C10G-E083A

SHIMADZU
Excellence in Science

Aiming to Improve the Marine Environment

Analytical Solutions for Microplastics

Diverse Solutions for Improving the Marine Environment

Tiny plastic fragments on the order of several μm to 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.

Applications for Microplastics

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.

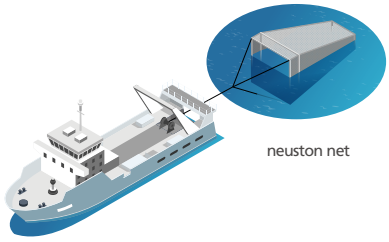
STEP 1 Sampling

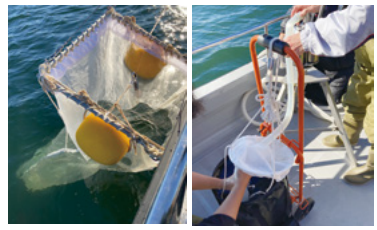
STEP 2 Preparation

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

NEW

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

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

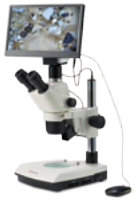
Advantages of the MAP-100

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.

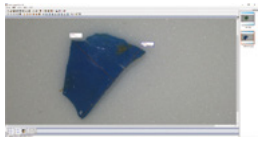
Stereoscopic Microscope
STZ-171-TLED
(Shimadzu Rika Corporation)



*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.

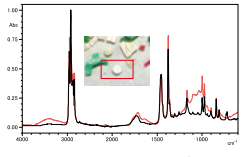
Software
Motic Images Plus



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

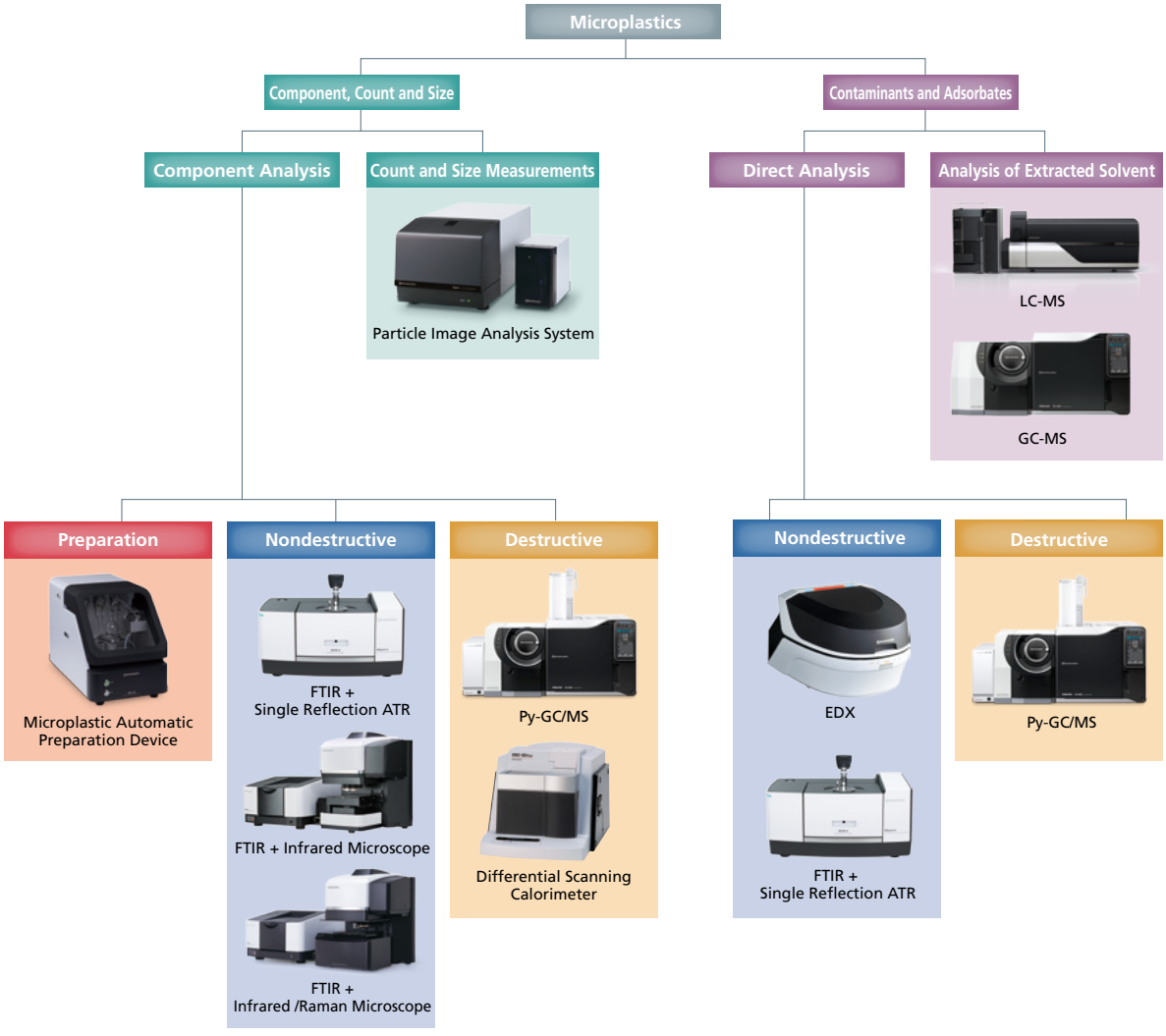


— Polypropylene irradiated UV-rays for 125 hrs
— White plastic shard

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.

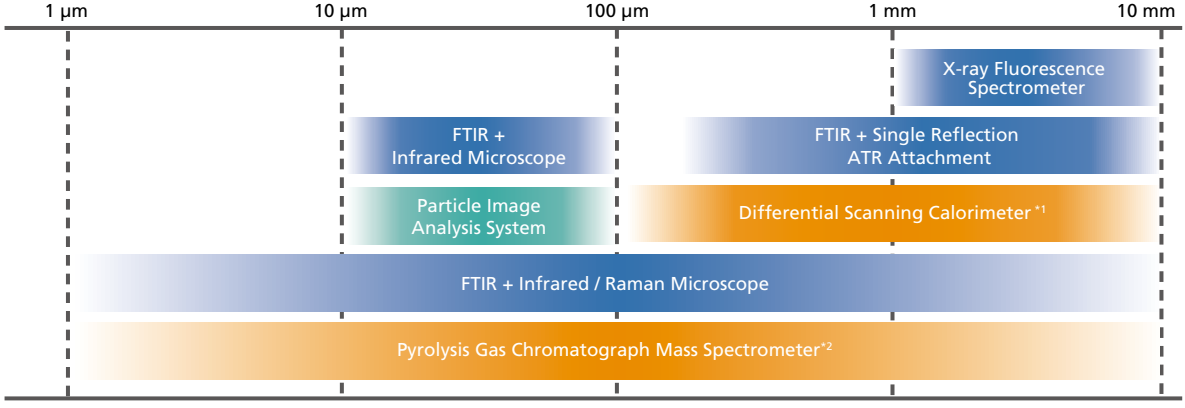
Workflow for Selecting an Analysis and Measurement Method

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 "River Microplastics Survey Guidelines" (revised in 2023) published by the Ministry of the Environment 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.

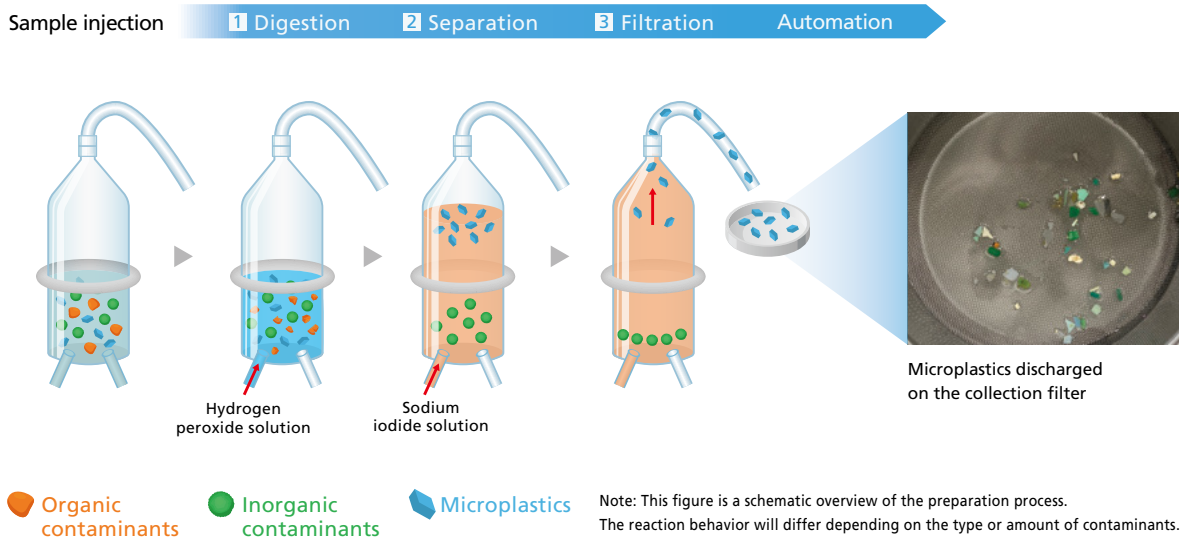


Fig. 1 Automated Sample Preparation Process

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.

