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FTIR TALK LETTER

vol. 7

February 2007

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The MCT detector is said to be a high-sensitivity detector,
but in what cases is it necessary?

FTIR Measurement Data Storage and Control

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This FTIR Talk Letter introduces topics related to the storage and control of FTIR data, as well as the backup for preventing the loss of important data.

1. Sample Measurement and Basic Data Storage

When using the Shimadzu FTIR control software, IRsolution, the file name for the data file to be saved can be specified prior to conducting the measurement. There is a data file name entry field in the IRsolution measurement screen, as shown in Fig. 1. By entering an appropriate file name and performing the measurement, the spectrum is automatically saved using that file name.
Moreover, by placing a checkmark in the [Auto increment] checkbox, upon conducting analyses and spectra subsequent analyses and generating new spectra, these are automatically saved as data files using the same name entered with the original measurement, but conveniently appended with sequential numbers to ensure that the files are not overwritten.

Fig. 1: Data File Name Entry

2. Data File Control

Basically, as described above, after entering a file name and conducting analysis, the spectrum data file is correctly saved. However, as the number of files increases, it can subsequently become difficult to find a particular file for viewing.
By using Windows Explorer, the file name can be later changed to a more meaningful, identifiable file name. Select the file name, right-click on it and select [Rename] from the right-click menu. In addition, folders can be created and named according to the analyst or sample type, etc., and by moving the data files to the corresponding folders, searching for the files at a later time is simplified.
If a file is currently opened in IRsolution, file operations related to that file cannot be performed in Explorer. It is necessary to first close the file in IRsolution before file operations can be performed in Explorer.

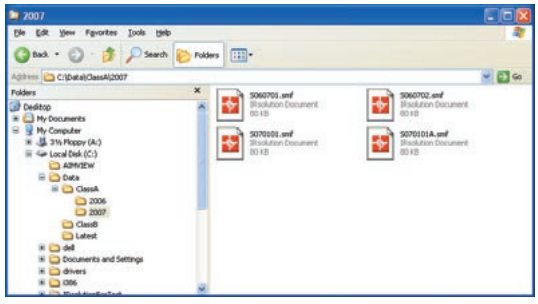

Fig. 2: Data Files Categorized According to Folder

Tips

To start up Explorer when using Windows XP, access the [Start] menu, then select [Programs]-[Accessories]-[Windows Explorer] in that order; however, it is also possible to execute it directly from the keyboard. While pressing the Windows logo key at the lower left on the keyboard, press the [E] key to easily open Windows Explorer.

As data files and folders can be named as desired, use easy-to-understand names. Note, however, that Windows only supports file names with up to 215 characters, and special characters “\ / : * ? " < > |” are not supported in file and folder names.

3. Changing Data Processing Result Name

As described above, appropriately changing the file names makes it easy to find them later. Similar to changing a file name, the data name inside of a data file can also be changed.
Many types of spectrum processing functions are available in IRsolution, and the data results are displayed in the IRsolution data tree below the original data. By default, the processed spectra are named according to the function that was performed. The names used for processed data can be changed using the following procedure. Use this function to better organize your data.

- Display the data processing result file in the display screen.
- Right-click on the displayed spectrum screen to display the menu shown in Fig. 3.

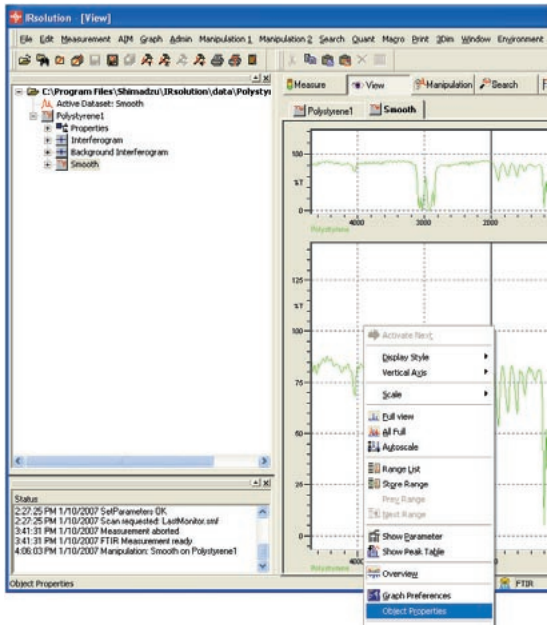

Fig. 3: Object Properties Menu Command

- From the menu, select [Object Properties].

