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On the Occasion of the Publication of FTIR TALK LETTER, Vol. 10

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It is with great pleasure that I am able to present the tenth volume of FTIR TALK LETTER, which was launched in the fall of 2006. The number of copies has increased with each publication, and is now nearly three times that of the first volume. In that first volume, we reported on FTIR-related changes in Japanese Industrial Standards and the Japanese Pharmacopeia. In this volume, we look back on the changes that have taken place in the field of FTIR and related peripheral devices since then.

As you know, FTIR is employed in a wide variety of fields and industries. One objective that it is applied to particularly often is the analysis of foreign substances performed as part of failure analysis. The analysis of foreign substances using FTIR, particularly with infrared microscope systems, started in response to demands from electrical and electronic fields that required the analysis of minute objects. Now, however, it is used widely in manufacturing and quality assurance departments in nearly all industries. Also, this form of analysis was previously regarded as work restricted to specialists with experience in infrared spectroscopy. Now, however, it is not unusual for novice users to perform FTIR for the analysis of foreign substances. These developments have been possible due in no small part to the appearance and improved performance of single-reflection ATR, the increased sensitivity of infrared microscopes, and improved operability achieved through the use of auto-stages, auto-apertures, and operation software.

Instruments capable of performing measurement over a wide wavenumber range using single-reflection ATR have been developed. These have come to be used in the checks performed on received materials and in the pre-delivery inspections of products, and have helped significantly reduce the labor that was required with earlier methods.

The application range of FTIR continues to expand in other fields too. In the field of new materials, it is used in the detection of substances modifying the surfaces of carbon nanotubes and fullerenes. In the field of electric and electronic materials, such as organic EL, it is used in the analysis of nano-order thin films. In the field of life science, which was previously regarded as unsuited to the application of FTIR because of the influence of water absorption, it is used in research related to the structure and function of proteins.

Aside from applications, in relation to FDA 21 CFR Part 11 and other regulations, a new approach to the storing and managing of measurement results is being introduced. In line with the switch from paper to electronic data as the medium used for data storage and management, from the perspective of reliability and consistency, the integrity and security of data with respect to loss or falsification have become important considerations, and systems that can meet these requirements while allowing easy operation are needed.

This year, our FTIR lineup was joined by IRAffinity-1. The word "Affinity" conveys the idea of familiarity. In FTIR TALK LETTER, in addition to presenting topics of an advanced nature, we will also try to cover a variety of basic, practical topics that our readers are familiar with. We look forward to your continued patronage.

Algorithms Used for Data Processing in FTIR

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In this article, I will present some of the algorithms used for a variety of data processing operations applied to spectra in FTIR. These algorithms are adopted in IRsolution software.

Smoothing

Smoothing is a process used to smoothen the shape of spectra.

For example, applying this process to a spectrum with a low S/N ratio makes it possible to reduce the influence of noise. Although the peak resolution decreases, the existence of peaks becomes easier to ascertain and the overall shape of the spectrum becomes clearer. So, in the analysis of unknown samples, this process is effective for obtaining qualitative information.

Smoothing a spectrum involves reducing the degree with which the spectral intensity changes at individual data points. A very simple way of smoothing would be to replace the intensity value of each individual data point with the value obtained by averaging the intensities of three points, which consist of the data point itself and two neighboring points. This does, to a degree, achieve the desired effect. In the figure shown below, the dotted line graph represents the result of applying this process to the solid line graph. The degree with which the spectrum changes at each point is reduced.
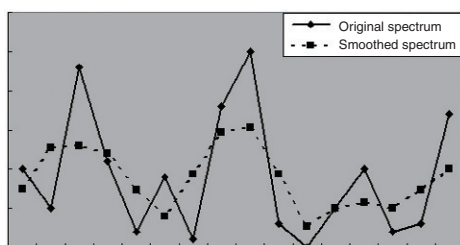

Fig. 1 Simple Smoothing Based on Replacement with Average Values

IRsolution uses a slightly more complex algorithm. Instead of taking the average of three points, it uses the value obtained by multiplying the intensity of each one of a specified number of smoothing points by a weighting factor and totaling the values thus obtained. This process is referred to as the application of a "third-order Savitzky-Golay smoothing filter" and the factors are determined by a function that is largest at the original data point and decreases as one moves away from this point. The number of smoothing points can be specified in IRsolution's smoothing command window. If this is set to a large value, the weighted average for data points covering a wide range is obtained and, in general, a smoother spectrum, with relatively few bumps, is produced.