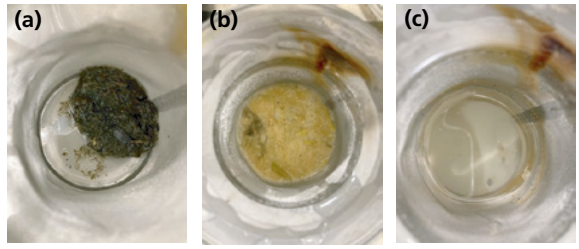


Fig. 2 Condition of Sample Before/After Preparation and During Digestion
(a) Before treatment, (b) During digestion (1 day after start of treatment), (c) After treatment

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

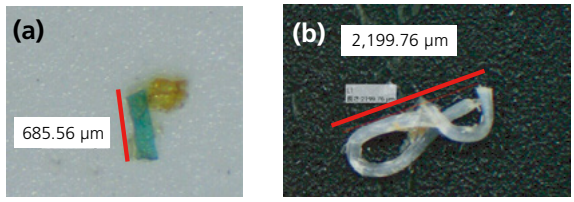


Fig. 3 Appearance of Microplastics

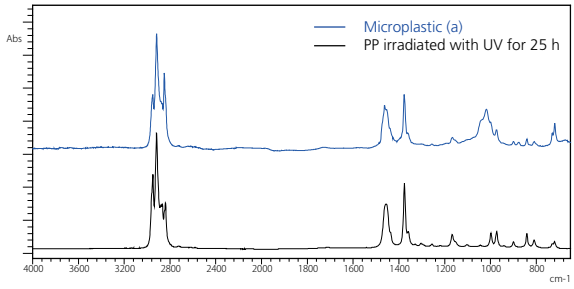


Fig. 4 Infrared Spectrum and Search Results for Microplastic (a)

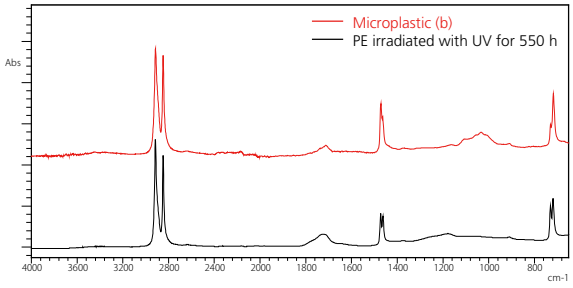


Fig. 5 Infrared Spectrum and Search Results for Microplastic (b)

MAP-100 Microplastic Automatic Preparation Device

The presence of microplastics in environmental surface waters such as oceans, rivers and lakes has been highlighted as an environmental problem all over the world. Microplastics research involves processes such as sample preparation, size and number measurement, and qualitative analysis. It is important to use the standard methodology for each process when comparing the results of the survey among analytical institutions. 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

Qualitative Analysis of Microplastics in Environmental Samples

For qualitative analysis of microplastics, one suitable analysis method is Fourier transform infrared (FTIR) spectroscopy since it excels at qualitative analysis of organic compounds. The Plastic Analyzer has a library that takes degradation conditions of microplastics in the environment into consideration, enabling anyone to perform highly accurate qualitative analysis with ease.

Application

Benefits

- By using the plastic analysis system "Plastic Analyzer", you can easily evaluate the deterioration of microplastics.
- Even those who are unfamiliar with FTIR measurement can easily analyze microplastics.

Qualitative analysis of degraded plastics in an environmental sample

Microplastics collected from rivers and oceans deteriorate due to ultraviolet rays. When plastic is exposed to ultraviolet light, its surface oxidizes and decomposes, changing its structure. In FTIR measurements, the infrared spectra of degraded plastics is different from non-degraded plastics. This makes it difficult for inexperienced analysts to distinguish between deterioration, mixtures, plastics, and deposits.

Microplastics collected in the ocean were measured by FTIR. Fig. 6 shows the appearance of the sample.

A search in a general library yielded standard PP hits with a match score of 918 out of 1,000 (Fig. 7). On the other hand, when using the UV-Damaged Plastics Library that reflects the degradation state, PP exposed to UV light for 50 hours was hit, and the match score increased by 25 points to 943 points (Fig. 8), showing that accurate qualitative analysis is possible with the UV-Damaged Plastics Library.

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

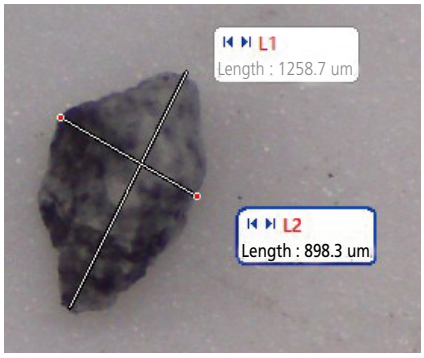


Fig. 6 Appearance of the Microplastic Sample

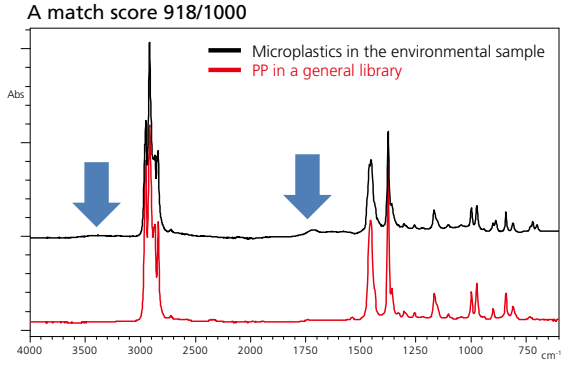


Fig. 7 Search Results Using a General Library

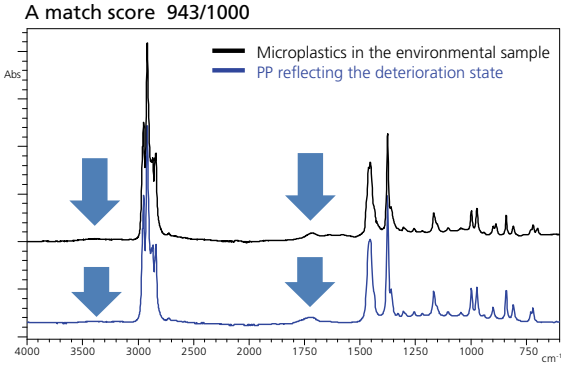


Fig. 8 Search Results Using the UV-Damaged Plastics Library

Degradation of Plastics

It is known that the surface of plastics is oxidized by ultraviolet rays and, at the same time, C=O groups, C-O groups, O-H groups, etc. are generated at the same time as when molecular scission occurs[1]. Fig. 9 shows the infrared spectra of polyethylene irradiated with ultraviolet light. The peak intensity at the arrow point increases from around the infrared spectra after 100 hours of irradiation. This is caused by the generation of functional groups due to degradation. Fig. 10 shows the infrared spectra of polypropylene irradiated with UV light. We can also confirm an increase in the peak intensity due to deterioration in the same way.

The UV-Damaged Plastics Library, which reflects the degradation caused by UV rays, is a unique Shimadzu library that contains a database of the infrared spectra of 14 types of plastics that have been exposed to UV radiation. Using a super-accelerated weathering chamber manufactured by Iwasaki Electric Co., Ltd., each plastic was irradiated with UV radiation at an intensity of 150 mW/cm^2 for 1 to 550 hours. This 550 hours of UV radiation by a super-accelerated weathering chamber is equivalent to about 10 years' worth of UV exposure. By reflecting the deterioration of microplastics in the environment in the infrared spectrum, highly accurate qualitative analysis becomes possible.

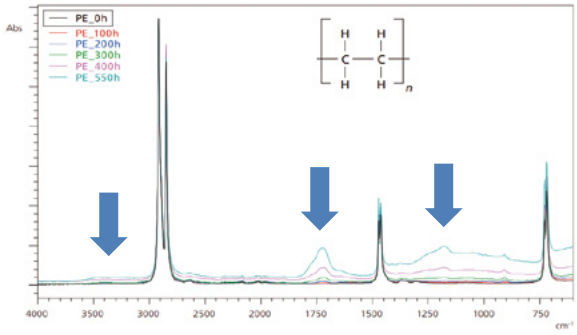


Fig. 9 Infrared Spectra of PE

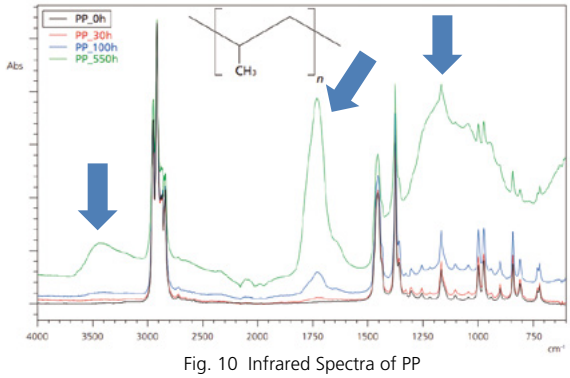


Fig. 10 Infrared Spectra of PP

Plastic Analyzer

Plastic Analyzer is a system consisting of a Shimadzu Fourier Transform Infrared Spectrophotometer: IRSpirit-X series, IRXross or IRTracer-100, Single Reflection ATR Attachment and Plastic Analyzer Method Package. The method package contains Shimadzu's unique UV-Damaged Plastics Library, Thermal-Damaged Plastics Library, and macro programs that include measurement conditions. In addition, the accompanying analysis handbook contains the structural formulas, infrared spectra, and characteristic peaks of 14 types of plastics, so anyone can easily start analysis regardless of their experience level.

IRSpirit-X Fourier Transform Infrared Spectrophotometer
QATR-S Single Reflection ATR Attachment

IRXross Fourier Transform Infrared Spectrophotometer
QATR 10 Single Reflection ATR Attachment

Product

Reference

(1) Nishioka Toshikatsu, Hamazaki Tatsuya, A Guide of Plastsic Analysis, Maruzen Publishing (2011)

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. 11 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

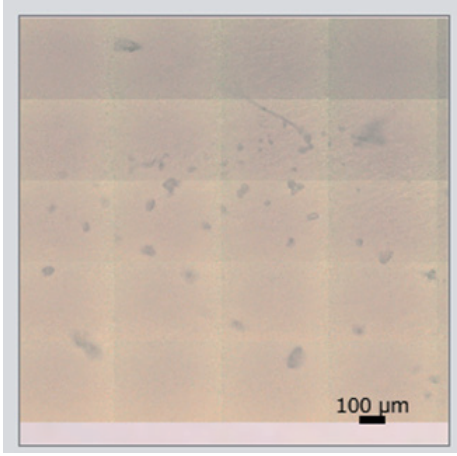


Fig. 11 Image of Microplastics on Filter Paper
Acquired with 15x Reflective Objective Lens

A mapping analysis of the microplastics collected on the filter paper was conducted by the transmission method with the AIMsight infrared microscope. Fig. 12 and Fig. 13 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. 12 was found to have a spectrum similar to that of polyethylene (PE) exposed to ultraviolet rays for 550 hours. Microplastics (b) in Fig. 13 was found to have a spectrum similar to that of polypropylene (PP) irradiated with ultraviolet light for 125 hours.

