Microplastics Related Activities in Our HORIBA Group, Japan

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In recent years, plastics pollution has become a widely discussed international problem. Drifting into the ocean from the urban areas, plastics gradually miniaturize into small particles called microplastics, that affect ecosystem in many various ways. HORIBA Group engineers and scientists in Japan and worldwide, are working to establish the measurement techniques for microplastics analysis. In this paper, we will introduce our HORIBA Group's efforts in Japan, in response to the microplastics analysis needs, including application examples.

Introduction

In the past several decades, plastics were widely used due to their many convenient benefits, but in recent years, the plastic pollution has become a widely discussed international problem. Drifting into the ocean from the urban areas, plastics gradually miniaturize into small particles that affect ecosystems in many various ways. These plastic particles are called Microplastics (MPs) when they get smaller than 5 mm.

The G20 summit held in Osaka in June 2019, resulted in the "Osaka Blue Ocean Vision" declaration which aims to stop any additional pollution being introduced into the ocean by 2050. To achieve this goal, the Japanese "Ministry of the Environment and Ministry of Economy, Trade and Industry" has introduced several programs: (1) reduction and replacement with alternative materials, (2) recycling and resource circulation, (3) countermeasures against sea pollution, and (4) introduction of various national movements for dissemination and awareness activities.

Analytical instruments for MPs characterization

MPs size range and evaluation parameters depend on analysis purposes and survey targets: sea, river, lake, pond, sewage treated water or factory drainage. Measurement conditions and the applied instruments are shown in Table 1. MPs research of sea water is focused on 300 µm to 5 mm, while for the sewage treatment and drinking water it is focused on the size smaller than 300 µm. In the life science field research is focused on particles smaller than 10 µm, because of their impact on the ecosystem.

Recently it is becoming common to consider to use several techniques for MPs characterization to provide a complete picture of information.

Table 1 Survey target, condition and applied instruments for MPs identification

Survey target	MPs size	Preparation	Analytical instruments
Sea, River, Lake and Pond	300 µm ~ 5 mm	Picking up	FT-IR, Raman pyrolysis-GCMS
Sewage water, Factory drainage	10 µm ~ 300 µm	Primary filtration ↓ Oxidization ↓ Gravity separation ↓ Secondary filtration	FT-IR Microscope Raman Microscope
Clean water, Drinking water	< 10 µm		Raman Microscope
Food Cosmetic			
Impact on Ecosystem (biocells)			

MPs measurement's issues

In the case of MPs characterization, analytical methods and measurement parameters depend on the evaluation target: particle size, composition, mass, surface area, and identification of plastic types and additional hazardous substances. Furthermore, the method of collecting the sample, the method of removing contaminants and pretreatment differ depending on the target sample. The smaller the MPs particle size, the more difficult characterization becomes. Many of above mentioned methods are currently performed using each researcher's personal knowledge. This now needs to be considered towards a standardization process for better reproducibility of research and for reliable data comparison moving forward. Currently it also requires a lot of time and effort to perform multiple measurements, because most of sample treatments are done manually. Therefore, automation and semi-automation for sample treatment should be prioritized to reduce significantly the time and labor required for MPs analysis.

Activities in Japan

As a reaction to the MPs pollution problem, many seminars and symposiums have been held in Japan's industry and academia societies. In various seminars, on the theme "Particle size analysis and Raman spectroscopy for MPs", HORIBA has introduced measurement examples using HORIBA products. Several instruments like: the Laser Diffraction Analyzer (LA-960V2), the Dynamic Laser Scattering (SZ-100V2) and the Nanoparticle Tracking Analyzer (ViewSizer™ 3000), are used to characterize particle size and distribution, particle number and concentration, zeta potential and aggregation conditions. Our capability to cover a wide size range of samples (mm ~ µm ~ nm) was introduced.

In addition, we have demonstrated that our Raman Microscopes (XploRA PLUS and LabRAM Evolution) equipped with the particle analysis function (ParticleFinder) enables users to associate chemical information with particle size, shape, number and compositions using automated image analysis functions for the Component analysis was performed using Fourier detection and positioning of small particles.

