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Using Infrared Detectors
—MCT Detector—

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In the previous issue, I presented the TGS (pyroelectric) detector, which is included with Shimadzu FTIR spectrophotometers as a standard feature. Another commonly used infrared detector is the MCT detector. In fact, an MCT detector is incorporated in Shimadzu infrared microscopes as a standard feature, and on FTIR spectrophotometers as an option.

Because the MCT detector and TGS detector are based on a different detection principle, there are various differences in the characteristics of the two.

(1) What Is an MCT Detector?

The "MCT" in "MCT detector" stands for "mercury cadmium telluride." The detection element in an MCT detector is an alloy of HgTe and CdTe. The notation "HgCdTe detector" is sometimes used.

The detectors used for the infrared region can be broadly divided into "thermal detectors" and "quantum detectors." The MCT detector is a quantum detector. As shown in Fig. 1, it detects changes in the electron-hole pairs formed by incident photons of infrared light.

Quantum detectors can be classified as either "photovoltaic" or "photoconductive." The former type detects changes in electrical current caused by changes in electron-hole pairs whereas the latter type detects changes in electrical conductivity. Incidentally, MCT detectors that operate as both photovoltaic and photoconductive detectors are currently being produced.

Pyroelectric detectors like the TGS detector are thermal detectors. They convert temperature changes caused by the absorption of infrared light to electrical signals using the pyroelectric effect. This difference in the detection mechanism gives rise to the contrasting characteristics of the two types of detectors. Refer to FTIR Talk Letter Vol. 12 for a detailed explanation on the TGS detector.

Conduction band

Light

Band gap

Electron

Valence band

Conduction band

Band gap
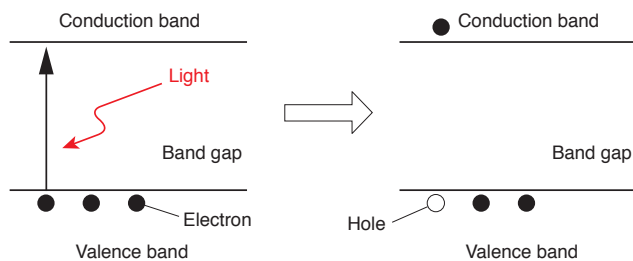
Hole

Valence band

When light of an energy exceeding the band gap energy strikes the material, an electron in the valence band is excited into the conduction band.

An electron in the valence band is excited into the conduction band, and an electron-hole pair is formed.

Fig. 1 Changes in Electron-Hole Pairs Caused by Incident Photons

(2) Characteristics of an MCT Detector

The following characteristics differentiate the MCT detector from the TGS detector.

(1) High Response Speed
One important characteristic of the MCT detector is the high response speed, and there is no change in sensitivity with the standard mirror speed. For this reason, the MCT detector is suited to applications that require measurement over a short time period, such as the analysis of samples that change over time. Fig. 2 and Fig. 3 show power spectra obtained with the diffuse reflection method using an MCT detector and a TGS detector.
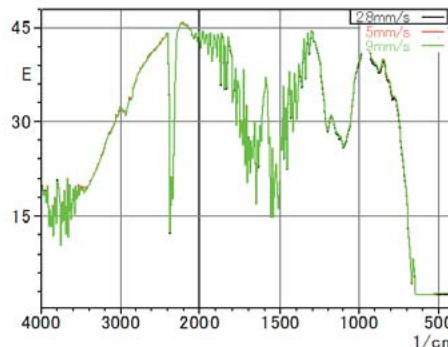
Fig. 2 Power Spectra Obtained with Diffuse Reflection Method Using MCT Detector
Black: Mirror speed of 2.8 mm/s; Red: Mirror speed of 5 mm/s; Green: Mirror speed of 9 mm/s
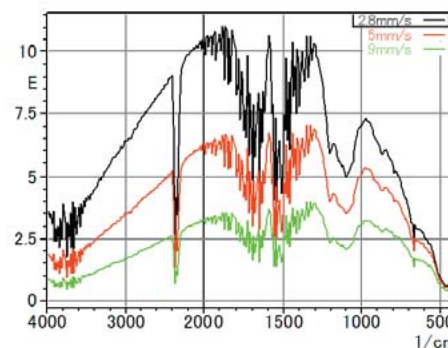
Fig. 3 Power Spectra Obtained with Diffuse Reflection Method Using TGS Detector
Black: Mirror speed of 2.8 mm/s; Red: Mirror speed of 5 mm/s; Green: Mirror speed of 9 mm/s

In the power spectra obtained using the MCT detector shown in Fig. 2, it can be seen that the spectrum intensity is not affected by changes in the mirror speed.

