

Identification of Environmentally Degraded Microplastics Using the Thermal-Damaged Plastics Library

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1. Introduction

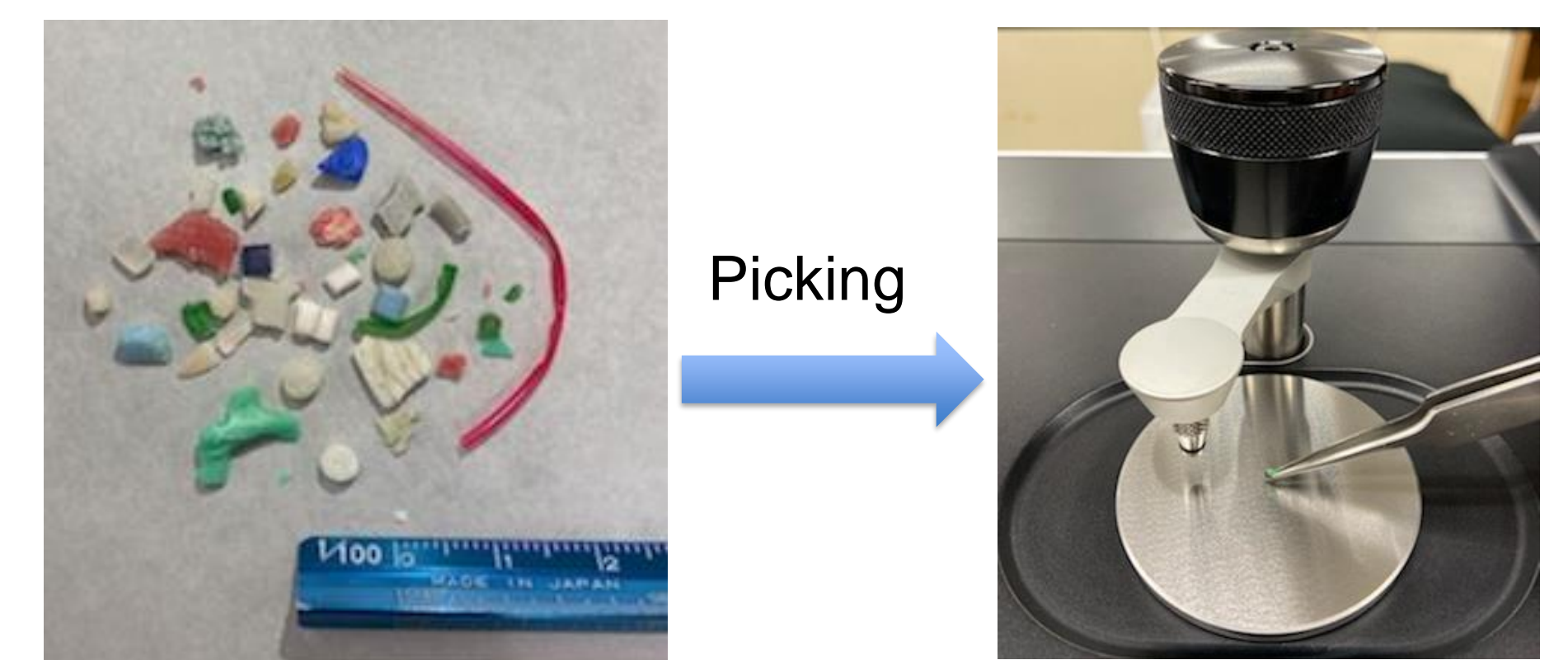
Microplastics are classified into two types, primary microplastics and secondary microplastics. Primary microplastics refers to substances that are used as raw materials in industrial abrasives, scrubbing agents, and so on. Polyethylene (PE) and polypropylene (PP) are frequently used in these purposes. Secondary microplastics are usually generated when large plastic products are reduced to a fine size of 5 mm or less by external factors such as ultraviolet radiation in the environment. There are several analytical instruments well known in the microplastic researches, and one of them is the Fourier transform infrared spectrophotometer (FTIR).

FTIR is generally used in the identification of plastics and is already utilized in many surveys of the actual condition of microplastic discharges into rivers or sea. However, since actual microplastics are normally degraded in the environment, mainly by ultraviolet radiation, there may be less matches with the infrared spectra referring from a standard FTIR library. In order to provide highly reliable identifications, the thermal-damaged plastics library has been introduced and utilized for real microplastics sampled from the environment.



2. Apparatus / Method

The compact FTIR, IRSpirit (Shimadzu Corporation), was used for the identification of microplastics with the QATR™-S ATR measurement accessory for the ATR method. ATR stands 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 reflected IR beam at the sample surface. The light penetration depth in ATR is several μm .

