

FTIR TALK LETTER

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What is an appropriate sample concentration for
the KBr tablet method or the diffuse reflectance method?

Resolution and Aperture

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1. What Is Resolution?

Resolution is one of the measurement parameters involved in obtaining spectra with FTIR .

The resolution can be set to values such as 16 cm⁻¹, 8 cm⁻¹, 4 cm⁻¹, or 2 cm⁻¹. It indicates the degree of fineness of the data obtained by measurement (i.e., the minimum peak interval that can be distinguished). For example, if 4 cm⁻¹ is selected, spectra will be obtained at intervals of approximately 2 cm⁻¹. To obtain sharper spectra (i.e., spectra with a higher resolution), a value such as 2 cm⁻¹ or 1 cm⁻¹ is set.

In fact, although this works for gaseous samples, there are cases with solid and liquid samples where the resolution of the data obtained does not improve even if a higher resolution is set. This is because the molecules of the solid or liquid are influenced by other molecules around them, causing the actual peaks to broaden.

Also, if the resolution is increased, a smaller aperture is selected in the way described later, and the intensity of the light entering the detector is reduced, increasing the relative amount of noise in the spectra. Therefore, it is undesirable for the resolution to be increased more than necessary.

For this reason, the resolution is usually set to approximately 4 cm⁻¹ for solid and liquid samples, and to approximately 1 cm⁻¹ or 0.5 cm⁻¹ for gaseous samples. On some occasions, a low resolution is set for gaseous samples if the purpose is quantification.

2. Comparing FTIR to a Camera

Although it is a rather crude analogy, I think that comparing the resolution setting for FTIR to the aperture and shutter speed settings for a camera can make it easier to understand.

FTIR	Camera
Infrared radiation source	Light from subject
Aperture (resolution)	Aperture
Number of integrations	Exposure time (shutter speed)
Gain setting (normally AUTO) Detector setting (TGS detector, MCT detector, etc.)	ISO sensitivity of film

Table 1 FTIR and Camera Settings

The aperture of a camera is a mechanism by which the light that is received from the subject is focused at the aperture position, and the quantity of light is adjusted. Narrowing the aperture gives a sharper photograph, but because this also reduces the light intensity, the resulting photograph is darker. In order to increase the brightness, the shutter speed is reduced, so that the cumulative amount of light reaching the film increases.

In FTIR, the clarity of the spectra (i.e., the sharpness of the peaks) obtained can be changed by selecting a different aperture.

With a camera, light from the subject is projected onto film. With FTIR, an infrared radiation source is incorporated inside the instrument, the sample is irradiated with infrared radiation, and the changes in light intensity are concentrated by a detector.

It is not easy to change the actual size of the radiation source, so it is changed artificially by focusing an image of the radiation source at the aperture position and then changing the size of the aperture.

3. What Is an Aperture?

The ideal form of radiation source is a point source. However, not only does such a source not exist in reality, a source of a certain size is used in order to ensure a sufficient level of light intensity at the surface of the infrared detector. As the source is not a point source, the light entering the interferometer does not consist solely of parallel light. The sample is also irradiated with grazing-incidence light, and this is ultimately received at the infrared detector, where it constitutes part of the measured signal.

This grazing-incidence light is handled in the same way as normal incident light, the long-wavelength component is incorporated in the obtained data, as a component with a wavelength longer than actual by an extent proportional to the angle of grazing incidence. The size of this grazing-incidence component varies according to the size of the radiation source. Consequently, the aperture diameter should be selected so that the measurement resolution is not affected by the spread of peaks due to the grazing-incidence light.