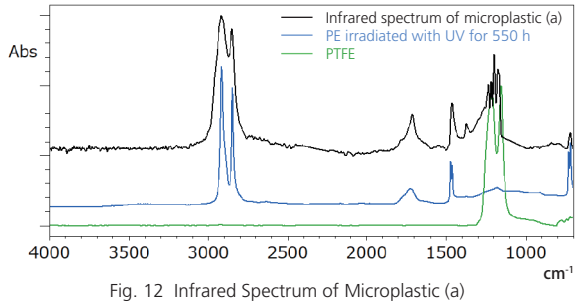


Fig. 12 Infrared Spectrum of Microplastic (a)
Acquired by Mapping Analysis and Search Results

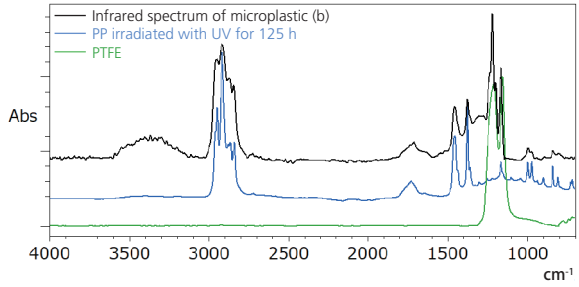


Fig. 13 Infrared Spectrum of Microplastic (b)
Acquired by Mapping Analysis and Search Results

Next, Figs. 14 (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.

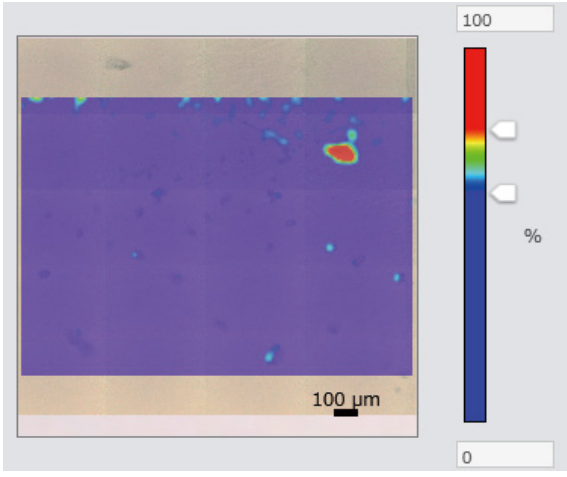


Fig. 14 (a) Distribution of PE
(Using corrected peak height of 718 cm^{-1} caused by rocking vibration of CH_2)

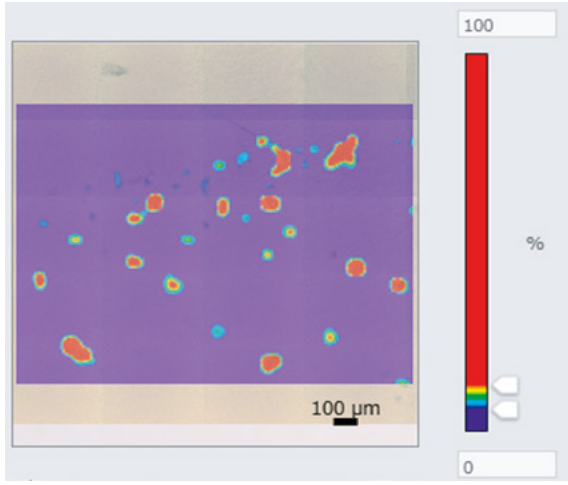


Fig. 14 (b) Distribution of PP
(Using corrected peak height of 1,373 cm^{-1} caused by symmetric bending vibration of CH_3)

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. 15 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. 15.

Fig. 15 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

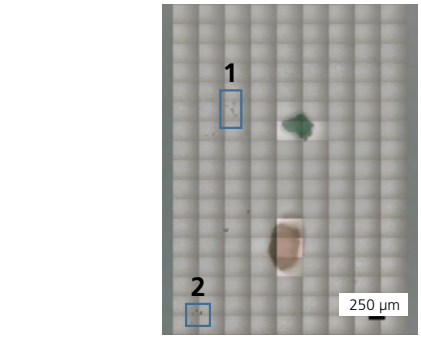
- By using AIRsight Infrared / Raman Microscope, analysis can be made on the same stage without moving the sample.
- Sample length can be measured from images acquired with a wide-field camera or an objective lens for infrared or Raman measurements.

Qualitative Analysis by Microscopic Infrared Spectroscopy

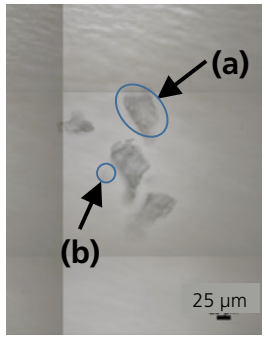
Fig. 17 shows images of microplastics (a), (b) and (c) on PTFE filter paper taken with the infrared and Raman objective lenses (Fig. 16). Microplastic (a) was measured by the transmission method with an infrared microscope. Fig. 18 shows search results using Shimadzu's unique UV-Damaged Plastics Library.

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

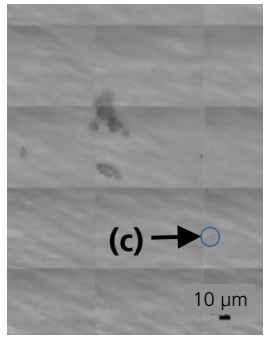


Fig. 17 Microplastic Image Taken with Objective Lens

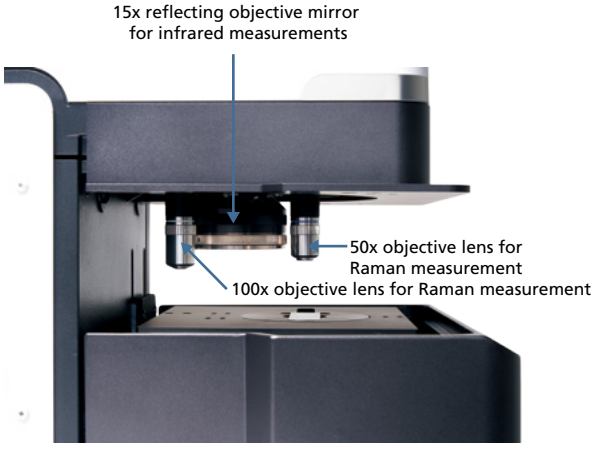


Fig. 16 Objective Lens for Infrared and Raman Measurements

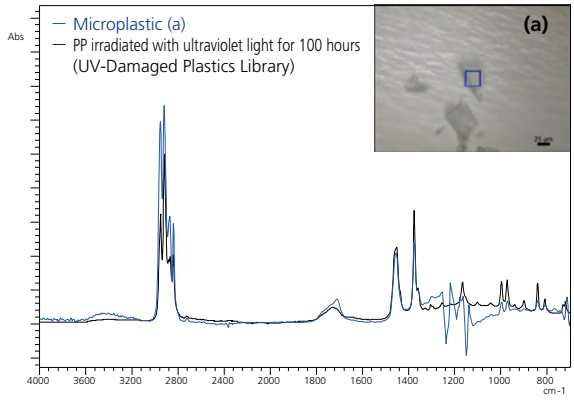


Fig. 18 Infrared Spectrum of Microplastic (a) on Filter Paper

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.19 and the resulting Raman spectra are shown in Fig. 20.

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

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

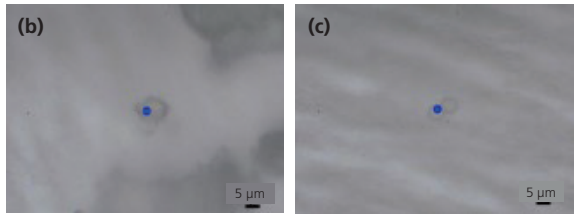


Fig. 19 Images of Microplastics (b) and (c) Taken with the Objective Lens

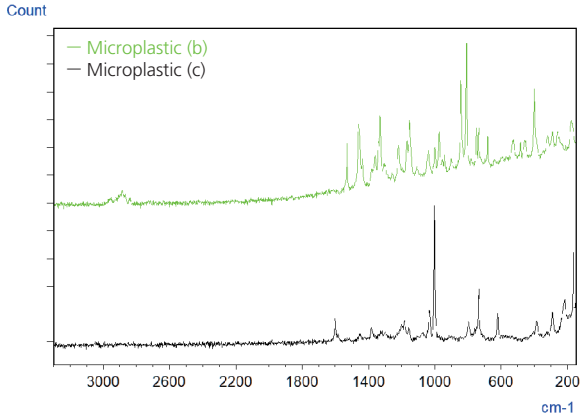


Fig. 20 Raman Spectra of Microplastics (b) and (c) on Filter Paper

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. 21. 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.

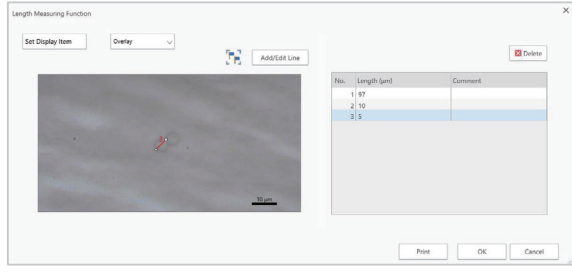


Fig.21 Length Measurement Operation Screen

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.

