Application News

No. A613

Spectrophotometric Analysis

Measurement of Microplastics and Use of Thermal-Damaged Plastics Library

Microscopic plastic with a size of several µm to 5 mm or less is called microplastic. As a marine environmental problem that adversely affects coastlines and marine ecosystems, and consequently may potentially affect human health, microplastics have become a global issue in recent years. As early action is necessary to protect the global environment, various analytical devices are used to designate the sources of microplastics and study countermeasures.

Microplastics are classified into two types, primary microplastics and secondary microplastics. Primary microplastics refers to substances that are used as law materials in industrial abrasives, scrubbing agents, and the like. Polyethylene (PE) and polypropylene (PP) are frequently used in these applications. Secondary microplastics, on the other hand, are substances that are generated when large plastic products are reduced to a fine size of 5 mm or less by external factors such as ultraviolet radiation, and include various types of plastics.

The Fourier transform infrared spectrophotometer (FTIR) is generally used in qualitative analysis of plastics and is already utilized in surveys of the actual condition of discharges into rivers. However, since many actual microplastics are degraded in the environment, mainly by ultraviolet radiation, there may be no matches in analyses using a standard FTIR library.

This article introduces measurement of microplastics with a size on the order of several mm and use of the Shimadzu thermal-damaged plastics library to identify the samples.

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Instrument: IRSpirit™ Compact FTIR

The IRSpirit Fourier transform infrared spectrophotometer has a compact, portable body with dimensions of 390 (W) × 250 (D) × 210 (H) mm and a footprint smaller than an A3 size sheet of paper. Featuring a unique design that enables access from two sides, it can be installed vertically in narrow spaces with the 250 mm side as the front. In addition to offering the highest SN ratio and resolution in its class, the IRSpirit also has the widest sample compartment in its class. By allowing installation of Shimadzu accessories and other commercially-available accessories, this feature realizes high expandability.

In this measurement, we used a system in which a Shimadzu QATR™-S ATR measurement accessory was integrated with the IRSpirit sample compartment in the IRSpirit unit. Fig. 1 shows the appearance of the IRSpirit + QATR-S.

Fig. 1 Appearance of IRSpirit™ + QATR™-S

Measurement Sample

Fig. 2 shows microplastics collected at a sea coast. The microplastics have various shapes, including spherical and pellet-like, and also have different colors.

Fig. 2 Microplastics Collected at Sea Coast

Measurement Method: ATR Method

In the ATR method used with the FTIR, ATR is an abbreviation for Attenuated Total Reflection. An absorption spectrum of a sample surface can be obtained by placing the sample on the ATR prism and measuring the total light reflected by the sample surface. The light penetration depth in ATR is several µm. Fig. 3 shows the condition of measurement.

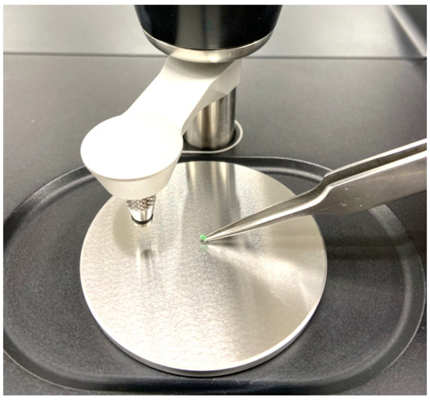

Fig. 3 Condition of ATR Measurement

Thermal-Damaged Plastics Library

The Shimadzu thermal-damaged plastics library is a library containing spectral data for 13 types of plastic in the unheated condition and when heated to various temperatures from 200 °C to 400 °C.

Degradation of plastics begins from the formation of carbon-centered radicals as a result of dissociation of hydrogen from carbon-hydrogen bonds caused by the energy of heat or light. When oxygen reacts with the radicals, formation of additional radicals and dissociation of hydrogen occur in a kind of chain reaction, and inert substances are also formed by bonding between pairs of radicals. Plastics are degraded by this process, which is accompanied by molecule scission and crosslinking [(1)]. Although large differences in the progress of degradation can be seen in ultraviolet degradation and thermal degradation, the factors that govern the progress of degradation are essentially the same [(2)]. Since the changes that occur in the infrared spectrum are often similar, the thermal-damaged plastics library can also be used in qualitative analysis of ultraviolet-degraded microplastics in many cases.

