C10G-E083B

SHIMADZU
Excellence in Science

Aiming to Improve the Marine Environment

Analytical Solutions for Microplastics

Diverse Solutions for Improving the Marine Environment

Tiny plastic fragments smaller than 5 mm are referred to as microplastics. In recent years, there have been growing concerns that microplastics are having a negative impact on marine environments and ecosystems. Not only the microplastic materials themselves but also the additives they contain, as well as harmful substances absorbed in the environment, may have a latent impact on humans via the food chain.

Shimadzu provides analytical and measuring instruments for the study of a variety of plastic materials: for R&D, characteristic evaluation of raw materials, quality control for plastic products, and deterioration analysis. With these diverse techniques, Shimadzu provides optimal solutions for microplastics research.

Microplastics and Their Effects in the Marine Environment

There are two types of microplastics. Primary microplastics consist of the plastic beads used in industrial polishing powders, scrubbing agents, and so on. Secondary microplastics consist of small fragments created by physical wear and UV degradation after plastics are released into the environment.

Their impact on the marine environment is becoming a serious problem. When plastics are swept out into the sea, they degrade into microplastics through physical wear and ultraviolet light. These microplastic pieces are then inadvertently consumed by marine animals. In addition to the risk of physical obstruction or damage to the digestive organs and digestive tracts in marine animals, the additives (such as flame retardants, plasticizers, and antioxidants) contained in the microplastics themselves, or the harmful substances (such as PCBs and DDT) which adhere to them within the environment, are accumulated in the organs and gradually become biomagnified.

Risks to Health

There is a concern that microplastics consumed by marine animals will also have an impact on human health as they pass through the food chain. While the main focus is on pollution in oceans and other environmental water, there are also reports that microplastics have been detected in the air. At the current time, however, the impact of microplastics on human health is not sufficiently understood, and further investigation is required.

Approaches to International Standardization

In response to the issue of microplastics released into the environment, starting from the Davos Forum in 2016, declarations of initiatives and policies have been made at the G20 Summit. As a result, promotion of the "3 R's (Reduce, Reuse, Recycle)," the development of biodegradable plastics, and the establishment of guidelines and standards are progressing worldwide.

With regards to the investigation and analysis of microplastics, unified measures have not been established worldwide, so there are difficulties when comparing and evalutating data, making the unification of guidelines desirable. As an ISO Commission member, Shimadzu is involved in the standardization of methods.

Applications for Microplastics >

Workflow for Monitoring Microplastics

At present, in order to evaluate environmental contamination by microplastics and the risks involved, research agencies and regional governments in countries around the world are promoting monitoring based investigations. Such investigations target diverse samples, not only from rivers, oceans, and other environmental waters, but also from tap water, soil, and in vivo. In line with the various targets, investigative guidelines summarizing sampling, pretreatment, and measurement methods are created separately by the various countries and institutions. One example is shown below.

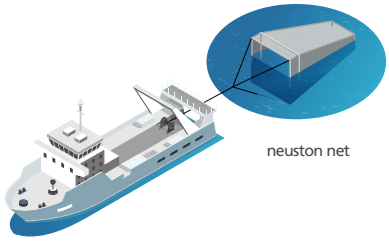
STEP 1 Sampling

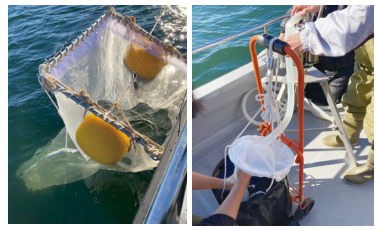
STEP 2 Preparation

STEP 3 Analysis and Measurement

Sampling

Ocean water is sampled from boats, and river water is generally sampled from bridges. Collection sites are determined in accordance with guidelines in each country. Note that a neuston net is generally used for sampling.





Collection of Microplastics from the Ocean

Preparation

Microplastic Automatic Preparation Device

MAP-100

Simplifies tedious monitoring tasks by automating the sample preparation process for microplastics.

Contaminants are automatically digested and separated so only microplastics are selected.

Advantages of the MAP-100

Labor savings	Significantly reduces the number of man hours.
Reproducibility	Enables highly reproducible preparation by reducing manual tasks.
Safety	Simplifies the handling of reagents by enabling the safe removal of contaminants.

Analysis and Measurement

The size of microplastic fragments after preparation is found by observation and particle size measurements using a stereoscopic microscope and special software. In addition, the use of Plastic Analyzer, a special Fourier Transform Infrared (FTIR) Spectrophotometer system is effective for component analysis.

Stereoscopic Microscope

STZ-171-TLED

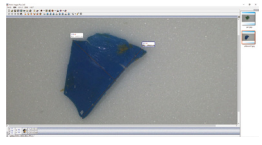
(Shimadzu Rika Corporation)

*Only available as a package sale with MAP-100.

With its wide field of view and 7.5 to 50 × zoom, this is the optimal stereoscopic microscope for making observations while working. In addition, the size of the microplastic particles can be measured by combining the instrument with our special software.

Software

Motic Images Plus

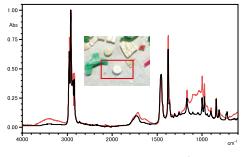


Fourier Transform Infrared Spectrophotometer

IRSpirit-X series / QATR-S

IRSpirit-X series is a compact, high-performance FTIR system. A special program with an analysis wizard (IR Pilot) is included as standard. With the QATR-S single-reflection ATR attachment, simply press the microplastics against the prism to perform a component analysis of the plastics.

UV/Heat Degradation Database

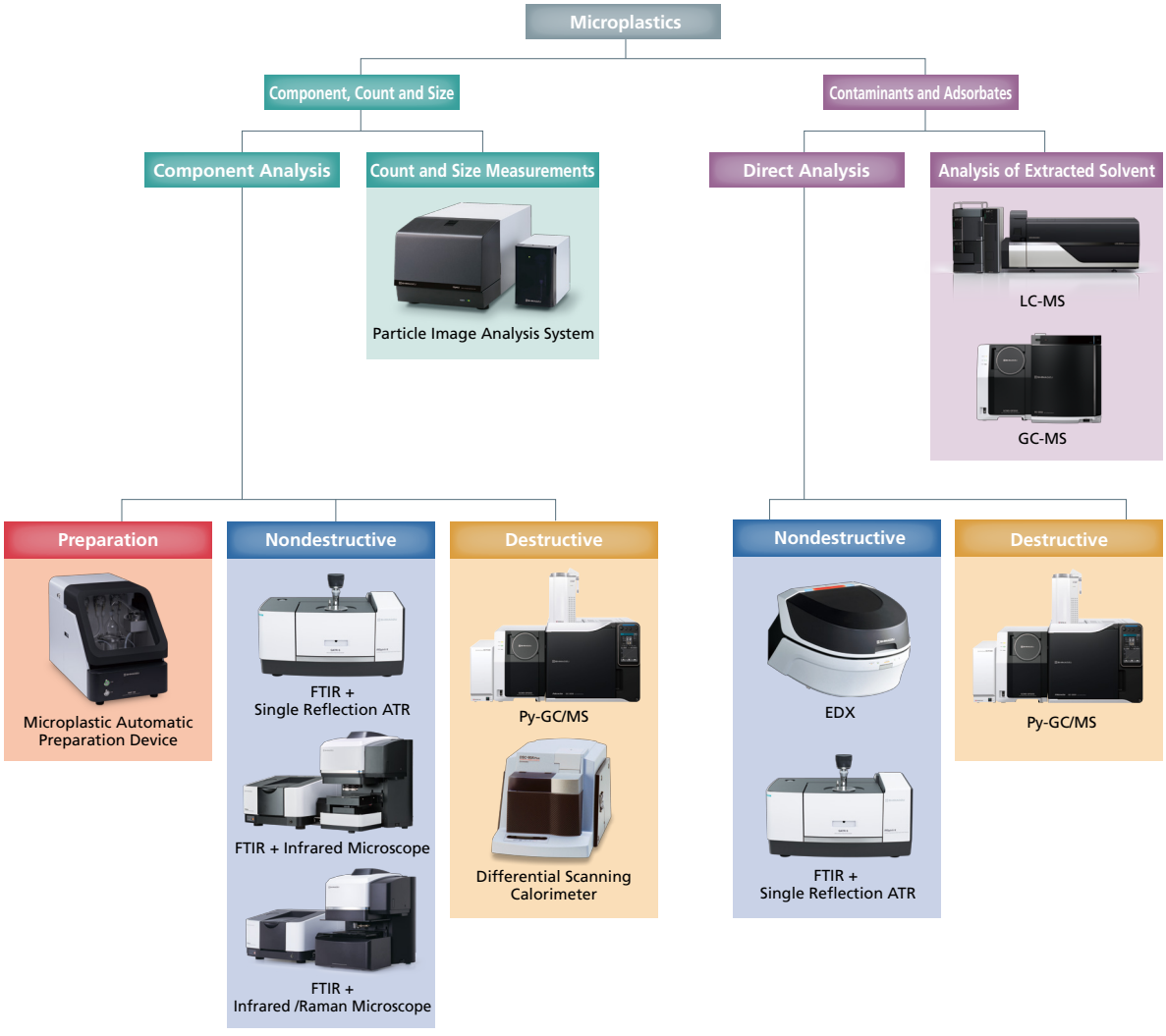


— Polypropylene irradiated UV-rays for 125 hrs
— White plastic shard

Microplastics are degraded by UV rays, so qualitative analysis using commercially available databases is not easy. Plastic Analyzer includes the infrared spectra of UV and heat-degraded plastics, which dramatically improves the qualitative accuracy of microplastics analysis.

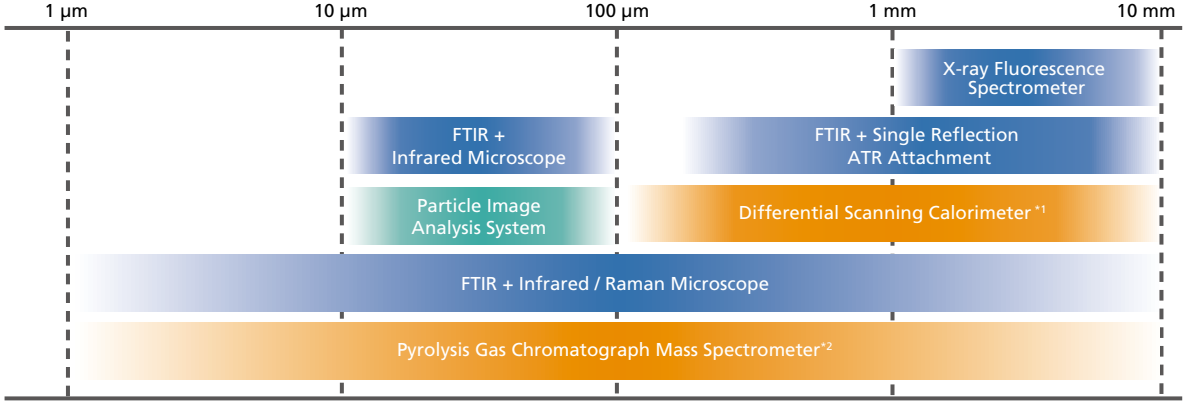
Workflow for Selecting an Analysis and Measurement Method

Microplastic analysis and measurement methods differ depending on what is being measured. A selection flowchart is shown below. Component analysis can be performed easily and nondestructively using a Fourier transform infrared spectrophotometer, an infrared microscope, or an X-ray fluorescence spectrometer. On the other hand, measurements using pyrolysis gas chromatography mass spectrometry, for example, will destroy the sample by pyrolysis, but such methods allow analysis of the interior of materials, and enable the simultaneous analysis of mixed samples containing multiple components of different types of plastics.



Microplastics by Sample Size Measuring Instruments

Analytical and measuring instruments capable of measuring samples ranging in size from 1 µm to 10 mm are shown below.



*1 Amount of sample: about 5 mg, *2 Amount of sample: about 0.1 mg

Analysis of Microplastics in Environmental Water

The MAP-100, Microplastic Automatic Preparation Device, is an automated device that uses a typical preparation method to extract microplastics from samples of environmental surface water. This device can be used in accordance with the "Guidelines for River Microplastic Monitoring Methods" published by the Ministry of the Environment Government of Japan since 2021. In addition, Shimadzu's proprietary technology in the MAP-100 achieves labor savings, high reproducibility, and enhanced safety.

Application

Benefits

- Automation of the sample preparation process reduces manual work by the analyst and enables sample preparation with high repeatability.
- Contaminants can be removed safely due to simplified handling of reagents.
- Accurate qualitive analysis of microplastics in environmental water is possible by utilizing the Shimadzu UV-Damaged Plastics Library.

Sample Preparation Process

In recent years, monitoring surveys and studies have been actively conducted in various countries around the world to obtain information on the distribution and scientific knowledge of microplastics. The microplastic investigation process includes sampling and preparation of samples, measurement of the size and particle count of the pretreated samples, and material analysis to determine the type of plastic. However, appropriate preparation to remove environmental contaminants contained in the sampled specimens is important for accurate measurement and analysis.

The sample preparation process consists of the following four processes: A: Screening (sieving) of the sampled specimen material, B: Digestion of contaminants (organic matter) by 30 % hydrogen peroxide water, C: Removal of inorganic contaminants with large specific gravities, such as stones, by separation using a 5.3 mol/L aqueous solution of sodium iodide, and D: Filtration of the microplastics. In particular, processes B to D place a heavy load on the analyst, as this work is complex and time-consuming. Moreover, if this work is done manually, this may cause differences in the results obtained by different analysts or analysis organizations, and handling of hydrogen peroxide water can harm analysts because this chemical is a corrosive reagent. By automating the processes shown in Fig. 1, the MAP-100 achieves labor savings, enhanced repeatability, and improved safety. The size of microplastics that can be extracted by preparation by the MAP-100 is from 0.3 mm to 5 mm (long diameter). However, due to the possibility of clogging the piping, samples taken from sites that contain a large amount of sand or mud, such as riverbeds, the sea bottom, and beaches, are not covered by preparation with this device.

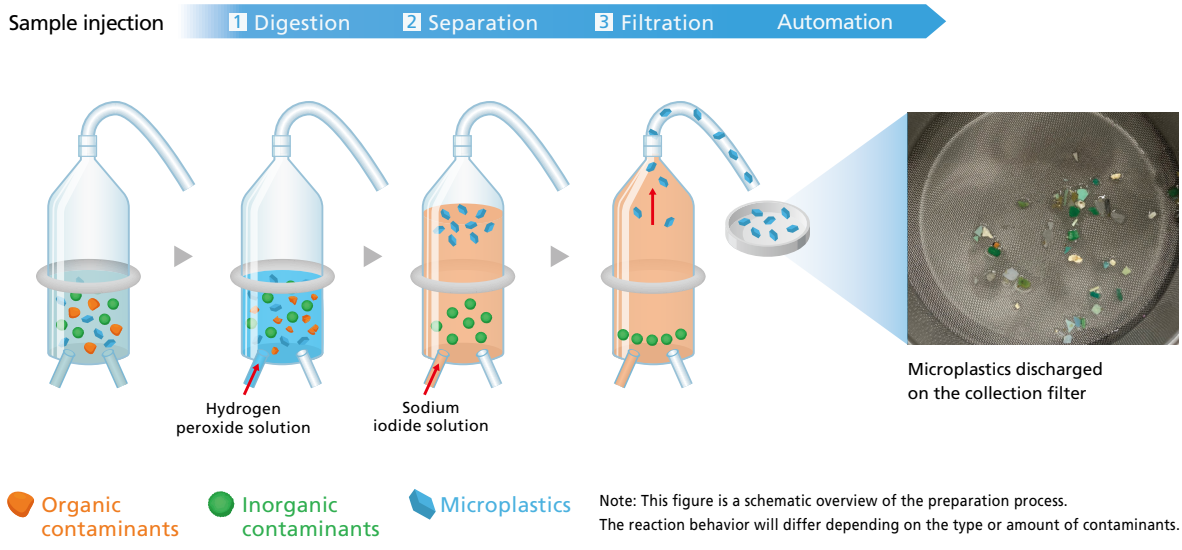


Fig. 1 Automated Sample Preparation Process

Preparation of Microplastics Collected from Environmental Surface Water

Samples collected from a river in Okinawa Prefecture were pretreated using the MAP-100. Based on Ministry of the Environment guidelines, digestion was conducted for 3 days, followed by separation for 3 hours. Figs. 2(a)-(c) show the condition of the sample before preparation, during digestion (1 day after the start of treatment), and after preparation. From Fig. 2(c), it can be understood that environmental contaminants could be removed with the MAP-100.