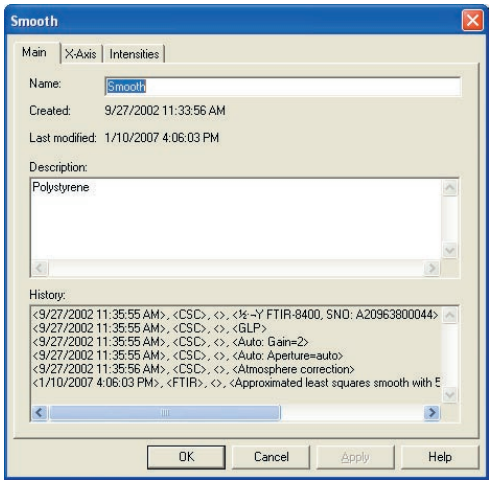

Fig. 4: Properties Window

- The current data processing result name is displayed in the [Name] field of the [Properties] window. This name can be changed using the keyboard entry, so after entering an appropriate name, click the OK button.

4. Data File Search

Even though the file and folder renaming operations make it easier to see files, as large quantities of data accumulate, it can become very difficult to find a specific file.

In such a situation, it is convenient to use the Windows Explorer Search function. From the Explorer menu bar, select [View]-[Explorer Bar]-[Search] to open the Search window. Here, a search for a file can be executed after specifying the date it was last modified, a portion of its name, its size or the folder in which it resides.

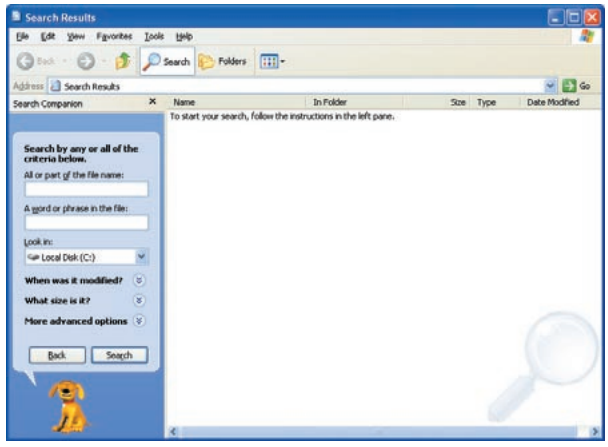

Fig. 5: Search Window

Tips

The [Search] window can also be opened using the Windows logo key. While pressing the Windows logo key, press the [F] key.

5. Data Backup

Importance of Backing Up

The term backup refers to the process of copying data from the computer's hard disk drive to another form of media to avoid the loss of data due to some kind of problem with the computer.

Measured spectral data is normally stored on the computer hard disk drive. Data on this hard disk drive can be read very quickly into IRsolution when it is started up, and is very conveniently available for viewing, printing, data processing, etc.

With all the convenience of this hard disk drive, which allows saving of files without any special operations, there is a real danger of losing data by carelessly overwriting stored data through mis-operation. Furthermore, there is a danger that the hard disk drive itself, spinning at high speed inside the computer case, can become damaged and crash, resulting in the total loss of data stored on the drive. In particular, the danger of a crash gradually increases with aging of the hard disk drive after years of usage.

To prevent the loss of data due to these types of incidents, the most certain approach is to regularly perform the above-mentioned backup procedure. It is strongly recommended to periodically back up important data to another disk.