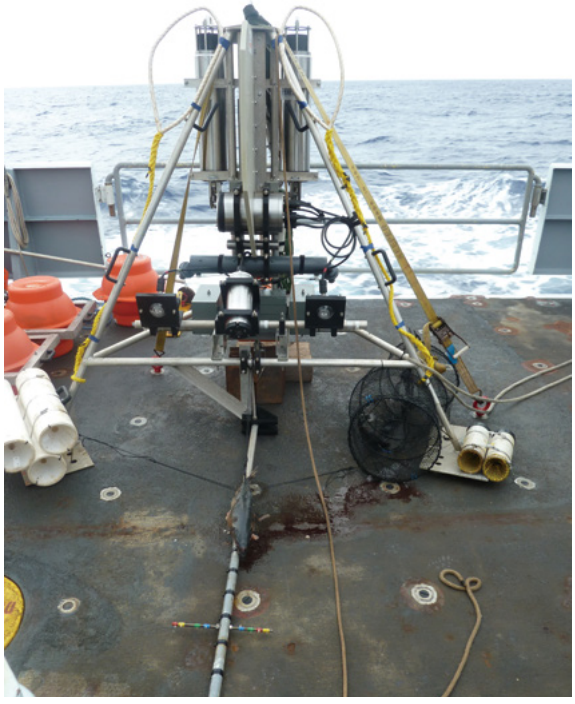
A group of scientists from Newcastle University in the UK and Wageningen Marine Research in the Netherlands collected the stomach contents of various marine creatures and separated microplastics of approximately 100 µm in size as part of a survey on the impact of marine debris [2].

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.



Marine Survey Equipment

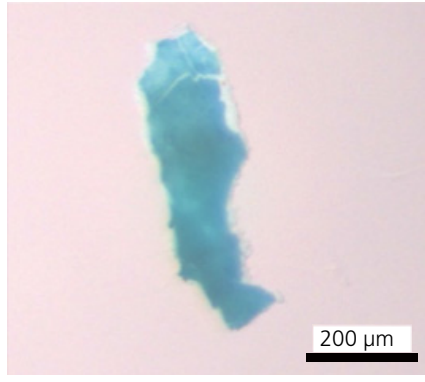


Fig. 22 Microplastic Collected from Polar Cod

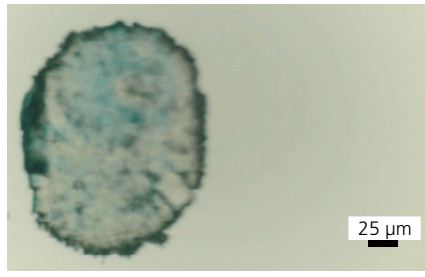


Fig. 23 Microplastic Collected from Deepwater Shrimp

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.

Deepwater Shrimp

Measurement Results

The blue microplastic piece collected from polar cod shown in Fig. 22 was measured with the microscopic ATR method (Fig. 24), and the microplastic piece collected from deepwater shrimp shown in Fig. 23 was compressed in a diamond cell and measured with the microscopic transmission method (Fig. 25).

From Fig. 24, 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. 25, 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. 22), 50 times (Fig. 23)
Apodization	: Happ-Genzel (Fig. 22) Sqr-Triangle (Fig. 23)
Aperture size	: 25 µm × 25 µm (Fig. 22) 15 µm × 15 µm (Fig. 23)
Detector	: MCT

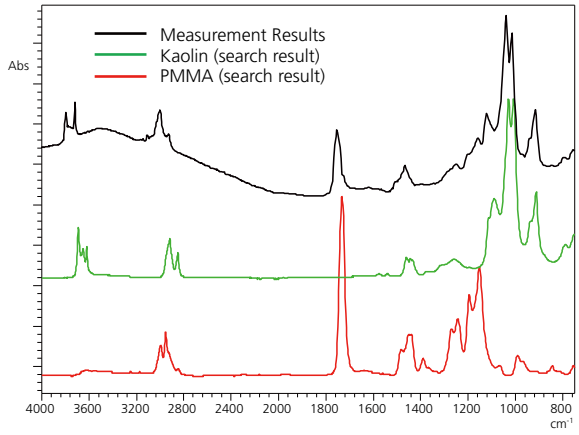


Fig. 24 Measurement Results for Microplastic Collected from Polar Cod

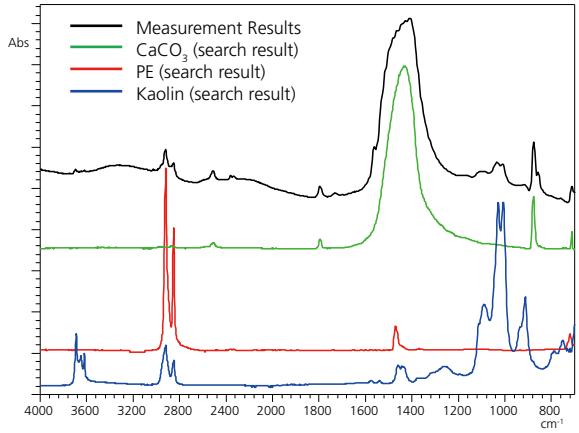


Fig. 25 Measurement Results for Microplastic Collected from Deepwater Shrimp

Reference

(2) 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

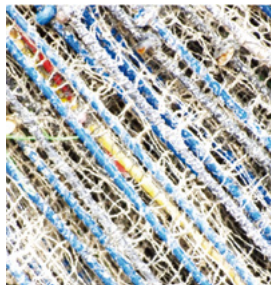
The causes of deterioration and breakup of fishing nets are contact with fish, algae, and stones in the sea and on beaches, as well as ultraviolet radiation from the sun. An example of a way to prevent this kind of naturally occurring damage is to give the surface of fishing nets used for aquaculture a protective coating of copper [3]. 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 [4].

Measurement Samples and Conditions

The measurement samples were fishing nets collected on the beach of Majorca island in Spain and others collected at a recycling plant. 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. 26). 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.



Fishing Net Used for Aquaculture

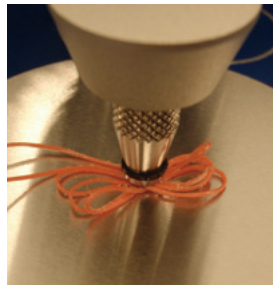


Fig. 26 ATR Measurement in Progress

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
Fourier Transform Infrared Spectrophotometer

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

Product

IRSpirit-X Fourier Transform Infrared Spectrophotometer
QATR-S Single Reflection ATR Attachment

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. 27 (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. 27 (c) and (d). In addition, the Cu content was estimated to be 15 wt% in the sample in Fig. 27 (c), and 8 wt% for the sample in Fig. 27 (d), which is more than others, so it could be inferred that it was part of a fishing net with a Cu protective coating.

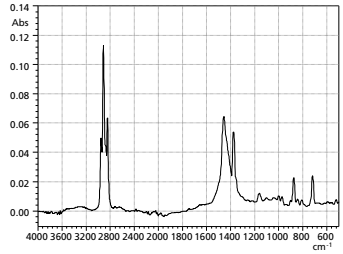
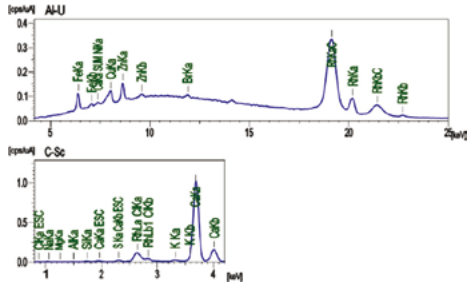
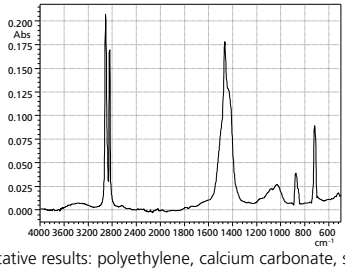
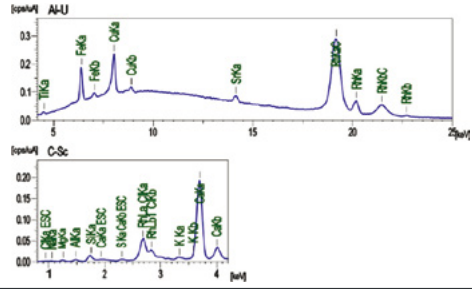
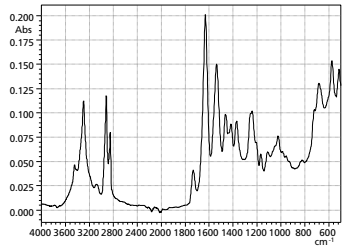
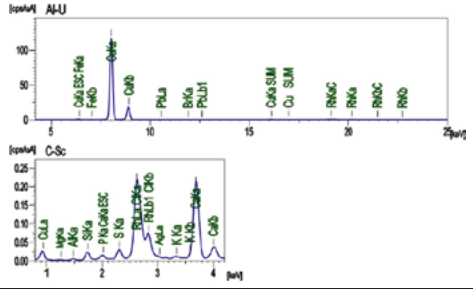
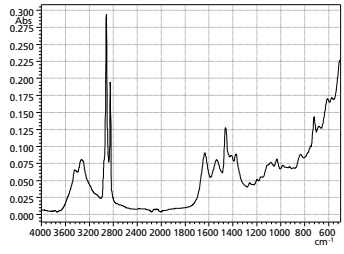
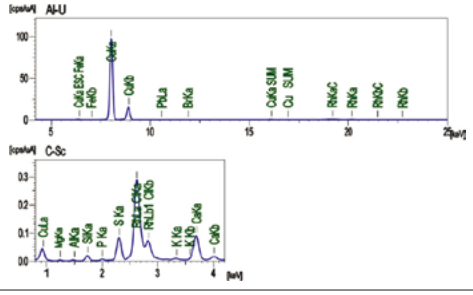
Measurement Samples	FTIR Measurement Results Infrared Spectrum	EDX Measurement Results Fluorescent X-ray Profile
(a) Collected at Playa de Muro, Majorca 	 Qualitative results: polyethylene, polypropylene	
(b) Collected at Playa de Muro, Majorca 	 Qualitative results: polyethylene, calcium carbonate, 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. 27 Measurement Samples and Measurement Results

References

(3) "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

(4) "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.

Qualitative and Elemental Analysis of Plastic Pellets

Large quantities of water are consumed for both domestic and industrial use each day. Although the Earth has abundant water resources, the amount of safe, drinkable water within these resources is extremely limited. Securing drinking water through the process of recycling wastewater is therefore a crucial issue.

The water treatment processes employed at wastewater treatment plants involve primary treatment for physically separating and removing solid material (physical treatment) and secondary treatment for removing organic matter using microorganisms (biological treatment). During biological treatment, cultivated microorganisms feed on the organic matter dissolved and suspended in wastewater which results in the oxidative decomposition of the organic matter. Plastic pellets (carriers for water treatment) serve the function of holding the microorganisms on the surface to improve purification of the wastewater. Plastic pellets play a role in purifying water used in a wide range of applications. However, there is concern that these pellets may turn into marine pollution (microplastics etc.) by flowing into the sea and river systems when heavy rain or other circumstances cause wastewater to overflow.