In the FTIR instrument, if "AUTO" is set for the aperture, then the aperture is automatically set in accordance with the set resolution. The aperture diameter, A (cm), required at each resolution level can be calculated using the following formula.

$$A \leq 2fc \sqrt{(\Delta\lambda/\lambda_{\max})}$$

f_c : Focal distance
Δλ : Spectral resolution
λ_{max} : Largest measured wavenumber

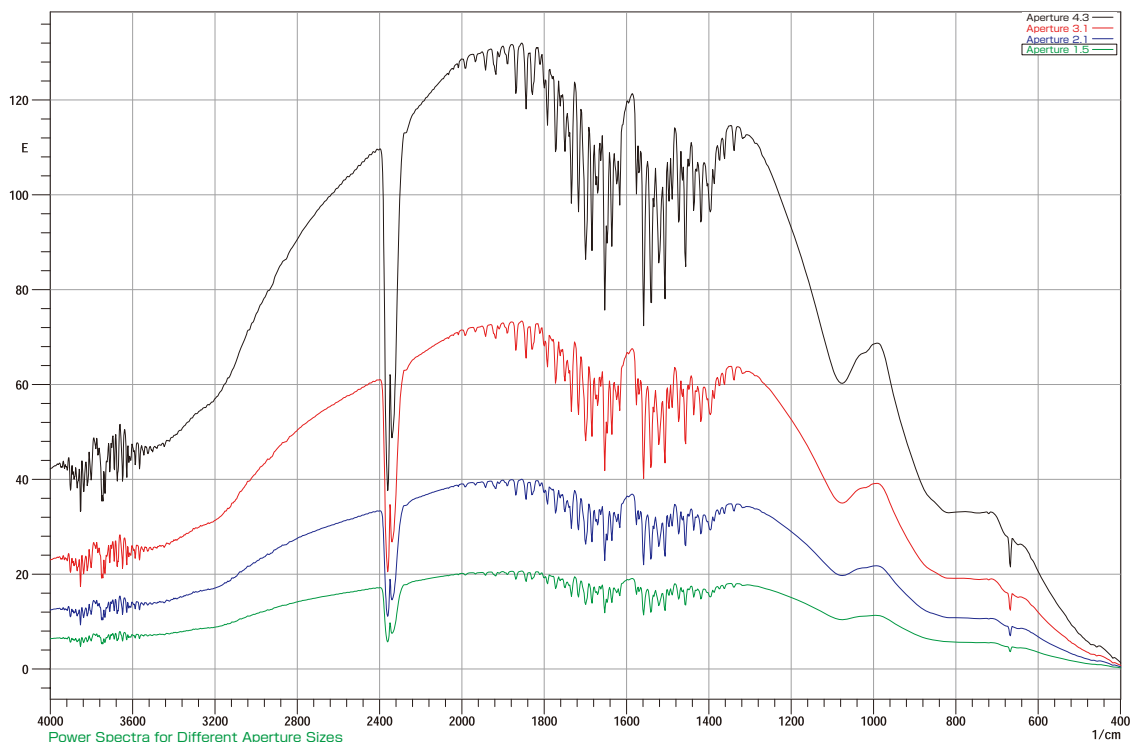


Fig. 1 Differences in Light Intensity for Different Apertures

Fig. 1 uses power spectra to show the differences in light intensity for different apertures.

In FTIR, a fast Fourier transform (FFT) is used to convert interferograms to power spectra so the numbers of data points for each resolution are all powers of two. (See Table 2.)

As can be seen from the figure, the light intensity is roughly halved when the resolution level is doubled. The apparent level of noise increases by an amount corresponding to the decrease in light intensity; so, with a high-resolution measurement, it is necessary to set a sufficiently high number of integrations to obtain clear spectra.

4. Resolution and Number of Data Points

With general-purpose infrared spectrophotometers, resolution is usually selected in the range of 16 cm^{-1} to 0.5 cm^{-1} . The following changes take place inside the instrument when the resolution is set:

The travel distance of the moving mirror (i.e., the optical path difference) is set in accordance with the set resolution.

The aperture is set in accordance with the set resolution.

With the Shimadzu IRPrestige-21, the following settings are used.

Resolution	16	8	4	2	1	0.5
Optical Path Difference	0.075	0.125	0.25	0.5	1	2
Number of Data Points	2048	4096	8192	16384	32768	65536
Data Interval (See note 1.)	7.72	3.86	1.93	0.96	0.48	0.24
Aperture Diameter	open	open	open	3.8	2.4	1.5

Table 2 Resolution and Parameter Settings

Note 1: The figures given are theoretical values. In practice, they are corrected in accordance with parameters associated with the selected aperture diameter.

