

FTIR

TALK LETTER

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Spectroscopic Analysis of Rechargeable Lithium-Ion Battery Electrolyte Solution by a Compact FTIR System located in a Glovebox



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1. Introduction

Raman spectroscopy and infrared spectroscopy in a vibrational spectroscopic technique are used in many fields and serves a major role in analyzing the composition and structure of substances¹⁾. At the same time, infrared spectroscopy has become very easy to use due to progress achieved in increasing instrument performance and reducing instrument size²⁾. Due to its wide availability as a measurement method, those involved in research and development often want to know “Can it measure this?” or “Can it measure samples in this state?” With a specialization in electrochemistry, the author is involved in in-situ spectroscopic measurements of electrochemical reactions occurring at the electrodes of rechargeable batteries. In-situ spectroscopic measurement is used to track the structural changes of electrodes as rechargeable lithium-ion batteries with charging/ discharging. Raman spectroscopy and infrared spectroscopy have been used to help improve battery performance by analyzing the electrode reactions at the cathode and anode interface of rechargeable lithium-ion batteries³⁾. However, exposure of rechargeable lithium-ion battery components to atmospheric oxygen or moisture can significantly affect battery properties. Therefore, if possible, it would be preferable to handle and characterize battery components within an environment where they are not exposed to oxygen or moisture. This article describes locating a compact FTIR system inside a glovebox controlled to extremely low moisture and oxygen levels and then using it to measure infrared absorption spectra for an electrolyte solution used in rechargeable lithium-ion batteries. The article compares the results to values measured in atmospheric air, describes how electrolyte solutions are affected by atmospheric air, and discusses considerations for measuring infrared absorption inside a glovebox.

2. FTIR Measurements in Atmospheric Air and an Inert Gas Atmosphere

Normally, measuring instruments and other laboratory devices are installed in an atmospheric air environment. However, material properties often need to be measured within more specialized environments, such as under high-temperature, low-temperature, high-pressure, or vacuum-pressure conditions. In such cases, samples are often placed in a specialized atmospherically-controlled cell, so that only the sample is kept in the required environment during measurements. However, completely eliminating the effects of atmospheric moisture, nitrogen, or oxygen can have a major influence on measurement results. One method of reducing such atmospheric effects is to install the entire measuring instrument within the necessary environment to minimize the effects of atmospheric air on the instrument and sample.

At the author’s laboratory, spectra are measured by a compact FTIR system installed inside a glovebox filled with an argon atmosphere that has a low dew point and low oxygen concentration. Fig 1. shows the compact FTIR system inside the glovebox. Inside the glovebox, the argon atmosphere is controlled to a maximum dew point of -70 °C (given a 2.58 ppm moisture content) and a maximum oxygen concentration of 0.3 ppm. Operating measuring instruments in such an atmosphere enables spectral measurements with minimal effects from the water vapor and oxygen present in atmospheric air environments. When experimental stuffs and instruments are moved from atmospheric air to an argon atmosphere with a low dew point and low oxygen concentration, the dew point and oxygen concentration levels in the argon atmosphere rise. That is presumably due to the oxygen or moisture present inside or attached to the experimental stuffs or instruments. Oxygen and moisture can be eliminated by applying a vacuum or high temperature to the atmosphere of the experimental stuffs or instruments, but it is often effectively impossible to move a

given experimental stuffs or instruments into such an environment. In reality, low-dew point and low-oxygen argon atmospheres are typically created by exposing the experimental stuffs or instruments to a low-dew point and low-oxygen argon atmosphere for a long time, by using a recirculating gas purification system to remove oxygen and moisture from the gas atmosphere, and by purging the oxygen and moisture from the box with argon gas. Once the system is installed inside the box, it can take from several days up to even one month to generate the low-dew point and low-oxygen atmosphere, depending on the size (gas volume) of the glovebox.

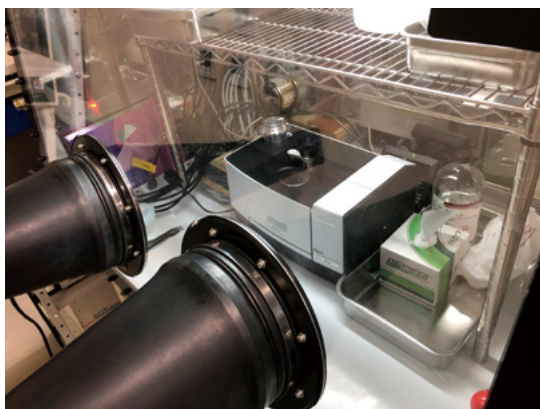


Fig. 1 Compact FTIR System Installed inside a Glovebox

Next, FTIR spectra were obtained both within the glovebox with the argon atmosphere and in atmospheric air and then compared. FTIR measurements normally involve measuring samples in an FTIR system located in atmospheric air; in this case, the FTIR spectra were obtained based on the optical properties of either atmospheric air or a vacuum. In the argon atmosphere, measurements require various experimental properties in argon atmospheres, which resulted in a variety of problems not observed in atmospheric air environments. For example, because argon has a different thermal conductivity than air, the system's heat exhaust system might stop functioning properly and prevent obtaining correct FTIR spectra. To avoid that problem, better heat removal was promoted by installing a fan-based exhaust system on the FTIR system. Also, argon gas has very different optical properties than air. To verify the effects of such differences, actual FTIR measurements were performed in atmospheric air and argon gas atmospheres and the spectra were compared. Fig. 2 shows FTIR spectra obtained in the glovebox (upper) and atmospheric air (lower) for an electrolyte solution containing a 3:7 ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) and containing 1 M LiPF₆. This electrolyte solution is an organic electrolyte typically used in rechargeable lithium-ion batteries. The close similarity of the spectra obtained in the glovebox with argon atmosphere and in