Backup Methods

Data backup basically involves copying data from the computer's hard disk drive to another form of media, which is maintained in a safe place. At this time, it is easy to find the data that must be copied if the data is normally categorized according to folders.

Use of commercial specialized backup software is very convenient for its availability of useful functions, such as the generation of periodic reminders to conduct backup, and copying only files that have been modified since the previous backup in order to save time.

However, for ordinary backup, use of Windows Explorer to copy files is perfectly adequate. Moreover, as described below, various commercial disk hard drives are often supplied with backup software, and utilizing these is also good.

Backup Destination Drives and Media

Now, what kind of drive or media should be used to back up data on the hard drive? Various types of drives and media are described below.

1) Floppy disk

PCs are sometimes equipped with floppy disk drives, and floppy disks can potentially be used for backup. However, as the capacity of floppy disks is only 1.44 MB (megabytes), one disk can only accommodate from just a few to up to 10 IRsolution data files. Moreover, their slow speed makes them inadequate for backing up today's large data files.

2) CD media including CD-R/CD-RW

These days, almost all PCs are equipped with CD-R drives which can write data files to CD disks. The CDs are available as CD-R or CD-RW types, enabling them to be written to once or multiple times, respectively. Both types have a relatively large capacity of 650 MB, making them suitable for backup. As the currently used Windows XP supports the function of writing to CDs, performing data backup is easy.

3) DVD-R/DVD-RW/DVD-RAM media

DVD media, the same physical size as CD media, has become popular for recording movies and music. However, this article focuses on their use as data backup media. These days, almost all PCs are also equipped with DVD drives; in addition, external DVD drives are commercially available.

With a capacity of 4.7 GB (gigabytes), nearly seven times that of CDs, DVD disks are suitable for backing up large amounts of data. There is also a dual-sided type DVD-RAM, writable on both surfaces, which has a capacity of 9.4 GB.

Among the DVD-RAM media, there is also a type that remains housed in a shutter-equipped case without ever being removed, so that the recording surface does not come in contact with people's hands or other objects. This provides an added degree of assurance with respect to stored data.

4) External Hard Disk Drive

The types of media described up to now have all been disks of some kind that can be inserted into a drive for copying data, and then removed and stored. Completely different from these is a method of using a hard drive separate from the drive housed in the PC for backing up data.

Almost all PCs these days are equipped with USB interface connectors. Commercially available external hard disk drives can be connected to a PC via the USB interface connector whenever desired, and can be used as a destination hard drive for backing up data on the PC.

The main benefit of this is that it is a hard drive with an extremely large capacity compared to any of the other media, and the backup operation and recovery operation in the event of a problem with the internal hard drive are easily accomplished because there is no need to insert or eject disks.

However, it is a hard drive, so the danger of a crash is the same as that with an internal hard drive, and reducing this risk is only possible by not using it on a steady basis. Therefore, a strategy like using the external hard drive for regular backup, and occasionally performing backup with other media is necessary for more certain data backup.

Tips

Windows XP supports the function of writing files to a CD. Insert a writable CD into the CD drive, and drag the appropriate files to the CD drive letter indicated in Explorer. Then, right-click on that CD drive and select "Write these files to CD" from the right-click menu. The actual write process will begin.

Storing the Backup Disk

Store the CD-R or other disks containing the backed up data in a safe place that is not exposed to direct sunlight or humidity. In the case of an external hard drive, take care to not impart any shocks to it when moving or transporting it.

Thin Film Sample Measurement Methods and Precautions

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Various measurement methods are available in infrared spectrophotometry, and appropriate use of these depends on the measurement object (sample), analytical objective and other factors. For measurement of thin film samples with a film thickness of up to 1μm, the high-sensitivity reflection method is widely used, but recently, single-reflection ATR is also being utilized. This FTIR Talk Letter introduces examples of thin film analysis using the high-sensitivity reflection and single-reflection ATR methods.