With FTIR, data is usually sampled at the interference fringe position using a helium-neon (He-Ne) laser with an operation wavelength of 632.8 nm. Converting this wavelength to a wavenumber gives 7,901 cm^{-1} . Dividing this by half of the number of data points (because data also appears on the negative side with an FFT) gives the data interval.

If measurement is performed at a resolution of 4 cm^{-1} , 8,192 data points are collected. As such, data is generated at the intervals of the following size:

$$7901 \div 8192 / 2 \doteq 1.93 \text{cm}^{-1}$$

This is a theoretical value. In practice, the optical wavenumber is corrected by applying a correction value that is set in accordance with the selected aperture diameter.

The travel distance of the moving mirror (i.e., half the optical path difference) is proportional to the number of sampling points. The numbers of data points required at each resolution, however, are as shown in Table 2.

5. Points to Note for Actual Measurements

Fig. 2 shows spectra obtained for water vapor in air at different resolutions. It can be seen that, as the resolution increases, the detail of the absorption peaks for the water vapor becomes clearer.

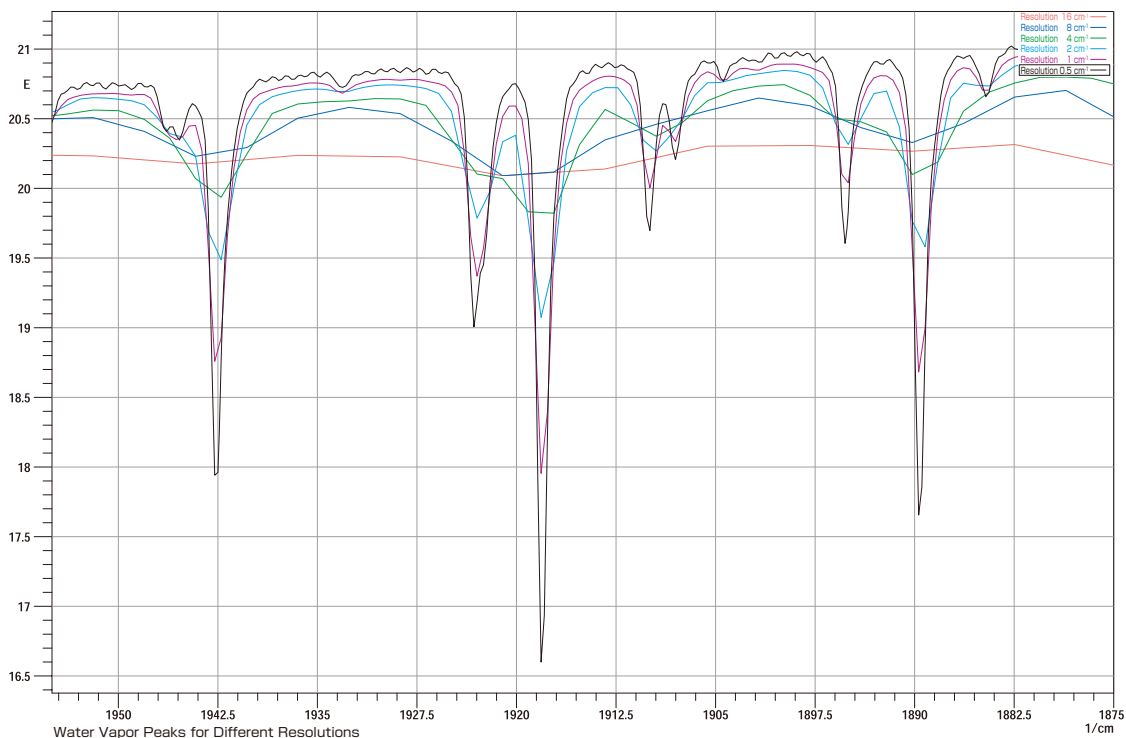


Fig. 2 Spectra of Water Vapor Obtained at Different Resolutions

The aperture is positioned at the image-formation position of the radiation source. The focusing position of the sample chamber is also set at the image-formation position of the radiation source. For this reason, if there is something in the sample chamber, such as a sample holder, that limits the light intensity in the same way as the aperture, there may be discrepancies in the wavenumbers or the waveform may be disrupted.