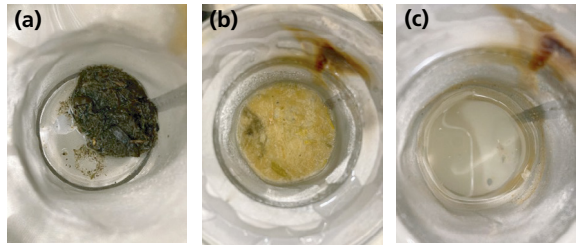


Fig. 2 Condition of Sample Before/After Preparation and During Digestion
(a) Before treatment, (b) During digestion (1 day after start of treatment), (c) After treatment

Qualitative analysis by FTIR

A material analysis of the microplastics obtained by preparation using the MAP-100 was carried out using FTIR. In this experiment, we used a plastic analysis system, Plastic Analyzer, which is effective in analyses of degraded microplastics. The measurement conditions are shown below. Fig. 3 shows the appearance of two measured microplastics while Figs. 4 and 5 show the measurement results of the obtained infrared spectra and the search results using the UV-Damaged Plastics Library, which is a unique Shimadzu database.

From Fig. 4, a hit for polypropylene (PP) irradiated with UV for 25 hours was obtained for microplastic (a), and from Fig. 5, a hit for polyethylene (PE) irradiated with UV for 550 hours was obtained for microplastic (b). The respective hit rates showed extremely high match scores of 876 points for (a) and 904 points for (b). It is thought that these excellent match scores were obtained because the infrared spectra of the simple plastic could be acquired by removing environmental contaminants with the MAP-100 Microplastic Automatic Preparation Device.

Measurement Conditions	
Instruments	: IRSpirit-TX, QATR-S (Diamond prism)
Resolution	: 4 cm^{-1}
Number of scans	: 20
Apodization	: Sqr-Triangle
Detector	: DLATGS

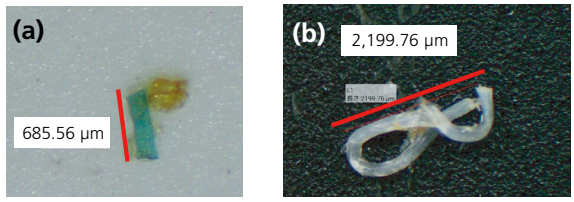


Fig. 3 Appearance of Microplastics

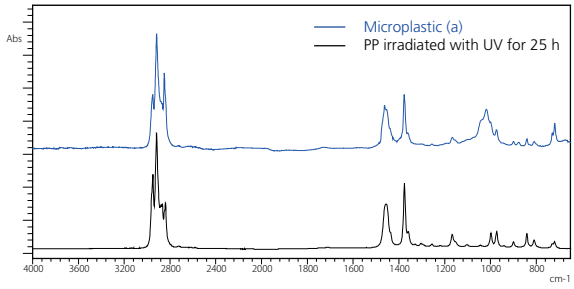


Fig. 4 Infrared Spectrum and Search Results for Microplastic (a)

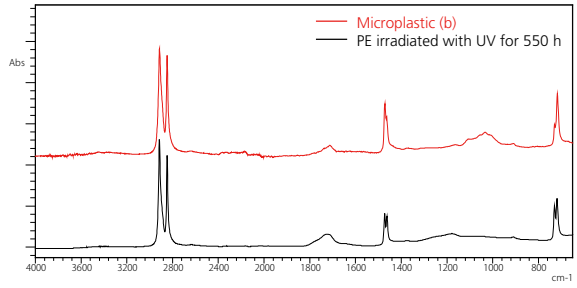


Fig. 5 Infrared Spectrum and Search Results for Microplastic (b)

IRSpirit-X Series
Fourier Transform Infrared Spectrophotometer

IRSpirit-X series is a compact, lightweight FTIR with an A3 size (420 × 297 mm) footprint and a weight of 8.5 kg. It delivers top-class sensitivity and resolution and, despite its small size, features a standard-sized sample compartment that accommodates most accessories, enabling a versatile range of applications.

Product

MAP-100
Microplastic Automatic Preparation Device

In order to correctly evaluate the microplastics contained in samples sampled from environmental surface water, proper preparation is required to exclude mixed environmental contaminants. This product is an automated preparation device that automates typical preparation methods for extracting microplastics from samples of environmental surface water, resulting in a more efficient workflow, high reproducibility, and a safer work environment.

Product

High-Speed, Efficient Measurement of Microplastics Collected on a Filter

Microplastics (MPs; plastic pieces ranging in size from a few µm to 5 mm) are widely recognized as a marine environmental issue. Smaller MPs (under 100 µm) have been raising concern due to reports of contamination in drinking water. To perform qualitative analysis while confirming the number and shapes of MPs smaller than 100 µm, samples are collected on a filter and analyzed using infrared or Raman microscopy. To reduce measurement and analysis time, we developed a high-speed mapping program and a particle-analysis program. Shown below are examples of measurement and analysis of MP reference materials.

Application

Benefits

- It enables high-speed measurements of microplastics (MPs) smaller than 100 µm collected on a filter.
- Particle analysis program can identify the types of MPs. In addition, it can count the number of MPs and even color-code them by type.
- In addition to calculating the size of MPs (minor axis, major axis, Feret diameter, and area), it can estimate the volumes and masses of particles.

Sample and High-Speed Mapping Program

We prepared CHIRON's Reference Material (tablet) as the sample. The tablet was dispersed in filtered ultrapure water, and the sample was collected on a Si filter (10 × 10 mm, pore size 5 µm). The Si filter was placed in a Particle Filter holder (PF holder) (Fig. 1), secured with a cover, and then mounted on the infrared microscope.

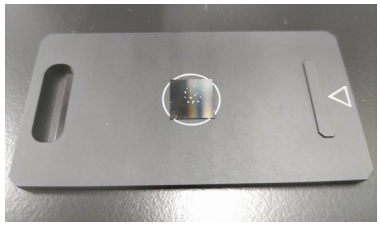


Fig. 1 Si Filter Installed in the PF Holder

Mapping measurements are especially useful for measuring samples with many target objects in the field of view. Normally, it takes longer to measure larger areas or a high number of measurement points, but this analysis can be shortened with the high-speed mapping program. In this example, a peak detection range of 3,200 to 2,800 cm^{-1} was specified for detecting the signal from hydrocarbons (C-H), and the data from peaks in that range were scanned the specified number of times.

Measurement Conditions	
Instruments	: IRTracer-100, AIMsight, PF Holder (13 mm dia.)
Software	: High-Speed mapping program and particle analysis program
Optical System	: Transmission (imaging acquired from reflection)
Resolution	: 8 cm^{-1}
Accumulation	: 30
Apodization Function	: Sqr-Triangle
Aperture Size	: 20 µm × 20 µm
Step Size	: 20 µm
Mapping Range	: 1,700 × 2,100 µm (1.7 × 2.1 mm)
Detector	: T2SL
High-Speed Mapping Conditions	
Noise Level	: 0.02
Threshold Value	: 0.4
Excluded Ranges	: 4,000 to 3,200 cm^{-1} and 2,800 to 700 cm^{-1}

The tiled image of the measurement range in Fig. 2 shows the large number of candidate measurement points. The 1.7 ×2.1 mm region highlighted in red was measured. The high-speed mapping program shortened the measurement time to approximately one-eighth of that required for conventional mapping measurements.

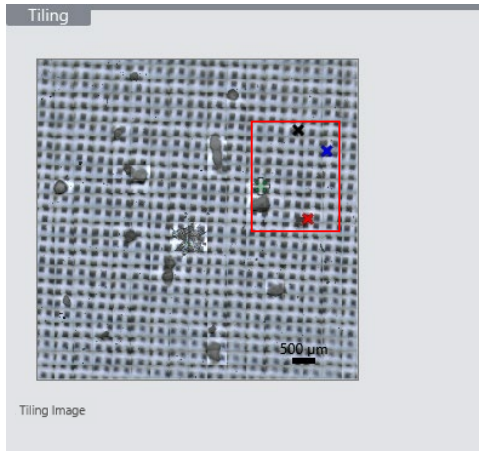


Fig. 2 Tiled Image and Measurement Range (Red Box) for the Measurement Range

Identifying the spectra of particle peaks confirmed the presence of polyethylene (PE), polyethylene terephthalate (PET), polystyrene (PS), and protein (Fig. 3). Typically, peaks are identified by searching for matching spectra one at a time.

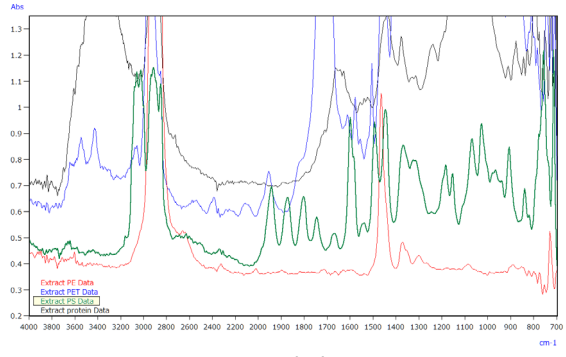


Fig. 3 Examples of Infrared Spectra

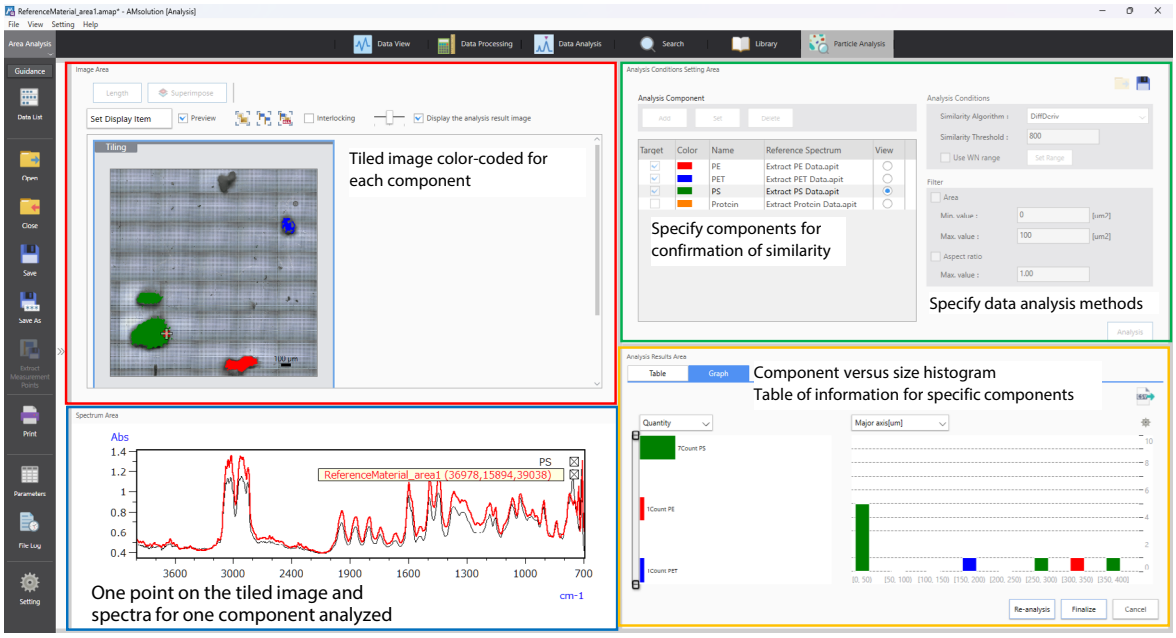


Fig. 4 Particle Analysis Program

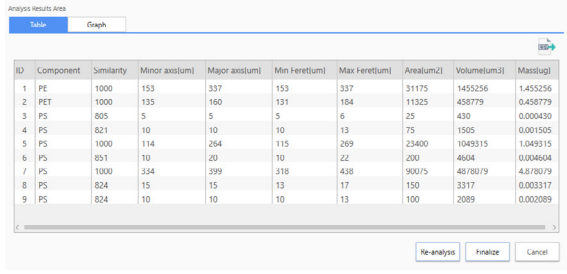
Measurement Result

A screenshot of the particle analysis tab page is shown in Fig. 4. The analysis components (upper right of the particle-analysis program) were set as PE, PET, and PS, which are contained in the measured MPs standard material (we registered the data from Fig. 3). Only components with a checked box are analyzed. Note that a built-in template for analysis of 15 typical components is available. Analysis conditions allow you to set the algorithm to use and the similarity threshold.

After pressing the Analysis button, components that match at or above the threshold are color-coded on the tiling image in the upper left according to the assigned colors. The lower right area of the particle-analysis program consists of a Table tab (Fig. 5) and a Graph tab. The analysis of the measurement area on the Si filter showed one PE, one PET, and seven PS particles. Also, from the histogram in Fig. 4 (right side), there are PS particles smaller than 50 µm in major axis and PS particles in the 150 to 400 µm size range. As shown in Fig. 6, magnifying the tiling image revealed small PS fragments surrounding a large PS cluster, which matched the image and the histogram results.

The Table tab shown in Fig. 5 displays detailed information for each analyzed component and calculates the minor axis, major axis, Feret diameter, and area. Individual volumes and masses inferred from the formula[*1] are also calculated. The table of analysis results can be exported in CSV file format.

Using the particle-analysis program, easy summation of counts and size distributions of MPs by type within the measured range can be achieved.



ID	Component	Similarity	Minor axis[um]	Major axis[um]	Min Feret[um]	Max Feret[um]	Area[um2]	Volume[um3]	Mass[ug]
1	PE	1000	153	337	153	337	31175	1455256	1.455256
2	PET	1000	135	160	131	184	11325	458779	0.458779
3	PS	805	5	5	5	6	25	430	0.000430
4	PS	821	10	10	10	13	75	1505	0.001505
5	PS	1000	114	264	115	269	23400	1049315	1.049315
6	PS	851	10	20	10	22	200	4604	0.004604
7	PS	1000	334	399	318	438	90075	48780/9	4.8780/9
8	PS	824	15	15	13	17	150	3317	0.003317
9	PS	824	10	10	10	13	100	2089	0.002089

Fig. 5 Analysis Results Area ([Table] Tab)

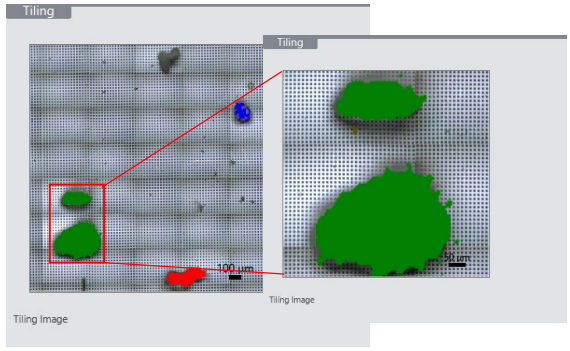


Fig. 6 Color-Coded Tiled and Enlarged Images

*1 Mass and volume are calculated based on the theoretical formula (Formula (1) [log10(M)=b·log10(S)+a]) used in the article referenced below. This theoretical formula applies only to microplastics. Shimadzu cannot guarantee the validity of the mass results.
Tomoya Kataoka, Yota Iga, Rifqi Ahmad Baihaqi, et al. Geometric relationship between the projected surface area and mass of a plastic particle. Water Research. 2024;261:122061.

