Dual Microscopy Technique for the Analysis of Microplastics

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1. Introduction

Microplastic pollution of rivers and oceans is spreading globally, and there are concerns about its impact on living organisms. In recent years, monitoring surveys and research have been conducted to gain scientific knowledge about the distribution of microplastics in many countries worldwide. When exposed to UV light, rain, wind, and physical friction that makes it brittle, the plastic released into the environment breaks up into even smaller microplastics; these particles are called secondary microplastics. Generally, microplastics are evaluated by observing their appearance, measuring their number and size, and qualifying their materials. Among these items, qualitative measurement of the material is one of the most important parameters for identifying the origin of the microplastic. Fig. 1 shows a decision tree tool for selecting the proper analytical instrument for analyzing microplastics according to the project' goals. Fig. 2 shows the analytical techniques traditionally used for analyzing microplastics based on the size that can be properly measured. The newly developed AIRsight Infrared/Raman microscope is an instrument that incorporates a Raman unit into an infrared microscope, enabling scientists to benefit from the use of the two techniques in one single platform. In addition to the increased sensitivity Raman grants, this instrument provides two lines of evidence for identifying the nature of the polymers constituting the particles. In this poster, we demonstrate performance of this dual technique for analyzing microplastics in environmental samples.

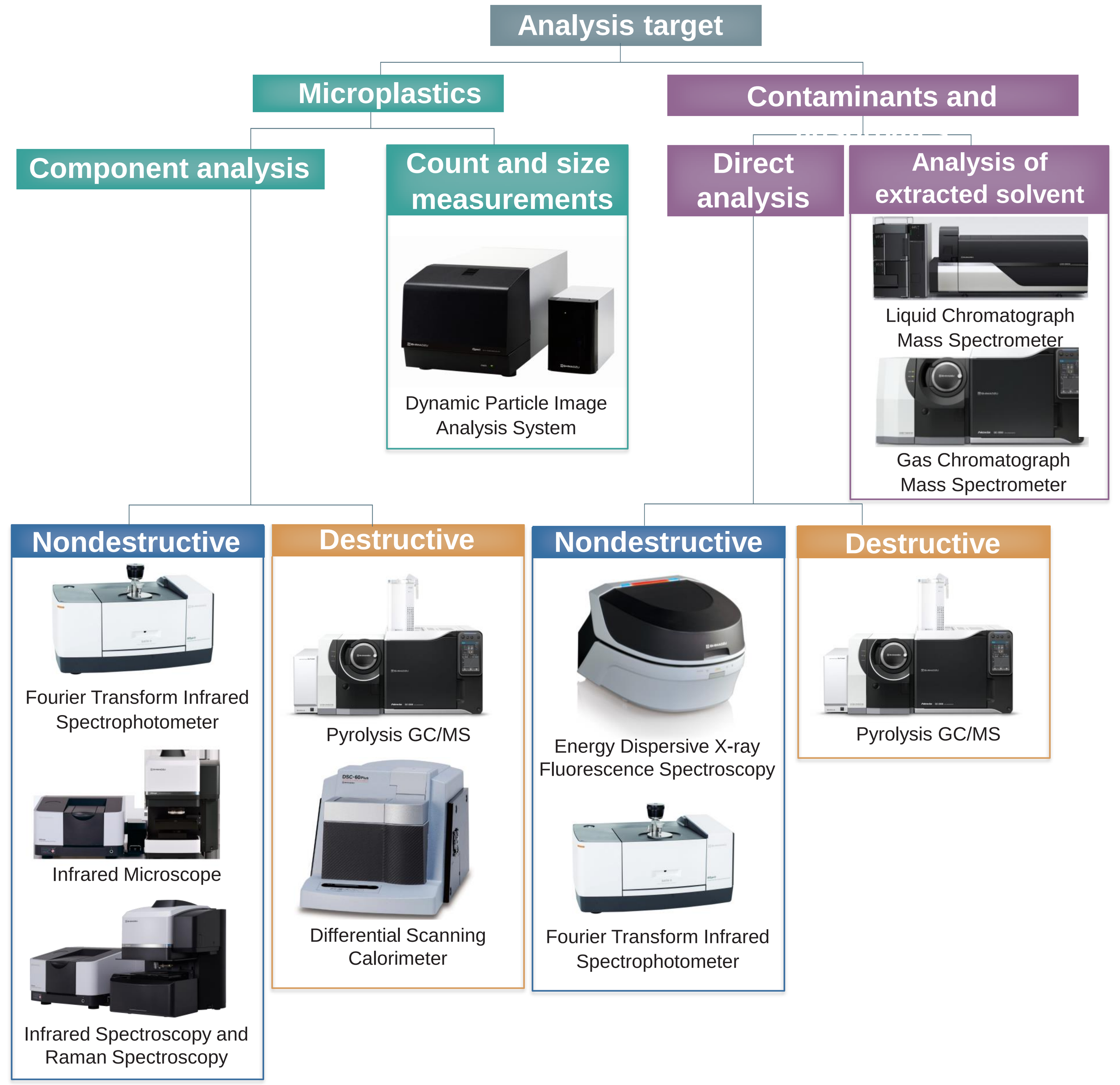
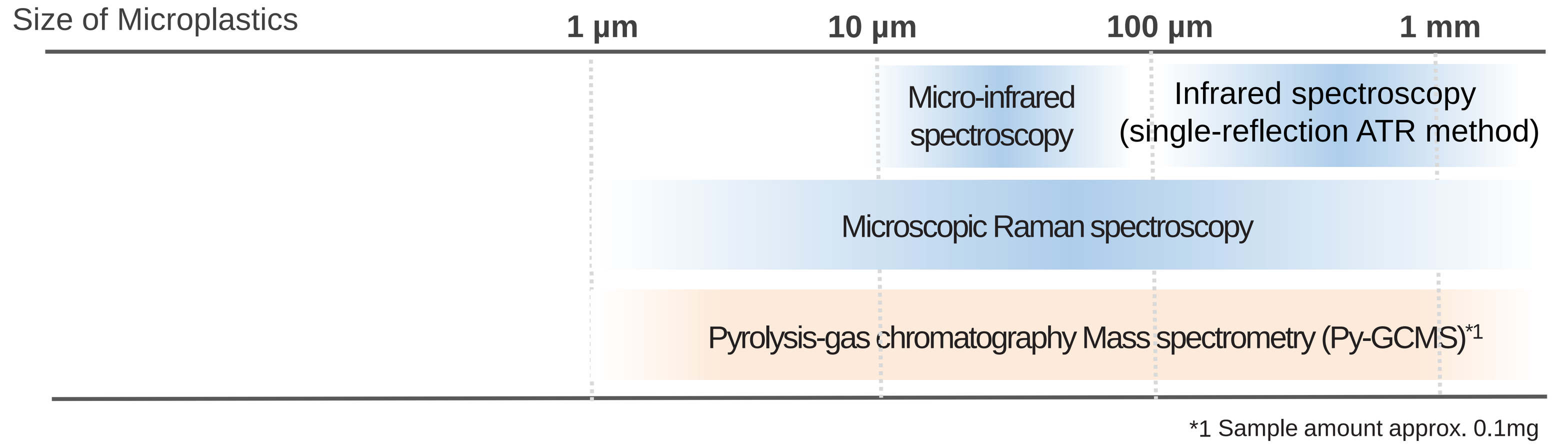