Interpolation

Interpolation is a process for obtaining spectral intensities at locations with no original data points from the spectral intensities of surrounding data points. It increases the number of data points.

This process is used, for example, when comparing two sets of data that have data points at different intervals because the original data was obtained with different resolutions. By applying the appropriate form of interpolation, the sizes of the intervals between data points can be unified.

There is a simple type of interpolation algorithm in which two points are joined by a straight line and a new point is created on that line. IRsolution, however, uses an algorithm based on the Laplace-Everett formula. This is an interpolation algorithm that creates new points using the intensities of several surrounding points, not just the neighboring points, and thereby reflects the trends of curves over a relatively wide range. With IRsolution, four surrounding points are used.

As an example, suppose that there are four points, P_0, P_1, P_2, and P_3 (in order), on a spectral curve and that their intensities are, respectively, I_0, I_1, I_2, and I_3. If P is a point that divides P_1 and P_2 internally in the ratio t:1-t, the intensity at P obtained with simple interpolation is as follows:

$$I = (1-t)I_1 + tI_2$$

However, the intensity obtained with the IRsolution algorithm is as follows:

$$I = (1-t)I_1 + \frac{t(1-t)(1+1-t)}{6}(I_0 + I_2 - 2I_1)$$
$$+ tI_2 - \frac{t(1-t)(1+t)}{6}(I_1 + I_3 - 2I_2)$$

IRsolution's interpolation function not only allows the sizes of the data intervals to be decreased by a specified factor (e.g., to intervals of one half or one quarter the size), but also makes it possible to switch to data intervals of any specified size. This is possible because the function obtains a curve using the original data points, and creates new data points by obtaining the intensities at the new specified data intervals. For this reason, even if the original data interval is a multiple of the new specified data interval, and data wavenumbers of the old and new data happen to coincide,
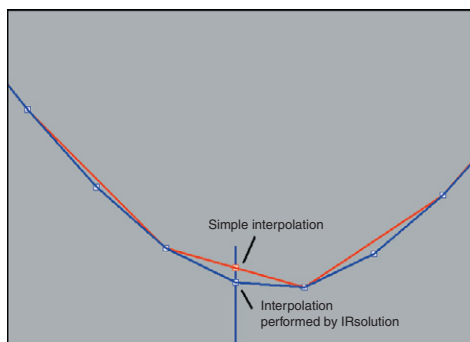
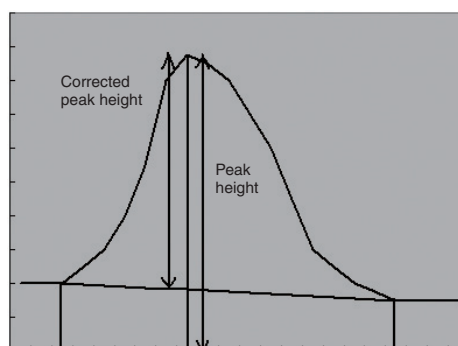Fig. 2 Interpolation Based on Laplace-Everett Formula

Fig. 3 Peak Height and Corrected Peak Height

the respective intensities will, in general, be slightly different. It must be remembered that interpolation is only a mathematical method for estimating intensity values and the values obtained may differ from the actual intensities.

Peak Detection

Peak detection involves the identification of absorbance at specific wavenumbers in a spectrum, and is used for the qualitative and quantitative analysis of sample substances. With IRsolution, the threshold value, the noise level, and the minimum area are required as parameters for peak detection. (Although these values differ according to whether the vertical axis of the spectrum represents transmittance or absorbance, the basic principle is the same. Here, an example where the vertical axis represents absorbance is used.)

First, the first- and second-order derivatives of the spectrum are calculated and the result is saved. Next, using these results, the wavenumber positions on the spectrum at which the first-order derivative changes from a positive to a negative value are detected, and these are considered to be peak candidates (because it is possible that they are positions where the spectrum takes maximum values). From these peak candidates, the ones for which the absorbance does not attain the threshold value are discarded. Then, the difference in first-derivative value between each candidate point and points before and after it is calculated, and the points for which the absolute value of this difference does not attain the specified noise level are judged to be noise and are discarded.