This article introduces an example of using FTIR and EDX to analyze plastic pellets before and after use in water treatment.

Application

Benefits

- FTIR can perform a qualitative analysis of organic compounds and some inorganic compounds, allowing quick determination of the main components in plastic pellets.
- Elemental information obtained using EDX can indicate detailed differences between materials, including the presence or absence of adhesions or additive consumption.

Measurement Samples and Conditions

Plastic pellets are approximately 5 mm in diameter, as shown in Fig. 28 (left). A large number of pores are visible upon inspection of the cross section as shown in Fig. 28 (right). Fig. 29 shows the measurement samples of unused and used plastic pellets. The used pellets have lost their original shape and exhibit significant unevenness on their surface. Analysis was performed using a system comprised of an IRTracer-100 Fourier transform infrared spectrophotometer connected to a Quest single-reflection ATR attachment and an EDX-8000 energy dispersive X-ray fluorescence spectrometer. There was no processing or special pretreatment of samples before analysis.

Fig. 28 (Left) Approx. 5-mm Diameter Plastic Pellet
(Right) Cross Section

Fig. 29 (Left) Unused (Right) Used

FTIR Measurement Conditions

Instruments	: IRTracer-100, Quest (Diamond prism)
Resolution	: 4cm^{-1}
Number of scans	: 100
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	: ø10 mm
Filter	: None
Integration time	: 100 seconds

IRXross
Fourier Transform Infrared Spectrophotometer

FTIR can perform a qualitative analysis of organic compounds and some inorganic compounds, so it can quickly determine the main components in plastic pellets.

Product

EDX-8100 X-ray Fluorescence Spectrometer

Elemental information obtained from EDX can indicate detailed differences between materials, including the presence or absence of adhesions or additive consumption.

Product

Measurement Results

Fig. 30 shows the results of measurement with FTIR and EDX. Measurement with FTIR was performed on both the sample surface and a cross section.

From the results of FTIR measurement, we found that the surface is a mixture of polyethylene and cellulose and the cross section is polyethylene for both the unused and used plastic pellets.

The results of qualitative and quantitative analysis using EDX show that $_{15}$P (red frame in Fig. 30) was detected in the unused plastic pellets but not in the used pellets. However, since there were no significant differences in composition between the two samples, we consider that contaminants that adhered to the surface or components that rubbed against the samples during use may be present in trace amounts.

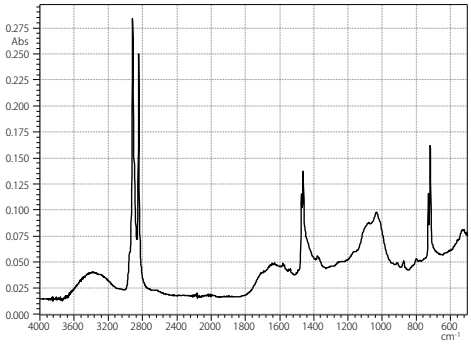
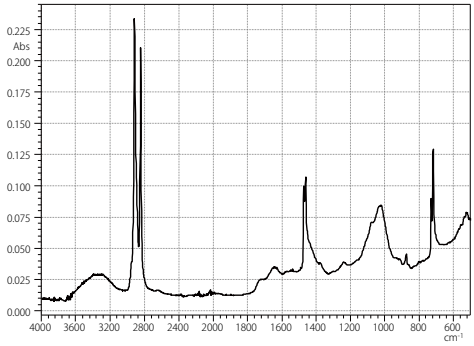
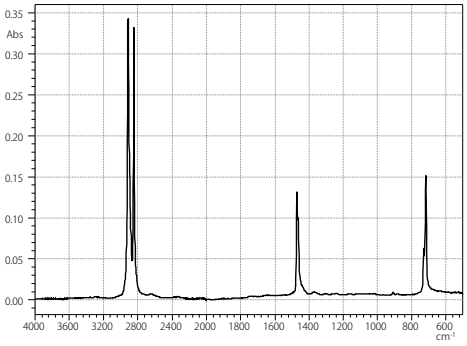
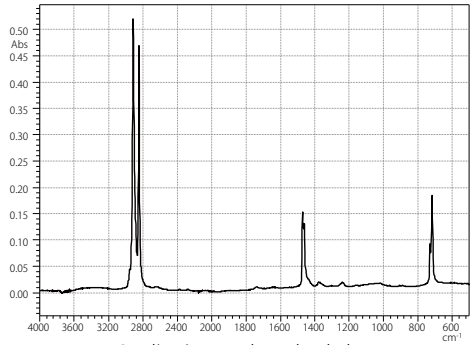
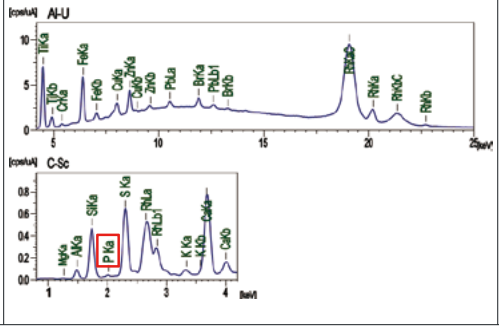
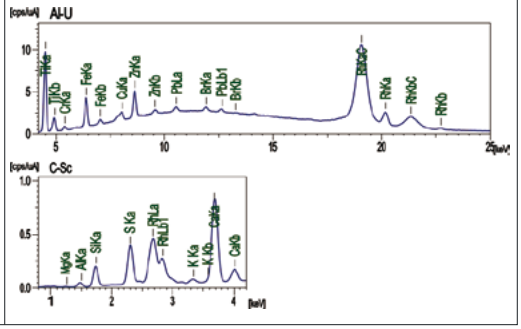
	Unused Plastic Pellets	Used Plastic Pellets
		
FTIR measurement result for sample surface Infrared spectrum	 Qualitative result: polyethylene, cellulose	 Qualitative result: polyethylene, cellulose
FTIR measurement result for sample cross section Infrared spectrum	 Qualitative result: polyethylene	 Qualitative result: polyethylene
EDX measurement result Fluorescent X-ray profile		

Fig. 30 Measurement Results

Acknowledgments

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

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. 31 shows some of the acquired particle images.

From Fig. 31, 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. 32 and Fig. 33 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. 33.

Measurement Conditions

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

Fig. 31 Particle Images

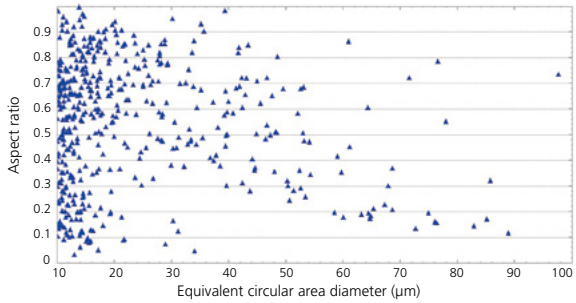


Fig. 32 Scattergram (Scatter Diagram)

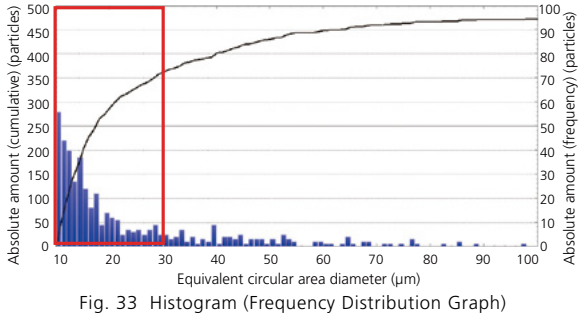


Fig. 33 Histogram (Frequency Distribution Graph)

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.

iSpect DIA-10

Product

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. 34 shows the visual observation image. As a result of the qualitative analysis of the infrared spectrum (Fig. 35) of the area in the red circle in Fig. 34, this particle was identified as polypropylene (PP).

Next, Fig. 36 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

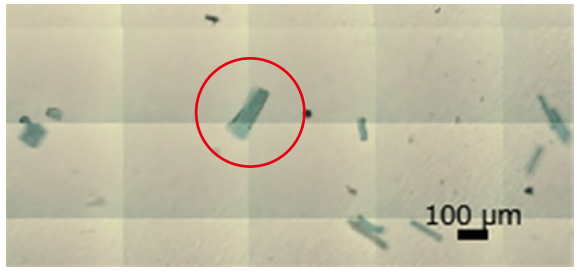


Fig. 34 Visual Observation Image

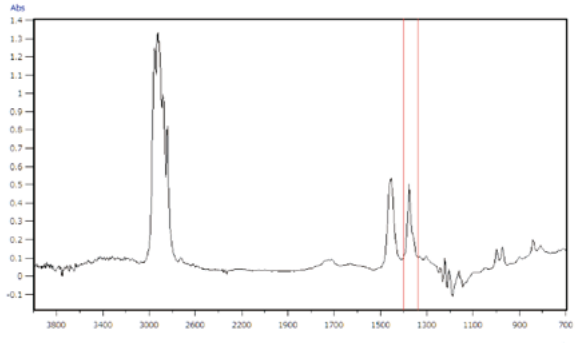


Fig. 35 Infrared Spectrum of Rod-like Microplastics
(The red box shows the peak used in preparing the chemical image in Fig. 36.)

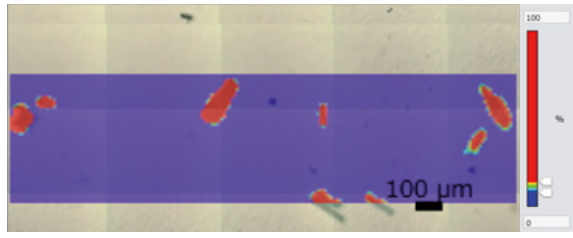
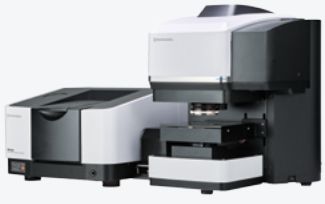


Fig. 36 Distribution of PP
(Corrected Area Value of 1,400-1,339 cm^{-1} Peak)

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. 37 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.