Figure 1. Decision tree for the selection of analytical instruments



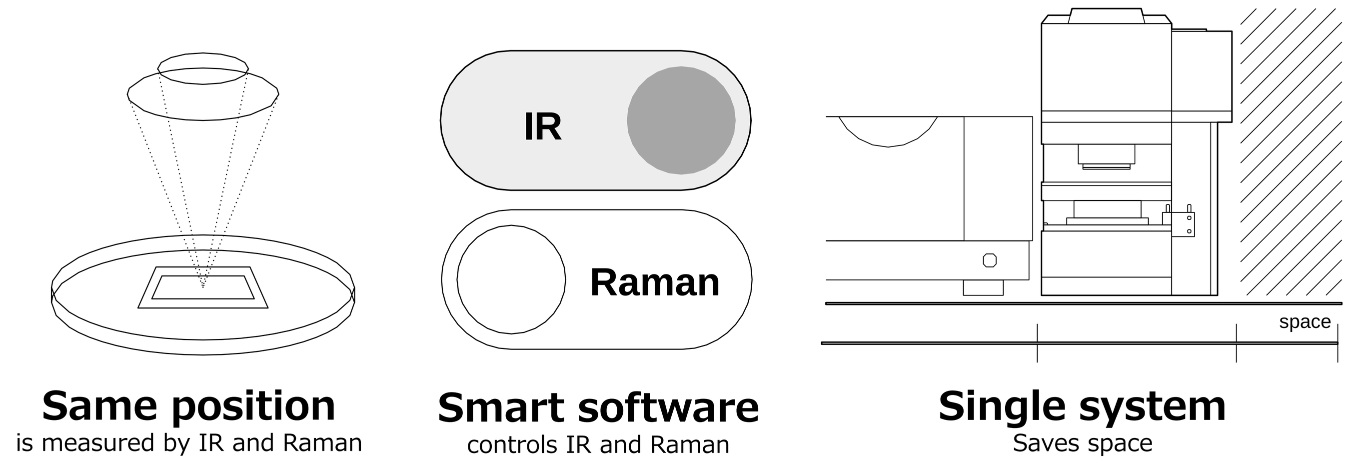
*1 Sample amount approx. 0.1mg

Figure 2. Methods for Analyzing Microplastics by Size

2. New Microscope AIRsight

The AIRsight Infrared/Raman microscope is a new type of microscope that incorporates a Raman unit into an infrared microscope, enabling both Raman and infrared analysis to be performed on a single instrument, analyses that previously required separate instruments. Figure 3 shows the instrument and summarizes three of its key features.

Figure 3. IRXross™(left) and AIRsight™(right)



First, the Same position in the sample can be measured by IR and Raman. Second, Smart software enables control of both acquisition modes, IR and Raman, in one software. Third, two spectra, providing the two lines of evidence for polymers' characterization, including the characterization of organic and inorganic components are collected with a Single system.

3. Method and Results

Microplastics in water were filtered using a PTFE-based filter. PTFE has no infrared absorption except at around 1200 cm^{-1}, so microplastics can be measured by a transmission method. The microplastics collected on the filter were placed on the stage of the AIRsight Infrared/Raman microscope for analysis. Figure 3 shows selected images of microplastics on the filter taken with the Infrared and the Raman objective lenses. In this work, three different sizes (a), (b), and (c) of microplastics were measured.

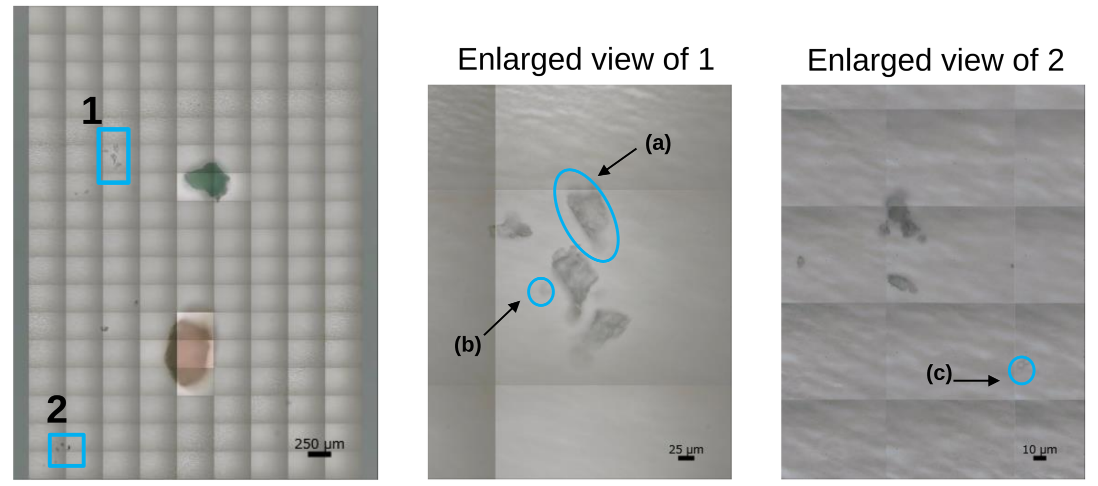


Figure 3. Microplastics Image Taken with Objective Lens

3-1. Qualitative Analysis by Microscopic Infrared Spectroscopy

Microplastic (a) collected on the filter paper was measured by the transmission method with the infrared microscope. The measurement conditions are shown in Table 1. In addition, Figure 4 shows search results using Shimadzu's UV-Damaged Plastic Library. Microplastic (a) was found to have a spectrum similar to that of PP (polypropylene) irradiated with UV light for 100 hours. The noise around 1,200 cm^{-1} is due to absorption by PTFE (filter material).

