP, PMMA, PET, and N66 were also detected. In conclusion, MPs in the sediment samples were able to be qualitatively and quantitatively determined by F-Splitless Py-GC/MS using the MP calibration standard and F-Search MPs.

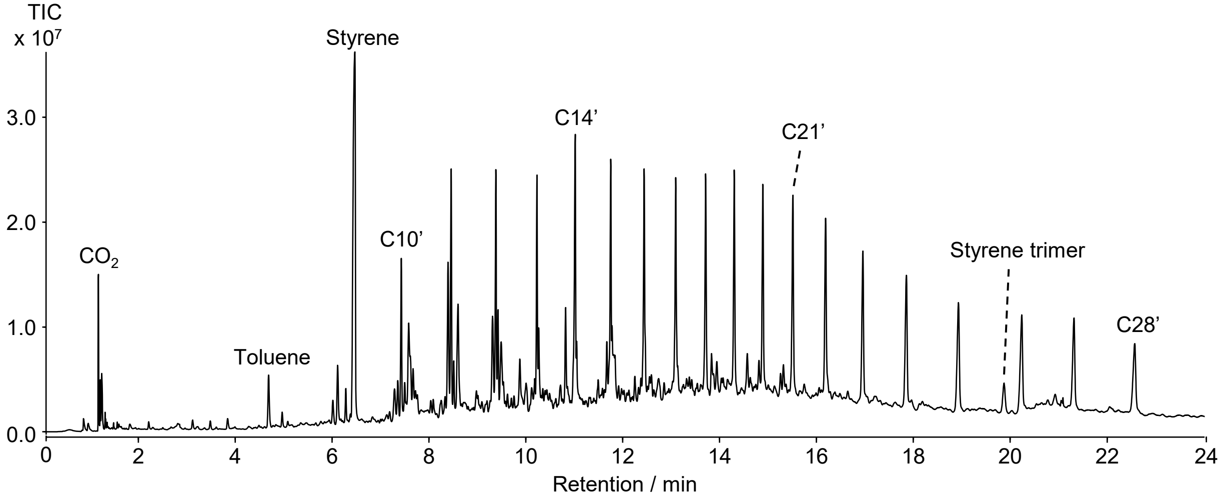

Fig. 1 Pyrogram of a sediment sample.

Table 1 Qualitative/quantitative results of MPs in sediment sample (4.047 mg).

Polymer*	Prob. [%]	Qnty [µg]
PE	98.6	10.22
PP	90.4	0.23
PS	99.0	1.12
PMMA	99.9	0.15
PET	90.8	0.12
N66	87.1	0.25

Prob.: Percent matching score with the summation spectrum of the library
Qnty.: Quantitative value
* PE : Polyethylene, PP: Polypropylene, PS: Polystyrene, PMMA: Polymethylmethacrylate, PET: Polyethylene terephthalate, N66: Nylon 6,6

1) M. Matsueda *et al.*, *J. Anal. Appl. Pyrolysis* 154 (2021) 104993.
2) K. Matsui *et al.*, *J. Anal. Appl. Pyrolysis* 149 (2020) 104834.

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