Technique for Measuring Microplastics Collected on Various Filters Using a Particle Filter Holder

Measuring MPs with an infrared microscope requires collecting samples on a filter. Various filters, each with unique characteristics, can be used with infrared microscopes. However, if a filter cannot be held horizontal during drying or measuring, it can develop wrinkles that might decrease measurement accuracy. Therefore, a particle filter (PF) holder was developed that can be placed directly on an infrared microscope stage while holding the filter horizontally.

Application

Benefits

- Particle filter holders provide clear microscope images of samples, enabling highly accurate measurements.
- Microplastics can be analyzed accurately and efficiently by using a particle filter holder in combination a high-speed mapping program and a particle analysis program.

Filter Selection

Table 1 summarizes the characteristics of typical filters used for MP analysis. Filters with diameters of 13 mm or 25 mm are commonly used. The infrared measurement range also depends on the filter material. Examples of transmittance data for filters alone are shown in Fig. 1. Due to the absorption of PTFE near 1,200 cm^{-1}, it can overlap with C-O-C stretching vibration peaks contained in the spectra of polyethylene terephthalate and other MPs, making it occasionally difficult to clearly recognize the peaks. Similarly, Al_2O_3 absorbs light in the 1,200 to 700 cm^{-1} range, which can make it difficult to recognize =C-H out-of-plane bending (benzene ring) peaks contained in polystyrene (PS) spectra. As another example, stainless-steel filters enable transmittance to be measured, depending on the pore diameter. To summarize, filters must be selected based on their characteristics and the material to be analyzed.

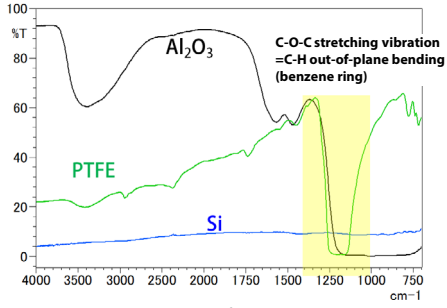


Fig. 1 Transmittance of Respective Filter Types

Table 1 Characteristics of Filters Compared in this Article

Filter	Material	Pore Diameter (µm)	Measurement Method*1	Pricing	Comments	Filtering Time (s)*2	Infrared Measurement Range*3
Hydrophilic PTFE	Polytetra-fluoroethylene	0.45	Transmission	Inexpensive	Easily wrinkled	30	4,000 to 1,300 cm^{-1} 1,000 to 700 cm^{-1}
SUS	Stainless-steel	8	Transmission /Reflection	Medium	Easy to achieve a flat surface	2	4,000 to 700 cm^{-1}
Au/PC	Gold-coated polycarbonate	0.8	Reflection	Expensive	Hight reflectance	12	4,000 to 700 cm^{-1}
Al_2O_3	Aluminum oxide	0.2	Transmission	Expensive	Brittle, easy to achieve a flat surface	53	4,000 to 1,200 cm^{-1}

Measuring Standard MPs

Polystyrene (PS), polyethylene (PE), and polypropylene (PP) particles that fell through a 100 µm mesh were dispersed in purified water. They were then collected by suction filtering through PTFE, Al_2O_3, Au/PC, and stainless-steel filters. After collecting the particles, the filters were dried using a PF holder. Fig. 2 shows the holders. The PTFE and Al_2O_3 filters were measured using the transmission method, whereas the stainless steel and Au/PC filters were measured using the reflection method. For the high-speed mapping program in this measurement, a peak detection range of 3,400 to 2,400 cm^{-1} was specified for detecting the signal from hydrocarbons (C-H). The range will be scanned for the specified number of times.

Fig. 2 PF Holders Holding PTFE Filters

Measurement Conditions

Instruments	: IRXross, AIMsight, PF holders
Software	: High-speed mapping program and particle analysis program
Resolution	: 8 cm^{-1}
Scanning Count	: 50
Apodization Function	: Sqr-Triangle
Aperture Size	: 20 µm × 20 µm
Measurement Interval	: 20 µm
Mapping Range	: PTFE: 480 × 400 µm Al_2O_3: 360 × 560 µm Au/PC: 780 × 500 µm Stainless steel: 480 × 400 µm
Detector	: T2SL
High-Speed Mapping Conditions	
Noise Level	: PTFE, Al_2O_3, Au/PC: 0.05, Stainless steel: 0.1
Threshold Values	: PTFE, Au/PC: 0.5, Al_2O_3: 0.1, Stainless steel: 0.2
Excluded Ranges	: 4,000 to 3,400 cm^{-1} and 2,400 to 700 cm^{-1}

*1 Measurement method recommended by Shimadzu
*2 The reference value was obtained by suction filtering 1 mL of standard MPs dispersed in purified water through a 13 mm diameter filter. The value depends on the concentration and size of particles contained in the solution.
*3 The measurement range was based on the range (700 to 4,000 cm^{-1}) of the infrared microscope.

Examples of infrared spectra obtained using the high-speed mapping program are shown in Fig. 3, showing that each type of plastic was more than adequately confirmed when collected on a PTFE filter.
The particle analysis program was used to color-code results (Fig. 4). Particle analysis results for a sample on a stainless steel filter are shown in Fig. 5. The particle analysis program can calculate not only particle count, major axis diameter, and Feret diameter values but also area, volume, and mass*4 values. In this example, the results indicate that 26 PS particles, 21 PP particles, and 1 PE particle were detected, and that the most common particle major axis diameter range was 20 to 40 µm.

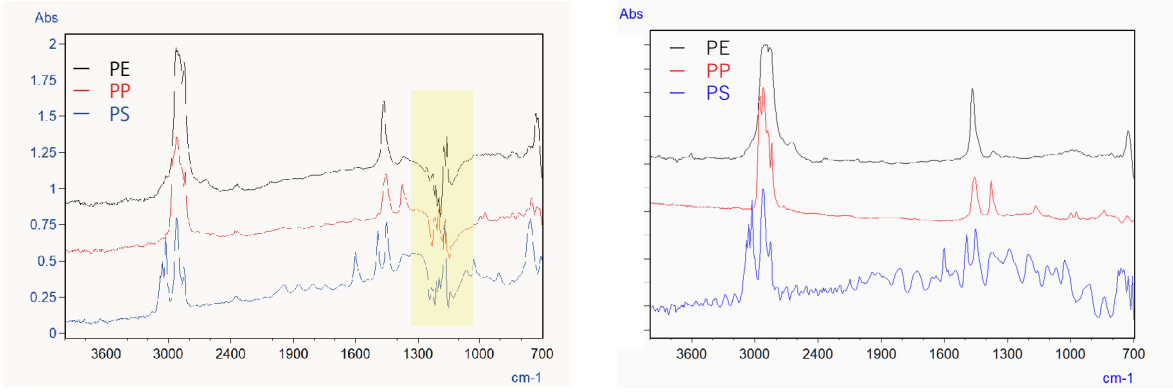


Fig. 3 Infrared Spectra of PE, PP and PS Particles on a PTFE (left) and Au/PC (right) filter

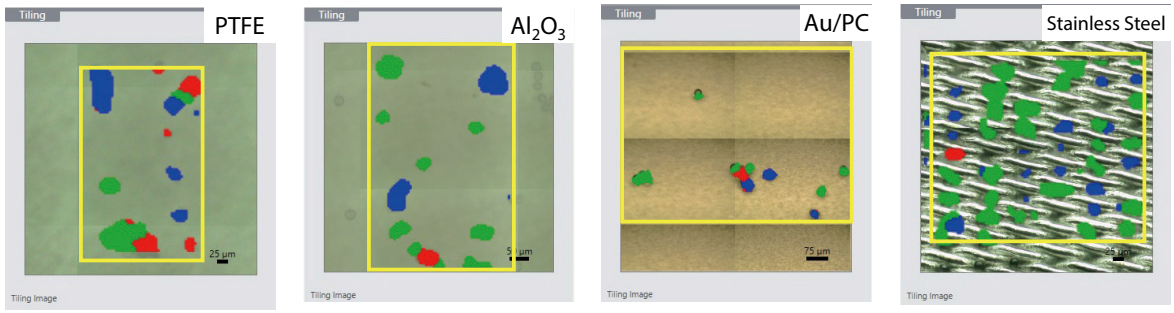


Fig. 4 Results from Analyzing Particles on Each Filter

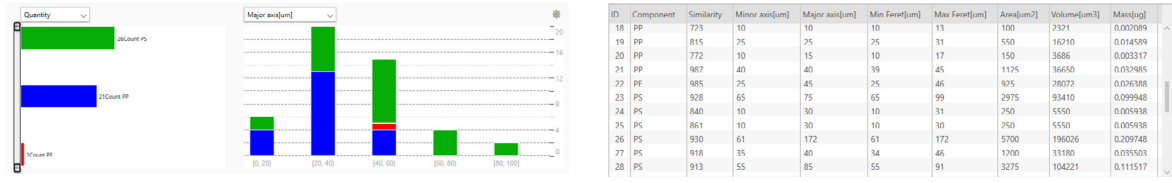
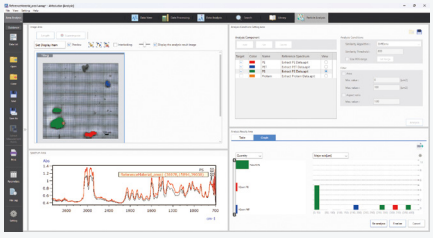


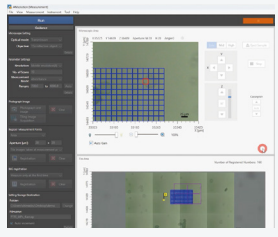
Fig. 5 Results from Analyzing Particles on a Stainless-steel Filter

Optional Products for the Infrared Microscope

We offer several optional products to enable efficient microplastic analysis.



Particle analysis program



High-speed mapping program

PF (Particle Filter) holder

Product

*4 Mass and volume are calculated based on the theoretical formula (Formula (1) [log10(M)=b·log10(S)+a]) used in the article referenced below.
This theoretical formula applies only to microplastics. Shimadzu cannot guarantee the validity of the mass results.
Tomoya Kataoka, Yota Iga, Rifqi Ahmad Baihaqi, et al. Geometric relationship between the projected surface area and mass of a plastic particle. Water Research. 2024;261:122061.

Qualitative and Mapping Analysis of Microplastics

Fourier transform infrared (FTIR) spectrophotometers are suited to the analysis of microplastics because they are optimal for the qualitative analysis of organic compounds. By adding the AIMsight infrared microsope to an FTIR system, highly-sensitive analysis of samples under 100 µm is made possible. Results can be referenced immediately against the comprehensive library provided as standard.

Application

Benefits

- Accurate determination of the material of microplastics in the environment is possible.
- Enables direct mapping analysis of microplastics collected on filter paper.
- The length of target objects in samples can be measured from images acquired by the wide-field camera or 15x reflective objective lens.

Mapping Analysis of Microplastics

Microplastics in water were collected using filter paper made of polytetrafluoroethylene (PTFE). The microplastics collected on the filter paper were placed on the stage of the AIMsight, and a mapping analysis was conducted. Fig. 1 shows an image of the microplastics on the filter paper taken with the 15x reflective objective lens of the AIMsight. Since the PTFE of the filter paper has no infrared absorption band except at around 1,200 cm^{-1}, the microplastics collected on the filter paper can be measured by the transmission method.

Measurement Conditions	
Instruments	: IRTracer-100, AIMsight
Resolution	: 8 cm^{-1}
Number of scans	: 10
Apodization	: Sqr-Triangle
Aperture size	: 30 µm × 30 µm
Detector	: T2SL

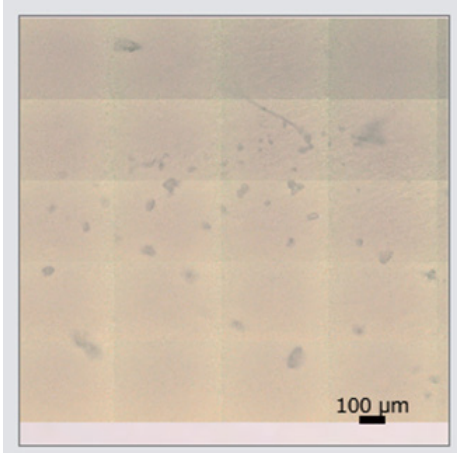


Fig. 1 Image of Microplastics on Filter Paper
Acquired with 15x Reflective Objective Lens

A mapping analysis of the microplastics collected on the filter paper was conducted by the transmission method with the AIMsight infrared microscope. Fig. 2 and Fig. 3 show the two types of infrared spectra acquired from the mapping analysis and the results of a search using Shimadzu's unique UV-Damaged Plastics Library. The absorption at around 1,200 cm^{-1} is due to the PTFE material of the filter paper.

Microplastic (a) in Fig. 2 was found to have a spectrum similar to that of polyethylene (PE) exposed to ultraviolet rays for 550 hours. Microplastics (b) in Fig. 3 was found to have a spectrum similar to that of polypropylene (PP) irradiated with ultraviolet light for 125 hours.

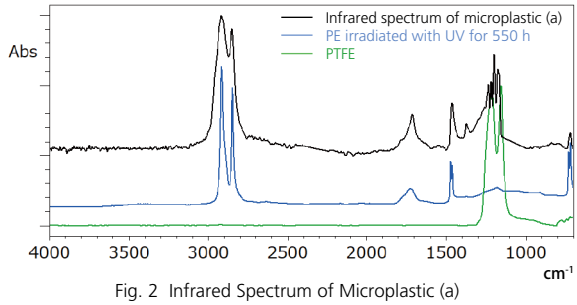


Fig. 2 Infrared Spectrum of Microplastic (a)
Acquired by Mapping Analysis and Search Results

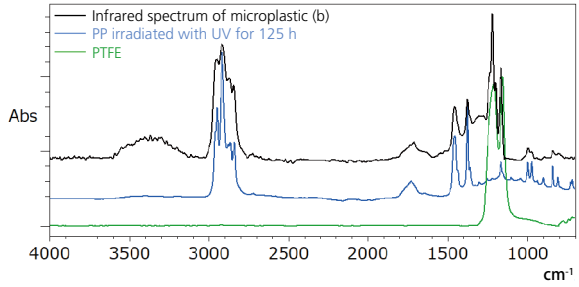


Fig. 3 Infrared Spectrum of Microplastic (b)
Acquired by Mapping Analysis and Search Results

Next, Figs. 4 (a) and (b) show the chemical images of distributions of PE and PP, respectively, prepared using the corrected peak height values (peak height from the baseline) of 718 cm^{-1}, caused by rocking vibration of CH_2, which is the characteristic peak of PE, and 1,373 cm^{-1}, caused by symmetric bending vibration of CH_3, the characteristic peak of PP. Areas where large numerical values were obtained for the plastic component are shown in red, while areas with small values are shown in blue. These mapping analysis results show visually that the larger part of the microplastics collected on the PTFE filter paper is PP, while some PE also exists in the sample.

