

FTIR TALK LETTER

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FTIR market situation in China --- 2

Mirrors Used with FTIR --- 4

**Near-Infrared Region Measurement
and Related Considerations Part 1 --- 6**

Question --- 9

When conducting measurement using the microscope transmittance method, quite a bit of noise is generated. What causes this?

FTIR market situation in China



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FTIR is one of the major analytical instruments in China nowadays. Of course, the main purpose to use an FTIR instrument is qualitative analysis of organic compounds. It is assumed that the market size of FTIR in China is US\$25M as an annual sales amount and 850 units as a number in year 2006. Last 5 years, FTIR market in China had been expanded, and we are expecting to continue the expansion of this market for another few years. With the growth of FTIR market, apparently, the developments of much more complicated applications are needed as the market requirements. The market segmentation for Shimadzu FTIR in 2006 is shown in Fig.1.

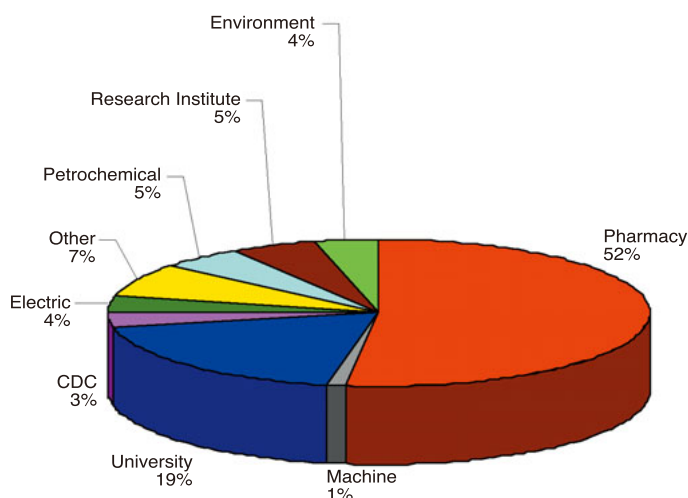


Fig.1 FTIR segments in China in 2006

Pharmaceutical industry is the biggest market, followed by University. Because of large population in China, pharmaceutical industry is one of most important industries. Thus, a lot of FTIR instruments have been sold for quality controls of the medicines. Main applications for pharmaceutical industry are identification of drugs as well as its package materials. ATR accessories, which can avoid complex sample pretreatment procedures, are often used to analyze package materials. The package materials are measured with an ATR accessory and their spectra are shown in Fig.2.

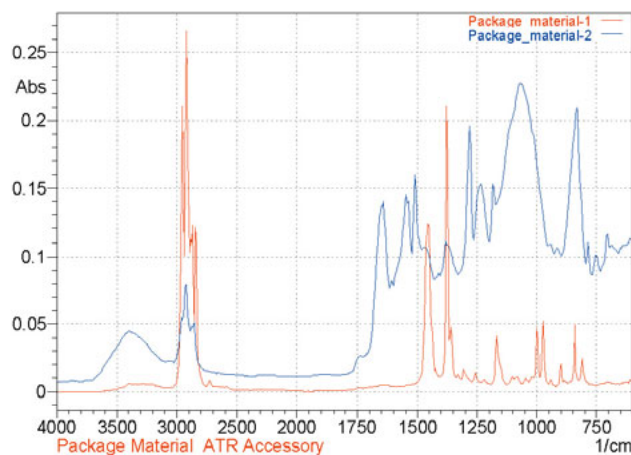


Fig.2 FTIR spectra of package materials

As the results of search, these materials are identified as polypropylene (Red line in Fig.2) and polyurethane (Blue line in Fig.2). In addition, as a historical reason, there is a specific application for an FTIR instrument in China market. This is the analysis of Traditional Chinese Medicine (TCM). Main ingredients of TCM such as ginsengs may depend on a harvest year, a growth area, etc. Therefore, identification of TCM is getting more complex. However, the use of infrared spectrum makes this identification much easier. Currently, 1103 numbers of infrared spectra are registered in Chinese Pharmacopoeia.

Compared to British Pharmacopeia and Japanese Pharmacopeia, the number of infrared spectra registered in Chinese Pharmacopeia is much larger than that of other Pharmacopeia. All raw materials and final medicines for TCM must be identified by FTIR. This is the main reason why more than 50 % of market segment in China is occupied by pharmaceutical industry.