A list of events and presentation titles are summarized in Table 2 and HORIBA product pictures, used for this study are shown in Figure 1

MPs mock sample analysis

The presence of MPs in our environment other than environmental water, such as our ocean and rivers, has also been reported, for example in air, drinking water and food.[2] In this article, we will introduce two analysis examples: mock MPs samples from environmental water and MPs obtained from the atmosphere.

A MPs mock sample was prepared by pulverizing a polypropylene (PP), polyurethane (PU), polymethylmethacrylate (PMMA), and polyethylene terephthalate (PET) mixture.

Component analysis was performed using Fourier Transform Infrared (FT-IR) microscopy. Particle size distribution and image observation were performed using a laser diffraction/scattering particle size analyzer with an optional built in Imaging Unit.[3] The respective measurement systems will be described below.

Table 2 List of events and presentation title

Event name	Date	Title	Organizer
JASIS conference	2019/9/6	Microplastic measurement and environmental impact	Japan Society for Environmental Chemistry (JSE) Japan Analytical Instruments Manufacturers" Association (JAIMA)
JETA seminar	2019/11/28	Measurement of microplastics in environmental water	Japan Environmental Technology Association (JETA)
AIST symposium	2019/12/2	Measurement and evaluation of microplastics	National Institute of Advanced Industrial Science and Technology (AIST)

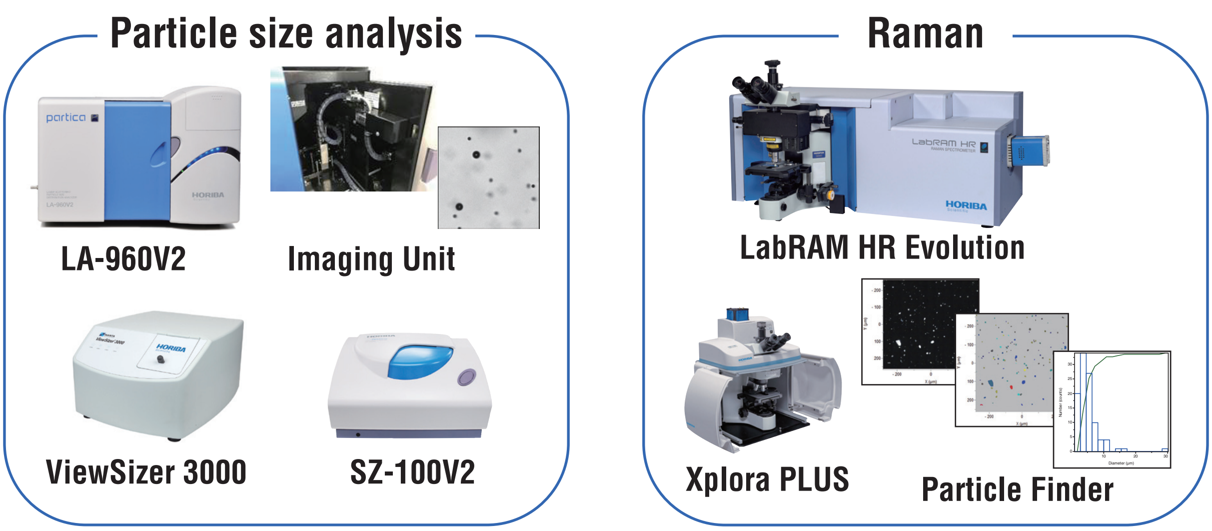


Figure 1 HORIBA product's pictures, used for this study

In infrared spectroscopic analysis, when a sample is irradiated with infrared light, an infrared absorption spectrum is obtained from an absorption value at each wavelength. A component analysis is performed using this infrared absorption spectrum. FT-IR microscopes use focused infrared light with a spatial resolution of about 10 µm, when combined with a motorized stage it is capable to obtain component infrared spectral images of a wide area.