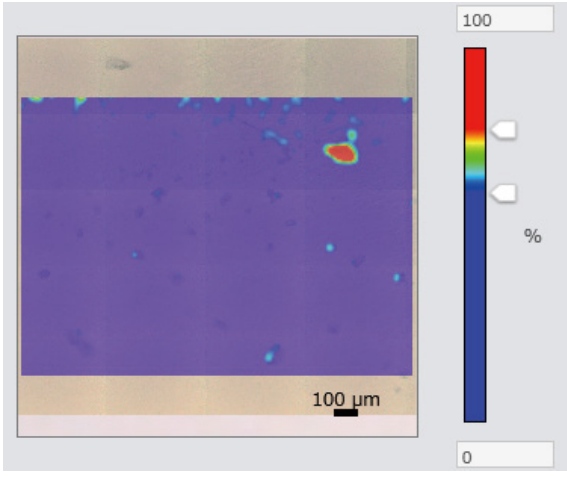


Fig. 4 (a) Distribution of PE
(Using corrected peak height of 718 cm^{-1} caused by rocking vibration of CH_2)

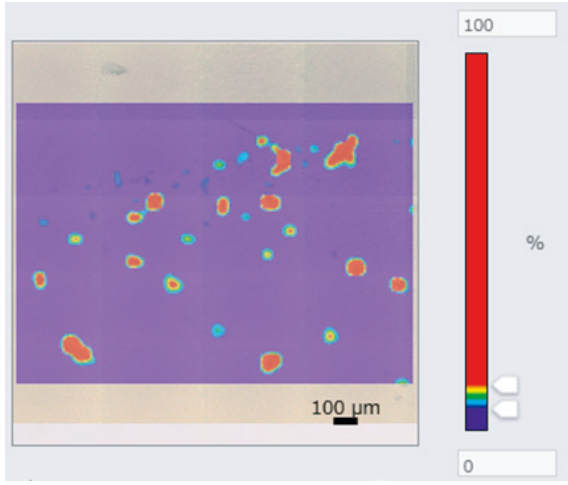


Fig. 4 (b) Distribution of PP
(Using corrected peak height of 1,373 cm^{-1} caused by symmetric bending vibration of CH_3)

Length Measurement Function

This section introduces the length measurement function, a new function in AMsolution software, which used to control AIMsight, using the microplastic images measured in this experiment. The length of the target objects in an image acquired by the wide-field camera or 15x reflective objective lens of AIMsight can be measured by setting the starting point and end point. Fig. 5 shows the operation screen of the length measurement function. Size information for microplastics can also be acquired by using this function. Length measurement results of multiple microplastics collected on the PTFE filter paper are shown in Fig. 5.

Fig. 5 Length Measurement Operation Screen and Measurement Length Results

Qualitative Analysis of Minute Microplastics Using an Infrared / Raman Microscope

The size of microplastics to be evaluated decreases each year, requiring the selection of appropriate analytical instruments. By using an infrared / Raman microscope, it is possible to measure minute microplastics on the order of several μm, which is difficult with an infrared microscope.

Application

Benefits

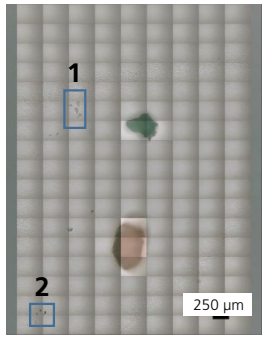
- By using AIRsight Infrared / Raman Microscope, analysis can be made on the same stage without moving the sample.
- Sample length can be measured from images acquired with a wide-field camera or an objective lens for infrared or Raman measurements.

Qualitative Analysis by Microscopic Infrared Spectroscopy

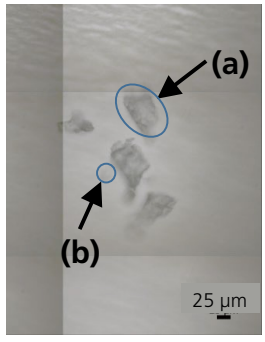
Fig. 2 shows images of microplastics (a), (b) and (c) on PTFE filter paper taken with the infrared and Raman objective lenses (Fig. 1). Microplastic (a) was measured by the transmission method with an infrared microscope. Fig. 3 shows search results using Shimadzu's unique UV-Damaged Plastics Library.

Microplastic (a) was found to have a spectrum similar to that of polypropylene (PP) irradiated with UV light for 100 hours. The noise around 1,200 cm^{-1} is due to absorption by PTFE ,the material of the filter paper.

Measurement Conditions	
Instruments	: IRXross, AIRsight
Resolution	: 8 cm^{-1}
Number of scans	: 30
Apodization	: Happ-Genzel
Aperture size	: 25 μm × 25 μm
Detector	: T2SL



Enlarged view of 1



Enlarged view of 2

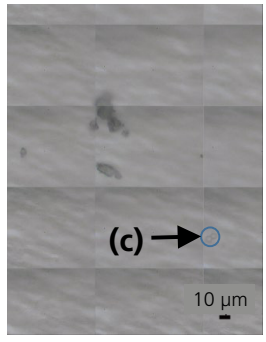


Fig. 2 Microplastic Image Taken with Objective Lens

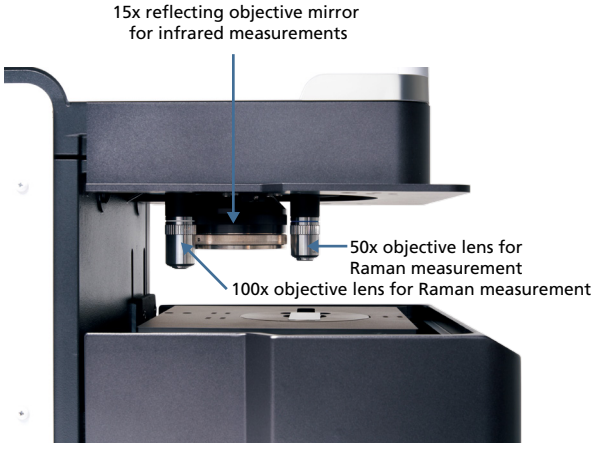


Fig. 1 Objective Lens for Infrared and Raman Measurements

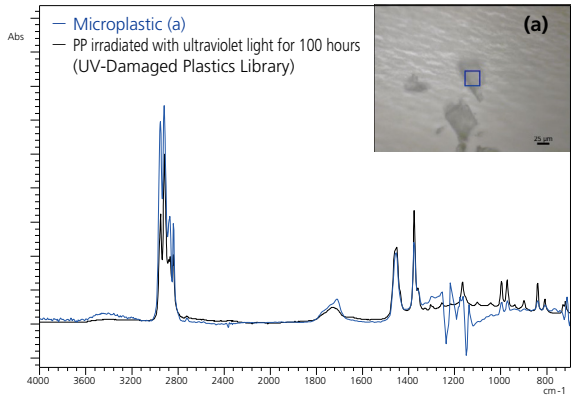


Fig. 3 Infrared Spectrum of Microplastic (a) on Filter Paper

Qualitative Analysis by Micro-Raman Spectroscopy

Micro-Raman spectroscopy was used to measure microplastics of smaller sizes, which are difficult to measure by infrared micro spectroscopy. The images of microplastics (b) and (c) taken by the objective lens are shown in Fig. 4 and the resulting Raman spectra are shown in Fig. 5.

It was determined from the Raman spectra that microplastic (b) was polyethylene (PE) and (c) was polystyrene (PS).

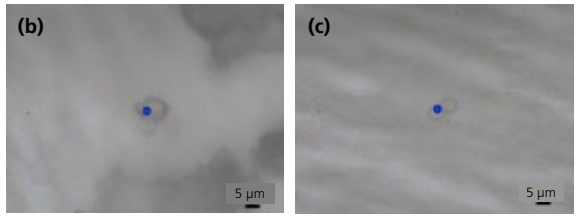


Fig. 4 Images of Microplastics (b) and (c) Taken with the Objective Lens

Measurement Conditions	
Instruments	: IRXross, AIRsight
Number of scans	: 40
Exposure time	: 5.0 sec
Objective lens	: 100x
Excitation wavelength	: 785 nm
Detector	: CCD

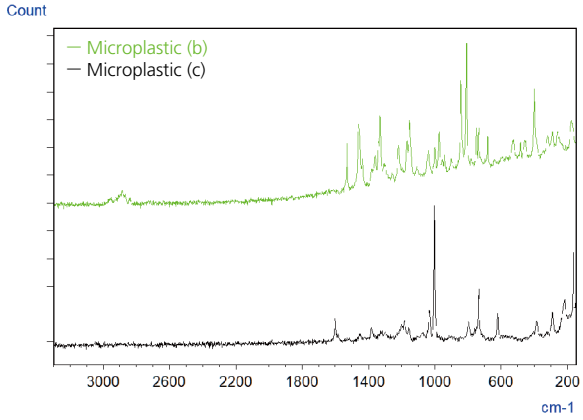


Fig. 5 Raman Spectra of Microplastics (b) and (c) on Filter Paper

Length Measurement Function

With the length measurement function, you can measure the length of an image captured with a wide-field camera or objective lens by setting its start and end points. The operation screen is shown in Fig. 6. This feature provides size information for microplastics as well as material information. The major diameters of microplastics (a), (b) and (c) were 97 µm, 10 µm and 5 µm, respectively.

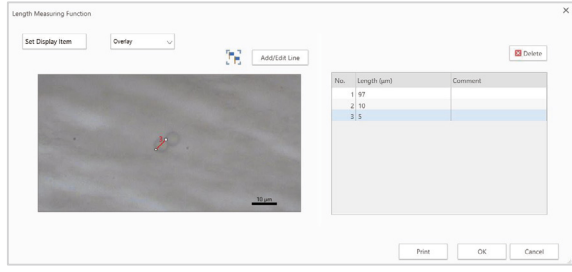


Fig. 6 Length Measurement Operation Screen

Analysis of Microplastics Collected from Marine Species

Pollution by marine debris including microplastics has become a serious environmental problem, and scientists all over the world are exploring the situation by carrying out surveys on microplastics accumulated in marine species. The effects of marine debris have spread through the food chain to marine species such as polar cod living in the Arctic Ocean and deepwater shrimp (order Amphipoda), which should have been hard for the impact of pollution to reach. Microplastics have even been found in the polar ice.

A group of scientists from Newcastle University in the UK and Wageningen Marine Research in the Netherlands collected the stomach contents of various marine creatures and separated microplastics of approximately 100 µm in size as part of a survey on the impact of marine debris [(1)].

This article introduces an example of analysis using an infrared microscope on microplastics collected from polar cod and deepwater shrimp.

Application

Benefits

- By using an infrared microscope, minute microplastics contained in living organisms can be measured with high sensitivity.
- Easy and accurate qualitative analysis is possible using Shimadzu's unique extensive library.

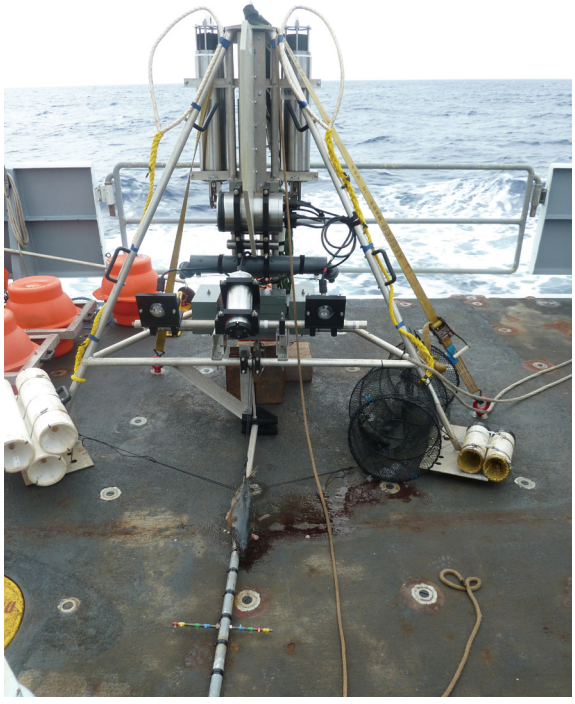


Fig. 1 Marine Survey Equipment

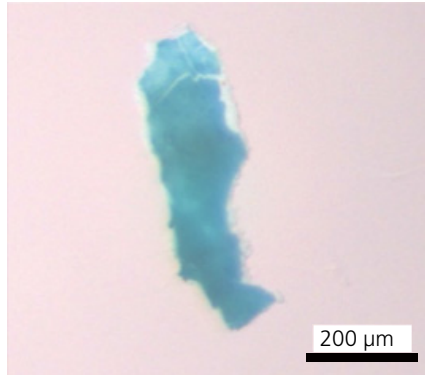


Fig. 2 Microplastic Collected from Polar Cod

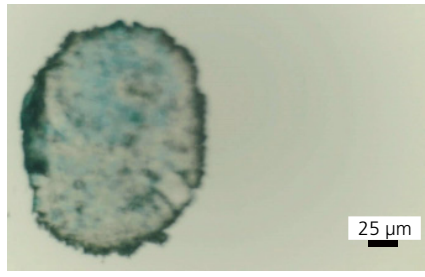


Fig. 3 Microplastic Collected from Deepwater Shrimp

Sample Pretreatment and Precautions

Microplastics analysis requires scrupulous attention to prevent contamination of samples. Direct touching could transfer sebum or dust and contaminate samples. Microfibers from clothing and minute particles floating in the air could also contaminate samples. If samples are contaminated, proteins and other residues need to be removed using an organic solvent or water. However, there is a possibility that the properties intrinsic to the samples may be lost by using an organic solvent. In this experiment, samples were washed with potassium hydroxide solution which removes organic contaminants without affecting the samples.

Fig. 4 Deepwater Shrimp

Measurement Results

Fig. 1 shows the marine survey. The blue microplastic piece collected from polar cod shown in Fig. 2 was measured with the microscopic ATR method (Fig. 5), and the microplastic piece collected from deepwater shrimp (Fig. 4) shown in Fig. 3 was compressed in a diamond cell and measured with the microscopic transmission method (Fig. 6).

From Fig. 5, we can see that the main component of the microplastic piece collected from polar cod was PMMA (polymethyl methacrylate) and that kaolin (aluminum silicate) was included as an additive. PMMA is a tough, lightweight resin with excellent resistance to weather, water and impacts, and is therefore used for everyday items and miscellaneous goods.

From Fig. 6, it can be seen that the main component of the microplastic piece collected from deepwater shrimp was a mixture of PE (polyethylene), $CaCO_3$ (calcium carbonate) and kaolin (aluminum silicate). PE is a common general-purpose resin used for packing materials and containers. It is often detected in microplastics.

Measurement Conditions

Instruments	: IRTracer-100, AIM-9000
Resolution	: 8 cm^{-1}
Number of scans	: 100 times (Fig. 2), 50 times (Fig. 3)
Apodization	: Happ-Genzel (Fig. 2) Sqr-Triangle (Fig. 3)
Aperture size	: 25 µm × 25 µm (Fig. 2) 15 µm × 15 µm (Fig. 3)
Detector	: MCT

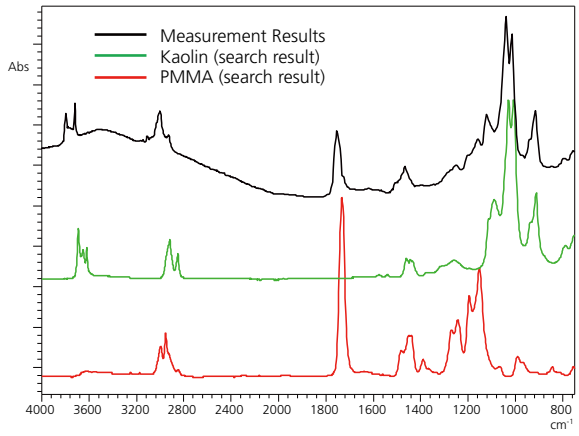


Fig. 5 Measurement Results for Microplastic Collected from Polar Cod

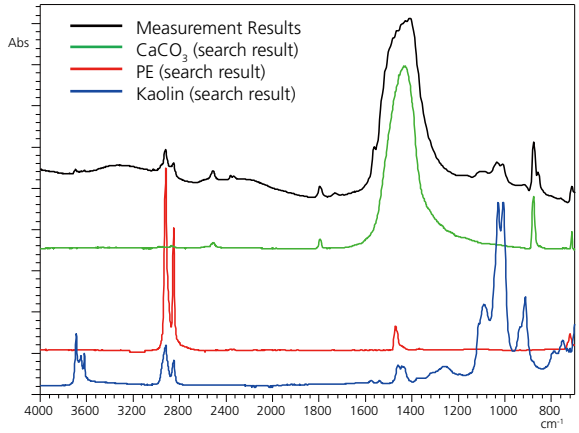


Fig. 6 Measurement Results for Microplastic Collected from Deepwater Shrimp

Reference

(1) In every ocean, at every depth - microfibers and microplastics, Micro FTIR analysis of smallest particles from deep sea to polar ice; Susanne Kühn, Wageningen Marine Research, The Netherlands Alan Jamieson, Newcastle University, Great Britain Robert Keighley, SUK, Great Britain Marion Egelkraut-Holtus, Shimadzu Europa GmbH, Germany, SHIMADZU NEWS, 2. 2018

Qualitative and Elemental Analysis of Marine Debris

Fishing nets, trawling nets, fishing lines, etc. used to be made from natural materials, but nowadays they are usually made of synthetic resin, which provides greater functionality. However, when such materials are not properly managed or disposed of, they become marine debris and are a factor in environmental destruction. Therefore, it is hoped that this kind of marine debris will be collected and reused as a raw material for new fishing equipment.