atmospheric air indicates that good FTIR spectra can be obtained either in the glovebox or atmospheric air. General spectra were obtained without any evidence of optical property or heat exhaust mechanism problems associated with the argon atmospheres noted above. To investigate the effects of moisture and oxygen in even more detail, the high-wavenumber regions of the spectra in Fig. 2 were further analyzed. The results are shown in Fig. 3. It shows FTIR spectra obtained in the glovebox (upper) and atmospheric air (lower) from a 3:7 electrolyte solution of EC and DEC and containing 1 M LiPF₆. In the 2800 to 3100 cm⁻¹ region, an absorption line caused by -CH-stretching vibration in the electrolyte solution is clearly observed in both FTIR spectra. Both spectra also include broad absorption or spectral fluctuation in the 3400 to 3700 cm⁻¹ region. In particular, the FTIR spectrum obtained in atmospheric air clearly shows broad absorption, which careful consideration of the frequency indicates is associated with symmetric and antisymmetric OH-stretching vibration in water molecules. The infrared absorption by water molecules is extremely large and can sometimes be observed from even trace quantities of water moisture. Presumably, the absorption in the FTIR spectra obtained in atmospheric air is due to the system sensitively identifying the presence of moisture in the atmospheric air or sample.

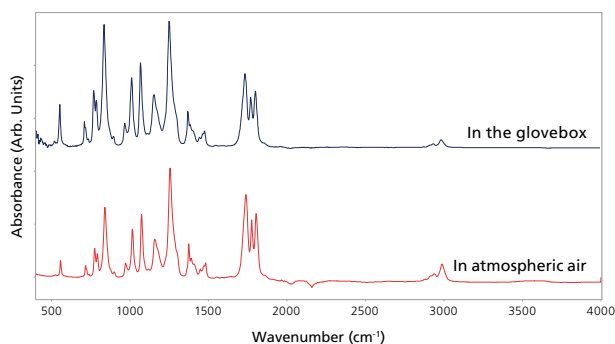


Fig. 2 FTIR Spectra of EC + DEC (3:7) Electrolyte Solution Containing 1 M LiPF₆

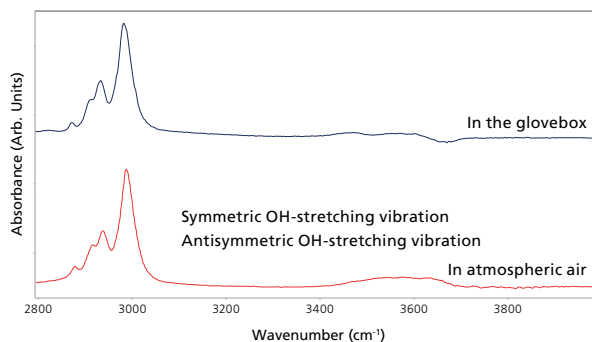


Fig. 3 FTIR Spectra of EC + DEC (3:7) Electrolyte Solution Containing 1 M LiPF₆ (High-Frequency Region)

Due to the small volume (gas volume) inside the glovebox and the extremely dry environment, the sample itself is prone to evaporation. If multiple samples are measured successively, the top of the ATR crystal must be cleaned with organic solvent or another solution to eliminate sample matter after measurements. For the measurements described, the ATR crystal was wiped with alcohol between each sample to ensure measurements were not affected by preceding samples. Fig. 4 shows an FTIR spectrum of EC + DEC (3:7) electrolyte solution after measuring 20 samples (after about three hours of measurements). In addition to absorption lines from EC and DEC, the FTIR spectrum in Fig. 4 also shows a new absorption line observed in the 3600 to 3700 cm^{-1} frequency region. Based on the frequency region, the absorption line in the 3600 to 3700 cm^{-1} region can be attributed to OH-stretching vibration caused by alcohol. Alcohol evaporates and becomes dispersed within the glovebox. Alcohol is removed by the recirculating gas purification system, but not fast enough to prevent the alcohol from becoming a high-concentration gas inside the glovebox, which has a relatively small volume of argon. As a result, absorption lines from the gaseous organic cleaning solvent appear in the FTIR spectrum, showing how evaporation of organic cleaning solvents or other substances has a large effect. That is not a problem if using a capped optical cell to obtain spectra based on the positioning of transmittance, but requires being careful about sample evaporation if using an uncapped cell. Typically, FTIR spectra are used after correction for the corresponding background spectrum, which is obtained without placing a sample and is subtracted from the FTIR spectrum obtained from the sample. The background spectrum used in Fig. 4 was obtained three hours before the sample was measured, with no consideration given to the effects of the evaporated organic cleaning solvent on the background spectrum. It is possible to correct spectra with a background spectrum obtained immediately prior to the sample spectrum, while also minimizing effects from the organic cleaning solvent, but that would require obtaining spectra with maximum consideration given to evaporation effects, such as by minimizing the quantity of organic cleaning solvent used. In recent years, FTIR spectra are typically obtained by the attenuated total reflectance method using a diamond crystal, which enables the measurement of extremely small sample quantities, such as a few drops. However, since only small sample quantities are involved, even small amounts of a foreign substance can significantly alter infrared absorption spectra. Therefore, extra caution is required.