For example, this problem might occur if background is measured without a sample holder, and then the sample is measured with a holder that greatly influences the diameter of the light beam. (See Fig. 3.) This problem can be prevented by measuring background with a sample holder (but without a sample), or by setting the aperture diameter used in sample analysis to 1.5 or 2.4. (See Fig. 4.)

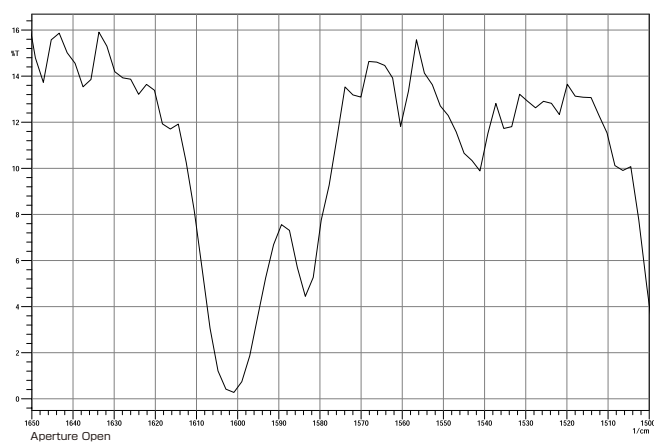


Fig. 3 Inaccurate Spectra Obtained by Measuring Background Without a Sample Holder

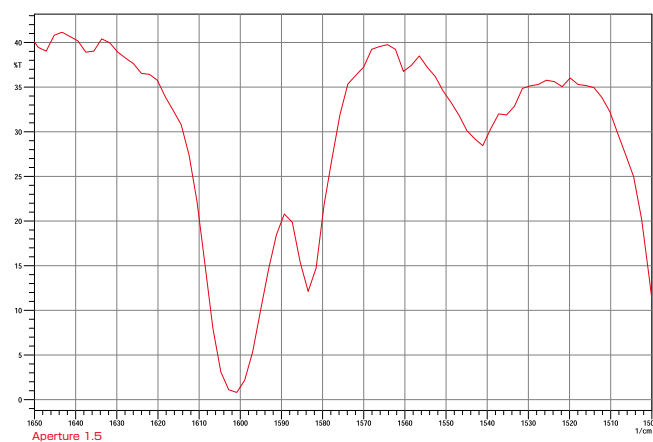


Fig. 4 Spectra Obtained Under the Same Conditions Used for Fig. 3 with an Aperture Diameter of 1.5

Polarization Measurement of Film Using Single-Reflection ATR

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There is a tendency for the long axes of the molecules of stretched polymers to line up in the stretching direction, and the extent of this can be ascertained using polarization measurement. Film samples are usually analyzed with a transmission method using a polarizer. Here, however, an example of polarization measurement using ATR is presented.

1. Polarization Measurement Using the Transmission Method

Polarization measurement uses linearly polarized light, which has an electric field that only oscillates in a certain direction. In order to create this linearly polarized light, a polarizer is required. Polarizers created by incorporating a wire grid into a KRS-5 substrate are commonly used.

The procedure of polarization measurement using the transmission method is as follows. First, BKG is measured with the polarizer at an angle of 0° (i.e., with the electric field oriented in a perpendicular direction), and then the sample is measured with its stretching direction aligned with the vertical direction. (At this time, the polarization direction and the direction of the stretching axis are parallel.) Then, the sample is rotated by 90° so that the stretching direction is perpendicular to the polarization direction and measured. The ratio of the absorbances, A_{\parallel} and A_{\perp} , of the spectra obtained in these two configurations, namely, with polarization parallel and perpendicular to the stretching direction, represents the dichroic ratio.

$$R = A_{\parallel} / A_{\perp}$$

2. Polarization Measurement Using ATR

With the transmission method, if the film thickness is too large, the peaks may become saturated, and measurement may not be possible. ATR has the advantage of not requiring consideration of film thickness.