Application

Benefits

- Toxic substances and metallic elements contained in fishing nets can be qualitatively and quantitatively determined easily using an X-ray fluorescence spectrometer.
- Plastic, which is the main component of fibers used in fishing nets and fishing lines, can be evaluated in multiple ways using FTIR.

Effects of Copper on Fish and Challenges in Recycling

The causes of deterioration and breakup of fishing nets are contact with fish, algae, and stones in the sea and on beaches, as well as ultraviolet radiation from the sun. An example of a way to prevent this kind of naturally occurring damage is to give the surface of fishing nets used for aquaculture (Fig. 1) a protective coating of copper [1]. In the past, paints containing toxic tributylin (antifouling paints for ships) were used as a protective coating on fishing nets, but copper came to be used instead in an effort to protect the environment. The heavy element copper (Cu) has an antibacterial effect and not only protects against bacteria and viruses but also has the function of preventing fouling, so it plays an important role in the manufacture of fishing nets. However, in recent years, the adverse effects of copper on fish have been reported. It is suggested that exposure of fish to high concentrations of copper sulfate over a long period of time may lead to damage to the gills, liver, kidneys and nervous system [2].

Measurement Samples and Conditions

The measurement samples were fishing nets collected on the beach of Majorca island in Spain (Figs 3 (a) and (b)) and others collected at a recycling plant (Figs 3 (c) and (d)). These samples were analyzed without undergoing any processing or special pretreatment.

The ATR method of FTIR stands for Attenuated Total Reflection. By measuring all of the light reflected by the sample surface, the absorption spectrum of the sample surface can be obtained (Fig. 2). The penetration depth of the light is several μm.

Fluorescent X-ray spectroscopy is a technique for analyzing the composition of a sample by irradiating it with X-rays and measuring the X-ray fluorescence generated from the elements contained in it. A ø3 mm collimator (irradiation diameter) was selected in accordance with the size of the sample.

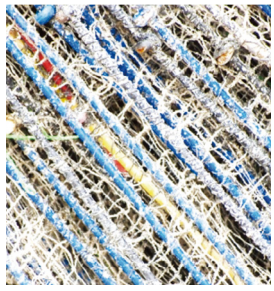


Fig. 1 Fishing Net Used for Aquaculture

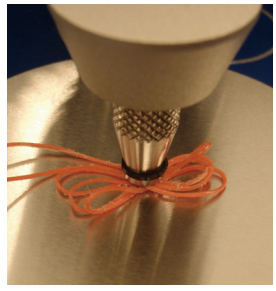


Fig. 2 ATR Measurement in Progress

FTIR Measurement Conditions

Instruments	: IRTracer-100, Quest (Diamond prism)
Resolution	: 4 cm^{-1}
Number of scans	: 45
Apodization	: Happ-Genzel
Detector	: DLATGS

EDX Measurement Conditions

Instrument	: EDX-8000
X-Ray tube target	: Rh
Voltage / current	: 50 kV (Al-U) / Auto, 15 kV (C-Sc) / Auto
Atmosphere	: Vacuum
Analysis diameter	: ø3 mm
Filter	: None
Integration time	: 50 seconds

IRSpirit-X Series
Fourier Transform Infrared Spectrophotometer

FTIR can determine the materials of the filaments used in fishing nets and fishing lines.

Product

EDX-8100 X-ray Fluorescence Spectrometer

EDX facilitates the elemental analysis of copper, etc. used in protective coatings, so both these instruments can be utilized in the management of recycled materials.

Product

Measurement Results

The results of measurement using FTIR showed that, for the samples in Figs. 3 (a) and (b), polyethylene was the main component in many cases, and the other components were polypropylene and, as additives, calcium carbonate and silicate. From the results of qualitative quantitative analysis by EDX, it was found that the Cu content of the samples was less than 0.03 wt%, and that they had no Cu protective coating.

On the other hand, it was found that various types of polymers, including polyethylene, polypropylene and polyamides, were used in the samples in Figs. 3 (c) and (d). In addition, the Cu content was estimated to be 15 wt% in the sample in Fig. 3 (c), and 8 wt% for the sample in Fig. 3 (d), which is more than others, so it could be inferred that it was part of a fishing net with a Cu protective coating.

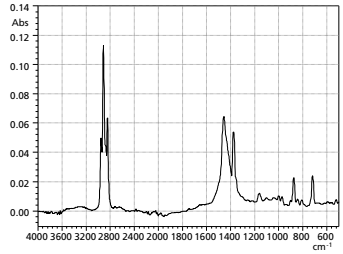
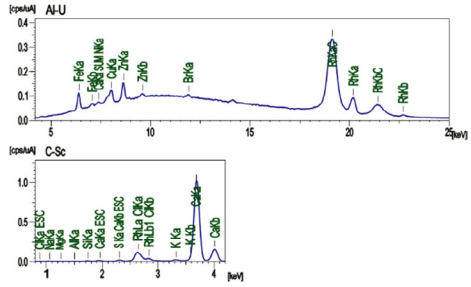
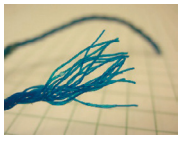
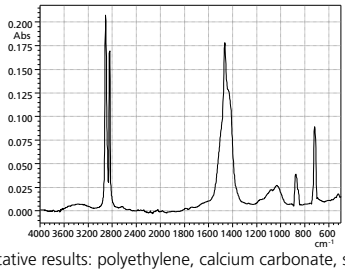
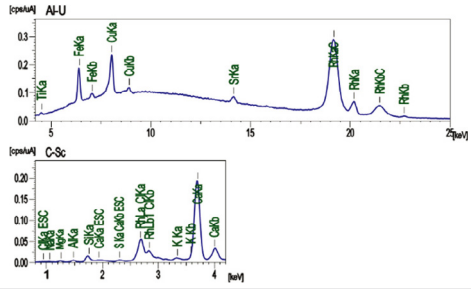
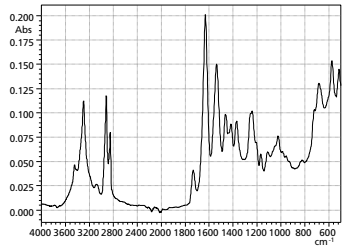
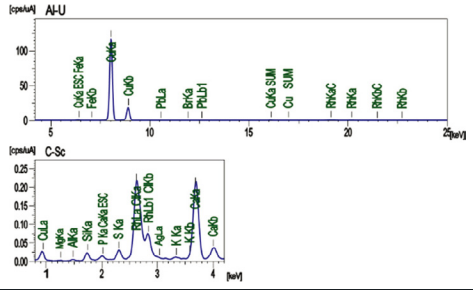
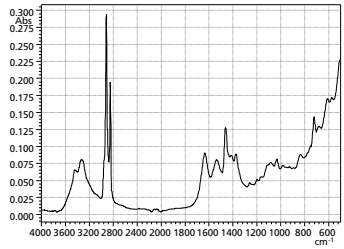
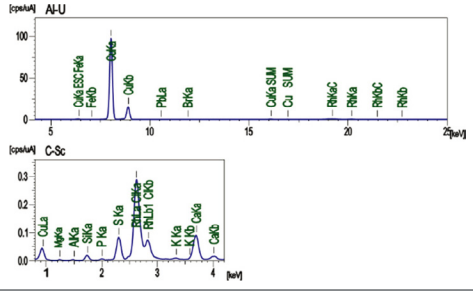
Measurement Samples	FTIR Measurement Results Infrared Spectrum	EDX Measurement Results Fluorescent X-ray Profile
(a) Collected at Playa de Muro, Majorca 	 Qualitative results: polyethylene, polypropylene	
(b) Collected at Playa de Muro, Majorca 	 Qualitative results: polyethylene, calcium carbonate, silicate	
(c) Fishing net obtained at a recycling plant 	 Qualitative results: polyamides, acetates	
(d) Fishing net obtained at a recycling plant 	 Qualitative results: polyethylene, polypropylene, polyamides	

Fig. 3 Measurement Samples and Measurement Results

References

(1) "Biofouling in the Marine Aquaculture Industry, with Particular Reference to Finfish – Current Status and Future Challenges", Mark G. J. Hartl, Douglas Watson and John Davenport, Nov. 2006, Marine Estate Research Report, (AQU/06/03), The Crown Estate

(2) "Fish farming and anti-fouling paints: a potential source of Cu and Zn in farmed fish", Marina Nikolaou, Nikos Neofitou, Konstantinos Skordas, Ioanna Castritsi-Catharios, Lamprini Tziantziou, June 2014, Vol.5: 163-171, Aquaculture environment interactions

Acknowledgments

We would like to thank Albert van Oyen (Carat GmbH, Bocholt, Germany), who is a collaborative researcher.

Comprehensive Approach for Successful Microplastics Analysis

A Fourier transform infrared (FTIR) spectrophotometer is a powerful instrument for microplastics (MPs) analysis because it can perform organic compounds qualification. A Dynamic Particle Image Analysis System (iSpect DIA-10) can obtain the pictures of the particles and other information, such as particle number and diameters. This article introduces how these products help the MPs analysis referring to ASTM determined method.

Application

Benefits

- Rapid measurement of the total number of particles, size distribution, and shape in particles < 100 µm by Dynamic Particle Image Analysis System.
- Qualitative and quantitative microplastics analysis for particles > about a few hundred µm using a benchtop FTIR system.
- Qualitative and quantitative microplastics analysis for particles < about a few hundred µm using an infrared microscope.

ASTM D8489 / WK87463

We actively participated in data acquisition for standardization [1] related to the evaluation of the total number of particles, particle size distribution, shape, etc., and ASTM D8489 (hereinafter referred to as D8489) was published in 2023 [2]. D8489 focuses on smaller particles between the range of 5 to 100 µm, and provides information on particle size, size distribution, concentration, and shape. On the other hand, infrared spectroscopy is a powerful method for evaluating the analysis of materials, and ASTM International is currently evaluating methods for standardization. ASTM WK87463, which is currently under investigation, is expected to be a standard for evaluating microplastics by FTIR and LDIR (Laser Direct Infrared) for particles between 20 µm and 5 mm. In this article, we introduce microplastics evaluation using iSpect DIA-10, a dynamic particle image analysis system in line with D8489, and microplastics material evaluation using FTIR.

Materials and Methods

We examined particles in the 5 to 100 µm range using the iSpect DIA-10 Dynamic Particle Image Analysis System and the IRTracer-100 Fourier Transform Infrared (FTIR) spectrophotometer equipped with a QATR 10 single reflection attenuated total reflection attachment to identify some of the larger particles. Additionally, we analyzed the entire < a few hundred µm fraction using an infrared microscope system using the Shimadzu IRXross FTIR spectrophotometer and AIMsight infrared microscope.

Microplastic particles were prepared according to procedure A of ASTM D8402 [3]. Sheets of polypropylene (PP), pieces of polyethylene (PE), and a food container of polystyrene (PS) were obtained and manually shredded into fragments using a grater as shown in Fig. 1. Next, the plastic particles were mixed, and about 50 mg of the combined plastic was added to 1 mL methanol to create a synthetic D8333 [4] mixture, then sieved through 212 and 100 µm.

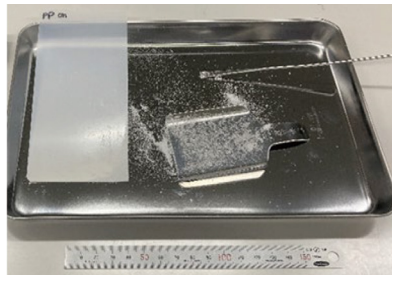


Fig. 1 Preparation of PP Microplastic Particles

Evaluation of Microplastic Using iSpect DIA-10

A <100 µm fraction of particles was analyzed by the Shimadzu iSpect DIA-10 Dynamic Particle Image Analysis System for determination of size distribution, shape, and counting of particles between 5 and 100 µm. A 250 µL aliquot of the < 100 µm fraction was added to 2,250 µL of 50% methanol and 50% glycerin according to D8489. Seven 150 µL replicates were introduced, captured, and analyzed. Figs. 2 and 3 show a particle size distribution and scattergram, respectively, with particle size distribution of one of seven replicates of the < 100 µm fraction. Fig. 4 shows a thumbnail display of particle images. The results indicate that particles are present in the size range of 5 to 100 µm for the < 100 µm fraction, and that the number of particles increases as they become smaller. Furthermore, from the scattergram and thumbnail display, it is apparent that the shredding process employed in this experiment has resulted in particles with a variety of aspect ratios.

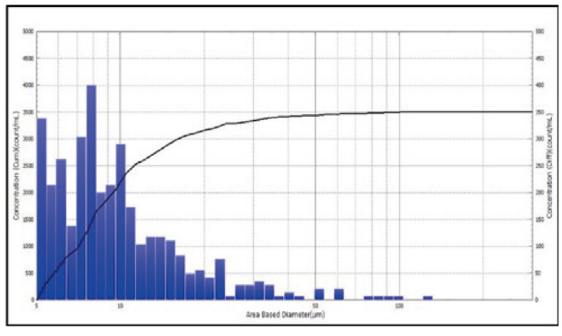


Fig. 2 Particle Size Distribution

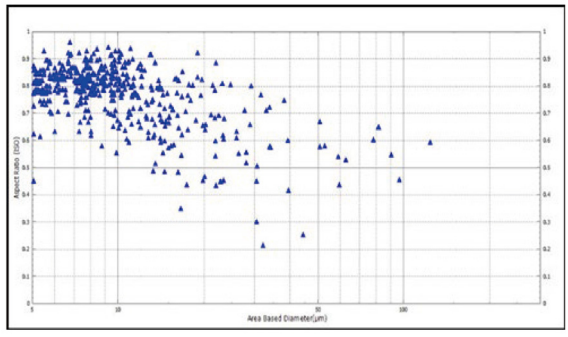


Fig. 3 Scattergram of Area Based Diameter (x-axis) and Aspect Ratio (y-axis)

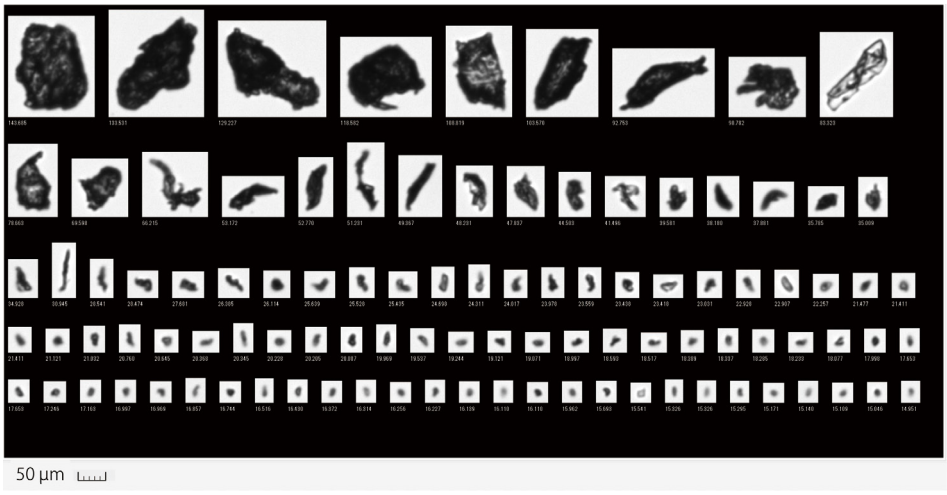


Fig. 4 Thumbnail Display of Particle Images Ordered by Area Based Diameter (µm)

Evaluation of Microplastics Using FTIR

We selected a few of the larger particles that did not pass through the 100 µm sieve for qualitative analysis using the Shimadzu FTIR and attenuated total reflectance attachment. Fig. 5 shows the three photographs, maximum length, and infrared spectra. The presence of particles from each mixed material was confirmed through qualitative analysis. Finally, we analyzed two < a few hundred µm fraction aliquots using the Shimadzu IRXross FTIR and the AIMsight infrared microscope. For this test, 200 µL of the D8333 mixture of microplastics in methanol was transferred onto a 25 mm diameter 15 µm stainless steel mesh screen and filtered. Three individual measurement areas of 1.232 mm^2 were selected from a filter, which had a filter area of 490.625 mm^2.