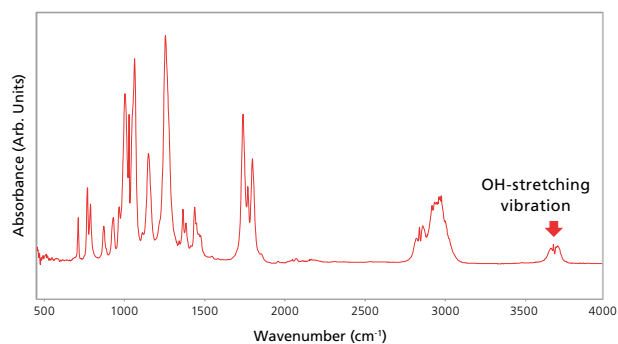


Fig. 4 FTIR Spectrum of EC + DEC (3:7) Electrolyte Solution Containing 1 M LiPF_6 (After Measuring 20 Samples)

3. FTIR Measurement of Rechargeable Lithium-Ion Battery Electrolyte Solution in Inert Gas Atmosphere

Moisture and oxygen present in atmospheric air can significantly affect performance due to sensitive reactivity with components in rechargeable lithium-ion batteries. Organic electrolyte solutions with strictly controlled moisture levels are used as electrolyte solutions. This section describes using the FTIR system in an inert gas environment to characterize such a rechargeable lithium-ion battery electrolyte solution. Fig. 5 shows FTIR spectra for an EC + DEC (3:7) electrolyte solution that contains 1 M LiPF_6 (red) and for an EC + DEC (3:7) solution (black). These spectra were obtained using an FTIR system installed inside a glovebox. Both spectra have excellent spectral form with FTIR peaks that indicate various components. The red and black arrows in the figure identify the characteristic absorption lines for respective components and indicate the areas where absorption lines are present or missing or where a small or large change in absorption level has occurred. Given that the only difference between the two samples is the presence of LiPF_6 , the spectra should only differ by the appearance or lack of absorption lines attributable to LiPF_6 . To highlight the differences between the two FTIR spectra, a differential spectrum for the two FTIR spectra is shown in Fig. 6. Differences in absorption intensity appear at 551.9 cm^{-1} , 719.8 cm^{-1} , 775.0 cm^{-1} , and 833.9 cm^{-1} . These four representative absorption lines cannot be explained by LiPF_6 vibration modes alone. Given that characteristic vibration modes of solvation between either EC or DEC and lithium ions appear in the 700 cm^{-1} to 1000 cm^{-1} frequency range⁴⁾, the four absorption lines are probably characteristic absorption lines of lithium ions solvated by EC or DEC. In this way, samples can be measured relatively quickly using an FTIR system installed in a glovebox to acquire accurate measurements that are not affected by moisture or oxygen, even for electrolyte solution characterization.

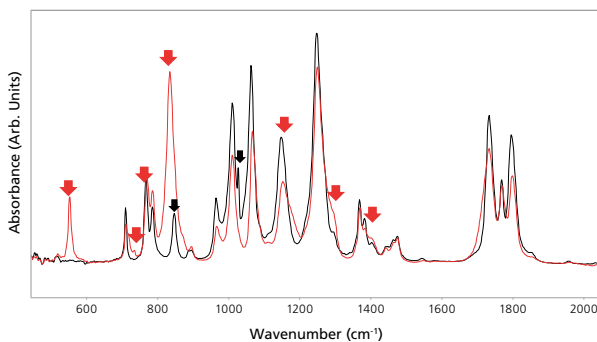


Fig. 5 FTIR Spectra of EC + DEC (3:7) Electrolyte Solution Containing 1 M LiPF₆ (Red) and EC + DEC (3:7) Solution (Black)

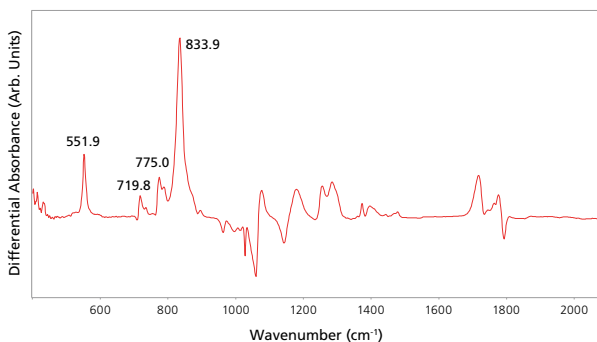


Fig. 6 Differential Spectrum of EC + DEC (3:7) Electrolyte Solution Containing 1 M LiPF₆ and EC + DEC (3:7) Solution

4. Summary

This article describes installing a compact FTIR system inside a glovebox controlled to extremely low moisture and oxygen levels, using it to obtain infrared absorption spectra from an electrolyte solution used in rechargeable lithium-ion batteries, and then comparing those spectra to spectra measured in atmospheric air. It also discusses the effects of atmospheric air on electrolyte solutions, factors to consider when measuring infrared absorption inside a glovebox, and so on. Glovebox users typically frown on placing measuring instruments inside a glovebox because it would increase moisture and oxygen levels. However, placing measuring instruments inside the glovebox can provide significant opportunities. Once an FTIR system is properly installed in the glovebox, FTIR measurements that are difficult to perform in atmospheric air can be performed as easily as in atmospheric air. For material development work, it also means a single glovebox can be used to perform all steps from composite material formation to characterization without any exposure to atmospheric air. The idea of placing an expensive instrument inside a glovebox may seem reckless, but the author believes the benefits from

the additional quantity and quality of information it can provide are immeasurable.

References

- 1) N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy Third Edition*, Academic Press Inc. San Diego, CA, 1990.
- 2) P. R. Griffiths and J. A. de Haseth, *Fourier Transform Infrared Spectroscopy*, Wiley & Sons Inc., Hoboken, NJ, 2007.
- 3) Takashi Itoh, In Situ Raman Spectroscopic Analysis of Electrochemical Reactions, *Electrochemistry*, 87(Spring), 2019, pp.43-56.
- 4) Masayuki Morita, Research of Solvation Structures by Raman Spectroscopy, *Electrochemistry*, 81(12), 2013, pp.991-994.