With single-reflection ATR, because the prism is smaller than it is with multi-reflection ATR, it is easier to rotate the sample and there is better adhesion, so spectra with good repeatability can be obtained.

One of the features of ATR polarization measurement is that, in cases of film samples with two-axis symmetry, as shown in Fig. 1, information can be obtained in relation to the orientation of the molecules with respect to the X, Y, and Z axes. In this diagram, the Y axis represents the stretching direction, the X axis the direction that is perpendicular to, and in the same plane as, the stretching direction, and the Z axis the direction that is perpendicular to the surface of the sample (i.e., the thickness direction). Four types of measurement are required. The sample is first measured with its stretching direction aligned with the direction of light

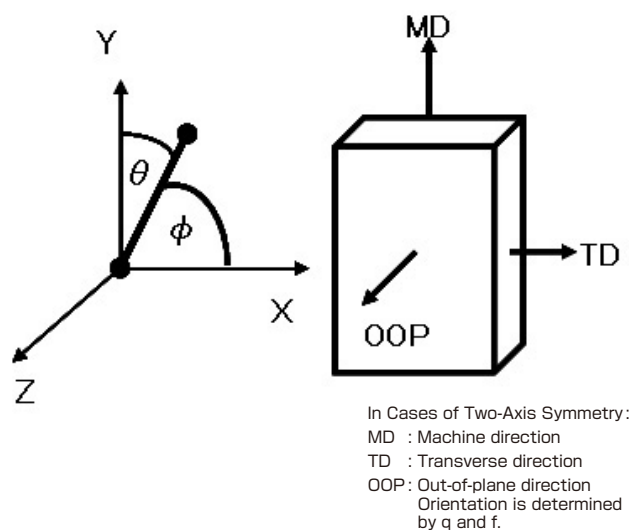


Fig. 1 Expressions of Molecular Orientation

propagation, while being irradiated with (1) parallel polarized light and (2) perpendicular polarized light. Then the sample is rotated by 90° and the measurements are repeated, with (3) parallel polarized light and (4) perpendicular polarized light. Here, "parallel polarized light" refers to linearly polarized light, which has an electric field that is parallel to the plane containing the incident light and reflected light, and "perpendicular polarized light" refers to linearly polarized light, which has an electric field that lies in the plane perpendicular to the parallel polarized light. The evanescent wave generated at the reflection point by perpendicular polarized light has a vector in the X direction. The evanescent wave generated at the reflection point by parallel polarized light has vectors in the Y and Z directions.¹⁾ (See Fig. 2.)

The spectra obtained with the above procedure reflect information about molecular vibrations in the X, Y, and Z directions. Detailed methods for expressing the orientation for all three directions are referred to in the reference material¹⁾. The spectra obtained in the actual analysis of PET (polyethylene terephthalate) film are presented here.

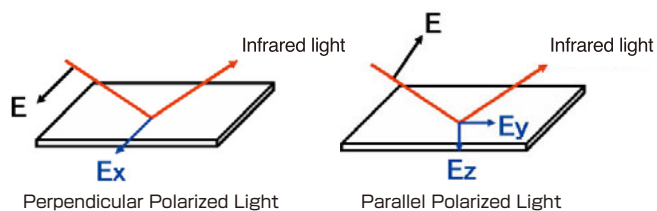


Fig. 2 Directions of Polarized Light and Evanescent Wave

3. Polarization Measurement for Stretched PET Film Using ATR

Fig. 3 shows the results obtained by analyzing unstretched PET film in four modes. There are hardly any differences between any of the four spectra, indicating that there is no molecular orientation. Fig. 4 shows the results obtained with the same PET film stretched by a factor of three.