Among points before and after the remaining peak candidates, points for which the first-order derivative changes from a negative value to a positive value and for which the second-order derivative is negative are searched for. If such points are found, they are judged to be the "valleys" before and after peaks. If valleys are not found, the corresponding candidates are judged to not be peaks and discarded. The valleys found before and after the peak candidate points are joined to form baselines, and the heights and areas of the corrected peaks are calculated. If these two values are greater than the specified threshold and minimum area respectively, the corresponding points are judged to be peaks.

The operations are basically the same in the case where the vertical axis represents transmittance. The transmittance values at the peak bottoms (rather than the peak tops), the depths of these peak bottoms from the baseline, and the areas bound by peaks and the 100% line and by peaks and the baseline are used instead.

Film-Thickness Calculation

This function calculates, from the number of interference fringes in a specified wavenumber range, the thickness of a film through which infrared light passes. In terms of algorithms, this function can be thought of as simple peak detection and its application.

As with standard peak detection, the first-order derivative of the spectrum is calculated, and the places where its value changes from positive to negative are detected. Precise noise level checks are not performed on the spectrum. Such characteristics are regarded as peaks.

The maximum and minimum peak wavenumbers in the specified wavenumber range are detected, and the number of peaks between them is counted. A calculation based on the following formula is performed on the number of counted peaks and the set refractive index and angle of incidence.

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2\theta}} \cdot \frac{1}{\left(\dfrac{1}{\lambda_2} - \dfrac{1}{\lambda_1}\right)} \quad , (\lambda_2 < \lambda_1)$$

Here, "d" represents the film thickness, "λ_1" and "λ_2" represent the wavelengths of the peaks or valleys at either end of the specified wavenumber range, "n" represents the refractive index of the film, "θ" represents the angle of incidence of infrared light with respect to the sample, and "Δm" represents the number of peaks between "λ_1" and "λ_2".

Atmospheric Correction

This is a corrective function that subtracts the component of a spectrum that corresponds to absorbance due to water vapor and carbon dioxide in the atmosphere, and thereby suppresses the influence of these factors. With IRsolution, the approximate shape of the background spectrum that is displayed in power spectrum format is calculated, and using this and the absorption peaks in the original background spectrum, the water vapor and carbon dioxide peaks are canceled out.
First, the approximate shape of the background spectrum is calculated. In order to do this, figures entered for water vapor and carbon dioxide in both the high and low wavenumber ranges via the parameter setting window are used. These figures are scale factors expressed as wavenumbers that are used to perform coarse graining of the spectrum. In the respective wavenumber regions, changes in small wavenumber ranges not exceeding the set figures are ignored, and an outline spectrum with no fine absorption peaks is calculated.
The wavenumber ranges are as follows:
   High wavenumber range for water vapor:
   3,540 to 3,960 cm^{-1}
   Low wavenumber range for water vapor:
   1,300 to 2,000 cm^{-1}
   High wavenumber range for carbon dioxide:
   2,250 to 2,400 cm^{-1}
   Low wavenumber range for carbon dioxide:
   600 to 740 cm^{-1}
The resulting spectrum has the form of an envelope curve created by removing small bumps from the original

background spectrum. From the difference between these spectra, an absorption peak pattern for the water vapor and carbon dioxide in the atmosphere is calculated. Furthermore, regarding the sample spectra displayed in power spectra format, the same kind of peak pattern is calculated, and the ratio of the background spectrum to this peak pattern is obtained. Subtracting the peak pattern obtained by performing scaling with this factor from the power spectrum makes it possible to obtain a spectrum from which the influence of the water vapor and carbon dioxide in the atmosphere is eliminated. (The final spectrum is given as a ratio of the sample and background spectra.)
IRsolution's atmospheric correction function, then, performs correction using power spectra for both the background and the sample. For this reason, correction is only possible for spectra obtained with IRsolution that are in a format bearing the .smf extension.

Library Searches

Many of the algorithms used for library searches are extremely complex. It would be impossible to give an exhaustive explanation of them all in such a limited space so, here, I will describe a relatively simple type of algorithm in the context of the operation of a typical library search. Shimadzu IRsolution software's search function supports many different types of search techniques. The most basic is called "spectrum search". When using spectrum search, various settings must be made, including the selection of the algorithm.
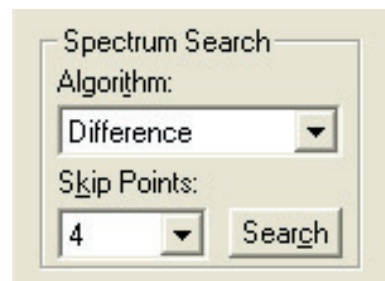

Fig. 4 Selection of Search Algorithm

Various algorithms can be selected in IRsolution's spectrum search. Of these, the algorithm "Difference" is relatively simple and I will describe the operation performed when this algorithm is used.