1. Measurement of Thin Film on Metal

Reflection absorption spectroscopy (RAS) is suitable for measurement of thin film on a metallic substrate. RAS is an external reflection (specular reflection method) method in which the angle of incidence is 70° or greater, whereby the substrate-associated peak vibration in the perpendicular direction is intensified. Using this, it becomes possible to measure thin film spectra that cannot be measured by the specular reflection method using an approximately 10° incidence angle.

Fig. 1 shows a reflection absorption spectrum of a mono-layer fibrinogen film on metal plating. Measurement was conducted at an 80° incidence angle. Fibrinogen, a water soluble protein present in blood, is a rod-like molecule with a molecular weight of about 340,000, a diameter of 9 nm, and length of about 45 nm. Amide I and amide II in the vicinity of 1666 and 1545 cm^{-1}, respectively, and the stretching vibration of N-H in the vicinity of 3312 cm^{-1} are clearly confirmed.

Fig. 2 shows a reflection absorption spectrum of a multi-layer sample (gold / hydroxyapatite / fibrinogen) consisting of a gold plating substrate, a hydroxyapatite layer (thickness about 10 nm) and a mono-layer fibrinogen film. The hydroxyapatite peak and fibrinogen peak are clearly seen in the vicinity of 1100 cm^{-1}. In the measurement of this sample, the infrared light irradiated on the sample was reflected from the fibrinogen surface as well as the interface between the fibrinogen and hydroxyapatite layers. However, compared to the reflected light from the gold, that amount is extremely small, leading to the assumption that the obtained spectrum is derived from light reflected off the gold surface after having been transmitted through the fibrinogen and hydroxyapatite layers. The analytical conditions used for the spectra in Figs. 1 and 2 are shown in Table 1.

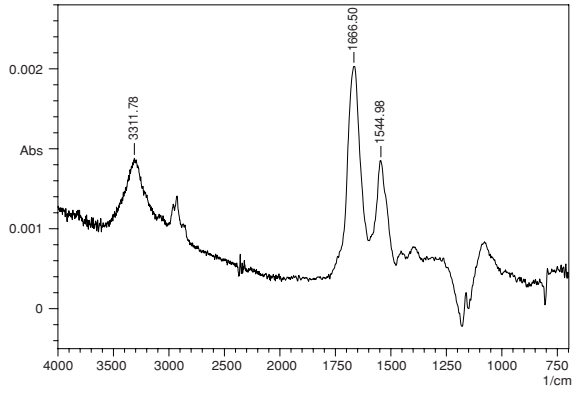

Fig. 1: Reflection Absorption Spectrum of Fibrinogen Thin Film on Gold Plating

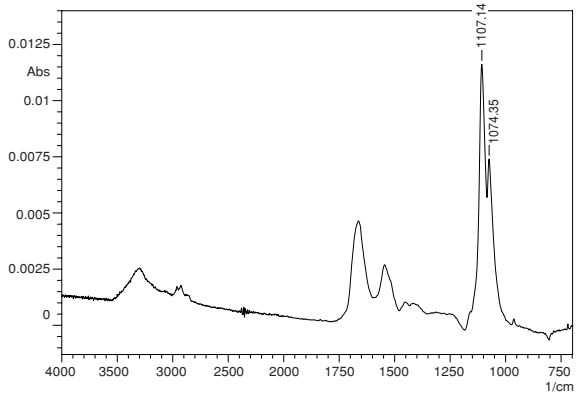

Fig. 2: Reflection Absorption Spectrum of Hydroxyapatite / Fibrinogen Multi-Layer Thin Film on Gold Plating

Table 1: Analytical Conditions 1

Accessory	:	VeeMAX
Incidence angle	:	80°
Resolution	:	4cm^{-1}
Number of scans	:	400
Detector	:	MCT

2. Precautions in Reflection Absorption Spectroscopy (RAS)

- Because a large angle of incidence is used in Reflection absorption spectroscopy (RAS), the light beam spreads widely on the metal surface (see Fig. 3). When the measurement sample is smaller than the light beam, a mask is used to eliminate reflected light other than that from the sample. The greater the angle of incidence, the higher the sensitivity that can be expected; however, since this is accompanied by wider spreading of the light beam, the light directed at the detector is reduced. Reducing the amount of light detected will result in increased noise. Therefore, when using RAS, it is essential to select the angle of incidence according to the sample and analytical objective. Now, when conducting analysis with a large angle of incidence and a small amount of light, an MCT detector is effective.