China has been called a factory of the world. In fact, a lot of electronics companies set up the factories in Southern China. The products manufactured by those factories are exported to Europe, USA, Japan, etc. In order to improve the product reliability and comply with some of regulations such as RoHS directive, screening of harmful compounds became big issues. Screening analysis always needs rapid quantitative information. An FTIR instrument can provide some of judgment information for existence of hazardous compounds in the products. In this point, big impact for FTIR application has come from RoHS (Restriction on Hazardous Substances) directive in the last few years. Brominated flame retardants such as Polybromobiphenyls (PBBs) and Polybromodiphenyl ethers (PBDEs) are banned by RoHS directive. To measure these residual PBBs and PBDEs, FTIR is one of effective method to identify these prohibited compounds in the plastic materials. In this regard, electronics industry is also one of rapid growth markets for FTIR instruments.

In all industries, failure analysis is one of the measurement purposes for an FTIR instrument. As an example of failure analysis, the result of contaminant analysis with an ATR accessory is shown in Fig.3.

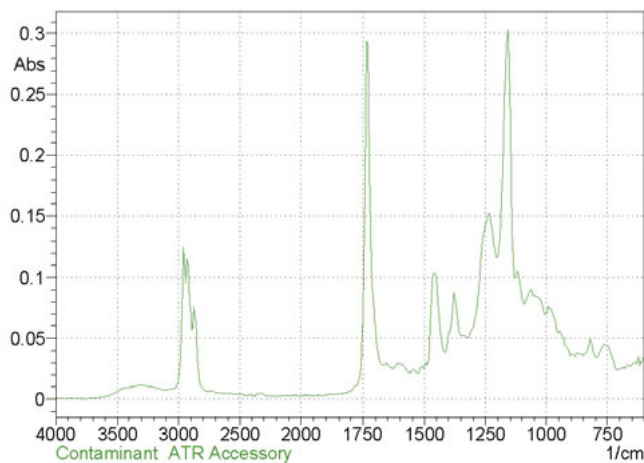


Fig.3 FTIR Spectrum of contaminant

As the result of search, a spectrum of acrylic compound is similar to the contaminant. The contaminant is guessed to be acrylic glue because the contaminant is adhesive. In the case of very small contaminants, microscope-FTIR is getting more demand for failure analysis.

As a factory of the world, FTIR market in China is steadily expanding in the pharmaceutical industry and some of material science industries. In order to meet versatile requirements, applications using FTIR accessories will take an important role.

SSL promotion activities

1. Seminars

Instrument promotion seminars and application seminars were held with some hot topics, such as RoHS and drug analysis in recent years.

2. User Meeting

To improve our after service, FTIR User Meeting was hold in every two years. User's papers were collected and famous FTIR experts were invited to give presentations. Through the meeting, the relationship between users and Shimadzu was highly strengthened.

3. Academic Conferences

The brand image of Shimadzu FTIR has been improved by attending academic conferences, such as National Molecular Spectrum Conference, where high quality papers by collaboration with famous universities were presented.

4. Internal Sales Training

In order to improve the sales of FTIR, internal training is held regularly. By training, sales become more confident in the competition.

Mirrors Used with FTIR

Spectroscopy Business Unit, Analytical & Measuring Instruments Division Tetsuo Okuda

Topics related to the internal workings of FTIR have been discussed time and again in the FTIR TALK LETTER, and this issue addresses the topic of mirrors used inside an FTIR.

1. Why is a mirror used instead of a lens?

In instruments that use light, like an FTIR, it is necessary to process light in various ways, such as focusing it or forcing its rays to travel in parallel. You may think of lenses as objects used for these purposes. Everyone has probably had the experience of using a magnifying glass to scorch a piece of paper by focusing the sun's rays at one point on the paper. In a camera, one of the most familiar devices which rely on light, multiple lenses are combined to form an image on the film (these days, most likely on a solid state image sensor like a CCD) of the picture we want to take. However, it is difficult to use a lens in an FTIR. In order for a lens to be applicable in an FTIR, that lens must satisfy the following conditions.

- (1) Have a wide wavelength range for transmission of infrared light, and be made of material that does not show large absorption within that range
- (2) Have a refractive index that is not too large
- (3) Be easy to fabricate
- (4) Be relatively inexpensive
- (5) Be environmentally-resistant

Up to now, a material that satisfies all the properties of (1) to (5) has not yet been developed. For example, an optical element known as a beam splitter is used inside the FTIR interferometer, and the material used for this is generally potassium bromide (KBr). This potassium bromide satisfies the conditions of (1) and (2), but because it is deliquescent (property of a crystal in air that takes in water and dissolves), it must be used in a low-humidity environment. Therefore, there is a problem with respect to environmental resistance, that is, condition (5).