Fig. 6 shows mapping images identifying the chemical identity of the individual plastic particles found. Areas with high absorbance originating from the plastic component are shown in red, and areas with low absorbance are shown in blue. Fig. 7 shows the spectra of the three plastics. Based on the measurement results, the measurement areas and the filter area, the number of particles retained on the filter was estimated to contain about 3,000 to 4,000 particles.

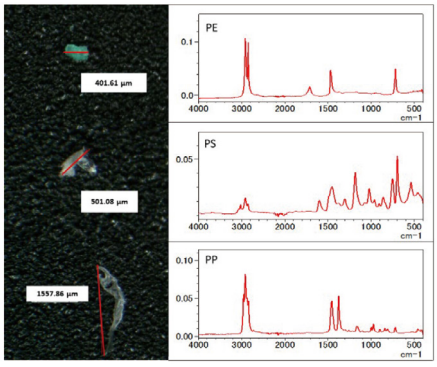


Fig. 5 Three Examples of Photographs, Maximum Length, and Infrared Spectra

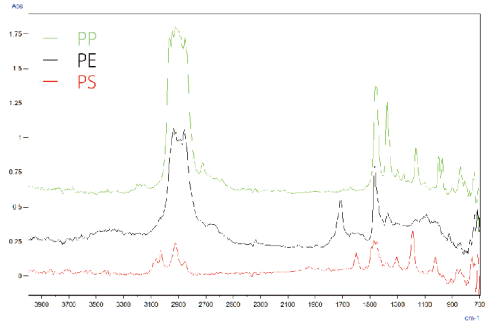


Fig. 7 Color-coded FTIR Spectra of the Individual Plastics

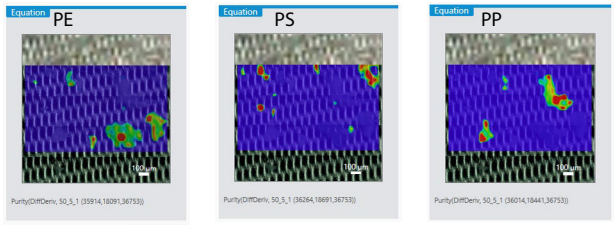


Fig. 6 Mapping Image Identifying Each Plastic in the Unit Area

References

(1) WK87463, New Test Method for Spectroscopic Identification and Quantification of Microplastic Particles in Water Using Infrared (IR) Spectroscopy
(2) ASTM D8489, Test Method for Determination of Microplastics Particle and Fiber Size, Distribution, Shape, and Concentration in Waters with High to Low Suspended Solids Using a Dynamic Image Particle Size and Shape Analyzer
(3) ASTM D8402, Standard Practice for Development of Microplastic Reference Samples for Calibration and Proficiency Evaluation in All Types of Water Matrices with High to Low Levels of Suspended Solids
(4) ASTM D8333, Standard Practice for Preparation of Water Samples with High, Medium, or Low Suspended Solids for Identification and Quantification of Microplastic Particles and Fibers Using Raman Spectroscopy, IR Spectroscopy, or Pyrolysis-GC/MS

Shape Observation, Particle Count Concentration Measurement and Qualitative Analysis of Microplastics

A dynamic particle image analysis system, which can automatically detect particles with sizes from 5 to 100 µm and analyze their shape and particle count concentration in a short time, is suitable for analysis of the shape and particle count concentration (particles/mL) of microplastics dispersed in solutions. An infrared microscope, which excels in the analysis of organic compounds, is suitable for qualitative analysis of microplastics with sizes of 100 µm or less that can be captured with filter paper. Here we introduce an example of analysis of the shape and particle count concentration of particles contained in environmental water and their qualitative analysis with a dynamic particle image analysis system and an infrared microscope.

Application

Benefits

- Images of microplastic particles 100 µm in size or smaller, as well as their maximum length and information on their concentration, can be obtained easily using a dynamic particle image analysis system.
- High-sensitivity measurements of microplastics 100 µm or smaller can be made using an infrared microscope.
- Faster analysis as there is no need for the laborious task of picking up each sample one by one.

Analysis of Shape and Particle Count Concentration of Particles

Environmental water containing microplastics was used as the sample, and the shape and particle count concentration of the particles contained in the sample were analyzed with an iSpect DIA-10. Fig. 1 shows some of the acquired particle images.

From Fig. 1, the shapes of particles with sizes of 100 µm and less have been captured clearly, and various shapes, such as rodlike and fibrous shapes, can be confirmed. Fig. 2 and Fig. 3 show the scattergram (scatter diagram) and histogram (frequency distribution graph), respectively (range shown on horizontal axis: 10 to 100 µm). Scattergrams and histograms can be prepared by selecting two desired measurement items (e.g., maximum length, aspect ratio, circularity). The results showed that the particle count concentration was 5,309 particles/mL. The average size was 24.315 µm, and the largest number of particles were in the size range of 10 to 30 µm, as shown by the red box in Fig. 3.

Measurement Conditions

Instrument	: iSpect DIA-10
Frame rate	: 8 fps
Analysis flow rate	: 0.1 mL/min
Total analyte	: 150 µL

iSpect DIA-10 Dynamic Particle Image Analysis System

The iSpect DIA-10 measures particles by the microcell method, in which image acquisition efficiency is enhanced by passing the particles through a narrow imaging area. Because fewer particles pass outside the imaging area (to the right or left sides), blurring in the front and back directions is small in comparison with the conventional method, and virtually all particles are captured. Moreover, this method supports the measurement of volumes as low as 50 uL, which is useful in the case of samples that are small or difficult to obtain.

Product

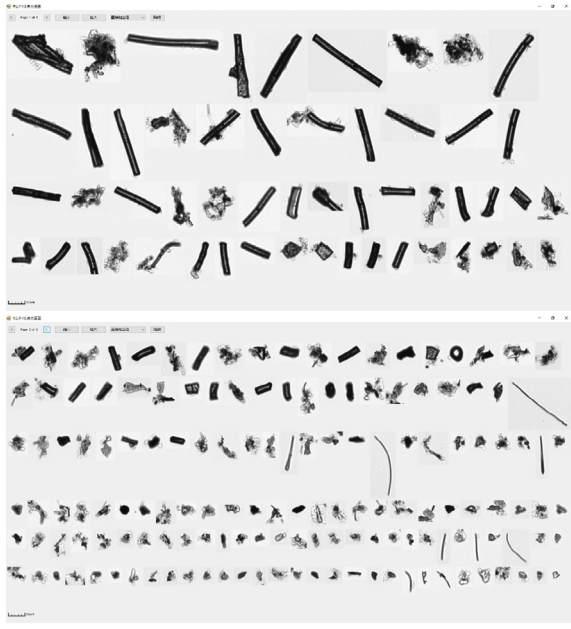


Fig. 1 Particle Images

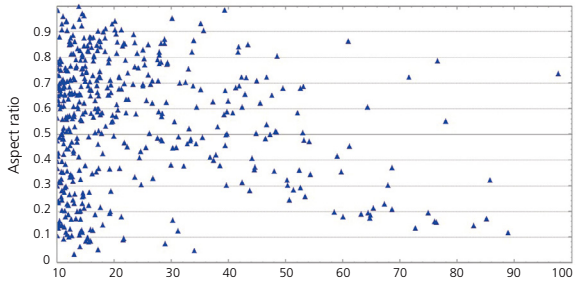


Fig. 2 Scattergram (Scatter Diagram)

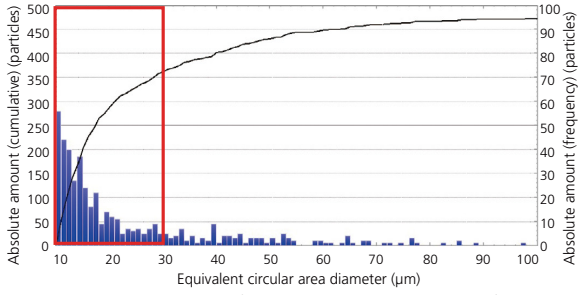


Fig. 3 Histogram (Frequency Distribution Graph)

Qualitative Analysis of Microplastics

After the measurements with the iSpect DIA-10, the particles contained in the sample were captured with polytetrafluoroethylene (PTFE) filter paper and a mapping analysis was carried out with the AIM-9000 infrared microscope.

Fig. 4 shows the visual observation image. As a result of the qualitative analysis of the infrared spectrum (Fig. 5) of the area in the red circle in Fig. 4, this particle was identified as polypropylene (PP).

Next, Fig. 6 shows a chemical image prepared using the corrected area value (area value of peak above the baseline) of the characteristic peak of PP in the range of 1,400 to 1,339 cm^{-1} (CH_3 bending vibration). Areas with high PP content are in red, and those with low PP content are in blue. This result confirmed that all of the rod-like microplastics that can be observed in the visual observation image are PP.

Measurement Conditions

Instruments	: IRTracer-100, AIM-9000
Resolution	: 8 cm^{-1}
Number of scans	: 40
Apodization	: Sqr-Triangle
Aperture size	: 20 µm × 20 µm
Mapping area	: 460 µm × 1780 µm
Detector	: MCT

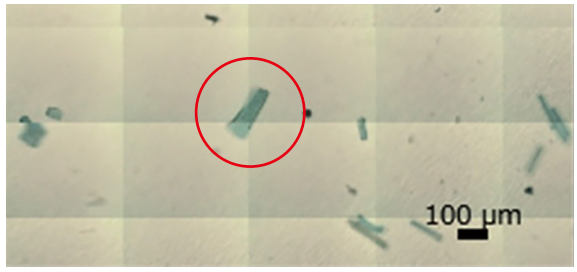


Fig. 4 Visual Observation Image

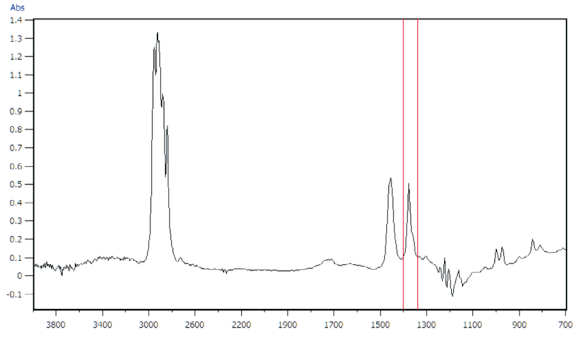


Fig. 5 Infrared Spectrum of Rod-like Microplastics
(The red box shows the peak used in preparing the chemical image in Fig. 6.)

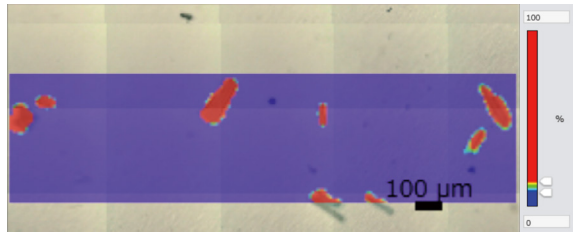
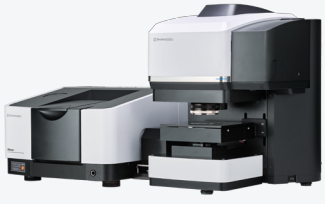


Fig. 6 Distribution of PP
(Corrected Area Value of 1,400-1,339 cm^{-1} Peak)

AIMsight Infrared Microscope

The infrared microscope system makes it possible to acquire information on microscopic areas with high sensitivity by using the aperture to narrow the infrared light beam to the designated size. Visual observation of microplastics on filter paper is also easy using the digital zooming function of the Shimadzu proprietary wide-field camera and microscope camera (with magnification up to 330x).



Product

IRXross Fourier Transform Infrared Spectrophotometer (Left)
AIMsight Infrared Microscope (Right)

Acknowledgments

We wish to express our deep gratitude to Associate Professor Yutaka Kameda of the Chiba Institute of Technology, who provided the samples used in these measurements and shared his knowledge of microplastics.

Determination of Component Ratios for Blended Plastic Samples

Polymeric materials are often created by blending two or more types of polymers in order to obtain properties which cannot be obtained with a single type. Mechanically blended polymeric materials show the characteristics of each component, such as melting and crystallization, so multiple changes derived from each component can be observed through measurement with a DSC (differential scanning calorimeter). If these materials are released to the environment, they become multiple types of plastic pollutants. In this case, the method described below can be used for the measurement of microplastics.

This article introduces the measurement results of blended plastic samples using low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene.

Application

Benefits

- The heat of fusion for each plastic is used, so the composition ratio of blended plastic samples is easily determined.
- Samples weighing a mere 5 mg can be measured.
- Pyrolysis can distinguish between plastics with a similar structure that are difficult to distinguish using FTIR.

Methods Using Individual Heats of Fusion

Using the Heat of Fusion of Individual Components

The content of LDPE and PP was determined from the individual heat of fusion of each component, and the heat of fusion of each component in the blend sample.

The blend sample data in Fig. 1 shows a sufficient temperature difference between the melting peaks of LDPE and PP to allow for separate detection. In this case, the content can be determined by simply dividing the heat of fusion (mJ) of the unknown sample by the known heat of fusion (J/g) of a component.

We prepared a sample with a known blend ratio of LDPE:PP = 80:20 and verified the component ratio using this method. A satisfactory result of 79.1 %:20.9 % was obtained with respect to the 80:20 ratio of LDPE and PP.

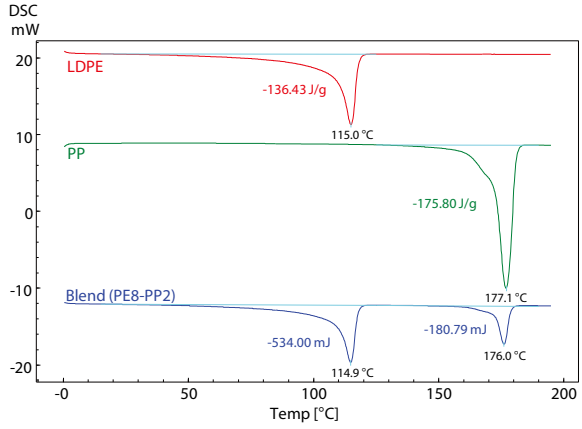


Fig. 1 DSC Curves of LDPE, PP, and Blend Sample

Using an Approximated Heat of Fusion

The component ratio of a sample was determined from the measured melting peaks for HDPE and PP, and a blend of these two components.