Table 1. Measurement Conditions

Instruments:	IRXross, AIRsight
Infrared Spectrometry	
Resolution:	8 cm^{-1}
Accumulation:	30
Apodization Function:	Happ-Genzel
Aperture Size:	25 µm
Detector:	T2SL

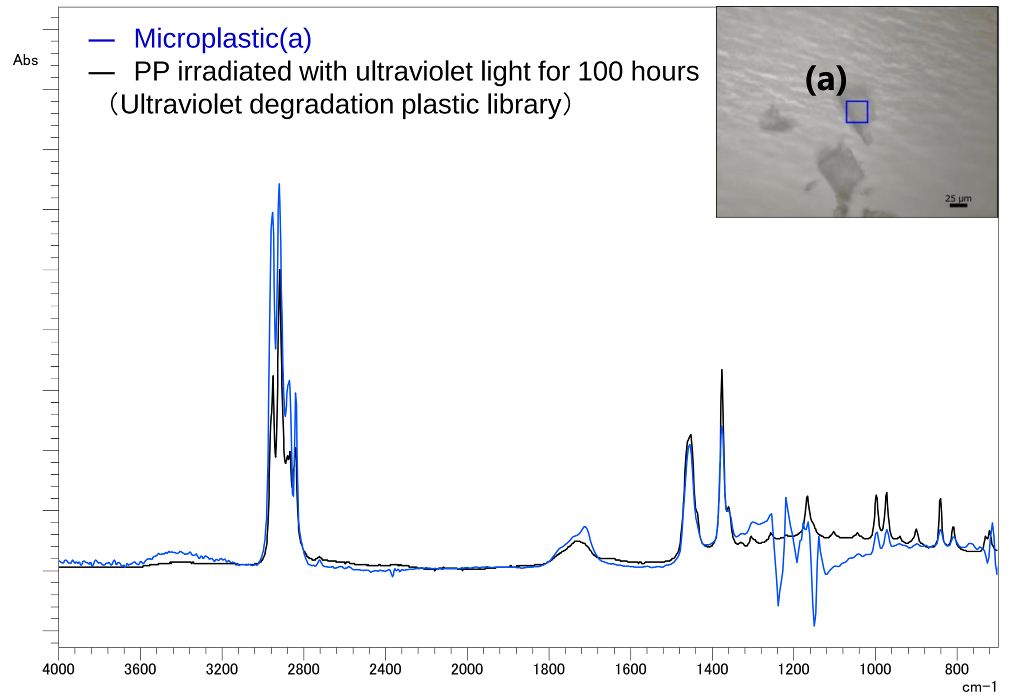


Figure 4. Infrared Spectrum of Microplastic (a) on Filter

3-2. Qualitative Analysis by Micro-Raman Spectroscopy

Micro-Raman spectroscopy was used to measure microplastics of smaller sizes, with sizes below the detection limit from IR microspectroscopy. The measurement conditions are shown in Table 2, and the resulting Raman spectra are shown in Fig. 5. In Raman spectroscopy, measurements are generally made at an excitation wavelength of 532 nm, where Raman scattering is strong. While the peak intensity is sufficient, it is difficult to obtain good data in the case of fluorescent samples because the baseline rises due to the fluorescence. Since many microplastics degraded by UV light are known to emit fluorescence at an excitation wavelength of 532 nm, measurements were performed at an excitation wavelength of 785 nm for this work. Compared to the excitation wavelength of 532 nm, measurement at 785 nm has a shorter wavenumber range due to the detector characteristics. However, it has the advantage of reducing fluorescence. It was determined through library searching from the Raman spectra that microplastic (b) was PE (polyethylene) and (c) was PS (polystyrene).