When a spectrum search is executed with IRsolution, processing of the wavenumber range is performed first. This is a selection function whereby the sample spectrum is compared with the library spectra within a specified wavenumber range, rather than the range of the entire spectrum. This function makes it possible to perform searches using only characteristic parts of spectra. Actually, this function converts the wavenumber range expressed in cm-1 units to an index (number) of the data points that configure the spectrum, and only the data points of the applicable index are transferred to the comparison function part of the software.

Next, the spectrum is normalized in terms of intensity. This process corresponds to the "Normalize" command that is displayed on IRsolution's "Manipulation" menu. A constant factor is applied to the entire spectrum so that the maximum absorbance becomes 1 while the shape of the spectrum is preserved.

In general, the sizes of spectra of unknown samples differ from those of library spectra; therefore, this processing is necessary to facilitate comparison based on appropriate spectral forms.

After the size of the spectrum has been normalized for all the data points in the set wavenumber range, the differences in intensity between the spectrum of the unknown sample and the library spectra are obtained as absolute values, and these values are totaled. If the spectrum of the unknown sample and a library spectrum are a perfect match, this value will naturally be zero. In practice, the value varies according to the degree of similarity between the two spectra. Multiplying this value by a certain factor and subtracting it from 1,000 gives an index (the "hit quality") that will equal 1,000 in the case of a perfect match. This operation is performed on all the library spectra used, and the results are displayed as a list with the spectra arranged in decreasing order of hit quality.

The operation of other types of algorithms is basically the same. The only difference may be, for example, that instead of the absolute values of the differences between the spectrum of the unknown sample and the library spectra, the squares of the differences are used.

Summary

Here, I have given a simple explanation of the algorithms used in some of the data processing operations performed by IRsolution. In the use of data processing functions, I do not think that it is usually necessary to be aware of the precise details of operation. Understanding the algorithms, however, can help the user appreciate the effects of the corresponding processes. Sometimes, when using a data processing operation, try to be aware of the utility of the operation.

Near-Infrared Region Measurement and Related Considerations Part 2

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In the article "Near-Infrared Region Measurement and Related Considerations Part 1" that appeared in FTIR TALK LETTER, Vol. 9, we mainly described the characteristics of transmittance measurement in the near-infrared region as well as some points that must be considered to perform this measurement. With measurement methods other than transmittance measurement, there are some characteristics and considerations that differ from those pertaining to measurement in the mid-infrared region here, in "Near-Infrared Region Measurement and Related Considerations Part 2", we introduce these with the aid of actual examples of sample measurement.

Characteristics of Near-Infrared Light Absorbance

First, we would like to review some of the characteristics of near-infrared light absorbance.
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). 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.

Diffuse Reflectance Measurement

In addition to transmittance measurement, there are several other methods that can be used to measure near-infrared light absorption. Diffuse reflectance measurement is a method that is often used for the near-infrared region.
As with transmittance measurement, there is relatively weak sample absorption when diffuse reflectance measurement is used in the near-infrared region, so dilution using KBr powder or any other form of pretreatment is not required, and direct measurement is possible. The attachments used for diffuse reflectance measurement include diffuse reflectance accessories and integrating spheres.
In diffuse reflectance measurement, a reference reflector called reference is used for background measurement (reference measurement). Unlike transmittance measurement, no simple, effective attachments that can obtain absolute values are commercially available; consequently, measurement is of the reflectance relative to that measured with the reflector used for background correction.