With the TGS detector, however, because the response speed is low, the intensity and form of the power spectrum vary with the mirror speed, as shown in Fig. 3. The influence of this is particularly noticeable in the high wavenumber (i.e., high-frequency) region.

(2) High Sensitivity

MCT detectors attain a D* value at least 10 times as large as that attained by TGS detectors.

For this reason, they are suitable for types of measurement associated with low levels of light intensity, such as microscope measurement, measurement performed with long-path gas cells, and heated vacuum diffuse reflection measurement. They also offer the advantage of allowing good spectra to be obtained with only a small number of scans.
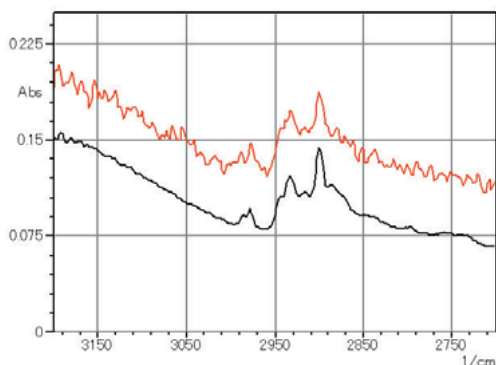

Fig. 4 Absorption Spectrum of Lactose Obtained with Diffuse Reflection Method
(Resolution: 4 cm^{-1}; One Scan)
Black: MCT detector; Red: TGS detector

It can be seen in Fig. 4 that using an MCT detector gives a better S/N ratio.

However, care is required when there is a high level of light intensity. This is because there will be a nonlinear relationship between the light incident on the detector and the output voltage. If the output voltage is nonlinear, there may be apparent power below 650 cm^{-1}, and if measurement is performed in this state, false peaks may appear in the region below 650 cm^{-1}. In this case, the light intensity must be reduced by, for example, using an aperture.

Supplementary Explanation
The "D* value" is an indicator of detector performance. Other indicators such as the "NEP" and "D value" are also used.
Noise equivalent power (NEP):
The "NEP" is the incident power that gives signals for which the S/N ratio is 1. Signals smaller than this value cannot be detected. This means that the lower the NEP of a detector, the better its S/N characteristics.

$$NEP = \frac{P \times A}{\frac{Sv}{Nv}} \times (\Delta f)^{1/2} \quad [W/Hz^{1/2}]$$

Sv: Signal output (voltage) [V]
P: Incident energy [W/cm^2]
A: Light-receiving surface area of detection element [cm^2]
Nv: Noise output (voltage) [V]
Δf: Noise bandwidth [Hz]

D value (detectivity), D* value (specific detectivity):
The "D value" is the inverse of the NEP. The "D* value" is the result of dividing the D value by the square root of the light-receiving area, and can be used to compare light-receiving elements of different areas.
This means that better detectors have larger D values and D* values.

$$D = \frac{1}{NEP} \quad [Hz^{1/2}/W]$$

$$D* = \frac{D}{A^{1/2}} \quad [cm \cdot Hz^{1/2}/W]$$

(3) Cooling Required

In general, the D* value of the MCT detector decreases as the element temperature increases, and if the detector is used when the temperature of the element is high, the element may be destroyed. For this reason, cooling with, for example, liquid nitrogen is required.

With Shimadzu FTIR spectrophotometers, PC software continually checks for the presence of liquid nitrogen. If the liquid nitrogen runs out, the software automatically stops the application of voltage to the MCT detector element in order to protect it and displays a warning message.

(4) Cut-Off Frequency

It can be seen in the power spectra in Fig. 2 that there is no intensity below 650 cm^{-1}. This is because no electrons are excited when a quantum detector receives light with an energy level smaller than the band gap; consequently, there is no sensitivity with respect to such light.