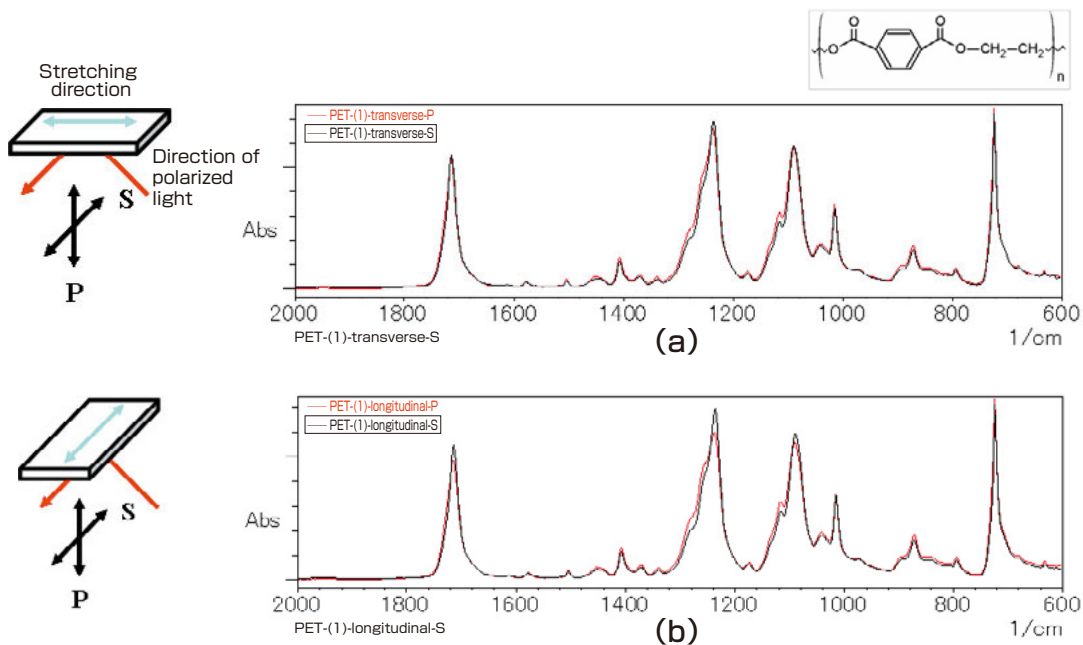


Fig. 3 Polarization Measurement Using Single-Reflection ATR Unstretched PET Film

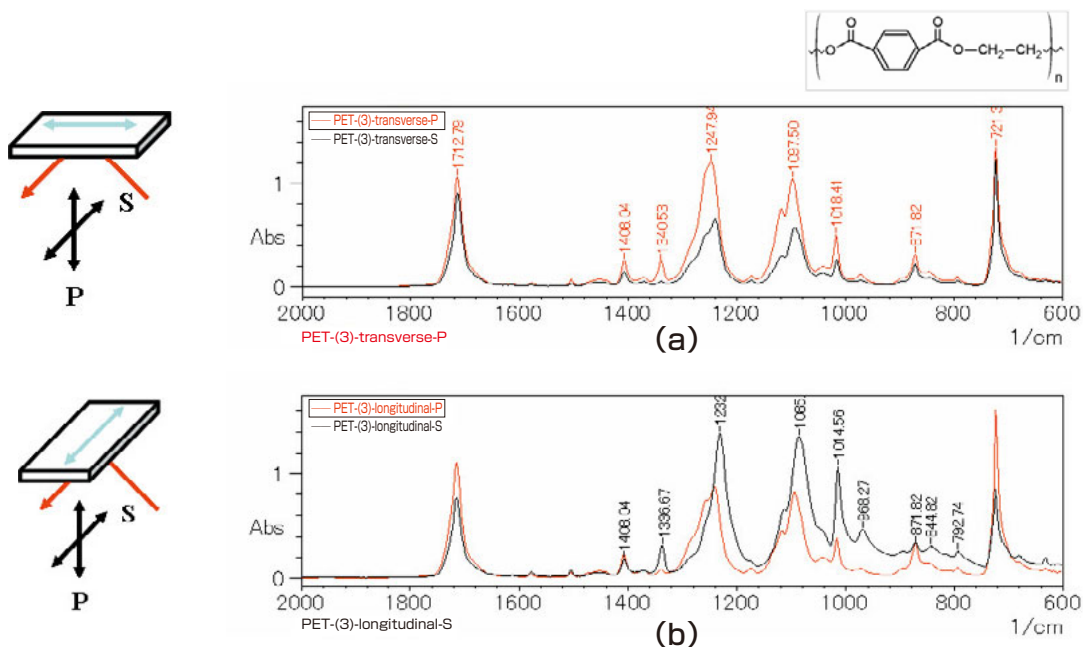


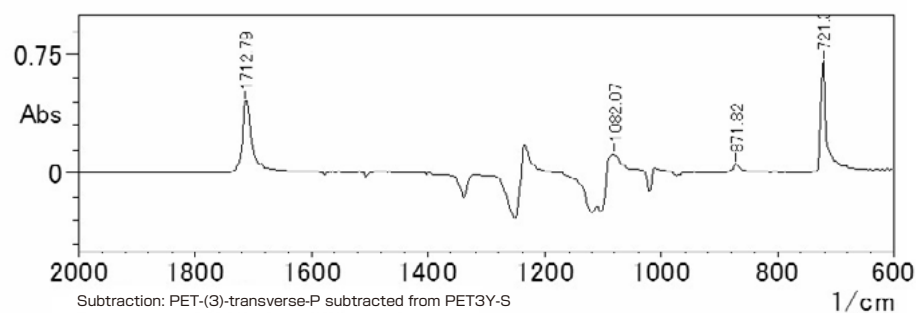
Fig. 4 Polarization Measurement Using Single-Reflection ATR PET Film Stretched by a Factor of 3

For each stretching orientation, differences can be observed in the spectra obtained with parallel polarized light and perpendicular polarized light. For example, the peak in the neighborhood of $1,340\text{ cm}^{-1}$ corresponds to the CH_2 wagging vibration and the mode in which the molecules oscillate in the direction of their long axes. In Fig. 4 (a), this peak is high for parallel polarized