A gold (vapor-deposited) mirror often acts as the reflector used for background correction. Although gold mirrors have absorbance in the visible light region, they exhibit extremely high reflectance in the near-infrared region. In some cases, an aluminum mirror or barium sulfate is used as the reflector.
One point to note about diffuse reflectance measurement is that the amount of near-infrared light absorption varies with the particle size and the density of the sample being analyzed. For smaller particles, the optical path is longer, and for denser samples, there are more opportunities for absorption by particles and, consequently, the absorption intensity is larger.
One of the attachments used in diffuse reflectance measurement is the NIR integrating sphere. This makes it possible to analyze various types of samples, including powders, tablets, and pastes.
A gold diffuse reflectance mirror with a rough surface (a scattering surface), rather than a mirror-finished surface, is used as the reference reflector. After reference measurement, the sample is placed on the window at the top of the attachment, and measurement is performed.
Fig. 1 shows the results obtained by analyzing L-arginine using a gold diffuse reflectance mirror as the reference.

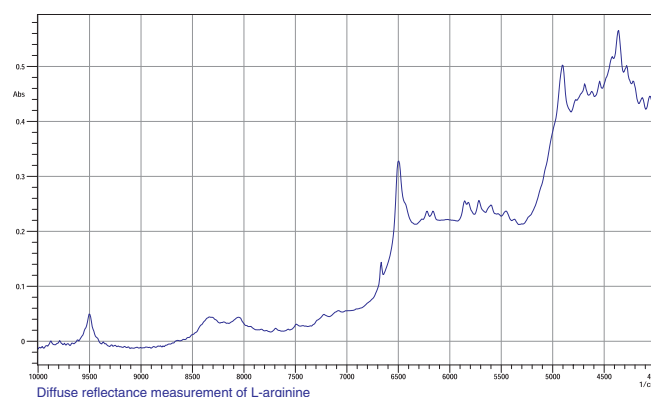Diffuse reflectance measurement of L-arginine

Fig. 1 Near-Infrared Diffuse Reflectance Spectrum of L-arginine

Measurement can be performed simply by placing the sample on the top of the integrating sphere. The sample does not need to be diluted.

In the near-infrared region, as in the visible light region, hardly any absorption is observed with glass or quartz. For this reason, diffuse reflectance measurement is possible for a sample placed inside a glass container.

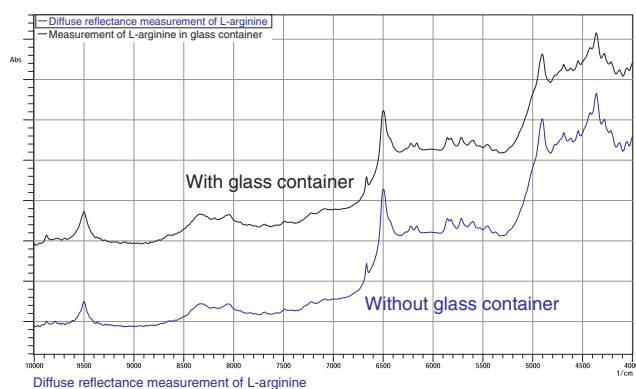Fig. 2 shows the results obtained by performing diffuse reflectance measurement on L-arginine placed in a glass container.

Fig. 2 Near-Infrared Diffuse Reflectance Spectrum of
L-arginine Obtained with and without Glass Container

To facilitate comparison, data obtained by measurement without a glass container (same as Fig. 1) is also shown. It can be seen that there is no difference between the two sets of data.

Using the fact that absorption is less in the near-infrared region than it is in the mid-infrared region, samples contained in plastic bags are sometimes tested by performing direct measurement through the plastic.

The absorption of a thin plastic bag is extremely small and a significantly greater amount of absorption is obtained for the contents.

Fig. 3 shows the results obtained by performing diffuse reflectance measurement on L-arginine in a plastic bag.
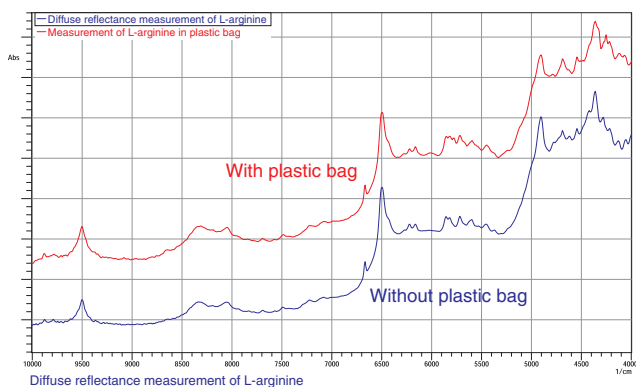

Fig. 3 Near-Infrared Diffuse Reflectance Spectrum of
L-arginine Obtained with and without Plastic Bag

To facilitate comparison, data obtained by measurement without a plastic bag (same as Fig. 1) is also shown. It can be seen that there is no significant difference between the two sets of data. Of course, a small amount of absorption by the plastic bag is observed in a neighborhood of 5,780 cm^{-1} and 4,250 cm^{-1}. Overall, however, no significant absorption by the plastic bag is observed, making it possible to obtain a spectrum for the contents.