On the other hand, the material calcium fluoride (CaF_2) is excellent with respect to conditions (2), (3), and (4). However, the range within which it transmits infrared light is narrow, barely transmitting any infrared light in the region referred to as the fingerprint region below 1000 cm^{-1} . Thus, its application is restricted.

Due to these factors, elements through which light must pass through, like lenses and prisms, are not used in FTIR, while mirrors, which reflect light, are used.

2. Types of Mirrors

The following types of mirrors are used to fulfill the roles of lenses and prisms in the FTIR.

(1) Plane mirror

As its name indicates, this is a mirror with a planar (flat) reflective surface. It is used to reflect light in a desired direction.

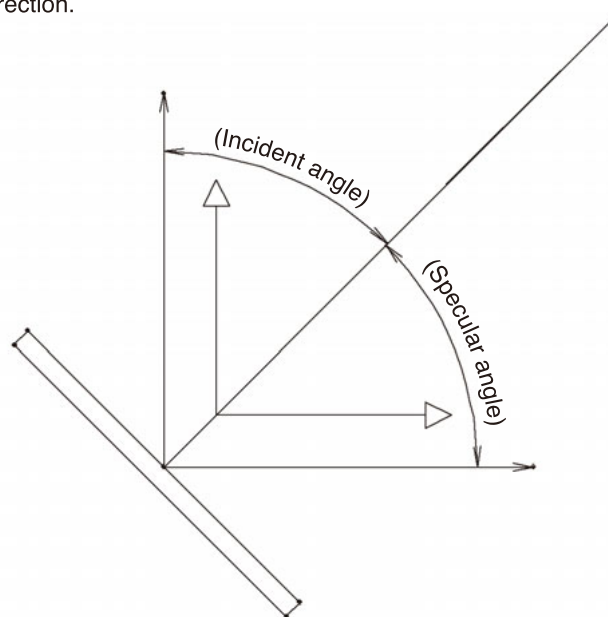


Figure 1 Plane Mirror

(2) Spherical mirror

This mirror uses part of the spherical surface as the reflection surface. Because there is point symmetry with respect to the center of the spherical surface, characteristically equal light can be created in any arbitrary direction.

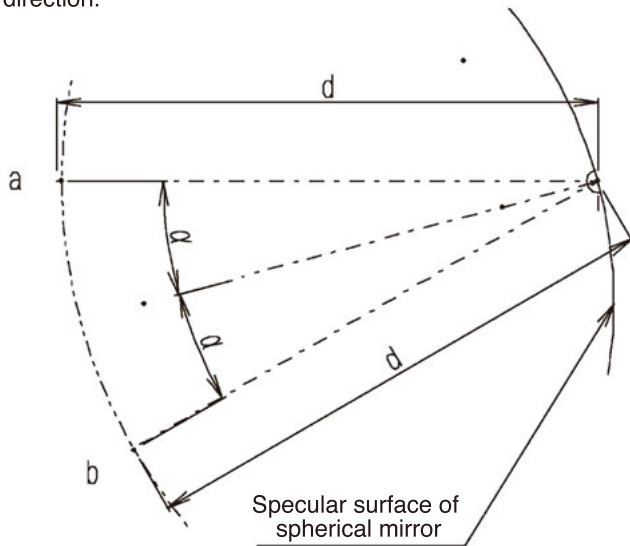


Figure 2 Principle of Spherical Mirror

Distance to center of the sphere surface is d .
Light from point a , at distance d from the sphere surface, is reflected by the spherical mirror.
An image the same as a is created at point b , separated from the sphere surface by distance d .

(3) Parabolic mirror

A mirror with a curved surface described by the rotation of a parabola expressed as $y=ax^2$ around axis y is a parabolic mirror. With a parabolic mirror, parallel incident light rays, illustrated by the arrows below, are concentrated at a single point. Therefore, it is used to focus parallel light rays to a single point, and to reflect light from a single point as parallel rays.

