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FTIR
TALK LETTER

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FTIR and Water

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Water is a ubiquitous and inseparable part of our daily lives. Without water, we could not live. However, for FTIR spectrophotometers, water (water vapor) is a dangerous substance that threatens both hardware and applications.

(1) Hardware and Water

FTIR spectrophotometers measure the infrared spectrum resulting from irradiating samples with an interference pattern generated from a light source. Functionally, the infrared light must be transmitted through the optical elements used in the optical measurement path, such as the beam splitter, which generates the interference pattern from the light, and windows separating the interferometer compartment from the sample compartment.

Optical elements that transmit infrared light are commonly made of alkali halides, such as potassium bromide (KBr) and cesium iodide (CsI). However, alkali halides are deliquescent (characteristic of crystals to melt by reacting with water vapor in air). Therefore, in humid locations, the water (water vapor) in air can erode the surface of optical elements until they are no longer viable as optical elements. Fig. 1 shows one KBr window with the surface eroded by moisture (right) and one without surface erosion (left).

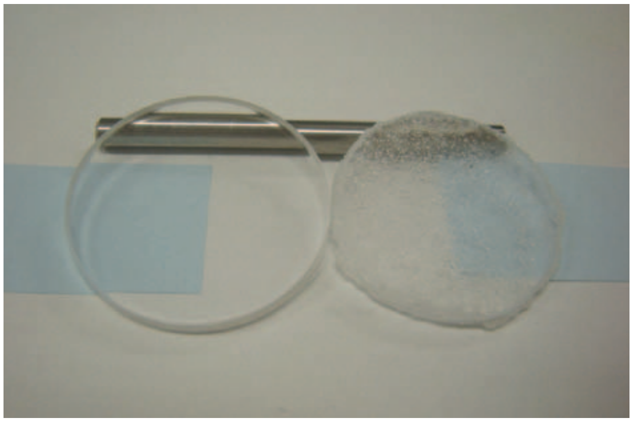

Fig. 1 KBr Window

(2) Applications and Water

Fig. 2 shows how water vapor absorbs infrared light between 4000 cm^{-1} and 3400 cm^{-1} and between 2000 cm^{-1} and 1300 cm^{-1}. If the peaks for water vapor coincide with other peaks, such as –OH and –NH group peaks between 4000 cm^{-1} and 3400 cm^{-1} or C=O and –CH$_2$– group peaks between 2000 cm^{-1} and 1300 cm^{-1}, the vapor peaks can interfere when analyzing infrared spectra.

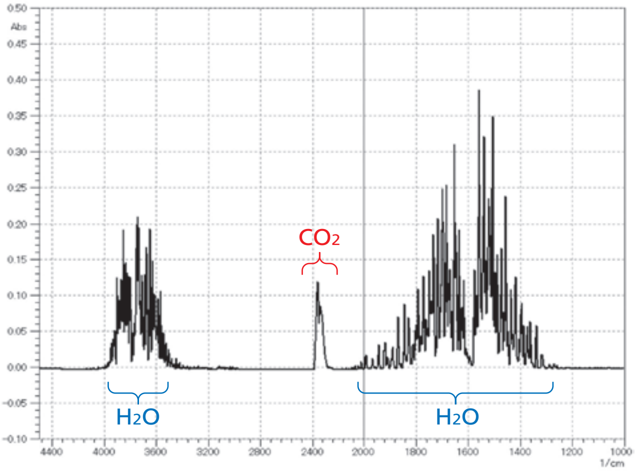

Fig. 2 Spectrum for Water Vapor

(3) Methods for Eliminating Water

Consequently, FTIR analysis is vulnerable to water both in terms of hardware and applications. The following describes hardware and software functions provided to eliminate moisture so that samples can be measured or analyzed precisely.

(1) Electric Dehumidifier (Included standard on IRPrestige-21 and IRAffinity-1 systems)

Shimadzu IRPrestige-21 and IRAffinity-1 Fourier transform infrared spectrophotometers are equipped with electric dehumidifiers in the interferometer compartment to protect optical elements from deliquescing.