The laser diffraction/scattering particle size analyzer can measure the particle size distribution of a sample. When the sample is irradiated with incident light at certain wavelengths, the scattered light angular distribution intensity changes according to the particles diameter size. By analyzing this pattern, the particle size distribution in the sample can be obtained. The sample dispersed in the liquid circulates in the flow cell. Since many particles are measured at the level of several millions, statistically high accuracy and measurement reproducibility can be obtained compared with the counting method using a microscope. Figure 2 shows the optical set up for the laser diffraction/scattering particle size analyzer.

The Imaging Unit is an optional built in unit used for image analysis. White light is emitted into the back surface of the cell, from a light source installed in the Imaging Unit, and a transmission image of particles in the cell is captured by a strobe camera. Particles in this circulated flow cell can be observed in real time, and a

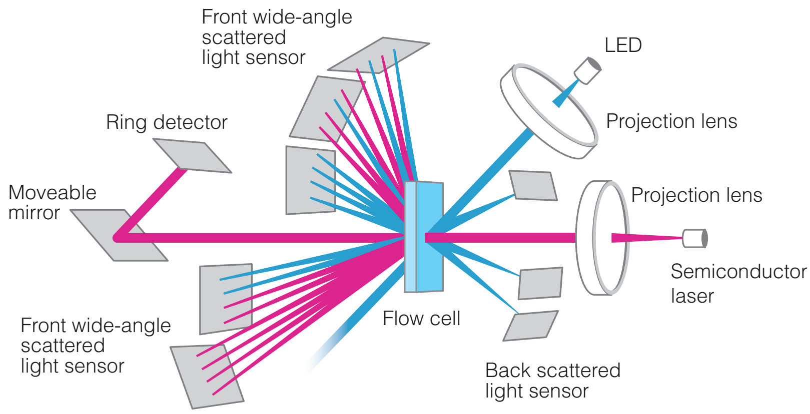
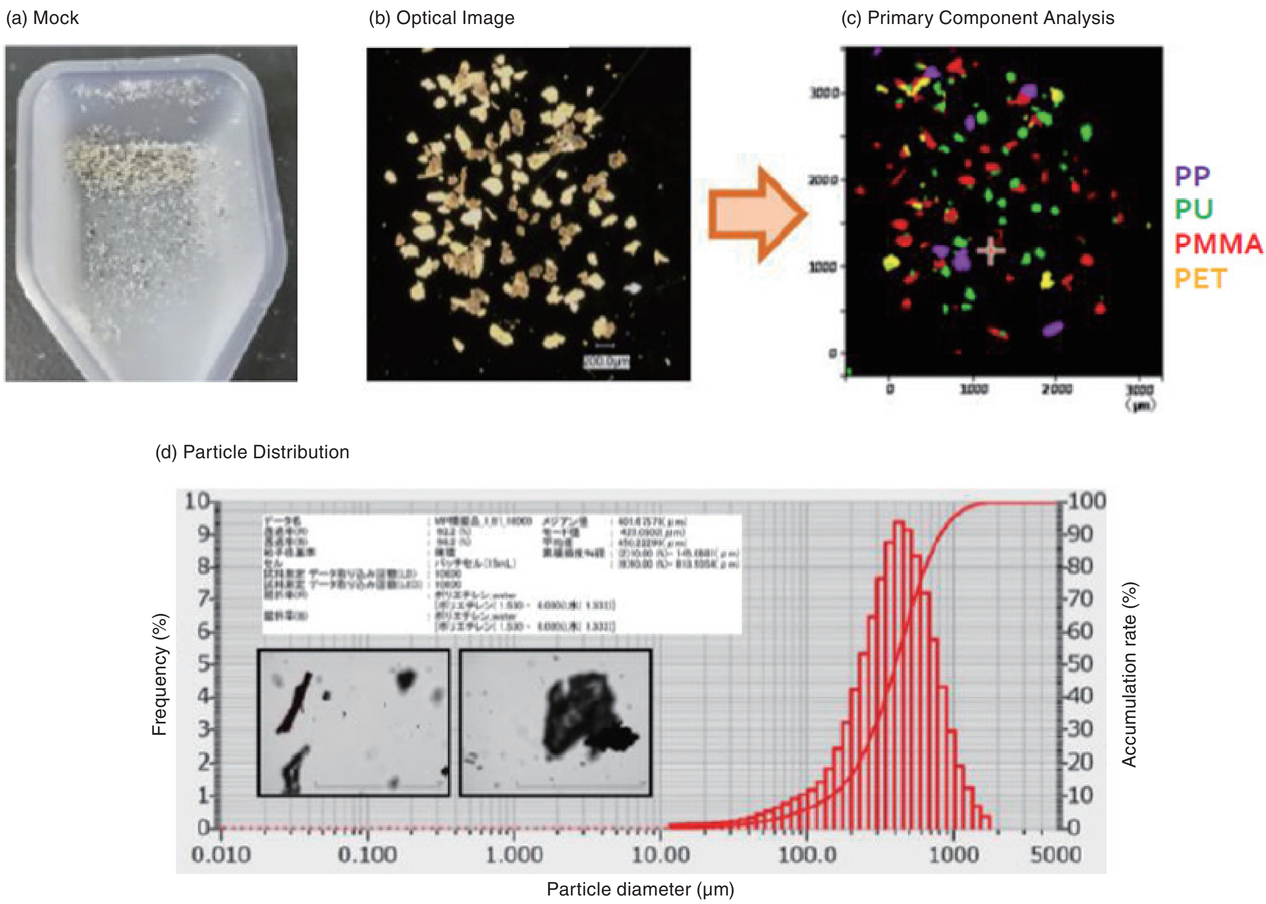