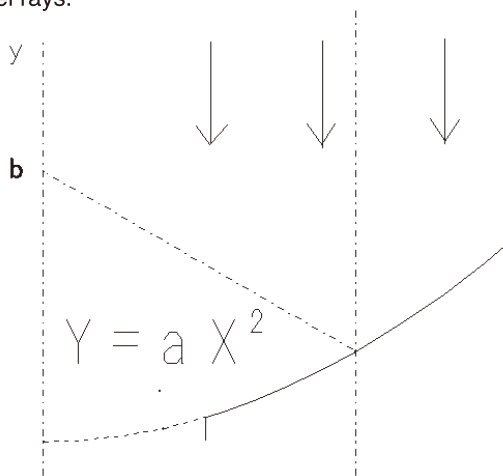


Figure 3 Principle of Parabolic Mirror

Parallel light, as illustrated by the arrows, is reflected and focused at point b .

(4) Ellipsoidal mirror

A mirror with a portion of the curved surface described by the rotation of an ellipsoid expressed as $x^2/a^2+y^2/b^2=1$ around axis y is an ellipsoidal mirror. There are 2 focal points on an ellipsoid surface, such that when light is irradiated from either of the points, it is focused on the position of the other focal point, and this is the property that is exploited. Specifically, it is used in the FTIR to refocus light that has been collected in the sample compartment on the infrared detector.

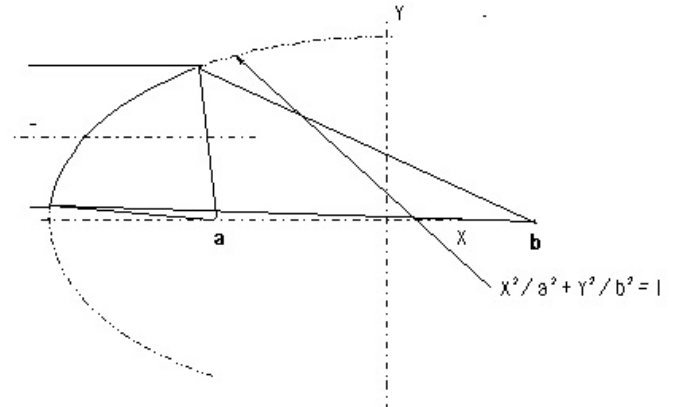


Figure 4 Principle of Ellipsoidal Mirror

Light irradiated from focal point a is concentrated at focal point b .

3. Conclusion

Here we introduced and discussed the use of the mirror in FTIR. In the Shimadzu FTIR, the infrared light can be taken out as parallel light from the side of the instrument. When we customize specialized attachments to conduct measurement using this parallel light, we use some of the mirrors explained above in combination.

Near-Infrared Region Measurement and Related Considerations Part 1

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Hirokazu Abo

Fourier Transform Infrared spectrophotometers (FTIR) are mainly used to measure light absorption of so-called mid-infrared light, light in the wavenumber range of 4,000 to 400 cm^{-1} (wavelengths 2.5 to 25 μm), in order to identify and quantify various materials. By modifying the FTIR's interferometer beam splitter and detector to accommodate near-infrared light, FTIR spectrophotometers that can be used for near-infrared light measurement have been developed and commercialized. Measurement of near-infrared light is different in some ways from that of mid-infrared light, and some of the characteristics and considerations associated with near-infrared light absorption should be noted.

Here we introduce some actual sample measurement examples to illustrate points that should be considered.

1. Characteristics of Near-Infrared Light Absorption

Near-infrared light generally refers to light within the wavenumber range of 12,500 to 4,000 cm^{-1} (wavelengths from 800 to 2,500 nm) (see Fig. 1). Absorption of near-infrared light, like that of mid-infrared light, is based on the vibration of the material. However, near-infrared light absorption is much weaker in intensity as compared with mid-infrared light absorption, since near-infrared light absorption is based on overtones and combined tones in the mid-infrared light region. Therefore, measurement of samples showing weak absorption is difficult, but the fact that samples can be measured without being diluted is an advantageous feature. Furthermore, as solvents themselves show weak absorption, aqueous solutions are also relatively easy to measure.

Various methods of near-infrared absorption measurement are known, such as the transmittance and diffuse reflectance methods, and these will be introduced using measurement examples.

2. Near-Infrared Transmittance Measurement of Liquids

Measurements that are often conducted in the near-infrared region include the transmittance measurement of solutions. There are a variety of measurement samples that fall into this category, and aqueous solutions are one type.