Note

The measurements discussed in this article were carried out under specific conditions, since the argon glovebox environment may lower the heat exhaust capabilities, affecting the operation of the equipment. Please contact us for details.

High-Speed Measurements Using the Rapid Scan Function

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Fourier transform infrared (FTIR) spectrophotometers are very useful tools for tracking chemical reactions and changes because of the rapidity of their measurement process. In particular, the IRTracer™-100 is equipped with a rapid scan function, which performs 20 spectral measurements per second, enabling faster reaction tracking.

This article describes the basic principles of the rapid scan function, cautions when performing measurements, and measurement examples.

1. Introduction

Time course measurements are a way to track chemical reactions. In time course measurements, data can be acquired at approximately 10-second intervals. (This changes depending on the measurement parameters.)

The sample is measured at set time intervals, and a time course graph is displayed indicating the time on the horizontal axis and specific peak intensities and areas on the vertical axis, thereby tracking sample reactions and measuring changes over time. For a detailed explanation of time course measurements, see FTIR TALK LETTER Vol. 21.

In contrast, with rapid scan measurements, as noted above, 20 spectra can be acquired per second, making this what could be called a high-speed time course measurement. When reactions finish in a very short time, temporal resolution is insufficient with time course measurements and peak changes are inadvertently missed. For this reason, rapid scan measurements, which feature high temporal resolution, must be performed.

At Shimadzu, measurements in which the moving mirror speed is up to 9 mm/s are referred to as time course, while measurements at 10 mm/s or higher are referred to as rapid scan. This does not mean that they are distinct with respect to their operating principles, however.

2. Rapid Scan Measurements

To heighten the temporal resolution, the moving mirror must be driven at high speeds. In FTIR, an interference wave is produced by driving a moving mirror in a Michelson type interferometer. By

performing a Fourier transform of the interference waveform, a spectrum can be acquired with the wave number on the horizontal axis and the energy on the vertical axis (Fig. 1).

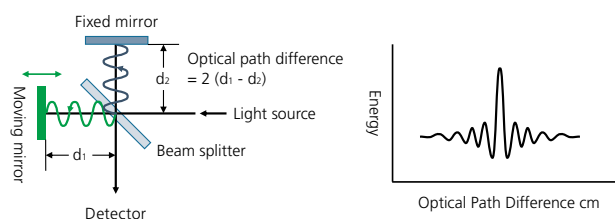


Fig. 1 Michelson Type Interferometer and Interference Waveform

For this reason, the moving mirror driving speed itself becomes the measurement time, and it is important to drive the moving mirror quickly and accurately.

In the Shimadzu IRTracer-100, when measurements are performed at the highest speed, data can be acquired at 50 ms intervals (which equals 20 spectral measurements per second). In addition, rapid scan software especially for high-speed measurements is used, rather than the standard LabSolutions™ IR software, in order to transfer the data from the instrument to the computer and to render the spectra smoothly (Fig. 2).

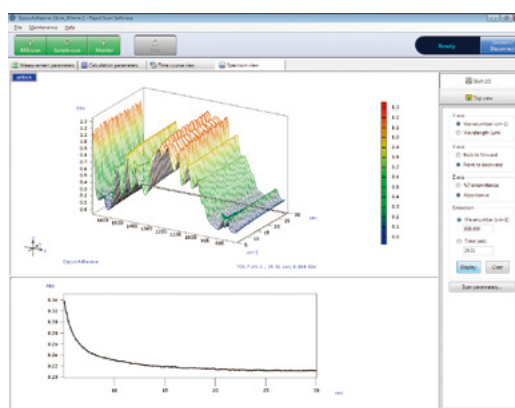


Fig. 2 Rapid Scan Software

An MCT detector is generally used. This is because the DLATGS detector that is provided as standard with FTIR has less sensitivity during high-speed measurements, while the MCT detector has a fast response rate, enabling faster measurements.

3. Example of High-Speed Measurement

An example of the tracking of the high-speed reaction of UV hardened resin is introduced below. UV irradiation started approximately 5 seconds after the rapid scan measurements started with respect to the UV hardened acrylate resin. The acquired results are shown in Fig. 3.

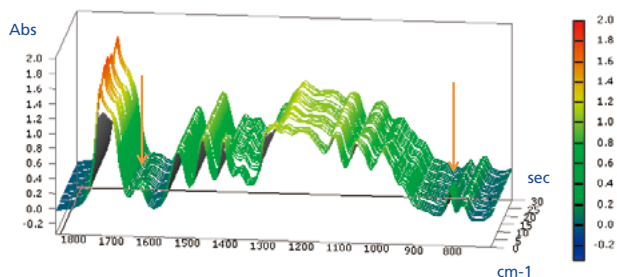


Fig. 3 Rapid Scan Measurement Results for UV Hardened Resin

Additionally, Fig. 4 shows a peak area time course graph for peaks in the vicinity of 1,635 cm⁻¹ and 810 cm⁻¹ originating from the vinyl shown in Fig. 3. It is evident that these peak areas decrease dramatically in the few seconds immediately following UV irradiation. Since this sort of time course graph makes it possible to specify multiple target peak wave numbers before the start of measurement, the changes can then be observed in real time during measurement.

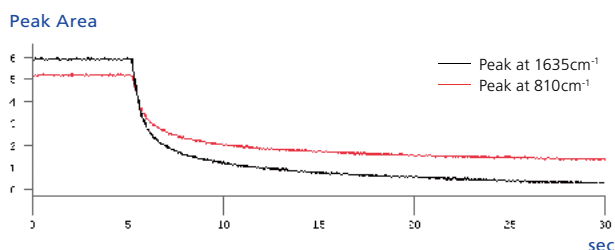


Fig. 4 Time Course Graph for Specified Wave Numbers

A specular reflectance attachment (SRM-8000 special model, Fig. 5) and ATR attachment (UV-GladiATR, Fig. 6) are available as accessories for performing measurements while irradiating a sample with UV rays.