Since the melting peaks of HDPE and PP are detected at very close temperatures, the peaks overlap and cannot be completely separated. In this case, the peaks are divided laterally as shown in Fig. 2 and the heat quantity (approximated) of each peak is calculated as the heat of fusion of each component. (An optional partial area analysis program is required to perform this calculation.)

Fig. 3 shows the data obtained using this method. The heat of fusion of 100 % HDPE and PP, and the approximated heat of fusion of each component in the blend sample, were used for the same calculation as in the previous section. Measurement results that provide a roughly close ratio of HDPE:PE = 85.1 %:14.9 % with respect to the actual blend ratio of HDPE:PE = 79.7 %:20.3 % were obtained. Note that significant overlapping of the two peaks reduces accuracy.

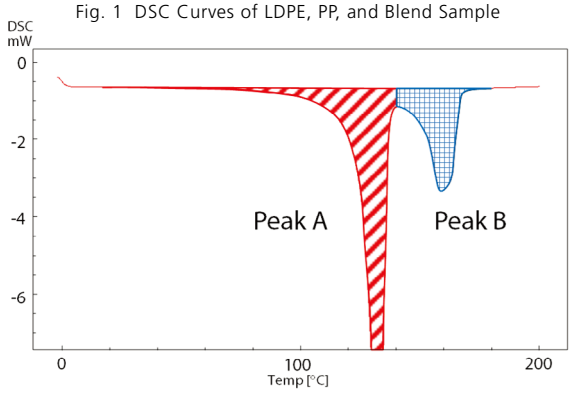


Fig. 2 Obtaining the Approximate Heat of Fusion

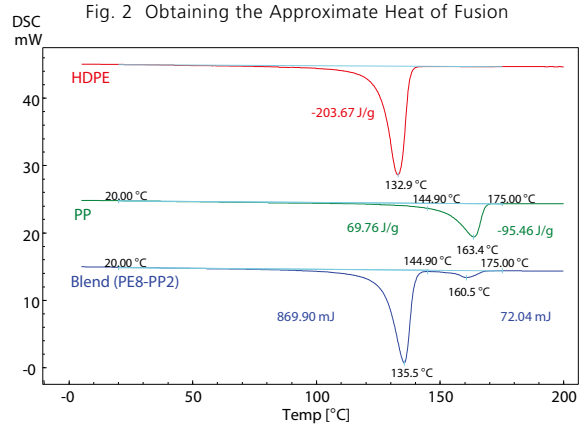


Fig. 3 DSC Curves of HDPE, PP, and Blend Sample

Method Using the Total Heat of Fusion

In the case when peaks overlap, the content ratio can be determined from the total heat of fusion (value obtained through a single integration of the area of both peaks, as shown in Fig. 4) as an alternative to the method using an approximated heat of fusion as described in the previous section.

First, a calibration curve is created by plotting and joining the heats of fusion of the separate 100 % samples with a straight line, as shown in Fig. 5. This calibration curve expresses the relationship between the blend ratio and the total heat of fusion. The blend ratio can be determined from the measurement results for total heat of fusion by using this calibration curve.

For example, a total heat of fusion of 200.68 (J/g) corresponds to a component ratio of PE:PP = 77.4:22.6. Table 1 compiles the results of blend ratios determined from the total heat of fusion using this method with respect to samples A through E (which have known blend ratios).

This shows that an approximate blend ratio can be obtained from the total heat of fusion measured using a DSC and a calibration curve.

Table 1 Samples of Various Blend Ratios and Measurement Results

	Blend Ratio		Total Heat of Fusion (J/g)	Result Determined from Calibration Curve	
Sample	HDPE	PP		HDPE	PP
PP	0.00	100.00	97.07	0.00	100.00
A	19.72	80.28	122.11	18.70	81.30
B	40.64	59.36	151.95	40.99	59.01
C	49.90	50.10	159.98	46.99	53.01
D	60.16	39.84	174.53	57.86	42.14
E	79.88	20.12	200.68	77.40	22.60
HDPE	100.00	0.00	230.94	100.00	0.00

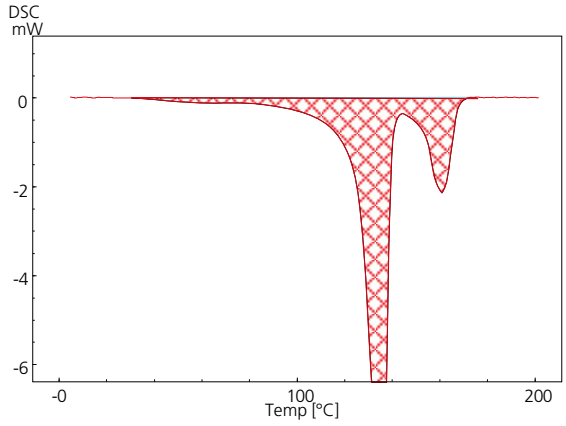


Fig. 4 Total Heat of Fusion of the Blend Sample

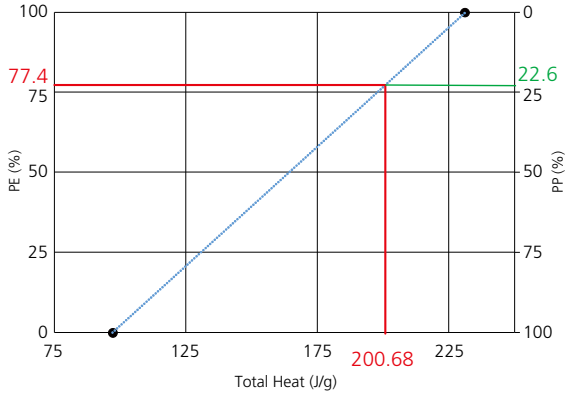


Fig. 5 Calibration Curve Determined from Separate HDPE and PP Samples

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

Tire wear particles that remain on roads can be transported to environmental waters by wind and rain, causing marine pollution, and can become airborne, contributing to air pollution; therefore, they are attracting attention as a source of microplastic contamination in the environment. Because these microplastics are small and consist of mixed particle types, isolating them from environmental samples is challenging.

Application

Benefits

- **Pyrolysis-GC-MS and F-Search MPs 2.0 software enable qualitative and quantitative analysis of multiple microplastics in environmental samples individually.**
- **By eliminating the tedious pretreatment steps needed to isolate microplastics from environmental samples, this method significantly reduces the workload of analysts.**

Preparation and Analytical Conditions

A microplastics calibration reference sample containing the twelve plastics with the highest global production quantities (MPs-CaCO3 from Frontier Laboratories Ltd.) was used as a standard 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 sample (Fig.1). The sample was a mixture of sand, soil, and other matter. About 4.1 mg of the 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 the table below. The twelve plastics 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 1.

Analytical Conditions

Pyrolyzer	: EGA/PY-3030D coupled with AS-1020E (Frontier Laboratories Ltd.)
GC-MS	: GCMS-QP2020 NX
Column	: UAMP Column Kit (Frontier Laboratories Ltd.)
[Pyrolyzer]	
Furnace Temp.	: 600 ˚C
Interface Temp.	: 300 ˚C
[GC]	
Injection Unit Temp.	: 300 ˚C
Carrier gas	: He
Injection Mode	: Split
Split ratio	: 50
Gas Flow Control	: 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
Acquisition Mode	: Scan (*m/z* 29-350)
Event Duration	: 0.2 sec

Fig. 1 Roadside Debris

Table 1 Twelve Plastics Included in the MPs Calibration Reference Sample, Thermal Decomposition Products Used for Qualitative Analysis, and Quantitative Ions Used for Quantitative Analysis

#	Plastic Type*1	Pyrolyzate	*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 (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)), PU (polyurethane), PET (polyethylene terephthalate), N-6 (Nylon-6), N-66 (Nylon-6,6)**

Pyrolysis GC-MS System (Pyrolysis Gas Chromatography Mass Spectrometry)

Py-GC-MS is an analytical technique that rapidly thermally decomposes a sample, separates the vaporized pyrolyzed products on a column, and detects them with a mass spectrometer. By detecting pyrolyzed products characteristic of each type of plastic, it is possible to analyze each plastic. It can analyze MPs less than 100 µm, and requires only a small sample amount —typically a few milligrams to several tens of milligrams.

Product

Result

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

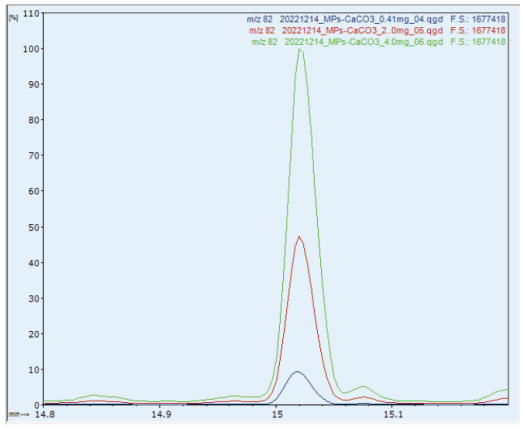


Fig. 2 Chromatogram Overlay from 0.4, 2.0, and 4.0 mg of MPs Calibration Reference Sample (PE, *m/z* 82)

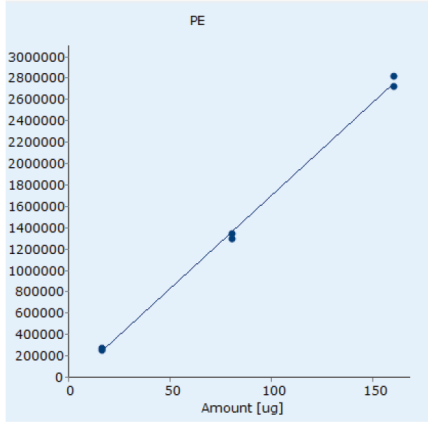


Fig. 3 Calibration Curve for PE (*m/z* 82, n = 2)

The sample was measured and a similarity search for the detected peaks was performed. The results showed a 90 % or more similarity to six plastics: PMMA, N66, SBR, PET, PE, and PS. For these plastics, quantitation values and their percent content were calculated based on the calibration curves created (Table 2). PE has the highest percent rate. It is assumed that it originated from container packaging materials, agricultural films, and other materials. SBR, used in the tire tread (the part in direct contact with the ground), and presumably derived from tire wear, has the second highest rate. Figs. 4 and 5 compare SIM chromatograms and corresponding mass spectra for PE and SBR in the sample and standard (2.0 mg MPs calibration reference sample).

Table 2 Qualitative and Quantitative Analysis Results

Plastic	Retention Time [min]	Result*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 more similarity.

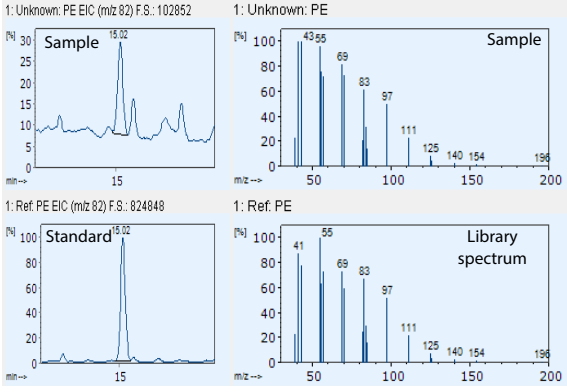


Fig. 4 Comparison of Mass Chromatograms and Mass Spectra for the Standard and the Samples (PE)
(Left: Mass Chromatograms, Right: Mass Spectra)

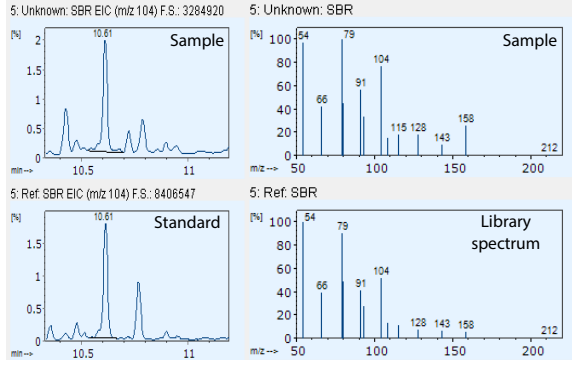


Fig. 5 Comparison of Mass Chromatograms and Mass Spectra for the Standard and the Samples (SBR)
(Left: Mass Chromatograms, Right: Mass Spectra)

This article described qualitative and quantitative analysis of MPs accumulated on road shoulders using Py-GC-MS. The calibration curves created from the MPs 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 without pretreatment steps, improving the overall efficiency of analysis.

Material Analysis of Microplastics in River Water

This article showcases a workflow of pretreating river water with the MAP-100 microplastic automatic preparation device, followed by analysis of microplastics (MPs) using FTIR spectroscopy and pyrolysis gas chromatography mass spectrometry (Py-GC-MS).

Application

Benefits

- Automated pretreatment of 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 the Cryogenic Mill (IQ MILL-2070).
- Py-GC-MS can measure the weight of multiple plastics even when they are mixed.

Flow of Material Analysis

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 directly. For Py-GC-MS analysis, extracted MPs were homogenized by freeze grinding.

Sampling → Pretreatment → MPs analysis with FTIR → Homogenizing → MPs analysis with Py-GC-MS

MAP-100

IRSpirit-TX + QATR-S

IQ MILL-2070 (Frontier Laboratories Ltd.)

EGA/PY-3030D + GCMS-QP2020 NX

Fig. 1 Flow of Material Analysis

FTIR Analysis Results

The extracted MPs were measured using FTIR+ATR. Polypropylene (PP), polyethylene (PE), and ethylene vinyl acetate (EVA) were detected in the 78 extracted MPs. There were also 62 PPs (79.5 %), 11 PEs (14.1 %) and 5 EVAs (6.4 %).

Py-GC-MS Analysis Results

The extracted MPs were freeze-ground before analysis by Py-GC-MS. 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.

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

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

Analytical Conditions of Py-GC-MS

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*1 (Frontier Laboratories Ltd.)
[Detailed Conditions]	
Pyrolyzer	
Furnace Temp.	: 600 ˚C
Interface Temp.	: 300 ˚C
Back Flush	: 22-50 min
GC	
Injection Unit Temp.	: 300 ˚C
Carrier Gas	: He
Injection Mode	: Split
Split Ratio	: 50
Gas Flow Control	: 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
Acquisition Mode	: Scan (*m/z* 29-350)
Event Duration	: 0.2 sec

*1 Precolumn : Smart COL (inactive 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)

Py-GC-MS Analysis Results

PE, PP, PS and EVA were detected from the MPs collected. Fig. 2 shows the mass chromatograms and mass spectra of PE output from F-Search MPs. It was confirmed that the elution time and mass spectra of the pyrolyzed products of each plastic were consistent between the standards and the samples and that they were correctly identified.

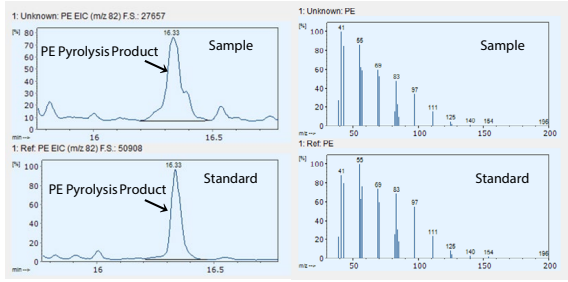


Fig. 2 Pyrolysis Products of PE
Mass Chromatogram (Left) and Mass Spectrum (Right)

Table 1 shows the results of the quantitative analysis of each plastic from the calibration curves. 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+SiO_2) 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 %.

Table 1 Results of Py-GC-MS Analysis*2

#	Sample Amount (mg)	Quantified 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 *3	2.30	97.2
%RSD	0.06	1.7	2.7	4.6	11.4	1.6

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

Samples collected from river water were automatically pretreated using the MAP-100, and the MPs were then analyzed by FTIR and Py-GC-MS. PP, PE and EVA were detected with both instruments, indicating that PP and PE are the main components (Fig. 3).