As is commonly known, the molecular extinction coefficient of water in the mid-infrared region is extremely large, and in most cases saturation occurs in absorption associated with the solvents. Therefore, there are many instances where the absorption associated with other substances cannot be confirmed. In contrast, when a 1 mm path length cell is used to conduct near-infrared transmittance measurement, in almost all regions, the absorption of substances present in the water can be confirmed (although this can be difficult at low concentrations).

In addition, in the near-infrared region, as in the visible region, the absorption of glass and quartz is barely seen. Therefore, chemically stable and easy-to-handle glass and quartz can be used as materials for window plates and cells for measurement.

	UV Light	Visible Light	Near-Infrared Light	Mid-Infrared Light	Far-Infrared Light	
<Wavelength>	200nm	400nm	800nm	2.5 μm	25 μm	1mm
<Wavenumber>			12,500 cm^{-1}	4,000 cm^{-1}	400 cm^{-1}	10 cm^{-1}

Figure 1 Near-Infrared Light Region

As an example of aqueous solution measurement, Figure 2 shows the near-infrared spectrum of an ethanol aqueous solution.

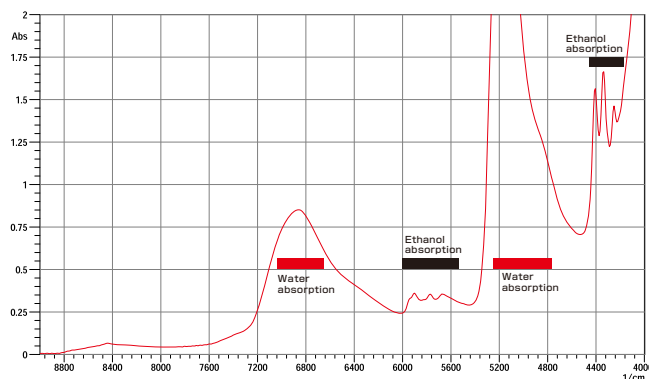


Figure 2 Ethanol Aqueous Solution Measurement

A cell with a path length of 1 mm was used. The absorption of water along with that of the dissolved ethanol was clearly confirmed. Thus, measurement of an aqueous solution, which is difficult in the mid-infrared region due to absorption saturation, is relatively easy in the near-infrared region.

In measurement of this type of aqueous solution and samples with high water content, it is necessary to consider the factor of temperature. Figure 3 shows the spectra of water acquired at different temperatures between 25 and 80°C.

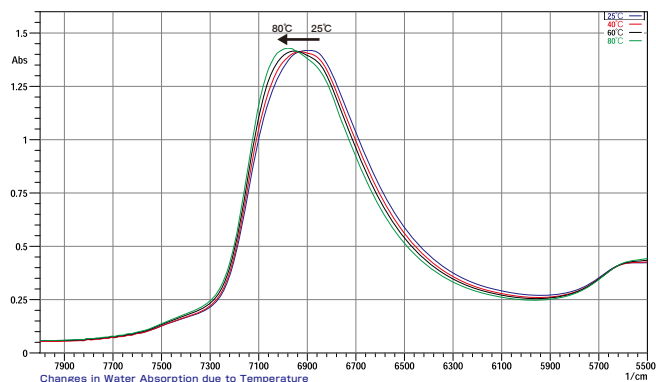


Figure 3 Changes in Peak Wavenumber of Water due to Temperature

It is clearly seen that, as the temperature increases, the peak around 7,000 cm^{-1} shifts toward the higher wavenumber side. Table 1 shows the absorbance values with respect to temperature changes at 6,890 cm^{-1} (peak position at 25°C).

Table 1 Temperature and Absorbance of Water at 6,890 cm^{-1}

Temperature (°C)	Absorbance
25	1.418
40	1.403
60	1.390
80	1.372

Thus, it can be seen that as the temperature changes, the absorbance also changes in accordance with the

wavenumber shift. For this reason, in near-infrared measurement of samples that contain water, absorbance around water absorption will fluctuate unless measurement is conducted at a constant temperature.

The main cause of peak shift shown here is said to be temperature-induced changes in the hydrogen bond of the water molecules.

Just to touch on the topic of the change in the hydrogen bond, in the near-infrared region, since there is a big difference in the peak positions of the hydrogen-bonded OH group and the non-hydrogen-bonded OH group, and since the peak intensity of the non-hydrogen-bonded OH group is relatively large, measurement is often conducted with respect to the hydrogen bond (Shimadzu Application News No. A365).