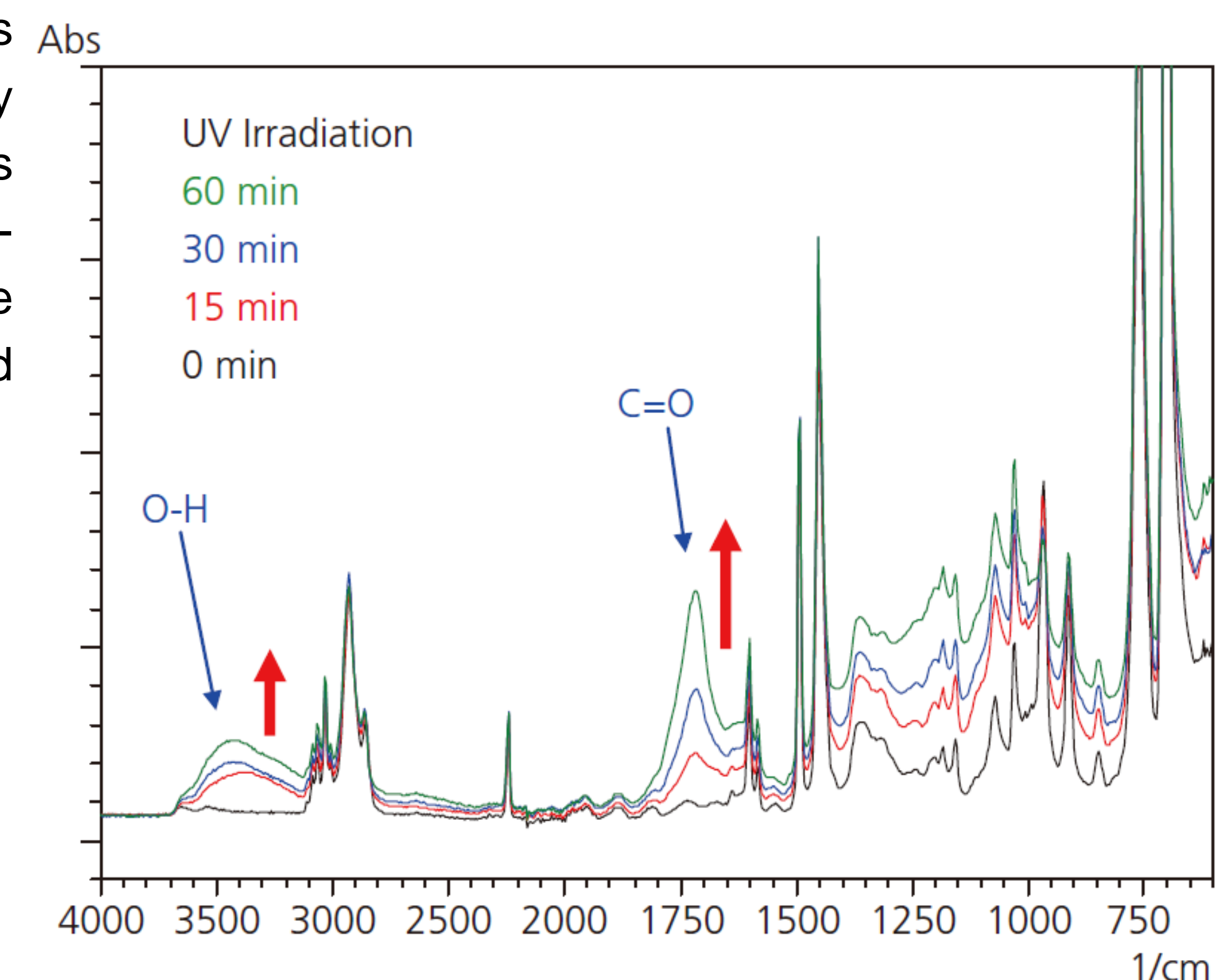


3. Thermal-Damaged Plastics Library

The thermal-damaged plastics library is a library containing spectral data of 13 types of plastics 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 radicals with the dissociation of hydrogen from carbon-hydrogen bonds caused by the energy of heat or light. Reaction of the oxygen connecting to those radicals generates different components with bonds like O-H and C=O, which shows specific absorption spectrum. This reaction process causes cross-linking and molecular scission, resulting to the degradation of plastics. Due to the reaction in the plastics, the FTIR analytical result often shows some differences in the infrared spectra between standard plastics and degraded plastics.