The band gap of an MCT detector varies with the ratio of HgTe to CdTe, and it is possible to make MCT detectors with various wavenumber ranges. For example, Shimadzu's infrared microscopes are available with two different measurement wavelength ranges: 5,000 to 720 cm^{-1} and 5,000 to 650 cm^{-1}.

Note, however, that the sensitivity decreases as the wavenumber range increases, as shown in Table 1, so it is necessary to select the product in accordance with the application.

Table 1 Wavenumber Ranges and S/N Ratios of Shimadzu Infrared Microscopes

	Type 1	Type 2
Wavenumber Range	5,000 to 720 cm^{-1}	5,000 to 650 cm^{-1}
S/N Ratio	2,600:1	2,000:1

Note: These S/N ratios are based on transmission measurement around 2,100 cm^{-1} with an aperture size of 50 × 50 μm, a resolution of 8 cm^{-1}, and 60 scans.

References

"Optical Detectors and How to Use Them," edited by Norihito Suzuki, Japan Scientific Societies Press, 1991, pp. 110-124

Spectral Emissivity Measurement Using FTIR Spectrophotometry

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As the issue of global warming becomes increasingly serious, various measures aimed at reducing CO_2 emissions are being implemented on a global scale. A representative example of this is the introduction of natural forms of energy (e.g., wind power, hydraulic power, and sunlight) as substitutes for fossil fuels, which are a major cause of CO_2 emissions. At the same time, from the viewpoint of energy conservation, it is also important to review our lifestyles and eliminate unnecessary energy consumption. Far-infrared radiation materials are used as heaters and refractory materials in industrial products and household electrical appliances, heating and insulating equipment in particular. There are increasing expectations that the efficient use of such materials will contribute to energy conservation.

Here, I present a measurement system and some measurement examples related to spectral emissivity spectra, which provide basic data that can be used to evaluate far-infrared radiation materials.

1. Spectral Emissivity

"Emissivity" is defined by Japanese industrial standard JIS Z 8117[1] as "the ratio of the radiant emittance of a body to the radiant emittance of a black body at the same temperature as that body." "Spectral emissivity" is defined as "the result of expressing the emissivity as a function of the component wavelengths (wavenumbers or frequencies)."[1]

A black body is "an idealized object that perfectly absorbs radiation at every wavelength."[1] The fact that the energy radiated from a black body can be expressed as a function of the wavelength and the temperature of the body is known as "Planck's law." Fig. 1 shows the spectral radiant emittance of a black body at temperatures of 100, 200, 400, and 600 °C calculated with Planck's law. (The vertical axis represents logarithmic values.)

In actual measurement, a black body furnace is used as a body whose properties approach those of an ideal black body. The emissivity of samples is measured using the black body furnace as a reference.

Planck's law
$$Me\lambda = (C_1/\lambda^5) / [\exp(C_2/\lambda T)-1] \ (W \cdot m^{-2} \cdot \mu m^{-1})$$

Here, C_1: First radiation constant, C_2: Second radiation constant
$C_1 = 2\pi hc^2 = 3.741771 \times 10^{-16} \ (W \cdot m^2)$,
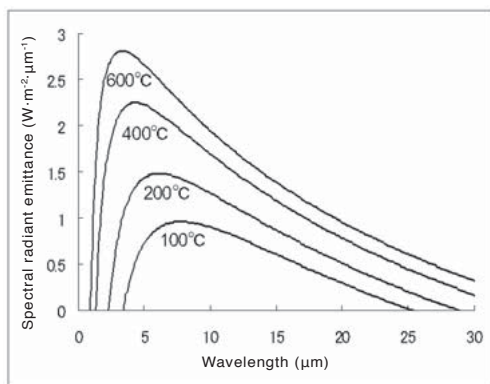$C_2 = hc/k = 1.438775 \times 10^{-2} \ (m \cdot K)$

Fig. 1 Spectral Radiant Emittance of Black Body

2. Spectral Emissivity Measurement System

A spectral emissivity measurement method using an FTIR spectrophotometer is detailed in Japanese industrial standard JIS R 1801[2]. Here, I present an emissivity measurement system consisting of an FTIR spectrophotometer (IRPrestige-21), a black body furnace, a sample heating furnace, a temperature controller, and a separate optical system. A photograph of the system is shown in Fig. 2.