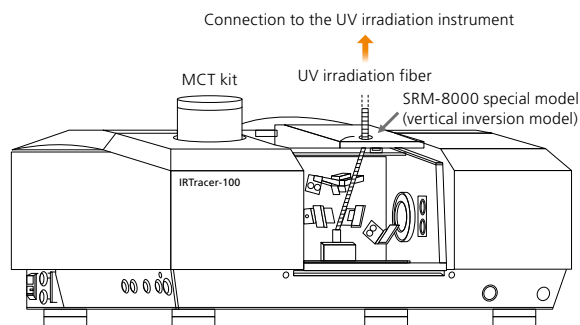


Fig. 5 UV Irradiation Type Specular Reflectance Attachment

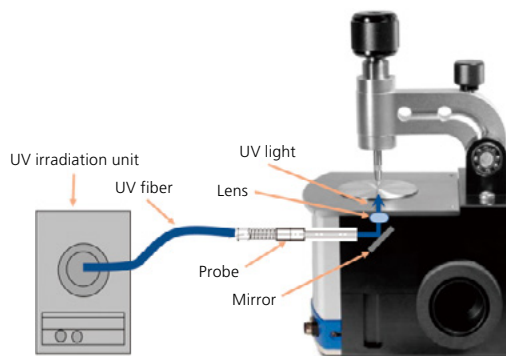


Fig. 6 UV Irradiation Type ATR Attachment (UV-GladiATR™)

4. Synchrony with External Equipment

In the high-speed measurement example noted earlier, UV irradiation started 5 seconds after the measurements started. However, synchronizing the start of UV irradiation with the start of the measurements is sometimes needed. The IRTracer-100 is equipped with a trigger function to signal the start externally, enabling the user to start the measurements in synchrony with external equipment.

Fig. 7 illustrates the synchronization of the start of measurements by the IRTracer-100 with UV irradiation from UV irradiation equipment. (Synchronization might not be possible depending on the UV irradiation equipment. Be sure to confirm in advance.)

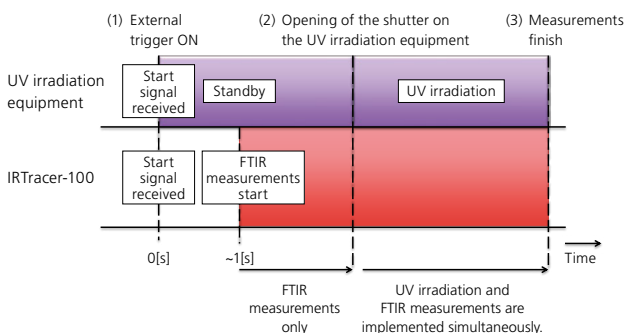


Fig. 7 Synchronization of Irradiation and Measurement Timing

As shown in Fig. 7, a start signal issued by an external switch is received simultaneously by the UV irradiation equipment and the IRTracer-100. After this, the LabSolutions IR software that controls the IRTracer-100 starts the measurements, and after a specified time has elapsed, the shutter on the UV irradiation equipment is opened, enabling synchronization of the UV irradiation and the infrared measurements.

5. Summary

This article has described the rapid scan function, which enables the acquisition of 20 spectral data sets per second. This is an effective tool for tracking reactions that occur at high speeds. For more information, feel free to contact your Shimadzu representative.

Analysis of Microplastics Using FTIR

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Risa Fuji

Environmental pollution from plastic waste has intensified, and the movement to avoid using plastics has accelerated worldwide. In addition, the impact on living organisms of microplastics drifting in rivers and oceans is a concern. In recent years, research aimed at investigating their distribution and specifying their origin has been extensively conducted. Against this background, there are calls for the development of effective methods for analyzing microplastics using various analytical instruments. This article describes analytical examples using an FTIR and infrared microscope system, typical instruments for the analysis of microplastics.

1. Introduction

Microplastics are designated as fine plastic particles between a few μm and 5 mm in size. They are further classified into primary and secondary types. An example of primary microplastics are the fine beads used as raw materials in industrial polishing powders and scrubbing agents. In contrast, secondary microplastics are designated as plastics produced through the degradation by external factors of plastic products that have been discarded. In actuality, plastic that is broken down by UV rays or impact with other plastic materials and which then flows into rivers and oceans becomes miniaturized to less than 5 mm in size through wave motion and physical impact with rocks and sand.

Microplastics consumed by marine life have an impact on human health through the food chain, which is a concern. At present, 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. In addition, in recent years, investigations have been implemented in order to assess the distribution of microplastics across extensive ocean areas as well as the amount of PCBs and other toxic chemical substances adsorbed. There have even been reports of observations of microplastics at the North Pole and South Pole, where the impact of garbage was initially thought unlikely to reach.¹⁾ Further, measures are being implemented to discontinue the use of micro beads in scrubbing materials and to avoid the use of plastic products.

A variety of analytical instruments is used to investigate the distribution of microplastics and to evaluate countermeasures for marine debris. Generally, a Fourier transform infrared (FTIR) spectrophotometer is used for the qualitative analysis of microplastics between about 100 μm and 5 mm in size, while an infrared microscope system is used for particles between about 10 μm and 100 μm in size. If the particles are under 10 μm in size, a Raman microscope spectrophotometer is utilized. In addition, gas chromatograph mass spectrometers (GCMS[™]) and liquid chromatograph mass spectrometers (LCMS[™]) are suitable for quantitative analysis or the qualitative analysis of trace components adsorbed to the microplastics. Further, in order to analyze the shape and particle concentration (particles/mL) of microplastics, a dynamic particle image analysis system can be applied to automatically detect particles between 5 μm and 100 μm dispersed in a solution, and to quickly determine their shape and particle concentration.