3. Near-Infrared Transmittance Measurement of Solids

Up to here, we have spoken about the near-infrared transmittance measurement of liquids; however, the near-infrared transmittance method is also effective for measuring solids. Figure 4 shows a near-infrared transmittance spectrum of 1 mm thick polystyrene. It is clear that in near-infrared measurement, there is almost no saturation in the absorption of the 1 mm thick sample. A mid-infrared transmittance spectrum of a polystyrene sample having the same 1 mm thickness is shown in Figure 5. Here, the absorption saturation is evident.

In measurement of solids, as shown here, samples of thickness that would be accompanied by absorption saturation in mid-infrared transmittance measurement can be measured without absorption saturation in the near-infrared region.

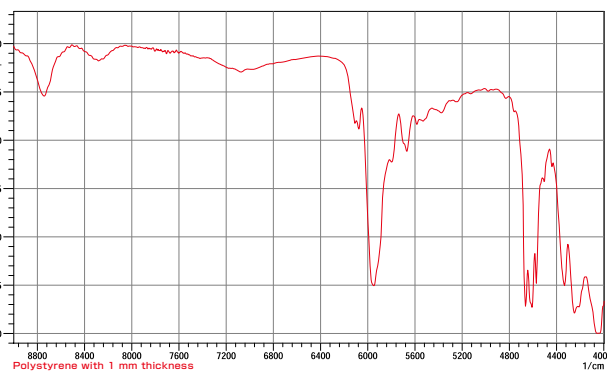


Figure 4 Near-Infrared Spectrum (1 mm thick polystyrene)

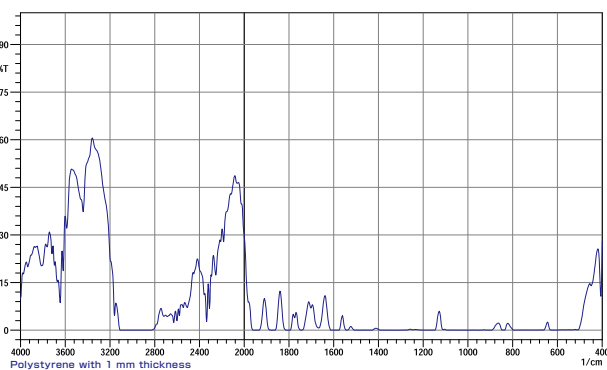


Figure 5 Mid-Infrared Spectrum (1 mm thick polystyrene)

4. Comparison with UV-Vis-NIR Spectrophotometer

Ultraviolet-visible near-infrared (UV-Vis-NIR) spectrophotometers are also capable of measuring near-infrared spectra. However, the construction of UV-Vis-NIR spectrophotometers is different from that of FTIR spectrophotometers, and there are differences in data obtained by these two types of instruments. Following are examples of o-xylene transmittance measurement. The measurement results using the FTIR are shown in Figure 6, and the measurement results using the UV-Vis-NIR Spectrophotometer are shown in Figure 7. The horizontal axis shows the wavelength to facilitate comparison.

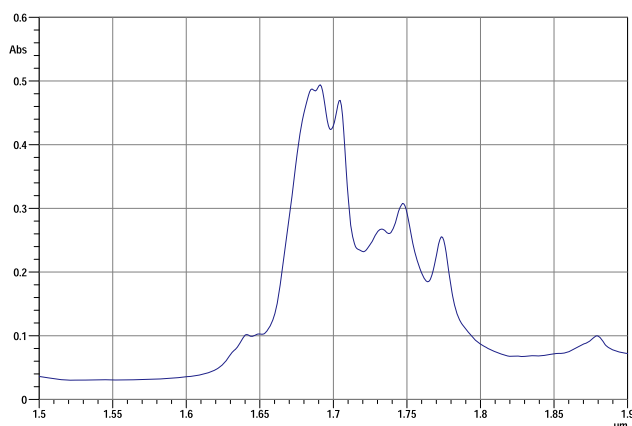


Figure 6 o-Xylene Near-Infrared Transmittance Spectrum (FTIR)