Fig. 2 Appearance of Spectral Emissivity Measurement System

JIS R 1801[2] specifies the method for performing measurement, using an FTIR spectrophotometer, in a range from "a wavelength of approx. 2.5 µm to approx. 25 µm." There is no clear definition of the wavelength range of "far-infrared," even in JIS Z 8117.[1] The definition varies with the industry; for example, the Japan Far Infrared Rays Association specifies a range of "the wavelength from 3 µm (micron) to 1 mm (millimeter)." Even if the sample is a "far-infrared radiation material," the type of measurement is referred to as "(infrared) emissivity measurement" or "radiation factor measurement," and not "far-infrared emissivity measurement," because the spectroscopic definition of far-infrared light is light of a wavelength minimum of 25 µm.

Explanations of the black body furnace, the sample heating furnace, and the FTIR spectrophotometer that form part of the system are given below.

2.1 Black Body Furnace

A black body is an object that completely absorbs any electromagnetic radiation that falls on it across all wavelengths. There are no true (i.e., ideal) black bodies in nature. Therefore, in emissivity measurement, a black body furnace is used as a body whose properties approach those of an ideal black body. A black body furnace is a device that closely replicates a black body, and is used as an illuminant. According to JIS Z 8117,[1] "there are black body furnaces in which a hollow formed out of metal, graphite, a ceramic, or some other suitable material is kept at a temperature in the range 300 to 1,500 K, and the radiant flux emitted from an aperture in the hollow is utilized." In general, a black body furnace has the kind of structure shown in Fig. 3, where a hole with a diameter of approx. 2 cm is opened in a spherical hollow surrounded by heaters.
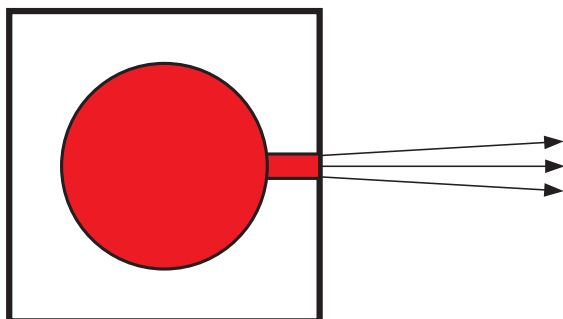

Fig. 3 Black Body Furnace

2.2 Sample Heating Furnace

A sample heating furnace is a device used to heat samples. There are furnaces that keep the sample in a vertical position but usually the sample mounting is horizontal, as shown in Fig. 4. Samples with diameters of up to a few centimeters can be set. As the spot size required for measurement is approx. 1 cm in diameter, note that the measurement results may be affected by a small positional displacement if the sample diameter is only around 1 cm. Also, because it is difficult to use large samples with sample heating furnaces designed for temperatures exceeding 1,000 °C, logistical coordination may be required to determine the specifications suitable for the samples. Regarding sample form, measurement is usually possible only for plate-like samples. Accurate measurement is not possible for curved or powdered samples. This is because the temperature is not even over the surface of such samples, making it impossible for the surface temperature to be measured accurately.
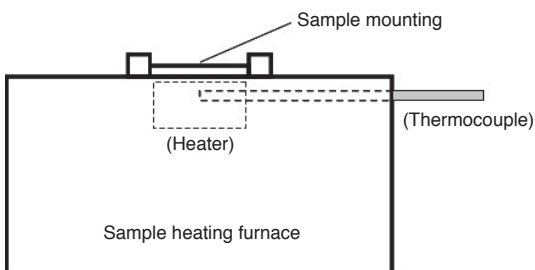

Fig. 4 Sample Heating Furnace

The black body furnace and sample heating furnace are equipped with thermocouples in order to monitor the temperature, and temperature control is performed by a temperature controller.