The IRPrestige-21 dehumidifies using a Peltier element. During the winter, it is common to see water droplets form and run down cold window panes. This is the same principle used in the IRPrestige-21. The interferometer compartment is dehumidified by exposing it to the cold side of a Peltier element, which condenses water vapor so it can be removed from the compartment as liquid water.

In contrast, the IRAffinity-1 uses a solid polymer electrolyte membrane to remove water from the interferometer compartment by electrolysis.

The anode side (dehumidification side) of the electrolytic dehumidifier is positioned inside the interferometer compartment, where it separates the water into oxygen and hydrogen ions.

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

The hydrogen ions pass through a solid polymer electrolyte membrane and to the cathode side (moisture discharge side) of the dehumidifier, located outside the interferometer compartment. At the cathode side of the dehumidifier, the hydrogen ions react with oxygen in the air to form water molecules.

$$2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$$

This process is illustrated in Fig. 3.

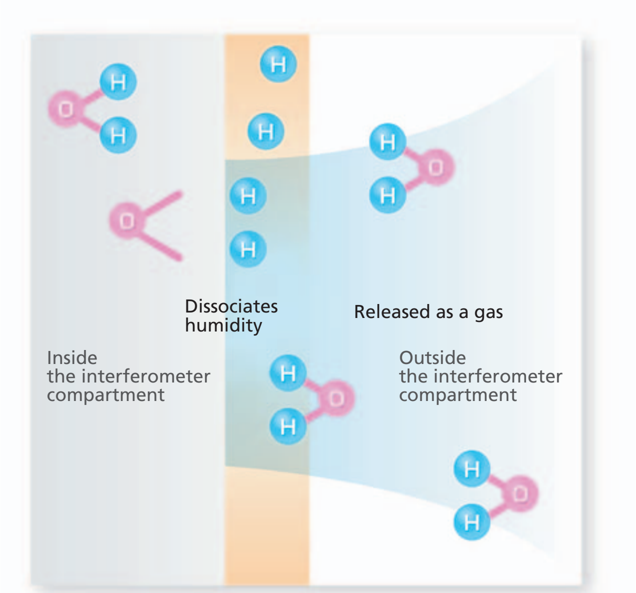

Fig. 3 Dehumidification by Solid Polymer Electrolyte Membrane

(2) Dry Air Supply System (special order accessory)

Used in conjunction with a purge control kit (special order accessory), this system is used to supply dry air to the FTIR interferometer, sample, and detector compartments. It purges water vapor from the measurement optical path so that samples can be measured more precisely. Fig. 4 shows power spectra measured before and after supplying dry air. It clearly shows a reduction in the size of water vapor peaks.

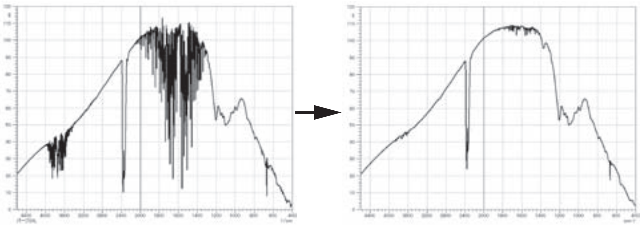

Fig. 4 Purging with Dry Air

(3) Purging with Nitrogen Gas

Instead of dry air, this system supplies high-purity nitrogen gas (nitrogen purging) to purge not only water vapor, but also carbon dioxide, which enables even more precise measurements.

(4) Atmospheric Correction (standard feature of IRsolution)

IRsolution includes an atmospheric correction function that allows using software to eliminate water vapor and carbon dioxide peaks.

When the background spectrum is measured, the software identifies peaks corresponding to water vapor and carbon dioxide in the power spectrum and then subtracts them from infrared spectra measured from samples.

Fig. 5 shows an infrared spectrum (black) measured after atmospheric correction, which clearly shows how water vapor peaks (red) are nicely eliminated between 4000 cm^{-1} and 3400 cm^{-1} and between 2000 cm^{-1} and 1300 cm^{-1} and carbon dioxide peaks (red) are eliminated near 2360 cm^{-1}.