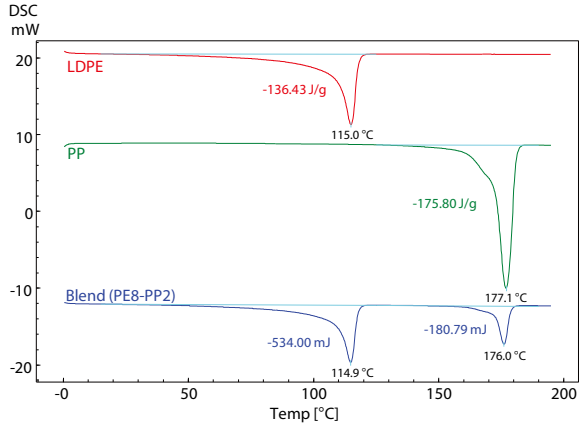


Fig. 37 DSC Curves of LDPE, PP, and Blend Sample

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. 38 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. 39 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.

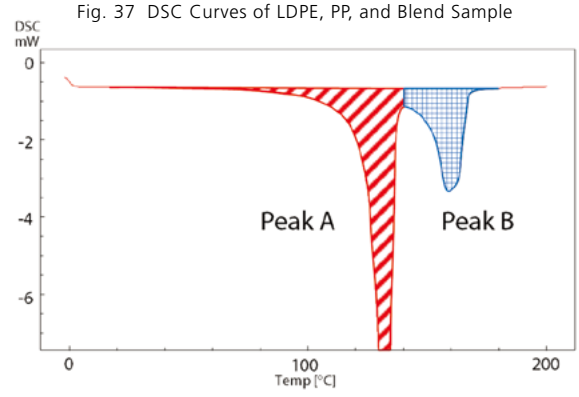


Fig. 38 Obtaining the Approximate Heat of Fusion

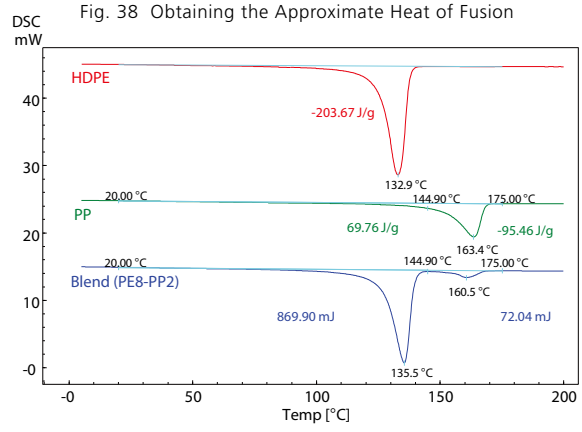


Fig. 39 DSC Curves of HDPE, PP, and Blend Sample

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. 40) 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. 41. 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

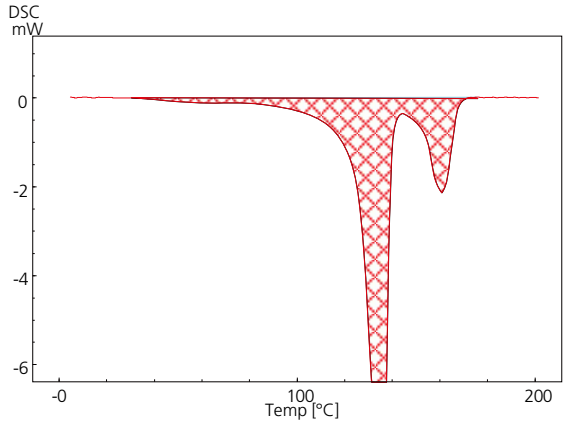


Fig. 40 Total Heat of Fusion of the Blend Sample

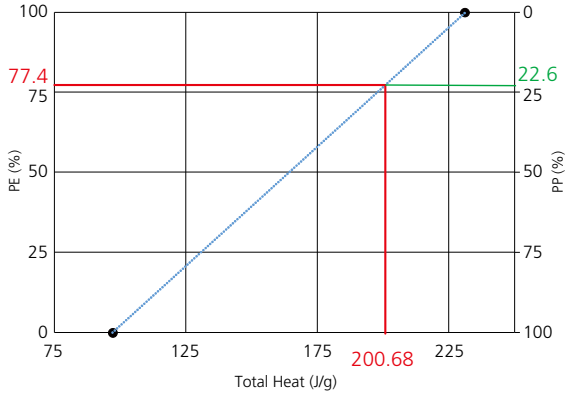


Fig. 41 Calibration Curve Determined from Separate HDPE and PP Samples

Qualitative Analysis of Mixed Polymer Samples

A Fourier transform infrared (FTIR) spectrometer is used in qualitative analysis of comparatively large microplastics, while an FTIR microscope is mainly used for fine microplastics which cannot be analyzed by the attenuated total reflectance (ATR) method of FTIR. An FTIR microscope enables highly sensitive analysis of fine microplastics with a size of approximately 10 µm. However, in cases where it is difficult to distinguish microplastics containing multiple types of fine particles, it has been reported that the pyrolysis gas chromatography/mass spectrometry (Py-GC/MS) method is effective. By using the Py-GC/MS method, qualitative analysis of individual polymers contained in mixed samples is possible due to highly sensitive detection of the distinctive pyrolysis products of each polymer.

Application

Benefits

- Analysis can also be performed when trace particles of different types are mixed together.
- Pyrolysis gas chromatograph mass spectrometers (Py-GC/MS) are useful when it is difficult to separate microplastics.
- The respective trace plastics in the mix can be qualitatively determined on an individual basis.

Measurement Samples and Conditions

This article reports on the results of a qualitative analysis of a sample, prepared by mixing multiple polymers to simulate microplastics, using the Py-GC/MS method. Approximately 0.05 mg each of fragments of four types of commercially-available standard polymer sample materials (polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC)) were introduced into a sample cup, and about 1 mg of wool was placed in the cup to prevent scattering. This sample was then set in the auto-shot sampler of the pyrolyzer. The Instruments and analytical conditions are shown below. According to References (5) and (6), the contents of the polymers were judged by detecting the pyrolysis products shown in Table 2 (however, some of these compounds were selected independently).

Measurement Conditions

[Instruments]

Pyrolyzer	: EGA/PY-3030D multi-shot pyrolyzer, AS-1020E auto-shot sampler (Frontier Laboratories Ltd.)
GC-MS	: GCMS-QP2020 NX
Column	: UA-5 (MS/HT)-30M-0.25F (Length 30 m, 0.25 mm I.D., df=0.25 µm) (Frontier Laboratories Ltd.)

[Pyrolyzer conditions]

Pyrolyzer furnace temp.	: 600 ˚C
Interface temp.	: 300 ˚C (Manual)

[GC conditions]

Vaporizing chamber temp.	: 300 ˚C
Column oven temp.	: 40 ˚C (2 min) - 10 ˚C/min - 320 ˚C (16 min)
Carrier gas	: Helium
Control mode	: Constant linear velocity
Injection mode	: Split (1:50)
Linear velocity	: 36.1 cm/min
Split Flow	: 100 mL/min
Purge flow rate	: 3 mL/min

[MS conditions]

Interface temp.	: 300 ˚C
Ion source temp.	: 230 ˚C
Ionization method	: EI
Measurement mode	: Scan/SIM (*m/z* 29 to 700)
Scan event time	: 0.3 sec
SIM event time	: 0.15 sec

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

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

Pyrolysis Analysis System

Pyrolysis gas chromatograph mass spectrometers (Py-GC/MS) can analyze trace samples of insoluble materials and composite materials in any form, including polymers, plastics, rubbers, paints, dyes, resins, coatings, cellulose, lumber, and fibers, all without the usual pretreatment.

Product

Measurement Results

Fig. 42 shows the total ion current chromatogram (TIC chromatogram) obtained by analyzing the mixed sample containing multiple polymers. Since the result of this analysis takes the form of a complex chromatogram in which the pyrolysis products of the respective polymers are intermixed, it was difficult to specify the individual polymers contained in the sample from this chromatogram alone.

Fig. 43 shows the SIM chromatograms of the pyrolysis products of the respective polymers. By tracing the distinctive pyrolysis products of the respective polymers, the contents of the polymers could be accurately specified, even multiple polymers that were intermixed in a sample.

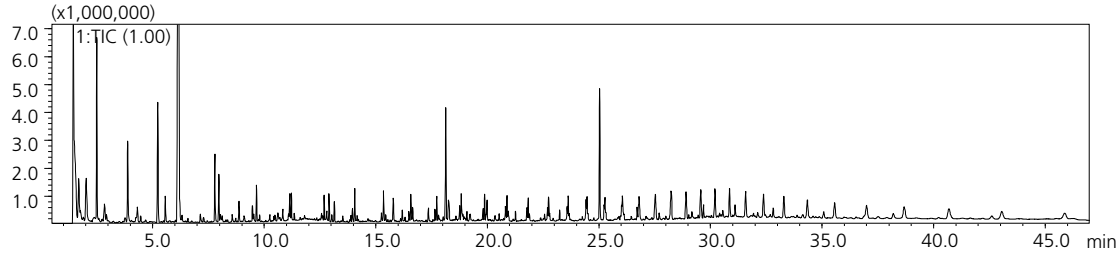


Fig. 42 TIC Chromatogram Obtained by Analysis of Mixed Polymer Sample by Py-GC/MS Method