Fig. 4 shows the infrared spectra of acrylonitrile butadiene styrene (ABS) resin when irradiated with ultraviolet light, and Fig. 5 shows the infrared spectra of ABS resin when subjected to heating. In the case of ABS, peaks associated with stretching vibration of the OH radical and C=O radical appear under both ultraviolet and thermal conditions, showing that oxidative degradation occurs due to exposure to ultraviolet radiation and heat.

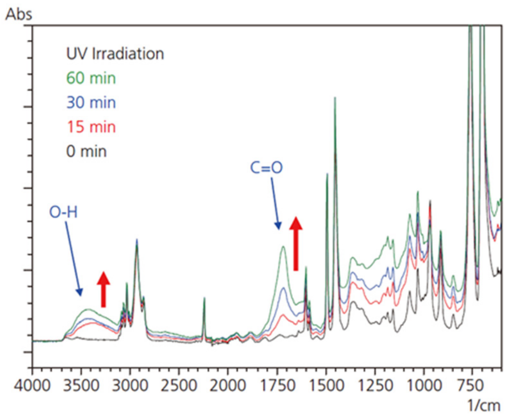

Fig. 4 Infrared Spectra of ABS Resin (Ultraviolet Irradiation)

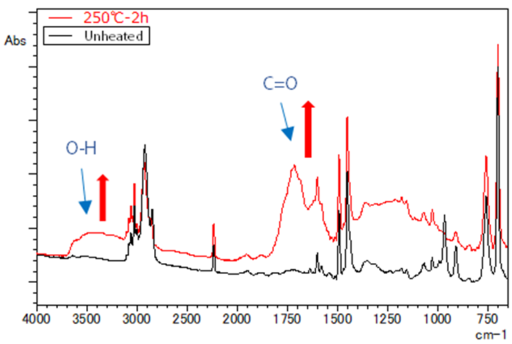

Fig. 5 Infrared Spectra of ABS Resin (Heating)

Measurement Results

Among the microplastics collected at the sea coast, those with sizes of 5 mm or less were measured. Table 1 shows the measurement conditions, and Fig. 6 and Fig. 7 show images of the samples and the measurement results for two samples.

From the results in Fig. 6, a hit for polypropylene (PP) heated at 200 °C for 4 h was obtained from the thermal-damaged plastics library for the white microplastic, and from Fig. 7, a hit for polyethylene (PE) heated at 200 °C for 2 h was obtained for the red microplastic. It can be inferred that both microplastics were degraded by oxidative degradation caused by ultraviolet radiation.

Table 1 Measurement Conditions

Instruments	: IRSpirit-T, QATR-S (diamond prism)
Resolution	: 4 cm^{-1}
Accumulation	: 40 times
Apodization function	: Happ-Genzel
Detector	: DLATGS

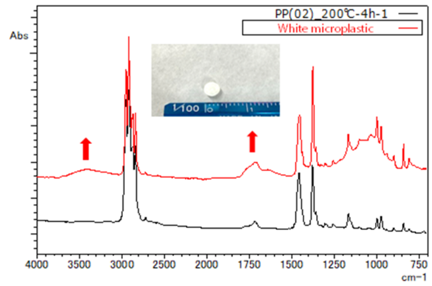

Fig. 6 Measurement Result and Library Search Result for White Microplastic

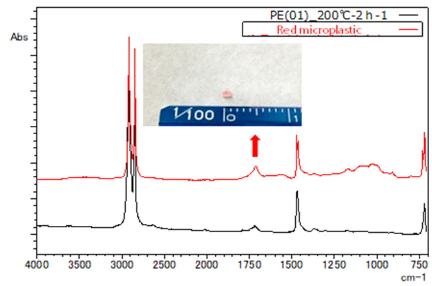

Fig. 7 Measurement Result and Library Search Result for Red Microplastic

Conclusion

Microplastics collected at a sea coast were measured with a compact IRSpirit FTIR. Simple and easy measurement was possible by the ATR method. Quick qualitative analysis of degraded microplastics was also possible by using the Shimadzu thermal-damaged plastics library.

In cases qualitative analysis by a more certain method is desired, we recommend measuring plastic which has been intentionally degraded by ultraviolet irradiation and comparing that sample with the actual sample.

<References>
(1) Hiroshi Yamanoi (2007), The Mechanisms of Polymer Degradation Discoloration and Stabilization, Journal of the Materials Life Society, Japan, 19(3), 103-108.
(2) Yoshio Oki (1973), Degradation of Plastic Materials, Journal of the Metal Finishing Society of Japan, 24(4), 229-238.

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