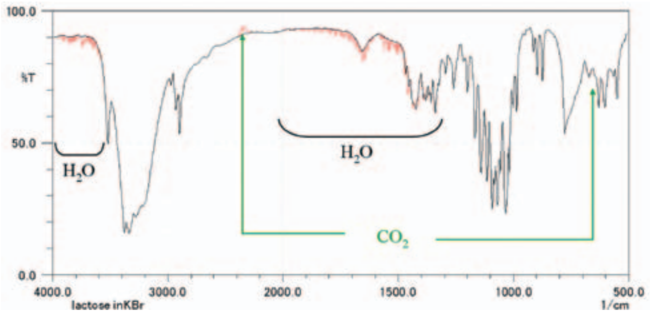

Fig. 5 Atmospheric Correction

As indicated above, water and water vapor can have a major effect on FTIR systems. However, by incorporating various hardware and software measures, Shimadzu FTIR systems can be used without worry.

Measurement Method ABCs: Multiple Reflection ATR Method

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The attenuated total reflectance (ATR) method is widely used because of its ability to easily obtain infrared spectra from samples in a variety of forms. Among ATR methods, the multiple reflection ATR method uses a prism to achieve multiple reflections. This principle provides peaks with higher intensity than single reflection ATR, which is especially advantageous for evaluating slight peaks from additives. The following describes some of the benefits of using the multiple reflection ATR method and key points to consider when measuring samples.

1. Attachments

Fig. 1 shows the HATR10 horizontal attenuated total reflectance attachment, which features an integrated sample compartment, used as a measuring attachment with the multiple reflection ATR method. Fig. 2 shows the HATR10 attachment installed on a Shimadzu IRAffinity-1 Fourier transform infrared spectrophotometer. Fig. 3 shows the ATR-8200HA horizontal attenuated total reflectance attachment, a model designed to be mounted inside the FTIR sample compartment.

The optical system of the multiple reflection ATR method is illustrated in Fig. 4. The infrared light is reflected repeatedly from the top and bottom surfaces of the ATR prism to obtain information about the sample from the side pressed against the sample. This information is then sent to the detector. Both the HATR10 and ATR-8200HA models reflect the light against the sample surface ten times. ATR prisms are typically made of ZnSe, which permits measuring samples with a pH value between 5 and 9. A Ge prism is used to measure samples with a high refractive index as well as highly acidic or alkaline samples. However, measuring acidic samples with a pH below 3 can corrode the prism or prism plate.

Fig. 1 HATR10 Horizontal Attenuated Total Reflectance Attachment with Integrated Sample Compartment

Fig. 2 IRAffinity-1 Unit with HATR10 Attachment Installed

Fig. 3 ATR-8200HA Horizontal Attenuated Total Reflectance Attachment

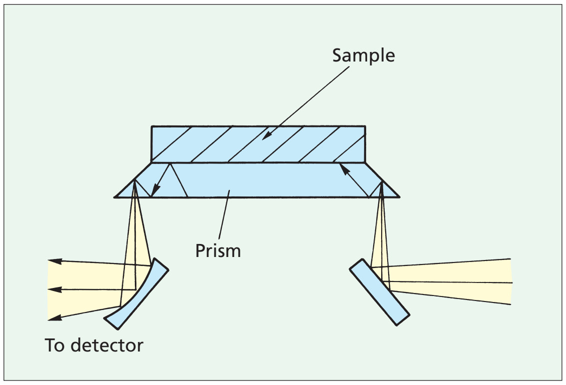

Fig. 4 Diagram of Optics for Multiple Reflection ATR Method

HATR10 and ATR-8200HA attachments are equipped standard with two types of prisms for measuring solid and liquid samples. ATR-8200HA attachments with solid and liquid sample prisms installed are shown respectively in Fig. 5 and 6. The solid sample prism is used to measure solid samples with a flat surface, such as flat film, rubber, or plastic samples. It is not suitable for measuring powdered or extremely small samples. In contrast, the liquid sample prism is fastened in a position slightly recessed from the prism plate surface, which allows holding liquid samples in the indentation during measurements.