With near-infrared diffuse reflectance measurement, then, dilution is not required as pretreatment, as it is with the mid-infrared region, and measurement is therefore relatively easy.

Measurement with Fiber

An attachment that is useful when the sample is too big to put in the instrument's sample compartment is the fiber probe. Fiber measurement is used for the mid-infrared region but fibers that offer high transmittance efficiency over the entire mid-infrared region are still in the development stage. When using fiber in this region, there are wavenumber regions in which measurement is not possible due to the absorption of the fiber material itself, and this method can only be used for a limited range of samples.

On the other hand, there are fibers that offer high transmittance efficiency over the entire near-infrared region, so fiber measurement is relatively simple in this region.

Fig. 4 shows the results obtained by performing reflectance measurement using a near-infrared reflection-type fiber probe. Because light attenuates as it passes along the fiber, there is more noise than there is with an integrating sphere. The data obtained, however, is similar to that obtained with an integrating sphere.
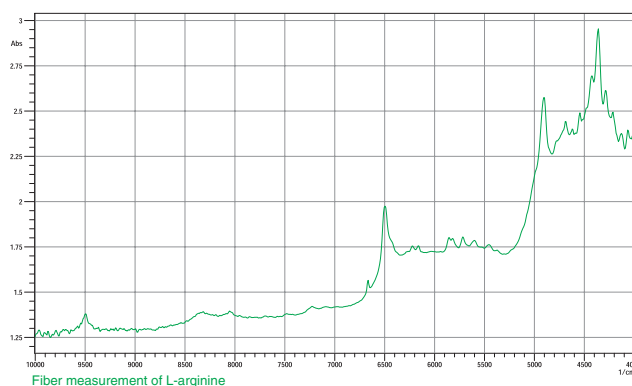

Fig. 4 Near-Infrared Reflection Spectrum of L-arginine Obtained with Fiber

As with an integrating sphere, fiber can be used in applications such as analyzing the contents of plastic bags.

Near-Infrared Specular Reflectance Measurement

In addition to diffuse reflectance measurement and fiber measurement, which we have described above, specular reflectance (reflectance absorption) measurement is also possible.

Specular reflectance measurement is performed using a specular reflectance accessory. Also, with specular reflectance measurement in the near-infrared region, a gold or aluminum mirror is used for reference measurement. As the absorption intensity is low, in comparison with measurement in the mid-infrared region, the measurement of thick layers formed on the top of metals is relatively easy. Fig. 5 shows the results obtained by performing near-infrared specular reflectance measurement using a specular reflectance accessory. The sample was a 0.5-mm-thick layer of polystyrene on metal.
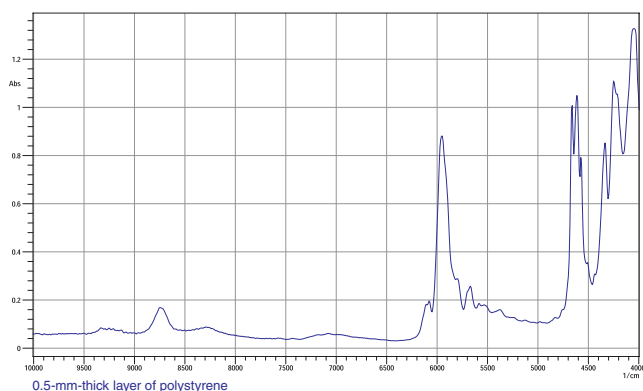
0.5-mm-thick layer of polystyrene