2.3 Fourier Transform Infrared (FTIR) Spectrophotometer

An FTIR spectrophotometer is a device with a built-in infrared light source that irradiates the sample in a sample compartment and obtains absorption spectra. When an FTIR spectrophotometer is used for emissivity measurement, the built-in infrared light source is turned OFF, and the spectrophotometer is set to analyze the radiation emitted from the black body furnace and the sample heating furnace. Because external radiation is introduced into the spectrophotometer in place of the radiation emitted by the light source, a separate optical system is required. In the photograph shown in Fig. 2, the separate optical system is set up on one side of the FTIR spectrophotometer, and the sample heating furnace and black body furnace are respectively positioned in front of and behind the optical system.

This system can also support standard measurement using the sample compartment.

3. Examples of Emissivity Measurement

The first step of the measurement procedure consists of setting the temperatures of the black body furnace and sample heating furnace to the temperature required for measurement. After the temperature of the black body furnace stabilizes at the set temperature, the radiant energy is measured as the background level. Then, the optical path is switched to the sample heating furnace, and after the sample surface is heated to the set temperature, the radiant energy emitted by the surface is measured. It is important to ensure that the temperatures of the black body furnace and the sample surface are the same. Because temperature control of the sample heating furnace is performed using the temperature in the area near the heater where the thermocouple is installed, the sample surface temperature is lower than the set temperature of the sample heating furnace. The sample surface temperature can be accurately made to conform with the temperature of the black body furnace by, for example, installing a thermocouple on the sample surface, or coating the sample surface with black coating material and measuring the emissivity, and adjusting the temperature as appropriate.
Examples of the analysis of an alumina ceramic and a glass plate are presented below.

3.1 Analysis of Alumina Ceramic

An alumina ceramic circular disc with a thickness of 1 mm was heated to 450 °C, and the spectral emissivity was measured. Fig. 5 shows the measurements obtained for the radiant energy of the black body furnace and the sample on a graph with the horizontal axis representing the wavelength. The spectral emissivity was obtained by calculating the ratio of the two sets of measurements, and the result of this is shown in Fig. 6. It can be seen that, in a wavelength range of approximately 6 to 10 μm, the emissivity is close to 100 %. If the spectral emissivity is known, multiplying the black body spectral radiant emittance obtained with Planck's law, which was given previously, by the emissivity of the sample makes it possible to obtain the spectral radiant emittance of the sample. Fig. 7 shows the spectral radiant emittance for a temperature of 450 °C obtained with Planck's law and the spectral emissivity of the alumina ceramic.
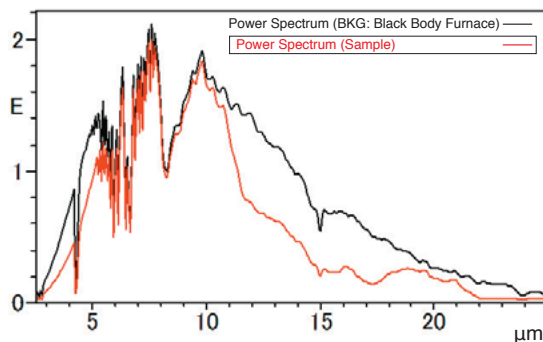

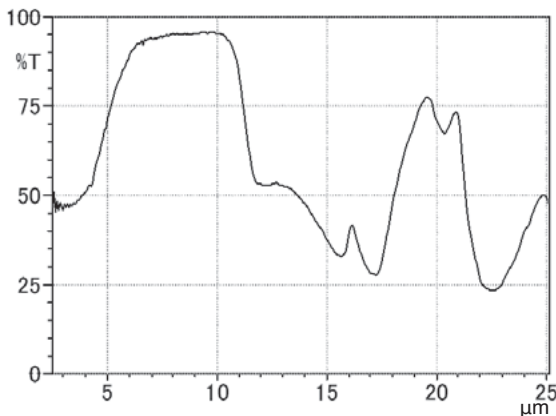Fig. 5 Radiant Energy of Black Body Furnace and Alumina Ceramic