Fig. 5 ATR-8200HA Attachment with Solid Sample Prism Plate Installed

Fig. 6 ATR-8200HA Attachment with Liquid Sample Prism Plate Installed

2. Example and Key Points for Measurement

The multiple reflection ATR method can be expected to provide higher peak intensity than single reflection ATR method, with the increase in intensity corresponding to the number of reflections. Fig. 7 shows the results from using a ZnSe prism to measure paraffin oil with both methods. It shows that the multiple reflection ATR method provided roughly 10 times higher peak intensity than the single reflection ATR method. Fig. 8 shows an enlarged view of the baseline in Fig. 7. It shows how the multiple reflection ATR method clearly detects the many tiny peaks.

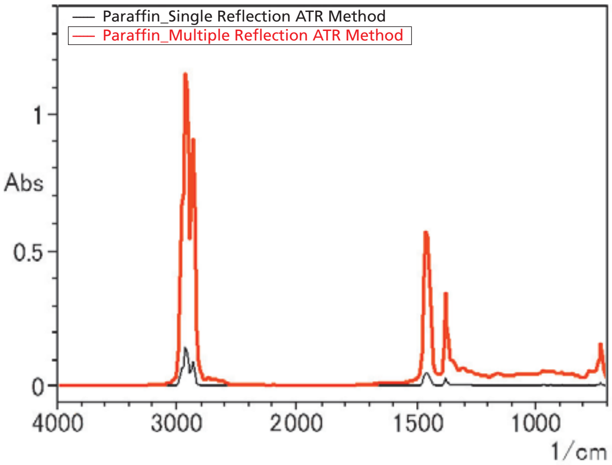

Fig. 7 Results from Measuring Paraffin Oil with Single and Multiple Reflection ATR Methods

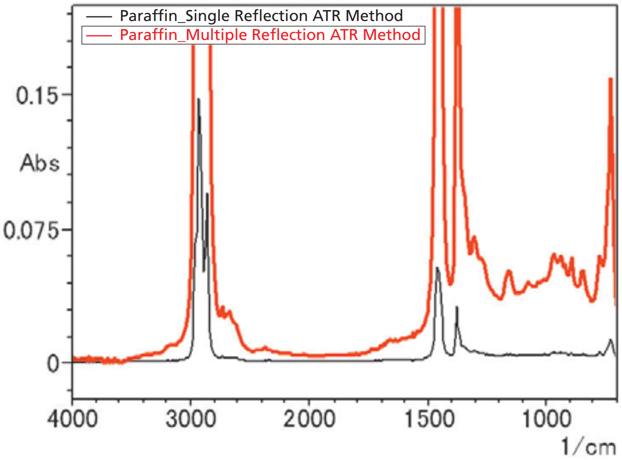

Fig. 8 Enlarged View of Baseline in Fig. 7

The ATR prism diameter on measuring instruments that use the single reflection ATR method (such as MIRacleA and DuraSamplIR II models) is typically about 2 mm. However, the ATR prism used in HATR10 and ATR-8200HA attachments that use the multiple reflection ATR method is about 80 mm × 10 mm. Therefore, the ATR prism must be cleaned with particular care after measurements. Cleaning typically involves using a cotton swab to wipe the prism with a solvent such as ethanol, acetone, or chloroform. To prevent scratching the ATR prism, it is important to repeatedly wipe it gently, rather than rubbing it with excessive force. Particular care is required for samples with high viscosity, which can tend to leave a residue on the ATR prism. Consequently, the multiple reflection ATR method is not as easy to operate as the single reflection ATR method.