Figure 2 Optical set up of a laser diffraction/scattering particle size analyzer distribution measurement device



Figures 3 Optical image and measurement results of MPs mock sample

*Figures 3 were kindly provided by Toray Research Center, Inc.

histogram of particle size distribution can be calculated from image particle analysis results.

After collecting water from the ocean or river, and pre-treatment for MPs separation, the measurement of particles number and a component analysis by FT-IR microscopy is widely adopted for the MPs analysis. The MPs mock samples used in this study were prepared by pulverizing a PP, PU, PMMA, and PET mixture. A photograph of the sample inside the plastic case is shown in Figure 3(a). This sample was dispersed on a metal substrate and infrared reflection-absorption imaging was performed by a FT-IR microscope. The spectrum obtained from each measurement point was subjected to principal component analysis to obtain a distribution chart of PP, PU, PMMA and PET. As shown in the Figure 3(b), (c), all the particles in the observed image could be identified.

The laser diffraction scattering particle size analyzer used for the same mock sample found the particle size distribution to be within a 10 μm to 2 mm range. As shown in Figure 3(d), it can be seen that the results can be obtained with high particle size resolution.
Inserted in part of Figure 3(d) shows images of particles with different shapes . Using the Imaging Unit it is possible to observe actual particles simultaneously with the particle size distribution.

Measurement of Airborne Microplastics by Raman Microscopy

Currently several researchers have reported Airborne microplastics (AMPs) found in the atmosphere of urban areas, high altitude mountains and the arctic circle.[4] These facts suggest that AMPs contamination is widely spread due to atmospheric circulation. In addition, AMPs smaller than 10 μ may have a bad influence not only on the environment but on the human health due to inhalation.[5]

In this study, we evaluated AMPs collected in the free troposphere (ca. 2000-11000 m a.s.l.) by researchers in Waseda University. AMPs collection was performed at night on the top of Mt Fuji at an altitude of 3776 m. A cyclone type High Volume Air Sampler (SIBATA SCIENTIFIC TECHNOLOGY LTD.) was used to collect PM2.5 particles on a Teflon filter. Chemical composition analysis was performed after removing natural organic or inorganic particles. In general, a FT-IR microscope is used to analyze larger microplastics, but because the expected estimated size of AMPs is smaller than 10 μm, the FT-IR microscope spatial resolution would be not sufficient. Therefore we decided to use Raman microscopy which has a much higher, up to sub-micron scale, spatial resolution.