light (P) and low for perpendicular polarized light (S). On the other hand, this is reversed in Fig. 4 (b), indicating that the molecules are oriented in the stretching direction.

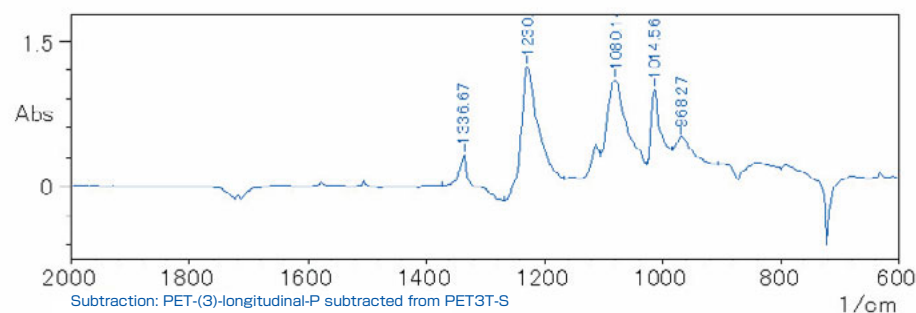
The peak at $1,410\text{ cm}^{-1}$ in Fig. 4 was thought to correspond to the in-plane bending vibration of benzene rings in a non-dichroic band. Figs. 5 (a) and (b) were obtained by

normalizing this peak, and generating differential spectra of the results for parallel polarized light and perpendicular polarized light shown in Figs. 4 (a) and (b). It can be seen that bands exhibiting infrared dichroism vary according to the orientation of the sample and the polarized light.