3. Contact Between a Solid Sample and an ATR Prism

To take full advantage of the superior operating principle offered by multiple reflection ATR attachments, it is important to be extra careful that solid samples are held tightly against the prism. As an example of a poor fit between the sample and a multiple reflection ATR prism, Fig. 9 shows results from measuring polyethylene (PE) film using a ZnSe prism in single and multiple reflection ATR attachments.
Compared to the single reflection ATR method, the multiple reflection ATR measurement results failed to provide peak intensity commensurate with 10 reflections. In particular, this situation tends to happen with hard films and plastics, which in some cases can even cause peak intensity from multiple reflection ATR measurement to be lower than from single reflection ATR measurement.
To improve the contact between a solid sample and ATR prism, we recommend that thin rubber or soft plastic be inserted as a spacer between the sample and clamp lever, as shown in Fig. 10. This spacer should be about 1 to 3 mm thick and be about the same size as the ATR prism (80 mm × 10 mm). That should improve the fit between the sample and ATR prism. Since the light penetration depth using HATR10 and ATR-8200HA attachments is about 5 µm, components in the spacer will not affect measurement results as long as the sample is at least 5 µm thick. The spacer can also be wrapped with aluminum foil to prevent components from the spacer adhering to the sample and affecting measurement results for samples that are smaller than the ATR prism. It is also important to be careful of other factors that affect the contact between the sample and ATR prism, such as by improving the flatness of curved samples by pressing them before measuring.
Measurement results obtained after using a spacer to improve the contact between the sample and ATR prism are shown in Fig. 11. An enlarged view of the high-frequency end of Fig. 11 is shown in Fig. 12. Measurement results from using a spacer clearly show two peaks from additives in the PE film between 3600 and 3000 cm^{-1}. Using a spacer can also be effective for single reflection ATR applications and is worth trying.

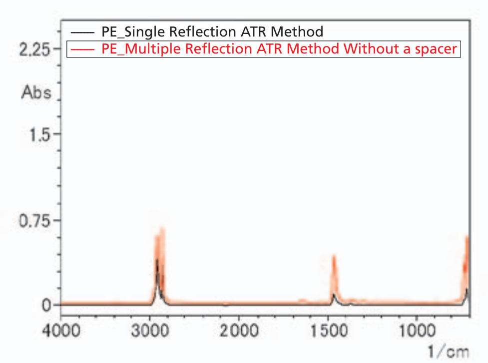

Fig. 9 Results from Multiple Reflection ATR Measurement of Sample Not Positioned Tightly Against the Prism

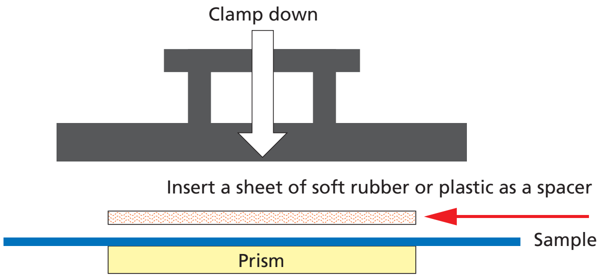

Fig. 10 Example of Method to Improve Contact Between Sample and ATR Prism

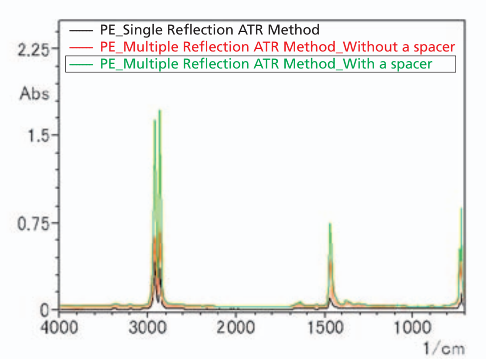

Fig. 11 Measurement Results After Improving Contact Between Sample and ATR Prism

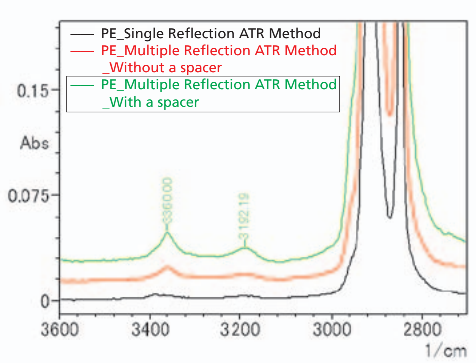

Fig. 12 Enlarged View from Fig. 11

4. Conclusion

As shown above, the multiple reflection ATR method can be a powerful tool for detecting and evaluating peaks from low concentration components, such as additives. Please consider it as a measurement method for applications that benefit from the advantages provided by its measurement principle. Also refer to Application News bulletins regarding applications using multiple reflection ATR method, such as Application News A432: Analysis of Degraded Machine Oil by FTIR, A401: Analysis of Biodiesel Blends by FTIR, and A332: Analysis of Human Skin by Horizontal ATR Attachment.