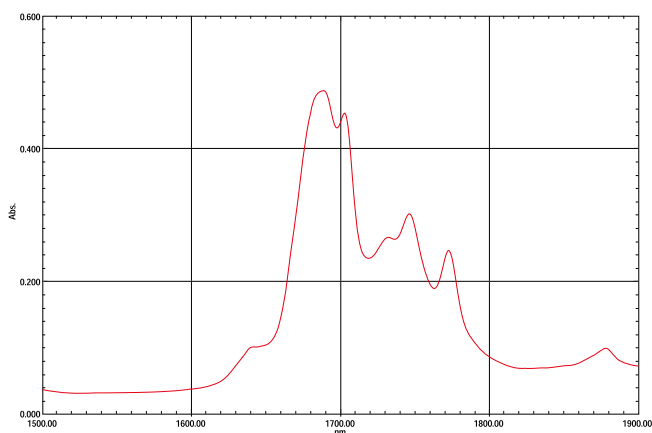


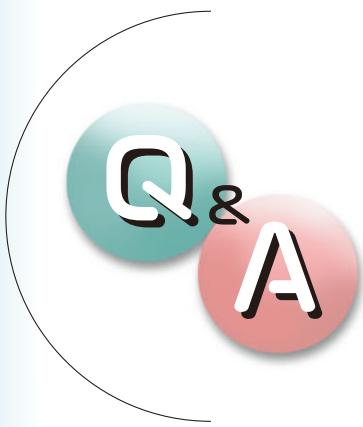
Figure 7 o-Xylene Near-Infrared Transmittance Spectrum (UV-Vis-NIR Spectrophotometer)

As can be confirmed from these figures, extremely high-resolution data can be obtained when measurement is conducted using the interferometer-equipped FTIR. The peak around wavelength $1.685\mu\text{m}$ ($5,950\text{ cm}^{-1}$) is separated into two. In contrast, the peak appears as a single peak in the case of the UV-Vis-NIR spectrophotometer, which uses dispersive elements. Although it depends on the instrument and measurement

attachments, in transmittance measurement, a resolution of 8 to 16 cm^{-1} can be obtained using the typical settings with the FTIR, while it is about 50 cm^{-1} (5 nm by wavelength) around $10,000\text{ cm}^{-1}$ with the UV-Vis-NIR Spectrophotometer. On the other hand, the UV-Vis-NIR Spectrophotometer is generally acknowledged to provide better repeatability of absorbance values than the FTIR.

5. Conclusions

Here we introduced characteristics and points to consider with respect to transmittance measurement in the near-infrared region. Next time, we will introduce methods of measurement other than the transmittance measurement method.



Question

When conducting measurement using the microscope transmittance method, quite a bit of noise is generated. What causes this?

Answer

One possible cause for the occurrence of noise in microscope transmittance

measurement is poor adjustment of the condensing mirror. In microscope transmittance measurement, even if a foreign body is clearly visualized in the visual image, the focus of light on the detector element might be shifted. In such a situation, adjustment of the condensing mirror below the sample stage is required.

Normally, when the microscope is installed, the mirror is adjusted so that the focal points of light are aligned on the MCT detector element without a window plate on the sample stage (see Fig 1, drawing at left). If measurement is to be conducted using the window plate, it is necessary to realize that the refractive index varies depending on the material used, thereby altering the optical path length to shift the focal point on the MCT element, as illustrated in the right-hand drawing of Figure 1 (while the refractive index of air is 1.0, it is 2.38 for diamond cells, and 1.42 for BaF₂ window plate). In such a situation, the amount of light used for measurement is reduced and, as a result, noise is increased.

In the case of the Shimadzu infrared microscope, in order to obtain the highest sensitivity, the focal point of light is aligned with the optical axis using the pinhole image in the visual observation screen, as shown in the left-hand image of Fig. 2.

Figure 3 shows a comparison of spectra obtained in the focused and unfocused condition. The sample was a minute particle on a diamond cell, and measurement was conducted using an aperture size of 10×10μm. A comparison of the spectra reveals that the noise is very large in the spectrum obtained in the out-of-focus state.

As the above-described method of adjustment differs depending on the instrument, customers who are using microscopes other than Shimadzu's should contact the appropriate manufacturer.