Table 2. Measurement Conditions

Instruments:	IRXross, AIRsight
Raman Spectrometry	
Accumulation:	40
Exposure Time:	5.0 sec
Objective Lens:	100x
Excitation Wavelength:	785 nm
Detector:	CCD

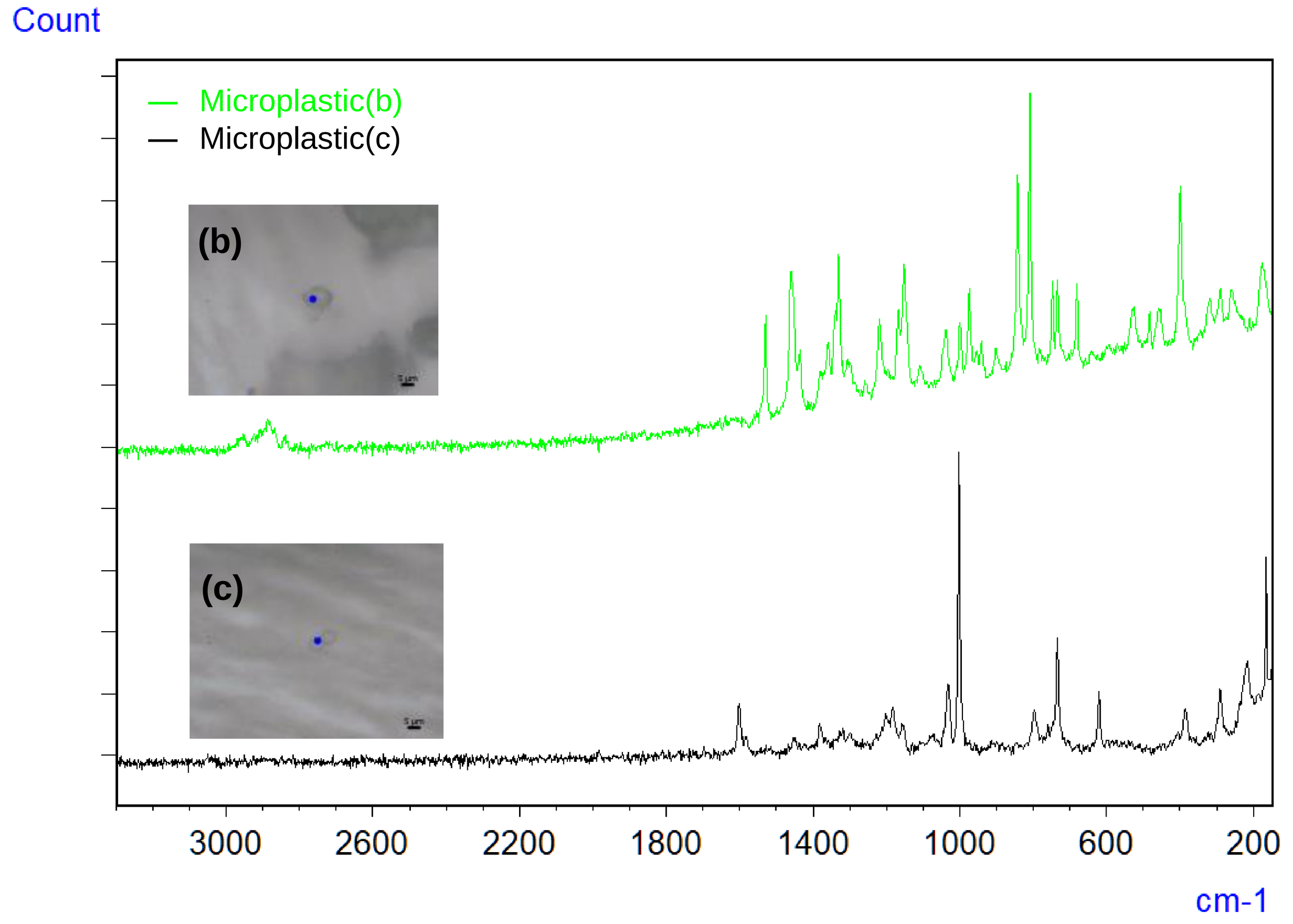


Figure 5. Raman Spectra of Microplastics (b) and (c) on Filter

4. Conclusions

In this work, microplastics of various sizes were analyzed using the AIRsight Infrared/Raman microscope. Micro-infrared spectroscopy allows the measurement of microplastics down to about 10 µm in size. However, by using this in combination with micro-Raman spectroscopy, it is possible to measure microscopic samples below 10 µm, which are difficult to measure by micro-infrared spectroscopy alone. When spectra are of the same microplastic are collected by FTIR and Raman, the confidence for identifying the material increases.