Q&A

Question

What are the key considerations when using a diamond cell for infrared microscope analysis?

Answer

The diamond cell shown in Fig. 1 is a type of infrared light transmission window used to compress thick samples or micro samples between two cells to an appropriate thickness. A diamond cell is an extremely useful tool in cases where the sample can be placed under the stereoscopic microscope to remove the target sample with a needle, tweezers, box cutter, or other device. The following describes the measurement procedure and key points. (*See* Fig. 2.)

(1) When sampling, place an appropriately sized sample near the center of the diamond window (hereafter "window"). The amount of infrared light is greater in the center than along the perimeter, which results in less noise in the data. Make sure part of the window is not covered by the sample. If the sample is placed across the entire window area, then there will be no area available for measuring the background spectrum.

(2) Next, place the other disk on top and compress the sample by tightening the three screws. To prevent damaging the window, tighten the screws by hand.

(3) Lastly, remove the screws and lift off the upper disk. Confirm which disk includes the sample. The sample can also stick to the upper disk. Measure the disk that includes the sample. If the sample is measured between both windows, it is extremely likely to cause interference fringes, due to the difference in refractive indices between the sample and windows.

Some samples cause saturated absorption peaks because they cannot be compressed adequately, whereas other samples spread out across the entire window. In such situations, samples must be re-sampled; sometimes good results can be obtained by simply placing the sample on the window and measuring ATR again. However, be careful not to scratch the prism or window, which is easy to do.

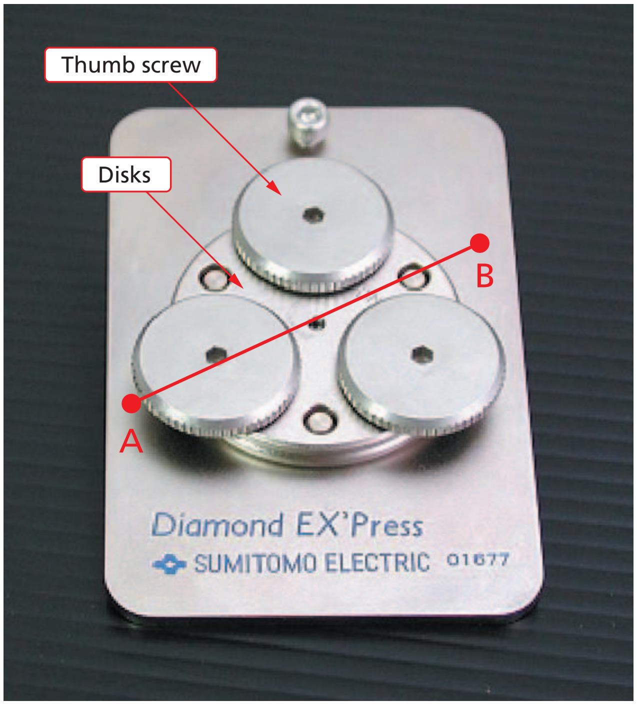

Fig. 1 Exterior of Diamond Cell

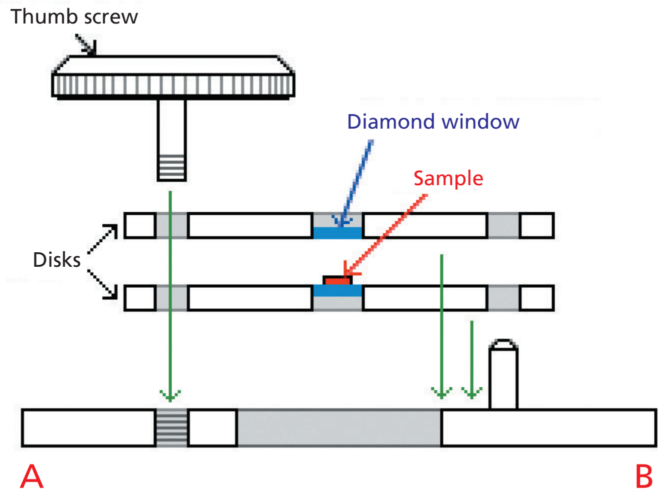

Fig. 2 Cross Section of Diamond Cell (A-B section)

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