Everall et al. report that, in experiments where the stretching factor was varied in the range of 1.0 to 3.5, for larger stretching factors, the degree of orientation in the stretching direction was greater while the degrees of orientation in the transverse direction (i.e., the direction in the plane of the film that is perpendicular to the stretching direction) and depth direction were smaller.¹⁾



(a)



(b)

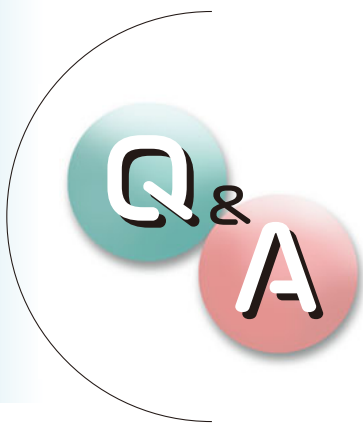
Fig. 5 Differential Spectra

4. Conclusions

It has been shown here that polarization measurement using ATR is extremely effective for investigating the orientation of film surfaces. Single-reflection ATR using a diamond prism, however, does present some problems. For example, there are concerns about the effect that the localized application of large forces may have on the molecular orientation, and in the analysis of polymers with a high refractive index, the peaks in bands of strong absorbance may be lopsided. Therefore, when investigating orientation with polarization measurement using ATR, in consideration of these potential problems, it is necessary to select the optimum peaks that exhibit dichroism.

References

- 1) Neil J. Everall and Arran Bibby *Appl. Spectrosc.* 51, 1083 (1997)



Question

What is an appropriate sample concentration for the KBr tablet method and the diffuse reflectance method?

Answer

With the KBr tablet method, a sample concentration corresponding to approximately 1% of the amount of KBr is generally considered appropriate. In practice, the molar absorbance coefficient varies with the sample so the concentration is adjusted in accordance with the transmittance and absorbance.

Adjusting the concentration so that the peak intensity of the largest peak in the spectrum corresponds to a transmittance of approximately 10% (or an absorbance of approximately 1 Abs) is considered appropriate. A spectrum obtained for lactose is given as an example. (See Fig. 1.)

If the maximum peak intensity is close to 100% (transmittance), the noise appears to be greater with respect to the peak. On the other hand, if the maximum peak intensity is close to 0%, the absorption peaks become saturated. This makes it impossible to obtain an accurate spectrum. (See Fig. 2.)

With the diffuse reflectance method, a concentration of approximately 5% with respect to the KBr is considered appropriate. Additionally, as in the KBr tablet method, the concentration is adjusted with the intensity of the maximum peak as a reference value. Note that with this method, because of the influence of the sample's surface reflection, the absorbance capacity may be saturated at a transmittance of 10%. Therefore, it would be better to adjust the concentration so that the transmittance is higher than this. (See Fig. 3.)

With the film method, the liquid membrane method, and transmission measurement methods based, for example, on microscope transmission measurement, it is appropriate, as a guideline, to adjust the sample thickness and optical path length so that the transmittance of the maximum peak becomes approximately 10%.

In some cases, a higher sample concentration is used in order to identify the peaks of trace constituents.

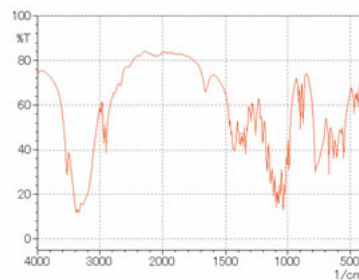


Fig. 1 Spectrum Obtained with KBr Tablet Method at Appropriate Concentration

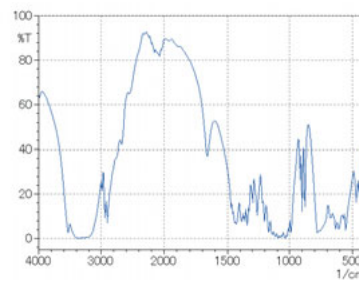


Fig. 2 Spectrum Obtained with KBr Tablet Method in Which Peaks are Saturated

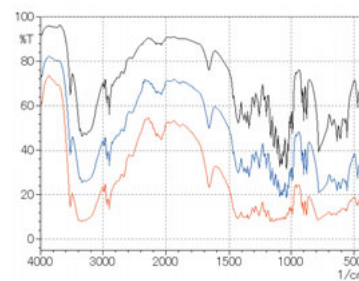


Fig. 3 Spectra Obtained with Diffuse Reflectance Method at Different Concentrations

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