In fact, 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. So we can see that the changes observed in the infrared spectrum are often similar. Due to this experience, the thermal-damaged plastics library has been introduced and utilized for real microplastics sampled from the environment.

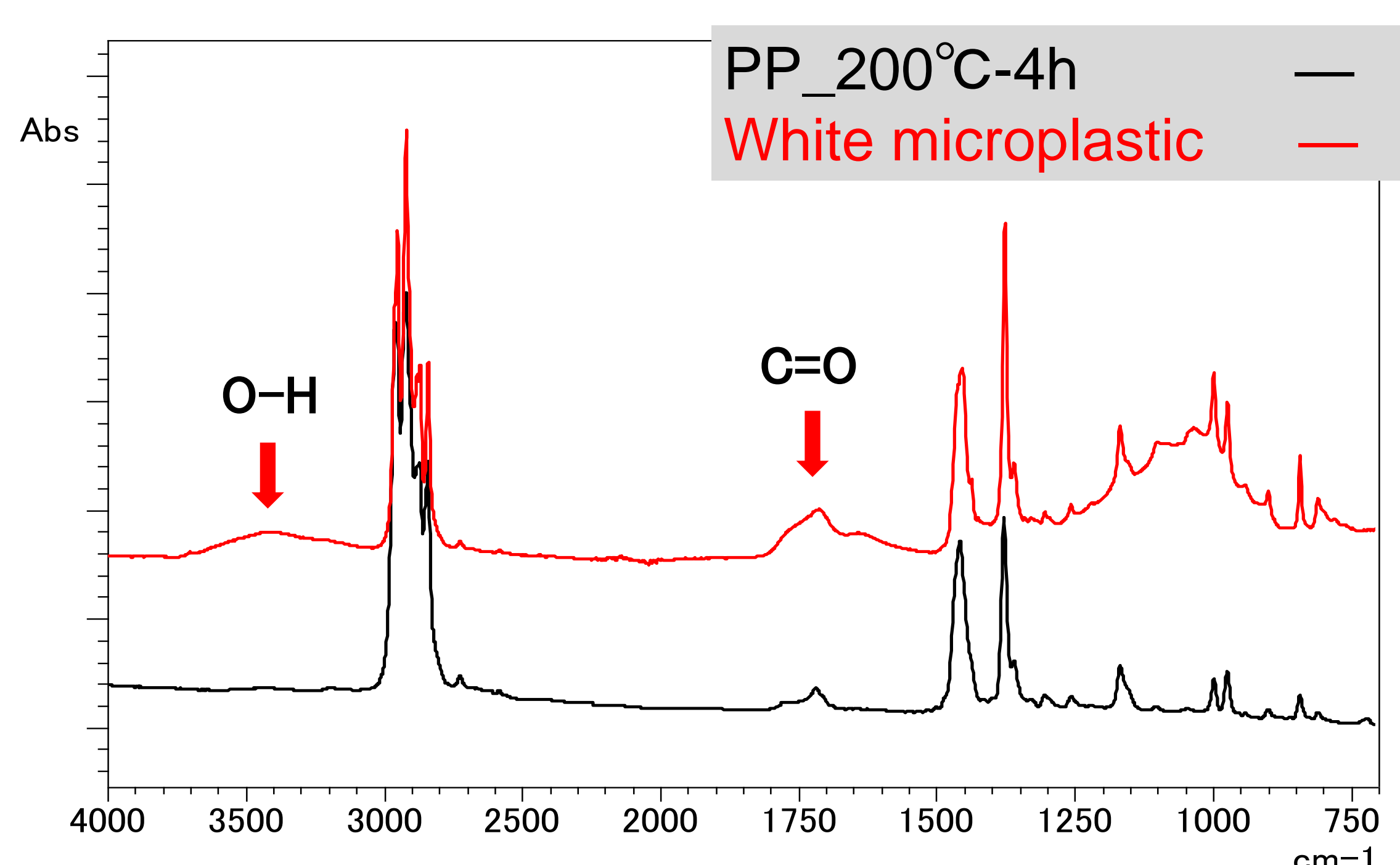
Right figure shows the infrared spectra of acrylonitrile butadiene styrene (ABS) resin when irradiated with ultraviolet light. In the case of ABS, peaks associated with stretching vibration of the O-H radical and C=O radical appear under ultraviolet conditions. Same experiment was tested under heat condition, 250 degrees for 2 h, and similar phenomena was observed in the spectrum.