Using an FTIR, individual qualitative results can be obtained easily, and the number ratios and densities can be calculated. Py-GC-MS provides a more accurate mass to material ratio (%). This workflow supports screening methods that take advantage of the features of each instrument, from preparation to analysis of MPs.

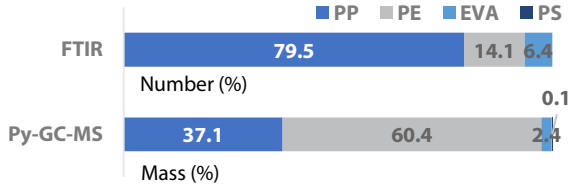


Fig. 3 Comparison of Quantitative Results of MPs in Each Instrument *4

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

MAP-100
Microplastic Automatic Preparation Device

Accurate evaluation of microplastics in samples collected from surface waters requires proper pretreatment to remove environmental contaminants. This product is an automated pretreatment system that standardizes common procedures for extracting microplastics from surface water samples, reducing labor, improving reproducibility, and enhancing safety.

Product

GCMS-QP2050 + EGA/PY-3030D
Pyrolysis GC-MS System

Py-GC-MS is an analytical technique that rapidly thermally decomposes a sample, separates the vaporized pyrolysis products by component on a column, and detects them with a mass spectrometer. By detecting pyrolysis products characteristic of each type of plastic, it is possible to analyze each plastic. It can analyze MPs less than 100 µm, and requires only a small sample amount—typically a few milligrams to several tens of milligrams.

Product

Analysis of Toxic Chemical Substances Adsorbed on Microplastics

There is a possibility that toxic chemical substances adsorbed on microplastics in the environment may impact the ecosystem by desorbing from the microplastics, migrating to the bodies of living organisms, and becoming concentrated in those organisms. The Shimadzu Group has been involved in evaluations of the adsorption characteristics of chemical substances on microplastics as part of its overall analysis of microplastics[1), 2)]. Here we introduce an example of an evaluation of the adsorption characteristics of polycyclic aromatic hydrocarbons (PAHs) and per- and polyfluoroalkyl substances (PFAS), which are known to have toxicity and bioaccumulation properties.

Application

Benefits

- It is possible to quantitatively evaluate the amount of polycyclic aromatic hydrocarbons (PAHs) and per- and polyfluoroalkyl substances (PFAS), which are known to be toxic and accumulative, adsorbed by the plastics.
- The characteristics of adsorption by the plastics can be evaluated from the compound.

Measurement Samples and Conditions

Particles of three plastics, polypropylene (PP), polystyrene (PS), and polyethylene (PE), were used as the microplastic samples.

First, an adsorption test of PAHs and PFAS on the microplastics samples was conducted (Fig. 1). The microplastics were immersed in water, to which PAHs or PFAS had been added, and the water was stirred gently for 24 h to promote adsorption. The amounts added to microplastics were 100 ng of PAHs and 8 ng of PFAS in 300 mL of ultrapure water. After the adsorption test, the microplastics were removed from the test system and dried. With some of the samples, ultrasonic extraction by hexane was used as a pretreatment for the PAHs, and ultrasonic extraction by methanol was used as a pretreatment for the PFAS (Fig. 2). The extracts obtained were injected into the GC-MS/MS and LC-MS/MS, respectively, for quantitative analysis of the PAHs and PFAS.

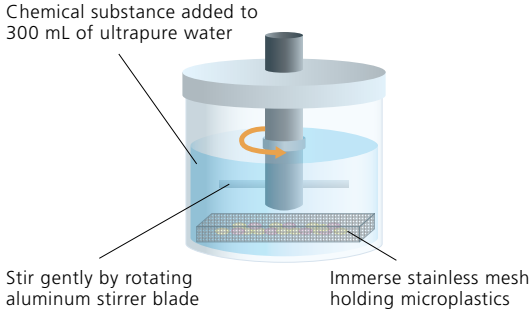


Fig. 1 Outline of Adsorption Test System

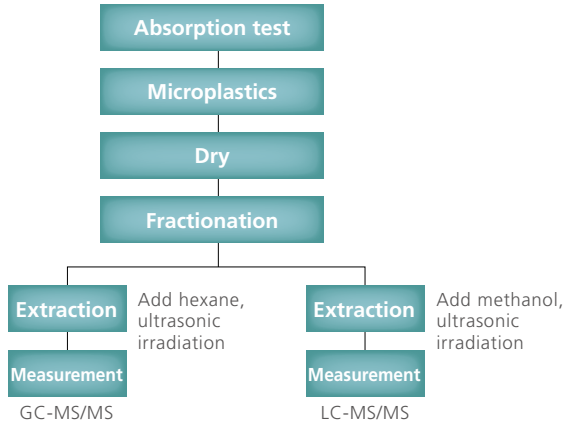


Fig. 2 Outline of Test Workflow

GC-MS/MS Measurement Conditions

GC	
Column	: DB-5ms (30 m x 0.25 mm I.D., 0.25 µm)
Column oven temp. program	: 60 °C (1 min) - 15 °C/min - 200 °C (0 min) - 8 °C/min - 320 °C (10 min)
Injection mode	: Splitless
Vaporizing chamber temp.	: 300 °C
Injection volume	: 2 µL
MS	
Ionization method	: EI
Ionization voltage	: 70 V
Interface temp.	: 300 °C
Measurement mode	: MRM

LC-MS/MS Measurement Conditions

LC	
Column	: Inertsil ODS-SP (150 mm x 2.1 mm I.D., 3 µm)
Column temp	: 40 °C
Injection volume	: 10 µL
Mobile phase A	: 10 mmoL/L ammonium acetate aqueous solution
Mobile phase B	: Acetonitrile
Mobile phase flow rate	: 0.2 mL/min
MS	
Ionization method	: ESI
Polarity	: Negative
Measurement mode	: MRM

GCMS-TQ8040 RX
Triple Quadrupole Gas Chromatograph Mass Spectrometer

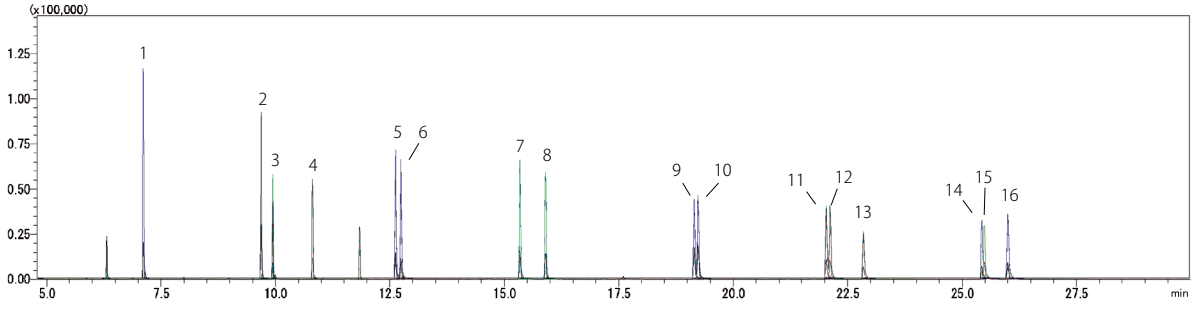
Product

LCMS-8060RX
Triple Quadrupole Liquid Chromatograph Mass Spectrometer

Product

Measurement Results

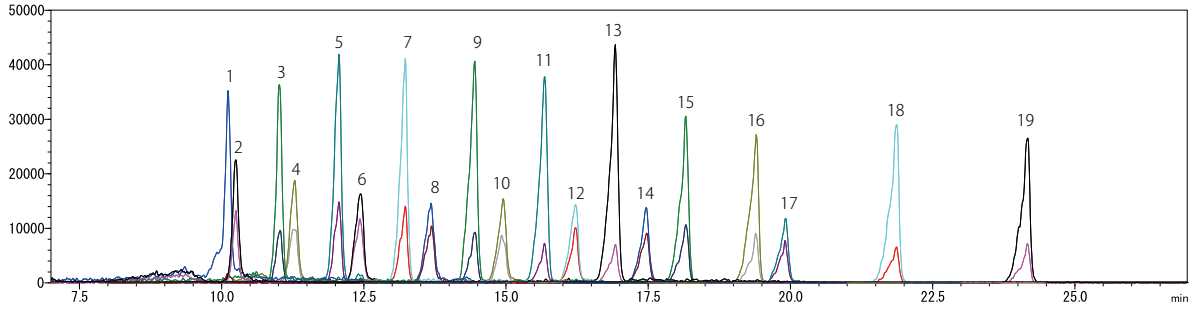
Fig. 3 shows the MRM chromatogram of the PAHs standard solution (2 ng/mL each) and Fig. 4 shows the MRM chromatogram of the PFAS standard solution (0.5 ng/mL each).



Compounds

1. Naphthalene	5. Phenanthrene	9. Benzo[a]anthracene	13. Benzo[a]pyrene
2. Acenaphthylene	6. Anthracene	10. Chrysene	14. Indeno[1,2,3-cd]pyrene
3. Acenaphthene	7. Fluoranthene	11. Benzo[b]fluoranthene	15. Dibenzo[a,h]anthracene
4. Fluorene	8. Pyrene	12. Benzo[k]fluoranthene	16. Benzo[ghi]perylene

Fig. 3 MRM Chromatogram of the PAHs Standard Solution (2 ng/mL each) (only target substances)



Compounds

1. PFHxA	5. PFOA	9. PFDA	13. PFDoDA	17. PFDoS
2. PFBS	6. PFHxS	10. PFOS	14. PFDS	18. PFHxDA
3. PFHpA	7. PFNA	11. PFUnDA	15. PFTrDA	19. PFOcDA
4. PFPeS	8. PFHpS	12. PFNS	16. PFTeDA	

Fig. 4 MRM Chromatogram of the PFAS Standard Solution (0.5 ng/mL each) (only target substances)

Fig. 5 shows the results of the analysis of PAHs with GC-MS/MS, and Fig. 6 shows the results of the analysis of PFAS by LC-MS/MS. Adsorption on the microplastics was confirmed for all PAHs and for some PFAS. Adsorption of the PAHs on PP and PE tended to be large. However, the adsorption of the PFAS tended to differ for each chemical substance. Because the adsorption characteristics on microplastics differed depending on the chemical substance, it is thought that some are easily affected by the type of microplastic, that is, its molecular structure, while others are not significantly affected.

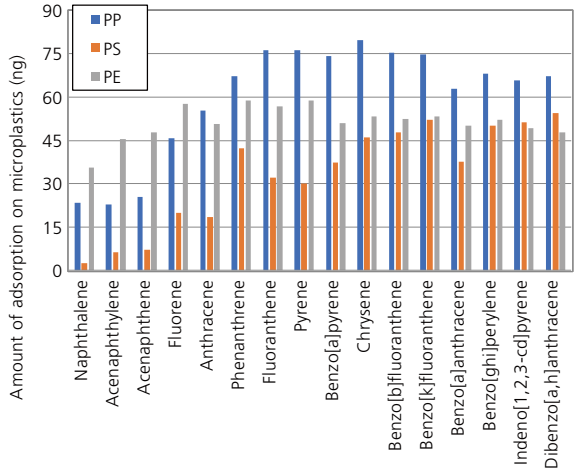


Fig. 5 GC-MS/MS Analysis Results: PAHs

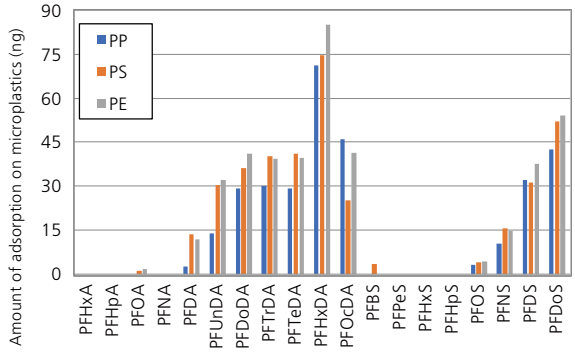


Fig. 6 LC-MS/MS Analysis Results: PFAS

References

(1) Makoto Yasojima, Haruna Mizuka, Takaki Mine, Hiroaki Takemori, Shinji Takeuchi, Yoshihide Yasui, "Adsorption Characteristics of Chemical Substances on Microplastics," Proceedings of the 22nd Symposium of the Japan Society on Water Environment (Sapporo; 2019)

(2) Makoto Yasojima, Haruna Mizuka, Takaki Mine, Hiroaki Takemori, "Existence of Unknown Chemical Substances Adsorbed on Microplastics Immersed in Rivers and Adsorption Characteristics of Chemical Substances on Microplastics," Proceedings of the 56th Environmental Engineering Research Forum (Okayama; 2019)

Plastics Analysis and Evaluation Techniques

Shimadzu provides a wide range of solutions for analysis and evaluation of plastic materials.

Test Evaluation Items	Materials Characteristics	Instruments/Products
Observation and Analysis	Observation	Scanning Probe Microscope
	Nondestructive internal observation	X-Ray Inspection System, X-Ray CT System
	Elemental analysis	Energy Dispersive X-ray Fluorescence Spectrometer
	Observation and elemental analysis	Electron Probe Microanalyzer
	Observation and component analysis	Imaging Mass Microscope
	Elemental analysis and analysis of chemical state	Imaging X-Ray Photoelectron Spectrometer
Material Properties (Research and Development, Quality Control)	Synthesis reaction analysis	Probe Electrospray Ionization Mass Spectrometer
		Fourier Transform Infrared Spectrophotometer
	High separation purification	Preparative Purification Liquid Chromatograph
		Supercritical Fluid Extraction / Chromatograph System
	Molecular weight distribution, molecular weight measurement	High Performance Liquid Chromatograph
		MALDI Mass Spectrometer
	Determination of material properties	Fourier Transform Infrared Spectrophotometer, Infrared Microscope, Infrared / Raman Microscope
	Color measurements and optical characteristics	UV-VIS-NIR Spectrophotometer
Additives and Harmful Substances	Foreign odors and gases produced	GC-MS Off-Flavor Analyzer, GC-MS Thermal Desorption System
	Heavy metals and trace elements	ICP Emission Spectrometer, Inductively Coupled Plasma Mass Spectrometer
		Atomic Absorption Spectrophotometer
		Ion Chromatograph
	Identification and quantitation of additives	High Performance Liquid Chromatograph
		Liquid Chromatograph Triple Quadrupole Mass Spectrometer
		GC-MS Pyrolysis System
	Residual solvent	GC-MS Headspace Analysis System
Thermal Characteristics	Endothermic/exothermic reaction and reaction rates	Differential Scanning Calorimeter, TG-DTA Simultaneous Measuring Instrument
	Relative heat capacity	Differential Scanning Calorimeter
	Evaporation, decomposition, gas adsorption, moisture content, and thermostability	TG-DTA Simultaneous Measuring Instrument
	Thermal expansion, contraction percentage, and softening point	Thermomechanical Analyzer
Physical Characteristics	Particle size distribution	Particle Size Analyzer
		Dynamic Particle Image Analysis System
Mechanical Performance	Tensile, compression, bending	Precision Universal Tester
		Micro Strength Evaluation Testing Machine
	Hardness	Micro Vickers Hardness Tester, Dynamic Ultra Micro Hardness Tester
	Friction force (tribology)	Scanning Probe Microscope
	Fatigue strain test	Fatigue and Endurance Testing Machine
		Electromagnetic Force Micro Tester
	HIgh-speed tensile and high-speed punching	High-Speed Impact Testing Machines
	Particle strength	Micro Compression Tester
Rheological Characteristics	Viscosity	Capillary Rheometer Flowtester
	Viscoelasticity evaluation	Mooney Viscometer
Mass	Specific gravity	Specific Gravity Measurement Balances
	Mass	Analytical Balances, Electronic Balances, Precision Platform Balances
	Moisture content	Moisture Analyzer
Preparation	—	Microplastic Automatic Preparation Device

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