In this way, various analytical instruments are used depending on the objective and the size of the microplastics, and research is advancing.

2. Pretreatment of Microplastics

When analyzing microplastics, pretreatment is required to remove any mixed impurities. An example of the pretreatment used when collecting microplastics from water sampled from rivers or oceans is shown below.

1. Acid Treatment

Extraneous organic matter adhering to the surface of the microplastics is treated using H_2O_2 .

2. Separation by Specific Gravity

An aqueous solution of NaI is added to raise the specific gravity of the water so that the microplastics float to the surface.

3. Filtration

Microplastics are collected in measurement filters (such as polytetrafluoroethylene (PTFE), alumina, or stainless steel filters).

Depending on the situation, it may not be possible to completely remove impurities using the above-mentioned pretreatment methods, and one could say that there is room for further investigation of pretreatment methods.

3. Example of the Analysis of Marine Debris Using FTIR

Recycling marine debris requires the strict management of fishing net materials or metals applied to protect their surfaces, as well as other toxic substances. For example, casting nets, trawling nets, fishing line, and other fishing gear were traditionally made of natural materials, but these days, they generally consist of synthetic resins. FTIR is the ideal instrument for the qualitative analysis of organic materials on the order of a few mm in size as well as some inorganic materials. It is useful for managing material properties in recycling and for the study of marine debris.

Fishing nets collected on a beach were measured using the FTIR ATR method. The ATR method measures light fully reflected from the surface of a sample in order to acquire the absorption spectrum of the sample's surface. The light penetrates the sample surface to a depth of a few μm . The process of measurement using the ATR method is shown in Fig. 1. The measurement conditions are shown in Table 1, and the measurement results are shown in Figs. 2(a) to (d).

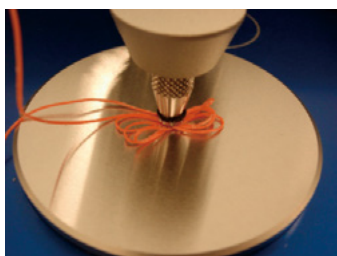
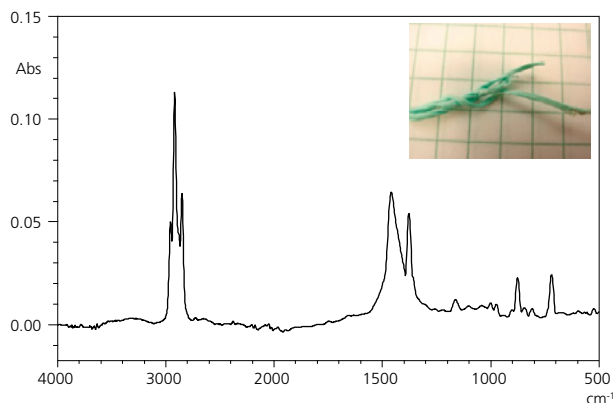


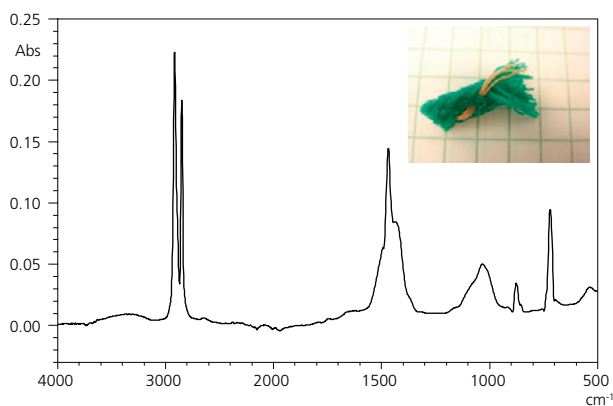
Fig. 1 Measurement Using the ATR Method

Table 1 Measurement Conditions

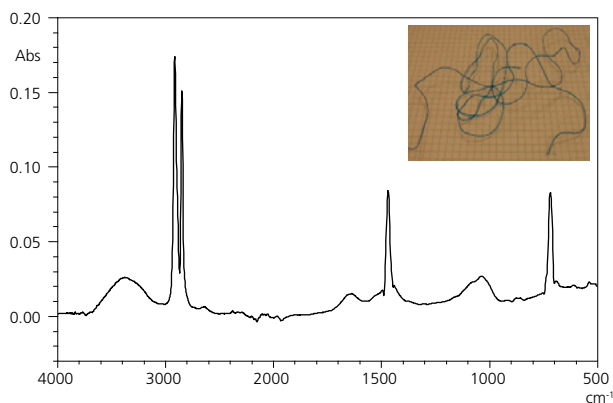
Main Unit/Accessories	: IRTracer-100 / Quest
Resolution	: 4 cm^{-1}
Scan Accumulation	: 45
Apodization Function	: Happ-Genzel
Detector	: DLATGS



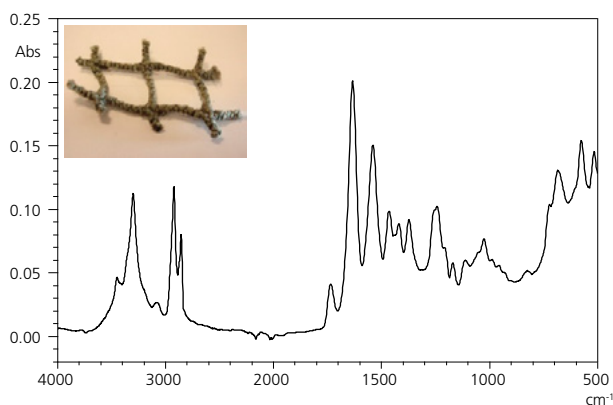
(a) Polyethylene (PE) + polypropylene (PP)



(b) Polyethylene (PE) + calcium carbonate (CaCO_3) + silicate



(c) Polyethylene (PE) + silicate



(d) Polyamide (PA) + acetate

Fig. 2 Qualitative Results

Figs. 2 (a) to (d) show the names of the components in the qualitative results. Here, it is evident that three of the four samples of marine debris are compounds consisting of multiple components. With FTIR, this sort of data analysis is easily performed by utilizing the libraries provided as standard with the instrument.