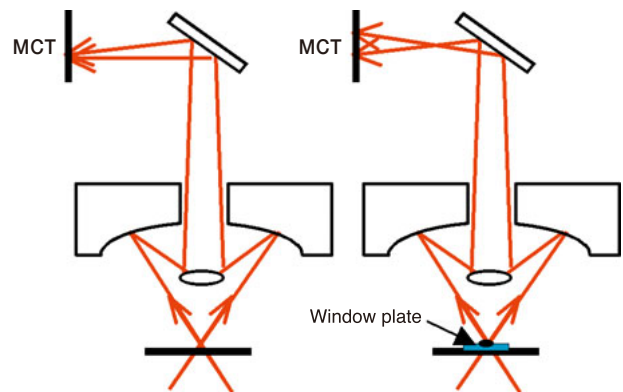


Figure 1
Optical Path in Microscope Transmittance Measurement

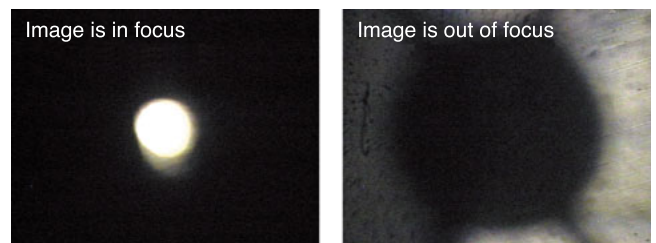


Figure 2
Pinhole Adjustment using Visual Image

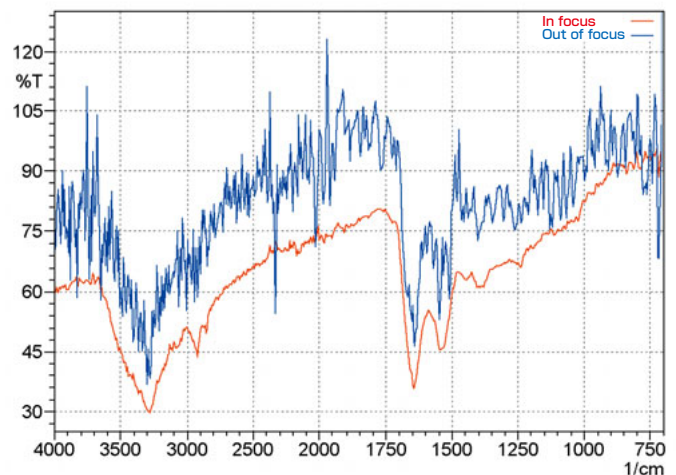


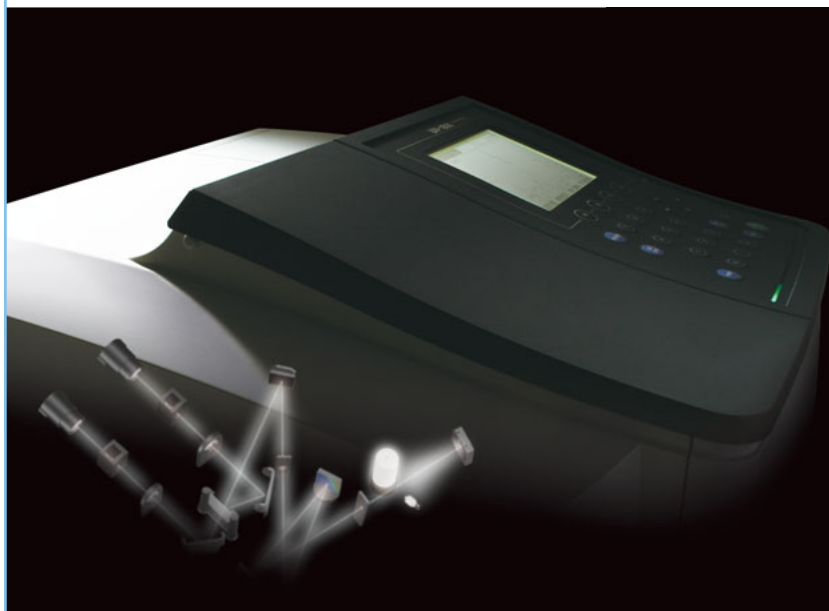
Figure 3
Microscope Transmittance Spectra of Foreign Particle

NEW PRODUCTS

Shimadzu UV-VIS Spectrophotometer

UV-1800

NEW



High Resolution

Highest resolution in its class at 1 nm*

Small Footprint

Setup space : W450 x D490 mm

Enhanced Ease of Operation

Equipped with USB Terminal

A compact, double-beam UV-VIS spectrophotometer wrapped in a sleek form, the UV-1800 uses the Czerny-Turner mounting for its monochromator, and boasts the highest resolution in its class*, a bright optical system, and a compact design. Available as either a stand-alone instrument or a PC-controlled instrument, the UV-1800 is USB-memory ready, which enables users to save measurement data to highly versatile USB memory, and perform data analysis and printing using a PC.

*As of August 2007, according to Shimadzu research.



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