- The mask used when the measurement sample is smaller than the light beam has a black coating on its surface to impart low reflectivity. However, as this reflectivity is not zero, there may be some influence due to reflected light from the surface of the mask when using Reflection absorption spectroscopy (RAS). This influence can be eliminated by applying soot to the surface of the mask to reduce the reflectance to zero. Application of soot is often performed using a candle.

  RAS is often conducted in combination with a grid polarizer. Since only parallel polarized light contributes to the above-mentioned "intensification of the metal substrate-associated peak that is vibrating in the perpendicular direction", the polarizer is used to cut the vertical polarized light, which has no effect on the peak, thereby giving the appearance of increased peak intensity. However, since use of the grid polarizer reduces the amount of light to less than one half, there is an increase in noise. In RAS, it is not absolutely necessary to use a grid polarizer.

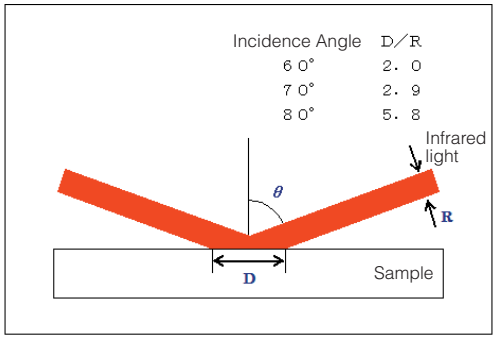

Fig. 3: Spreading of Light Beam in High-sensitivity Reflection Method (D/R is calculated assuming parallel light beams)

3. Measurement of Thin Film on Non-Metallic Substrate

Reflection absorption spectroscopy (RAS) is extremely effective for measurement of thin films on metallic substrates; however, this method is unsuitable for measurement of thin films on non-metallic substrates such as glass, silicon wafer and plastics. Fig. 4 shows the reflection absorption spectrum of a fibrinogen mono-layer film on a mirror-polished hydroxyapatite sintered plate. The inset in Fig. 4 is a magnification of the range from 1900 to 1300 cm^{-1}. As the reflectivity of hydroxyapatite is lower than that of metal, the "intensification of the peak that is vibrating in the perpendicular direction due to parallel polarized light" is not seen. Furthermore, the amide I and amide II peaks are inverted due to the influence of reflection from the fibrinogen film surface. Although peak shapes are apparent in the vicinity of 1250 to 1000 cm^{-1}, these are the residues of the hydroxyapatite reflectance spectrum.

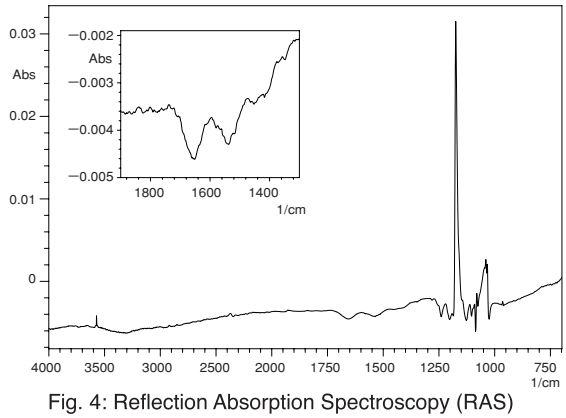

Fig. 4: Reflection Absorption Spectroscopy (RAS) of Fibrinogen Thin Film on Hydroxyapatite