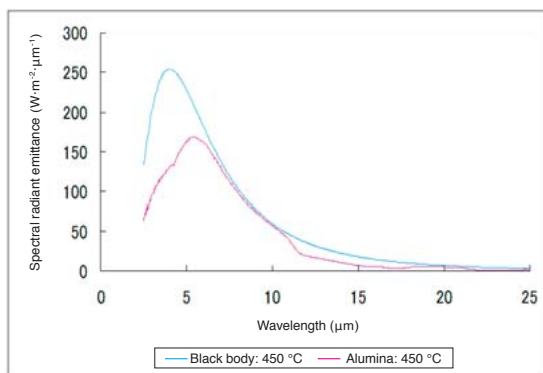
Fig. 6 Spectral Emissivity Spectrum of Alumina Ceramic

Fig. 7 Spectral Radiant Emittance at 450 °C

3.2 Analysis of Glass Plate

Fig. 8 (a) shows the spectral emissivity spectrum obtained for a glass plate with a thickness of 5 mm at a temperature of 300 °C. Fig. 8 (b) and Fig. 8 (c) show the reflection spectrum and transmission spectrum obtained for the same sample.

Taking 1 as the total amount of energy in the light that strikes the object, the law of conservation of energy gives the following:

$$1 = α + ρ + τ$$
 (α: Absorptance, ρ: Reflectance; τ: Transmittance)

In the case of an opaque body, $τ = 0$, and applying Kirchoff's law, which states that the emissivity, ε, of a body equals its absorptance at thermal equilibrium, the emissivity can be obtained by subtracting the reflectance from 1 ($ε = 1 − ρ$).

The results shown in Fig. 8 indicate that, at wavelengths greater than 4 μm, the transmittance of this glass is almost 0 %, so $ε ≈ 1 − ρ$. It can be seen from this that the emissivity spectrum shown in Fig. 8 is reasonable.
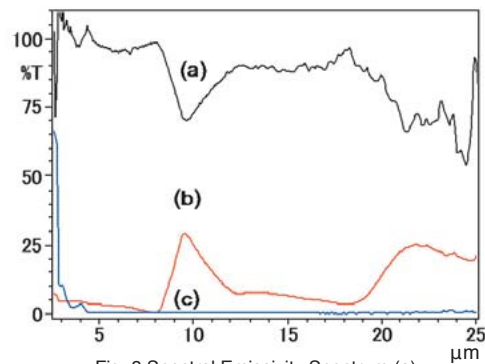

Fig. 8 Spectral Emissivity Spectrum (a),
Reflection Spectrum (b), and Transmission Spectrum (c) of Glass Plate

4. Summary

In the 1970s, Japan experienced energy crises that resulted from a disruption of the world's oil supplies. This experience greatly encouraged the country to develop far-infrared radiation materials as a means of energy conservation. Now, faced with the issue of global warming, we are entering an age in which new energy sources and energy conservation are pressing issues. While the efficient use of far-infrared radiation materials is being promoted with increasing intensity, it is important to advance a correct understanding of spectral emissivity measurement, the technique used to evaluate these materials. Dr. Hiroo Takashima's book[3] provides a detailed explanation on the effects and characteristics of far-infrared radiation, and includes a description of spectral emissivity measurement.

References
1) Japanese industrial standard JIS Z 8117: "Glossary of Far Infrared Radiation Terms"
2) Japanese industrial standard JIS R 1801: "Method for measuring spectral emissivity of ceramic radiating materials for infrared heaters by using FTIR"
3) Hiroo Takashima, "Far-Infrared Engineering Made Easy," Kogyo Chosakai Publishing, Inc., 1988.

I am having trouble with the qualitative analysis of rubber constituents. Is there an effective method that you can recommend?

Answer Various substances, including vulcanizing agents, vulcanization accelerators, fillers, and plasticizers, are added to rubber. When FTIR is used in the qualitative analysis of rubber, the absorption of these additives may coincide with the absorption of the rubber constituents and make analysis difficult. Some points that must therefore be observed in the analysis of rubber are given below.

Carbon black is added as a strengthening agent to black rubber products such as tires. In the analysis of rubber containing carbon black, measurement is difficult with the transmission method because carbon absorbs infrared light. Although analysis using the attenuated total reflection (ATR) method is effective, with rubber containing a large amount of carbon black, a germanium (Ge) prism must be used for reasons related to the refractive index. Refer to FTIR Talk Letter Vol. 11, "Points to Note in Rubber Analysis: Black Rubber," for details.