Raman spectroscopy can perform composition analysis and crystallinity evaluation from inelastic light scattered (Raman scattering) on a laser irradiated sample. By combination of a microscope and motorized sample stage, sub-micron spatial resolution Raman chemical imaging is achievable.

In order to perform Raman measurements, we transferred AMPs to an Almina filter and carried out mapping measurement in 4 areas, 1 mm^2 each, followed by the imaging of CH stretching mode intensities. This image illustrates distribution of the existing organic compounds in the AMPs. 30 pieces of AMPs were detected in the 4 mapping areas. By conducting point measurement of detected AMPs with longer acquisition times, a total of 15 different polymer species there identified. Figure 4 shows the optical image of part of the detected AMPs on the Almina filter using a X100 objective lens. Figure 5 shows the

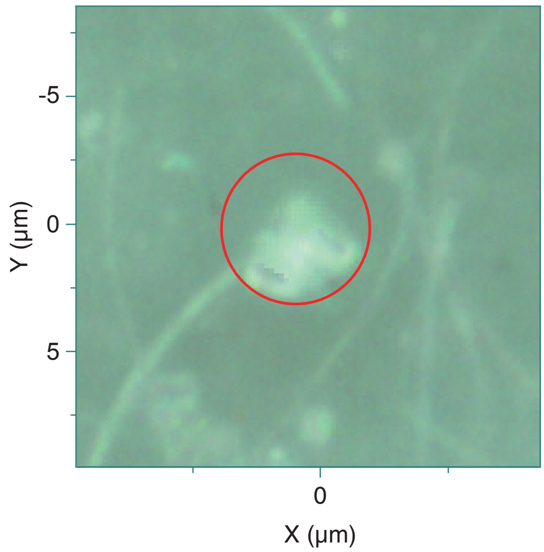


Figure 4 Optical image of detected AMPs

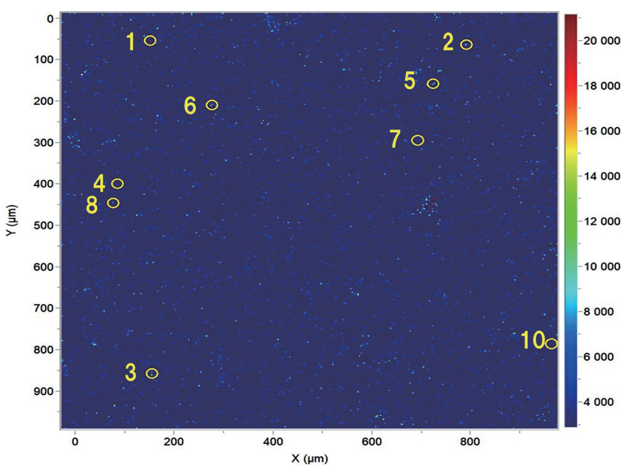


Figure 5 Image of CH stretching mode intensity

Table 3 AMPs size and identified species chemical names

target	Size/μm	identified compound by Library search
1	8(diameter)	Polystyrene (PS)
2	6(Maj axis), 4(Min axis)	Unidentified polymer + TiO_2
3	3(diameter)	Polyester
4	4(diameter)	Polypropylene (PP)
5	6(Maj axis), 4(Min axis)	Polyurethane (PU)
6	12(Maj axis), 3(Min axis)	Polyethylene (PE)
7	1.4(diameter)	Poly-3-Hydroxyl Butyl acid
8	2(diameter)	Polyolefin
9	28(Maj axis), 2(Min axis)	Palytetrafluoro ethylene (PTFE)
10	ND	Polyolefin

image of CH stretching mode intensities in one of the mapped areas. In Table 3 the AMPs size and identified species chemical names are summarized. Most of the AMPs were smaller than 10 μm. 37% of detected particles were made from Polypropylene material, followed by bio-degradable plastics such as Polyhydroxybutyric acid.

The AMPs number concentration in the atmosphere, calculated in this study, was found to be 4.47 particles/m^3. These results show that Raman microscopy is suitable for the qualitative analysis of MPs composition for particles smaller than 10 μm.

Acknowledgments

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* This content is based on our investigation at the year of issue unless otherwise stated.

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