4. Example of the Analysis of Microplastics Using an Infrared Microscope System

• Microplastics Collected from Marine Life

The impact of marine debris has spread even to living organisms inhabiting marine regions where contamination was initially thought unlikely to reach. This includes arctic cod living in the Arctic Ocean and deep sea shrimp, amphipods living in the deep seas. Newcastle University in the UK and the Dutch Wageningen Marine Research group have separated microplastics on the order of 100 μm in size from the stomach contents of a variety of living organisms, and are investigating the impact of marine debris.²⁾

Microplastics collected from arctic cod and deep sea shrimp were measured using an infrared microscope system. Images of the samples are shown in Figs. 3 (a) and (b). The blue microplastic collected from the arctic cod shown in Fig. 3 (a) was measured with the microscopic ATR method. The microplastic collected from the deep sea shrimp shown in Fig. 3 (b) was rolled with a diamond cell, and then measured by the transmission microscopy method. The measurement conditions are shown in Table 2, and the measurement results are shown in Figs. 4 and 5.

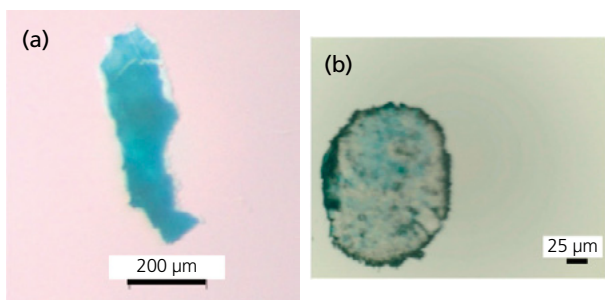


Fig. 3 Sample Images

(a) Collected from Arctic Cod (b) Collected from Deep Sea Shrimp

Table 2 Measurement Conditions

Main Unit/Accessories	: IRTracer-100 / AIM-9000
Resolution	: 8 cm^{-1}
Scan Accumulation	: 100 (Fig. 3a), 50 (Fig. 3b)
Apodization Function	: Happ-Genzel (Fig. 3a) Sqr-Triangle (Fig. 3b)
Detector	: MCT
Aperture Size	: 25 μm \times 25 μm (Fig. 3a) 15 μm \times 15 μm (Fig. 3b)

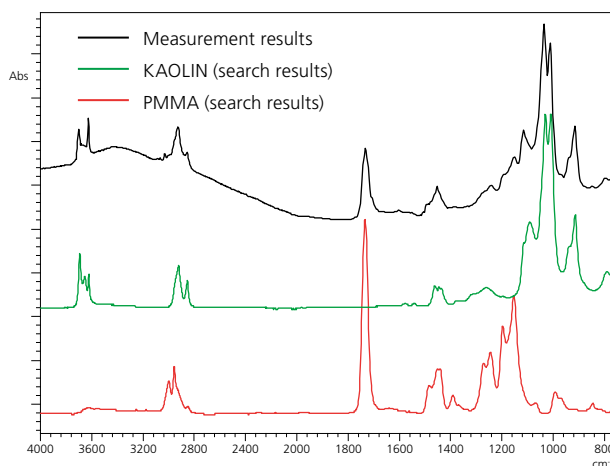


Fig. 4 Measurement Results for Microplastic Collected from Arctic Cod

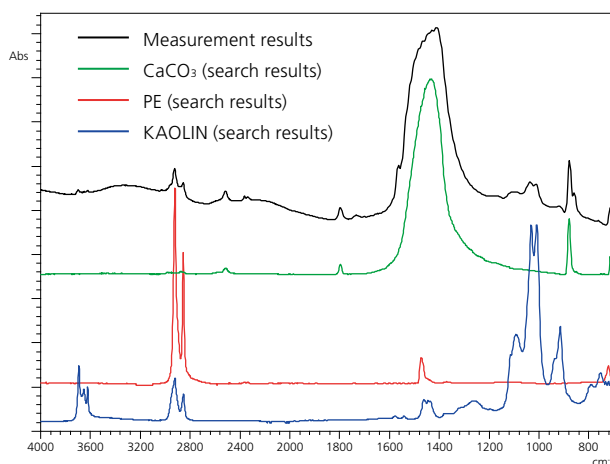


Fig. 5 Measurement Results for Microplastic Collected from Deep Sea Shrimp

From Fig. 4, it is evident that the main component of the microplastic collected from the arctic cod is polymethyl methacrylate (PMMA), and that it contains the additive KAOLIN (aluminum silicate). PMMA is a resin used in general merchandise and everyday items because it is light and tough, and features superior weather resistance, water resistance, and impact resistance. In addition, from Fig. 5, it is evident that the microplastic collected from the deep sea shrimp is a mixture of polyethylene (PE), calcium carbonate (CaCO_3), and KAOLIN (aluminum silicate). PE is a very common resin used in packaging and containers, and is often detected as a microplastic.