Fig. 5 Near-Infrared Specular Reflectance Spectrum of Polystyrene

Also, film-thickness calculation is easier in the near-infrared region than it is in the mid-infrared region. Fig. 6 shows the results obtained in the measurement of a thin film on metal. In the near-infrared region, because there is little absorption by the sample, interference fringes can be observed with hardly any influence of sample absorption. For this reason, near-infrared spectra are effective for film-thickness measurement.
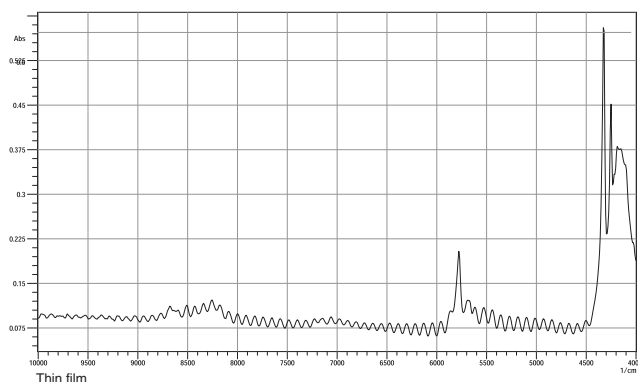
Thin film

Fig. 6 Near-Infrared Specular Reflectance Spectrum of Thin Film

For the sample whose results are shown in Fig. 6, performing calculation of the film thickness for the wavenumber range 7,000 to 6,000 cm^{-1} by entering a refractive index of 1.5 gave a result of 39.5 μm. Fig. 7 shows the actual film-thickness calculation window.
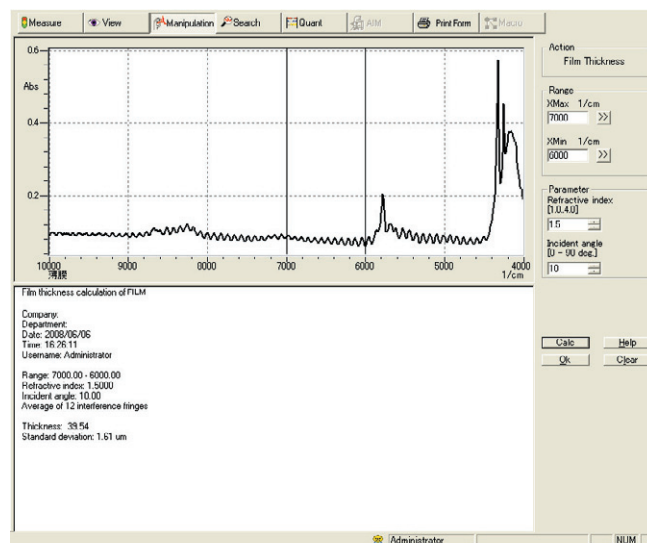
Fig. 7 Film-Thickness Calculation Window

Summary

Here, we have described the characteristics of diffuse reflectance measurement, fiber measurement, and specular reflectance measurement in the near-infrared region, and have detailed some points to be considered to ensure execution.

Compared with measurement in the mid-infrared region, there are many advantages, such as the ability to perform measurement without pretreatment. There are disadvantages, however, such as the fact that the spectrum database is not as comprehensive as that for the mid-infrared region and the fact that absorption exists that is difficult to associate with functional groups (e.g., combination tones), making it difficult to obtain qualitative information.

By understanding the various characteristics of the measurement methods used for the near-infrared region, together with the points to be considered for proper execution, you can expand the range of measurement and analysis techniques at your disposal and perform measurement with greater efficiency.

In addition to the methods we described so far, various other types of measurement are used for the near-infrared region, such as simultaneous multicomponent quantitation based on chemometrics.

On another occasion, we would like to make a presentation on chemometrics.

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IRAffinity-1 Supports a Wide Range of Analytical Applications

Shimadzu Fourier Transform Infrared Spectrophotometer

IRAffinity-1

Levels of sensitivity and performance that surpass those of general-purpose instruments
Easy-to-use, high-performance software: IRsolution
Expanded application range.

IRAffinity-1 is a compact Fourier transform infrared spectrophotometer with a stylish design. It is equipped with a dynamic alignment mechanism that performs continuous optimization of the interferometer, and has a built-in dehumidifier that ensures easy maintenance. It offers an S/N ratio of 30,000:1 (resolution 4 cm^{-1}, 1-minute accumulation, neighborhood of 2,100 cm^{-1}, peak-to-peak), the highest level among instruments in the same class*, a maximum resolution of 0.5 cm^{-1}, and a compact design. The high-performance software package IRsolution, which was developed with an emphasis on operability, and analysis support programs (contaminant analysis program and a Japanese Pharmacopoeia-compliance program) facilitate simple data processing and analysis.

*As of January 2008, according to Shimadzu investigations

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