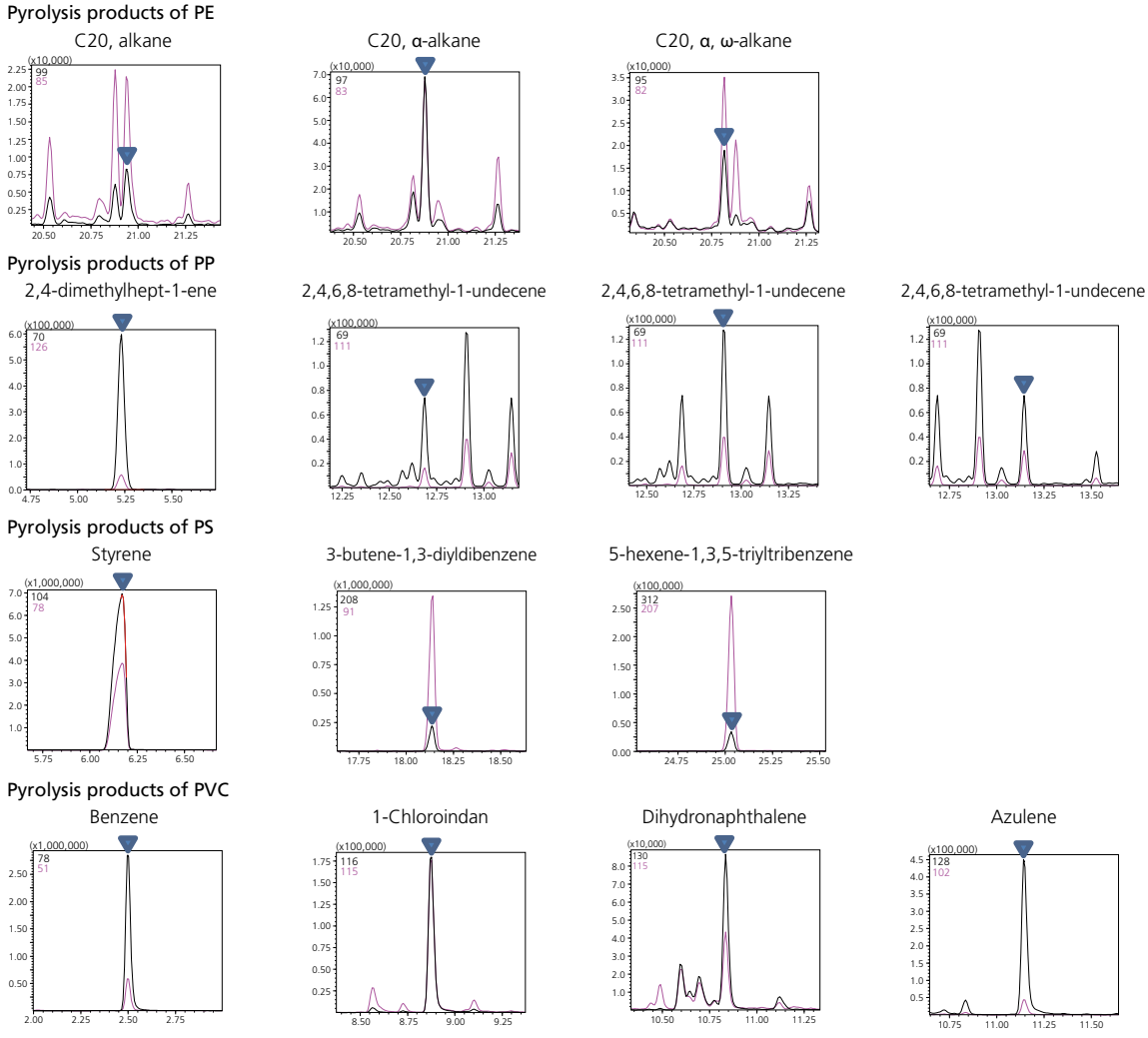


Fig. 43 SIM Chromatograms of Pyrolysis Products of Polymers in Mixed Polymer Sample

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

References

(5) M. Fisher and B. M. Scholz-Böttcher, Environ. Sci. Technol., 51, 5052–5060 (2017)

(6) S. Tsuge, H. Ohtani, C. Watanabe: Pyrolysis-GC/MS Data Book of Synthetic Polymers –Pyrograms, Thermorgams and MS of Pyrolyzers–, 1st Edition, Elsevier, 420 (2011)

Identification and Quantitation of Unknown Microplastics in the Environment

Microplastics are a concern because they are contaminating oceans and having an impact on ecosystems, so factual investigations and toxicity evaluations are being performed. ASTM International examines methods for testing microplastics using Py-GC/MS, looking to construct a workflow for screening analyses that can conveniently provide qualitative and quantitative analysis.

Here, calibration curve linearity, repeatability, recovery rates, and limit of quantitation were checked using the Py-GC/MS method for the 12 polymers with the largest volume of production worldwide.

Application

Benefits

- Microplastics in environmental samples can be qualitatively and quantitatively analyzed separately using the Py-GC/MS method.
- Calibration curves are easily created using microplastic calibration standard samples.
- Troublesome pretreatment procedures to separate out only the microplastics from the environmental samples are not needed.

Measurement Samples and Conditions

A microplastic calibration standard (MPs-$CaCO_3$ from Frontier Laboratories Ltd.) consisting of the 12 polymers with the largest volume of production worldwide was used as the sample. The ratios of the various plastics in the standard microplastic calibration sample are shown in Fig. 44.

The microplastic calibration standard was weighed using a balance and placed in a sample cup. Quartz wool weighing 1 to 2 mg was added to prevent scattering and the sample was analyzed. Samples (1) to (4) were prepared in line with the evaluation objectives (Table 3).

Table 3 Measurement Samples and Evaluation Purpose

Sample	Evaluation purpose	Sample weight (mg)	Number of repetitions
(1)	Calibration curve	0.2, 0.4, 0.8, 2.0, 4.0	n=4
(2)	Repeatability Percent Recovery	0.2	n=7
(3)	Lower limit of quantification	0.1, 0.2, 0.4, 0.6, 1.0	n=1
(4)	Calibration curve compatibility	0.8	n=4

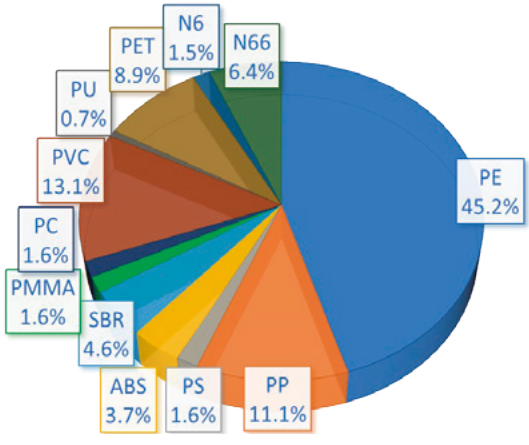


Fig. 44 Percentage of Polymer Composition in Microplastic Calibration Standard

Measurement Conditions

[Instruments]

Pyrolyzer	: EGA/PY-3030D multi-shot pyrolyzer, AS-1020E auto-shot sampler (Frontier Laboratories Ltd.)
GC-MS	: GCMS-QP2020 NX
Column	: UAMP Column Bracket (Frontier Laboratories Ltd.) UA precolumn 50: Ultra Alloy-50 (2 m x 0.25 mm I.D. x 1.0 µm) Separation column: Ultra Alloy-5 (30 m x 0.25 mm I.D. x 0.5 µm)

[Pyrolyzer conditions]

Pyrolyzer furnace temp.	: 600 ˚C
Interface temp.	: 300 ˚C

[GC conditions]

Injection port temp.	: 300 ˚C
Carrier gas	: He
Injection port mode	: Split mode (1:50)
Flow control mode	: Constant 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 conditions]

Ion source temp.	: 230 ˚C
Interface temp.	: 300 ˚C
Ionization method	: EI
Measurement mode	: Scan (*m/z* 29-350)
Event time	: 0.2 sec

Pyrolysis Analysis System

The pyrolysis gas chromatograph mass spectrometer (Py-GC/MS) can perform individual qualitative and quantitative analyses of multiple plastics, without requiring troublesome pretreatment to extract each of the microplastics individually.

Product

Measurement Results

The TIC chromatogram for a 4.0 mg microplastic calibration standard is shown in Fig. 45. Qualitative analysis was performed based on the degradation products characteristic of each plastic. The degradation products and retention times are shown in Table 4. Sample (1) was analyzed, and the area values for the quantitative ions with respect to the weight of each plastic in the microplastic calibration standard were used to create 12 calibration curves. The linearity (R^2) of the calibration curves was 0.9947 or larger for all the plastics, which is a favorable result (Table 4). The calibration curve for PE, one of the 12 plastics, is shown in Fig. 46.

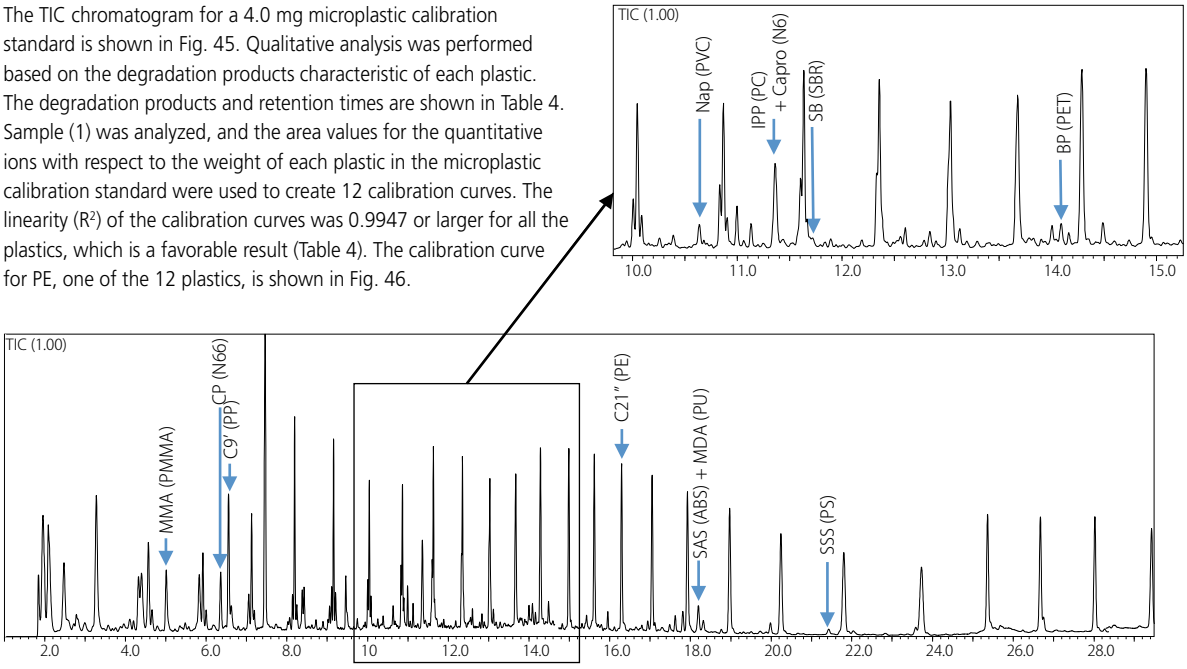


Fig. 45 Pyrogram of 4 mg Microplastic Calibration Standard Showing Elution Order of the 12 Characteristic Pyrolyzate