In the analysis of microplastics on the order of a few dozen to a few hundred μm , an infrared microscope system is suitable because it is capable of qualitatively analyzing organic compounds and some inorganic compounds. It can quickly identify resin components and additive components.

5. Example of the Analysis of Microplastics Using an Infrared Microscope System

• Microplastics Collected from Environmental Water

Microplastics in environmental water were collected using a polytetrafluoroethylene (PTFE) filter. A mapping analysis was then performed using an infrared microscope system. PTFE does not absorb infrared rays in the vicinity of 1200 cm^{-1} , so it is convenient for measuring samples as is using transmission microscopy after they are collected by a filter. The measurement conditions are shown in Table 3, and the visible observation image is shown in Fig. 6.

Table 3 Measurement Conditions

Main Unit/Accessories	: IRTracer-100 / AIM-9000
Resolution	: 8 cm^{-1}
Scan Accumulation	: 5
Apodization Function	: Sqr-Triangle
Detector	: MCT
Aperture Size	: $20\text{ }\mu\text{m}\times 20\text{ }\mu\text{m}$
Mapping Range	: $460\text{ }\mu\text{m}\times 1780\text{ }\mu\text{m}$

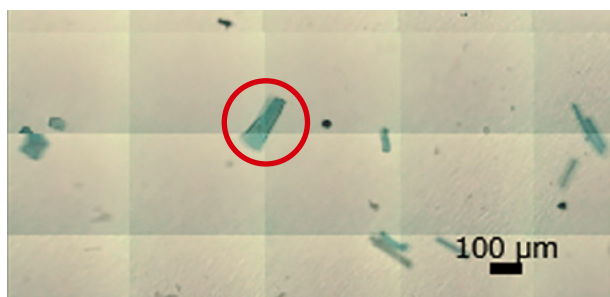


Fig. 6 Visible Observation Image

The infrared spectrum for the rod-shaped microplastic circled in red in Fig. 6 is shown in Fig. 7.

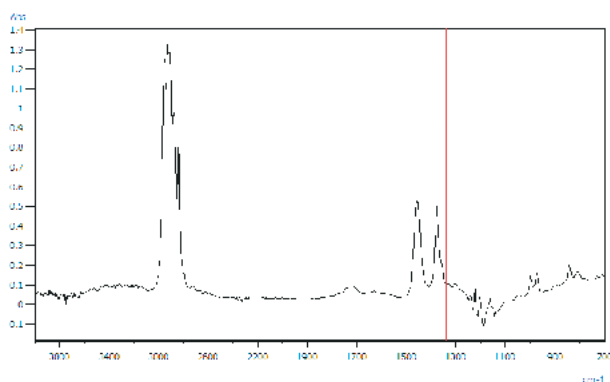


Fig. 7 Infrared Spectrum of Rod-Shaped Microplastic (The red frame contains the peaks used to create the chemical image indicated in Fig. 8.)

Though not shown here, from the results of the library search, it was determined qualitatively that the microplastic was polypropylene (PP).

Fig. 8 shows the chemical image created using the corrected area value (peak area value from the baseline) for the peaks in the range of $1400\text{ to }1339\text{ cm}^{-1}$ (CH_3 bending vibration), which are characteristic of PP. The sites with a lot of the component are shown in red, and the sites with little of the component are shown in blue. It is clear that all of the rod-shaped microplastic that can be confirmed in the visible observation image is PP.

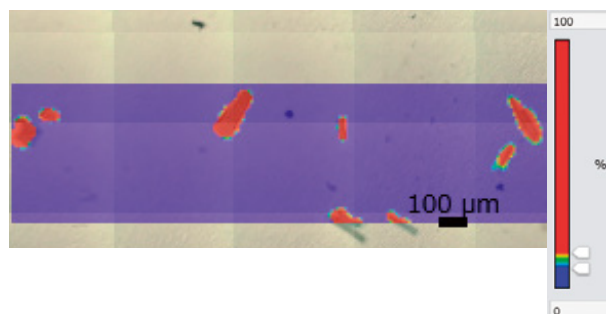


Fig. 8 PP Distribution—Corrected Area Values for $1400\text{--}1339\text{ cm}^{-1}$ Peaks

With mapping analysis using an infrared microscope system, the components of the microplastic were quickly qualified based on the visible observation image, and their distribution was clearly shown in the chemical image.

<Acknowledgments>

The samples used in these measurements as well as information related to the microplastics were provided by Yutaka Kameda, associate professor at the Chiba Institute of Technology. His cooperation is greatly appreciated.

6. Conclusion

Shimadzu handles a variety of analytical instruments capable of performing multifaceted evaluations of microplastics. We will continue to monitor analysis trends, and will report effective pretreatment techniques and measurement techniques.

References

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Application News No.A586, 589, 605



Tests of Pharmacopeia Grade Ethanol (Ethanol for Disinfection)

Ethanol acts as a disinfectant. Products containing ethanol at the optimal concentration are sold as ethanol for disinfection. The alcohol used in pharmaceuticals is tested using confirmation test methods specified in the Japanese Pharmacopeia, thus ensuring its quality. Confirmation tests on ethanol and dehydrated ethanol used as ethanol for disinfection are specified based on an accord in three pharmacopeias. Basically, the same test method is indicated in the Japanese Pharmacopeia (JP), the United States Pharmacopoeia (USP), and the European Pharmacopeia (EP).

Shimadzu offers applications and instruments for implementing a variety of tests, including ethanol confirmation tests, purity tests, and checks for inclusions.



Fourier Transform Infrared Spectrophotometer
IRSpirit™

UV-VIS Spectrophotometer
UV-1900i



Gas Chromatograph
Nexis™ GC-2030



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