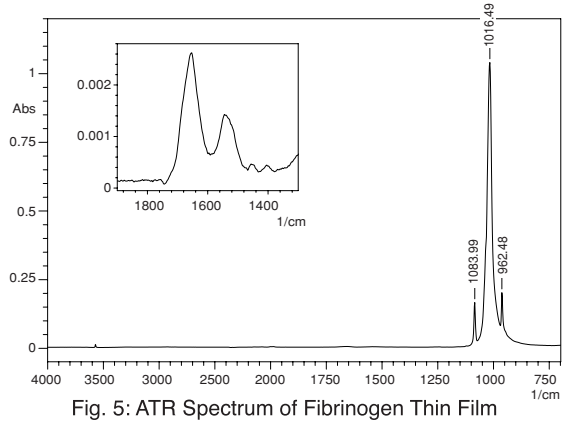

Fig. 5: ATR Spectrum of Fibrinogen Thin Film on Hydroxyapatite

Fig. 5 shows an ATR spectrum of the same sample measured by single-reflection ATR. A Ge prism was used. The peaks in the vicinity of 1084, 1016 and 962 cm^{-1} are peaks derived from hydroxyapatite. The inset in Fig. 5 is a magnification of the range from 1900 to 1300 cm^{-1}. The inverted amide I and amide II peaks seen in Reflection absorption spectroscopy (RAS) are obtained normally in this spectrum.

Fig. 6 shows the ATR spectra of N, N'-di (1-naphthyl)-N, N'-diphenylbenzene (NPD) thin film measured by the single-reflection ATR method (Ge prism) (after subtraction with ITO spectrum). NPD is a substance known as a material of the electron hole transport layer in organic EL displays, and the NPD film thicknesses (measured here) are 1 nm and 10 nm. A good spectrum was obtained even with the 1 nm thickness.

The analytical conditions used for the spectra in Figs. 5 and 6 are shown in Table 2.

Table 2: Analytical Conditions 2

Accessory	:	MIRacle
Prism	:	Ge
Resolution	:	4cm^{-1}
Number of scans	:	100
Detector	:	DLATGS

4. Precautions in Thin Film Measurement using Single-Reflection ATR

- In ATR methods, measurement is contacted with the sample tightly pressed against the prism, and the spectrum is influenced by the contact condition. In particular, if the state of contact is poor when measuring thin film, a spectrum may not be obtained. Therefore, it is necessary to perform measurement after ensuring that the contact surfaces of the sample and prism are clean and without any adhering substances. Furthermore, if the substrate has a rough surface, contact will be poor, and good results will probably not be obtained.
- Theoretically, better results with higher sensitivity can be obtained with multi-reflection ATR as compared to single-reflection ATR due to the strong intensity of peaks generated through a greater number of reflections. In actuality, however, it is common to obtain peaks by single-reflection ATR that cannot be obtained using multi-refection ATR. This is because the prism used in multi-reflection ATR is large, and minute particles of dirt and other adhering substances from the sample can easily create a gap to make it difficult to obtain good contact with the prism. In single-reflection ATR, the prism is small, and even if there are minute particles on the surface of the sample, they can be avoided to allow good contact.

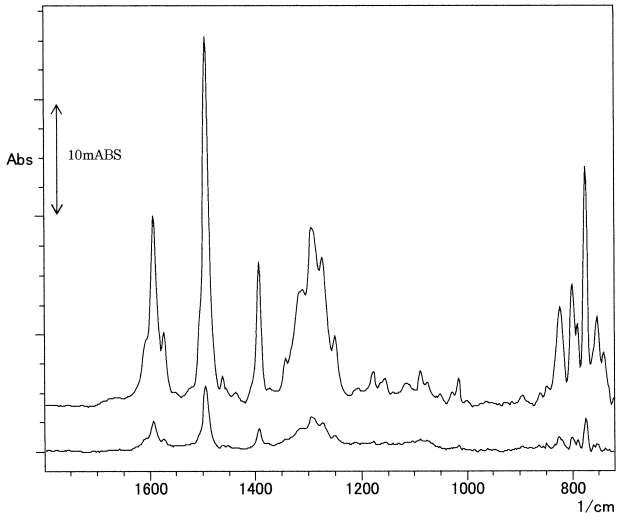

Fig. 6: ATR Spectra of NPD Thin Film on ITO Film
(Upper:10nm, Lower:1nm)