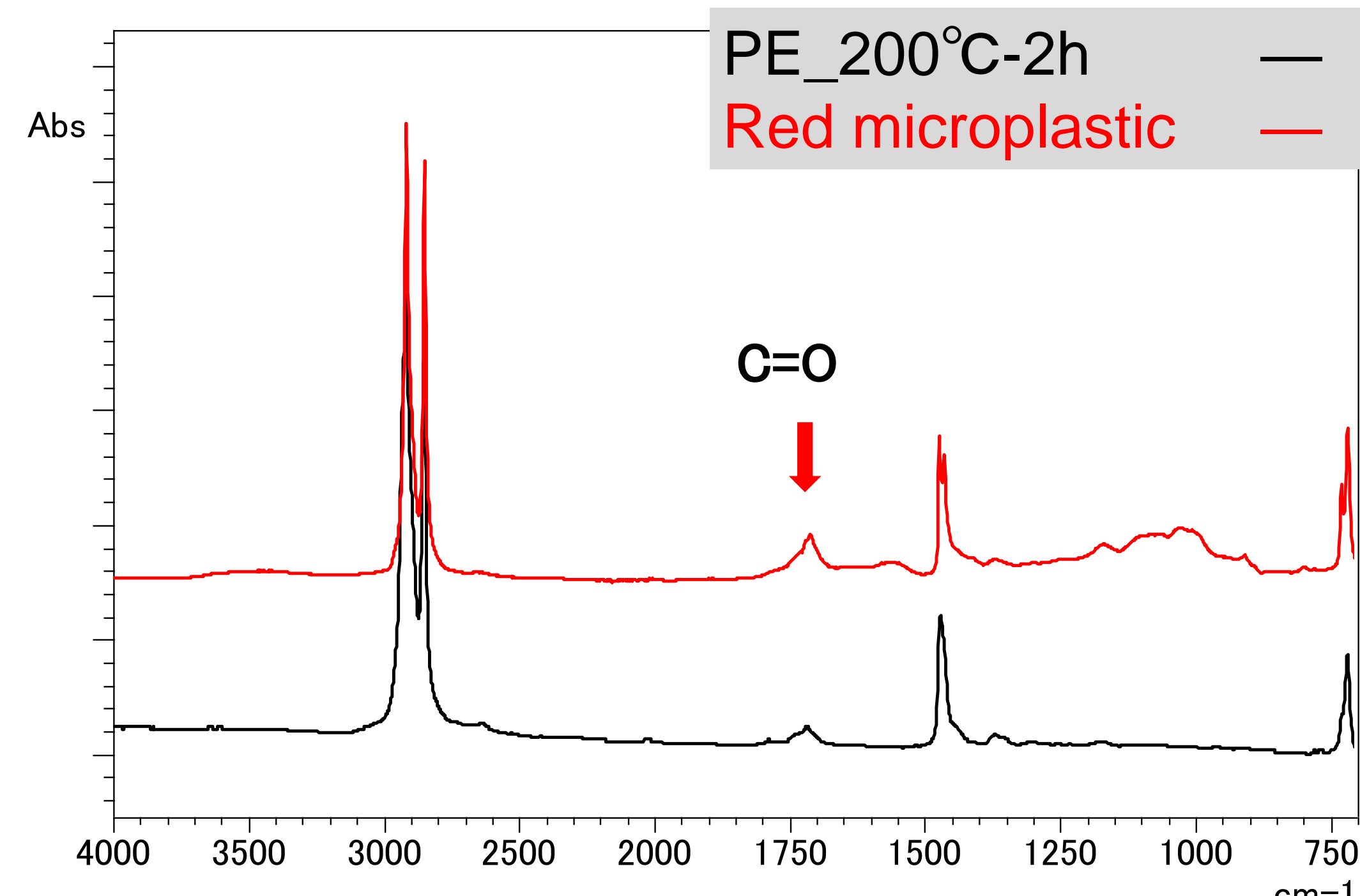
4. Result

Among the microplastics collected at the sea coast, those with sizes of 5 mm or less were measured. 2 sample measurement results are shown below.

From the results in left figure, 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 right figure 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.



Identification: Polypropylene
Spectrum: due to the effects of degradation, O-H and C=O absorption were confirmed



Identification: Polyethylene
Spectrum: due to the effects of degradation, C=O absorption was confirmed

5. Conclusion

Microplastics collected at a sea coast were measured with a compact FTIR. Simple and easy measurement was possible by the ATR method. Quick qualitative analysis of degraded microplastics was also possible by using the thermal-damaged plastics library. But in case of desiring higher accurate identification, we recommend measuring plastic which has been intentionally degraded by ultraviolet irradiation and comparing that sample with the actual sample. This is our next challenging task to be solved.