Calcium carbonate is also used as an additive in many types of rubber because it makes them easier to mold. With rubber containing calcium carbonate, there is broad and strong absorption of CO_3^{2-} near 1,430 cm^{-1}. (This may shift depending on the measurement technique used.) As a result, absorption originating from rubber constituents may be obscured by the absorption of calcium carbonate, making qualitative analysis difficult. In this case, the rubber is treated with hydrochloric acid in order to remove the calcium carbonate. With rubber from which the calcium carbonate has been removed, the CO_3^{2-} peak does not appear; as a result, the qualitative analysis of rubber constituents becomes significantly easier. Fig. 1 shows the ATR spectra obtained for EPDM (ethylene propylene diene monomer) rubber containing calcium carbonate, talc, and carboxylic acid ester both before and after hydrochloric acid treatment. As a result of this treatment, the broad and strong peak of CO_3^{2-} disappears, and peaks originating from C-H bending vibrations of EPDM can be observed.

It is known that many of the additives contained in rubber are precipitated to the surface. This phenomenon is called "bleeding" or "blooming," and is illustrated in Fig. 2. Due to influence of the additives that are precipitated to the surface, the absorption of the rubber constituents is obscured. On the other hand, inside the rubber material, the influence is less, and the qualitative analysis of rubber constituents is relatively easy. Fig. 3 shows the results of analyzing butyl rubber (IIR) with the ATR method. While the peaks of the

additives aluminum hydroxide and calcium carbonate are detected with high intensity at the surface, the absorption of the rubber constituents can be observed with a cross section. Using the ATR method to analyze both the surface and a cross section enables the qualitative analysis of both rubber constituents and additives.
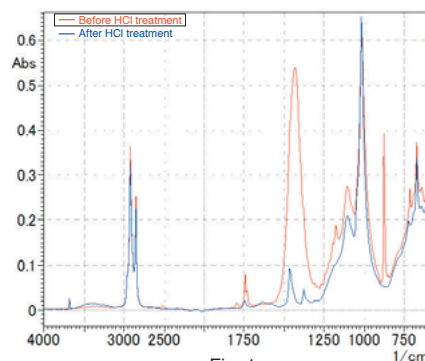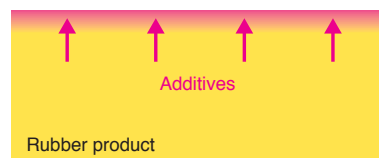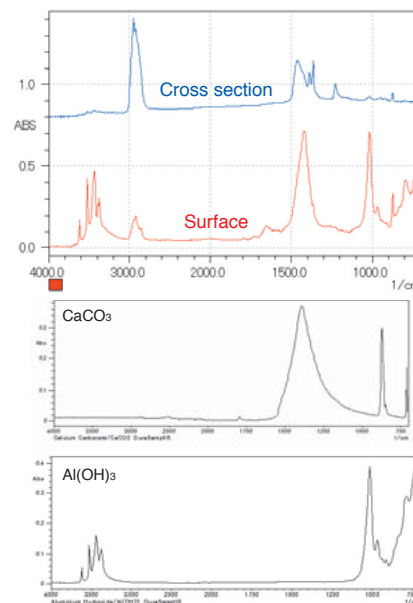

Fig. 1

Additives

Rubber product
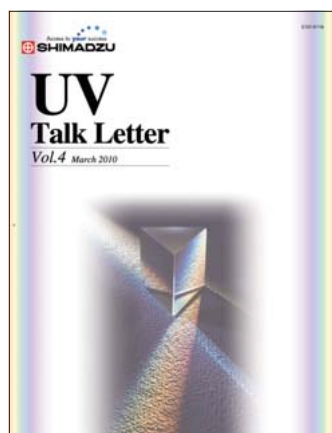
Fig. 2

Cross section

Surface

CaCO₃

Al(OH)₃

Fig. 3

Related Publications

UV TALK LETTER

UV Talk Letter is a pamphlet containing information related to ultraviolet-visible spectrophotometers. It covers a wide range of material, from the latest topics to analytical techniques that do not appear in books.

UV Talk Letter
First published: 2008

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