5. Conclusion

This FTIR Talk Letter introduced Reflection absorption spectroscopy (RAS) and the single-reflection ATR technique as methods for measuring thin film samples. RAS is unsuitable when the substrate is non-metallic, but thin film on a metallic substrate can be easily measured in a non-contact state. On the other hand, single-reflection ATR requires that the sample and prism be in close contact; however, it is extremely effective for measurement of thin films on non-metallic substrates.

Of the measurement examples introduced in this article, the samples for Figs. 1 to 5 were provided by Mr. Ikoma and Mr. Monkawa of the Biomaterials Center, National Institute for Materials Science, Japan. The sample for Fig. 6 was provided by Mr. Ide of the Optoelectronic Industry and Technology Development Association Yamagata Research Center, and Shiroto Research Laboratory, Faculty of Engineering, Yamagata University, Japan.

Q&A

Question

The MCT detector is said to be a high-sensitivity detector, but in what cases is it necessary?

Answer

In general, MCT detectors are used in IR microscope measurement, vacuum heating dispersion reflectance measurement, measurement using a long optical path gas cell, GC-FTIR measurement and some other types of measurement. The common aspect in these measurement types is that only a small amount of light reaches the detector. The effectiveness of the MCT detector is evident in this situation. However, if the MCT detector is used when the amount of light is sufficiently abundant, rather than achieving high sensitivity, the detector may become saturated and correct spectrum may not be obtained.

We compared a standard detector with an MCT detector using 1-mm diameter and 18-mm diameter masks to measure transmission spectra of white film. To check the peak linearity, the measurement results of a single film layer and a double layer were superimposed, as shown in Figures 1 through 4 (red line: single layer, black line: double layer). The analytical conditions were 4 cm^{-1} resolution and 10 scans.

Compared to the results of Fig. 1, in which the 18-mm diameter mask is used with the standard detector, the MCT detector results of Fig. 2 reveal a lack of peak intensity linearity. On the other hand, when the 1-mm diameter mask is used, the S/N ratio is poor with the standard detector, as shown in Fig. 3, but with the MCT detector, as shown in Fig. 4, the S/N ratio is good and linearity is well maintained.

As indicated above, the premise for using the MCT detector is that the amount of light is sufficiently small. In cases where there is strong light, it is necessary to reduce the amount of light by using an attenuator or other measures. Additionally, it is also necessary to consider the wavenumber range characteristics to select the optimum detector (refer to FTIR Talk Letter Vol. 3 Q&A).

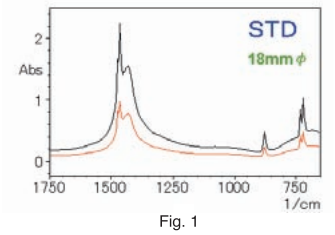

Fig. 1

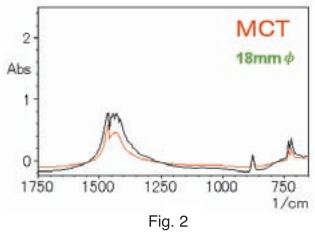

Fig. 2

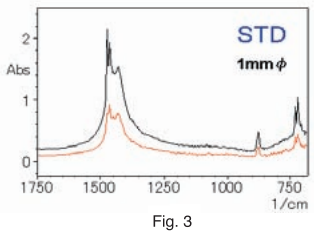

Fig. 3

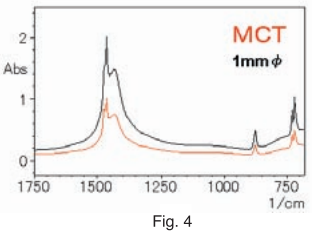

Fig. 4

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Printed in Japan 3295-12606-30A-NS

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