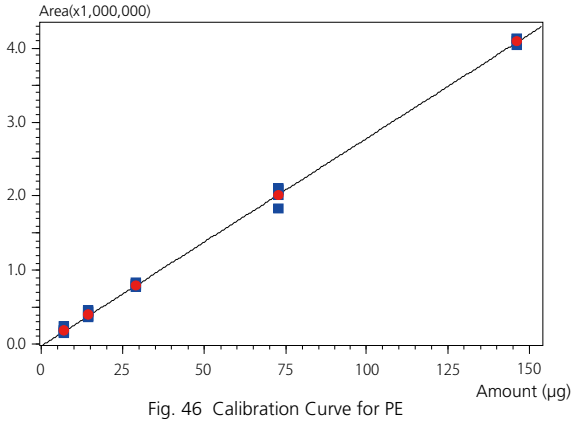


Fig. 46 Calibration Curve for PE

Sample (2) was analyzed, and the repeatability and recovery rate were checked. The weight of each of the plastics was calculated using the calibration curves created, and the relative standard deviation (%RSD) of the calculated quantitative values and recovery rate were checked. The %RSD ranged from 3.6 to 24 %, and the recovery rate ranged from 66 to 145 % (Table 4).

Sample (3) was analyzed, and the lower limit of quantitation (LLOQ) was checked. In this analysis, the weight resulting in a S/N ratio of at least 10 for the polymer with the lowest sensitivity of the 12 plastics was taken as the LLOQ. The LLOQ values for the 12 plastics ranged from 0.1 to 7.3 µg (Table 4).

Table 4 Summary of Method Performance

Polymer	Pyrolysis products	Retention time (min)	R^2	%RSD	Recovery (%)	LLOQ (µg)
PE	1,20-Heneicosadiene (C21')	16.2	0.9999	9.7	100	7.3
PP	2,4-Dimethyl-1-heptene (C9')	6.60	0.9999	9.2	111	1.8
PS	Styrene trimer (SSS)	21.3	0.9947	24	66	0.3
ABS	2-Phenethyl-4-phenylpent-4-enenitrile (SAS)	18.1	0.9999	7.8	107	0.6
SBR	4-Phenylcyclohexene (SB)	11.7	0.9997	6.8	122	0.8
PMMA	Methyl methacrylate (MMA)	5.00	0.9985	8.5	104	0.3
PC	4-Isopropenylphenol (IPP)	11.4	0.9999	7.1	123	0.3
PVC	Naphthalene (Nap)	10.6	0.9997	9.3	114	2.1
PU	4,4'-Methylenedianiline (MDA)	18.1	0.9972	3.6	145	0.1
PET	Benzophenone (BP)	14.1	0.9995	13	127	1.4
N6	ε-Caprolactam (Capro)	11.4	0.9998	11	112	0.3
N66	Cyclopentanone (CP)	6.40	> 0.999	8.1	122	1.0

Click here for an example of the analysis of microplastics in environmental samples.
Microplastics in a sample of dirt from the side of a road were analyzed without pretreatment.

Application

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[7), 8)]. 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. 47). 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. 48). The extracts obtained were injected into the GC-MS/MS and LC-MS/MS, respectively, for quantitative analysis of the PAHs and PFAS.

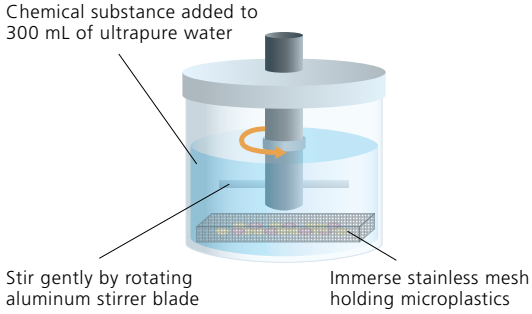


Fig. 47 Outline of Adsorption Test System

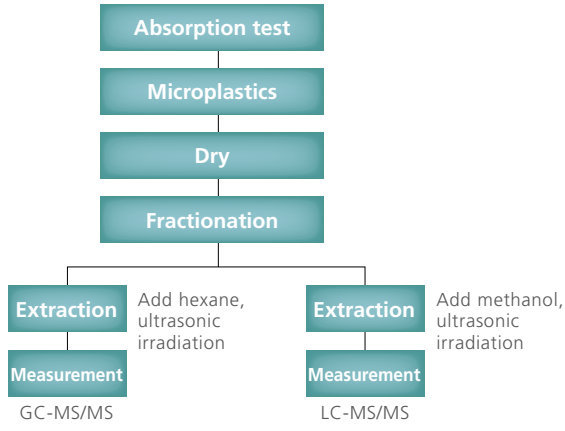


Fig. 48 Outline of Test Workflow

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 NX
Triple Quadrupole Gas Chromatograph Mass Spectrometer

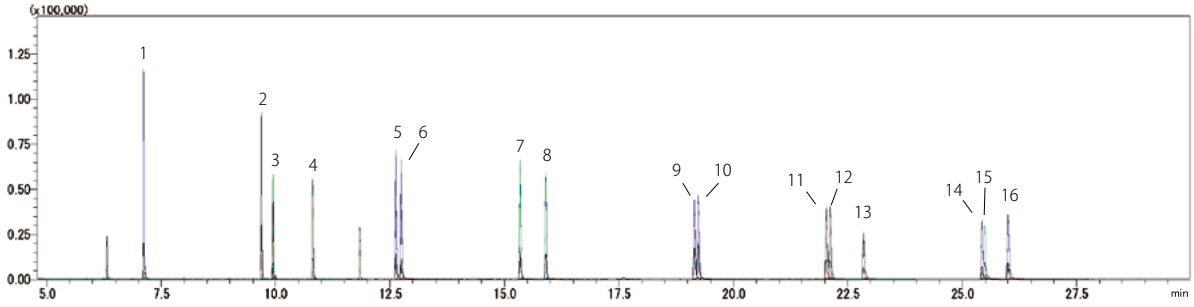
Product

LCMS-8060NX
Triple Quadrupole Liquid Chromatograph Mass Spectrometer

Product

Measurement Results

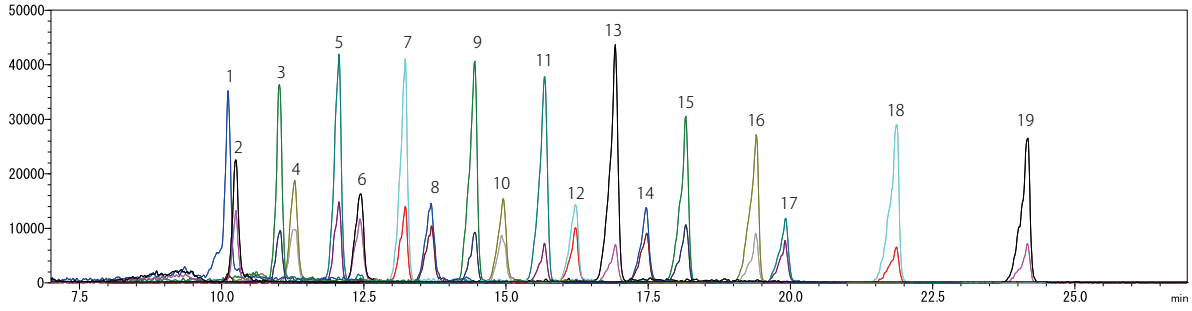
Fig. 49 shows the MRM chromatogram of the PAHs standard solution (2 ng/mL each) and Fig. 50 shows the MRM chromatogram of the PFAS standard solution (0.5 ng/mL each).



Compounds

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

Fig. 49 MRM Chromatogram of the PAHs Standard Solution (2 ng/mL each) (only target substances)



Compounds

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

Fig. 50 MRM Chromatogram of the PFAS Standard Solution (0.5 ng/mL each) (only target substances)

Fig. 51 shows the results of the analysis of PAHs with GC-MS/MS, and Fig. 52 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.

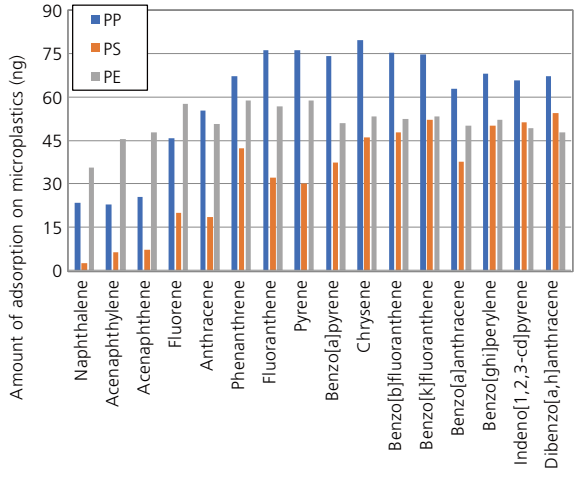


Fig. 51 GC-MS/MS Analysis Results: PAHs

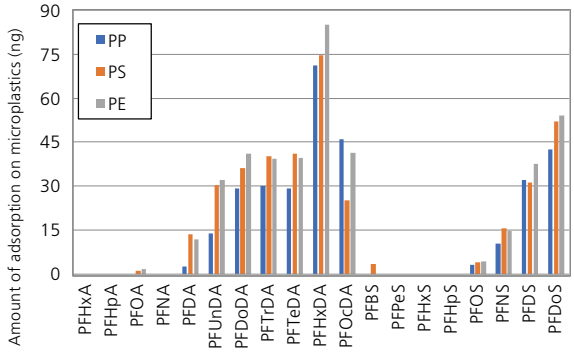


Fig. 52 LC-MS/MS Analysis Results: PFAS

References

(7) 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)

(8) 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 / 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

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