

UV

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Vol. 12



Application:

Solid Sample Reflectance Measurements — 02

How to Choose Integrating Spheres and White Reference Plates — 08

Q&A:

Sometimes when using a 10 mm cell to measure the transmittance in the near infrared region, the peaks cannot be confirmed due to saturation.

What should I do? — 12



UV Talk Letter

Application – Solid Sample Reflectance Measurements –

In addition to measuring liquids, UV-VIS spectrophotometers are used to measure the transmittance and reflectance of solid samples. UV TALK LETTER vol. 11 discusses measuring the transmittance of solid samples. For the next two issues, starting with this one, we will discuss measuring reflectance. Of the two types of reflectance measurements—relative reflectance and absolute reflectance, this issue is mainly focused on relative reflectance measurement.

1. Reflectance Measurement

Reflectance is measured by shining light on a sample and measuring the light reflected from the sample. Reflected light consists of specular reflected light and diffuse reflected light, which when combined together is referred to as total reflected light (specular reflected light plus diffuse reflected light). Fig. 1 shows a diagram of these types of light. The light shone onto the sample is called the incident light and the angle formed between the incident light and sample is called the angle of incidence. In Fig. 1, the incident angle is represented with the symbol θ .

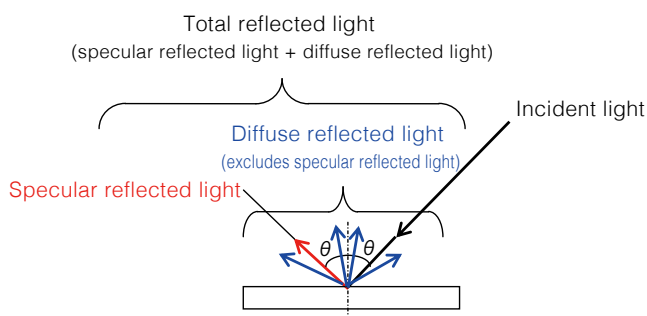


Fig. 1 Types of Reflected Light

Specular reflected light is the light reflected from shiny mirror-like surfaces at the same angle as the incident angle. Diffuse reflected light is the diffuse light reflected in all directions from rough surfaces, such as paper and powder surfaces. Total reflected light is the total combination of specular and diffuse reflected light. Total reflected light is often measured when measuring samples that have both rough and shiny characteristics, such as plastic and painted samples. The methods used to measure specular, diffuse, and total reflected light are referred to as specular, diffuse, and total reflected light measurement methods, respectively.

Reflectance measurements measure either the relative or absolute reflected light, with measurement values expressed in terms of reflectance. Relative reflectance measurements calculate the proportional amount of reflected light measured from a sample surface, relative to the amount of reflected light measured from a reference plate, such as barium sulfate or a mirror. The relative reflectance is calculated based on assuming the reference plate has a reflectance of 100%. Therefore, it is very important to manage reference plates properly because different reflectance values can be obtained if reference plates are substituted or if they become contaminated or change characteristics.

$$\text{Relative Reflectance (R\%)} = \frac{\text{Amount of Light Reflected from the Sample}}{\text{Amount of Light Reflected from the Reference Plate}} \times 100$$



In contrast, absolute reflectance measurements calculate the proportional amount of reflected light relative to the amount of light measured directly from a light source, not using a reference plate such as barium sulfate or a mirror. Reflectance

measurement values are based on assuming a 100 % reflectance for air. Absolute reflectance measurements allow determining the true reflectance of samples, which is referred to as absolute reflectance.

$$\text{Absolute Reflectance (R\%)} = \frac{\text{Amount of Light Reflected from the Sample}}{\text{Amount of Light Used}} \times 100$$

Reflectance measurements can be categorized as shown in Fig. 2.

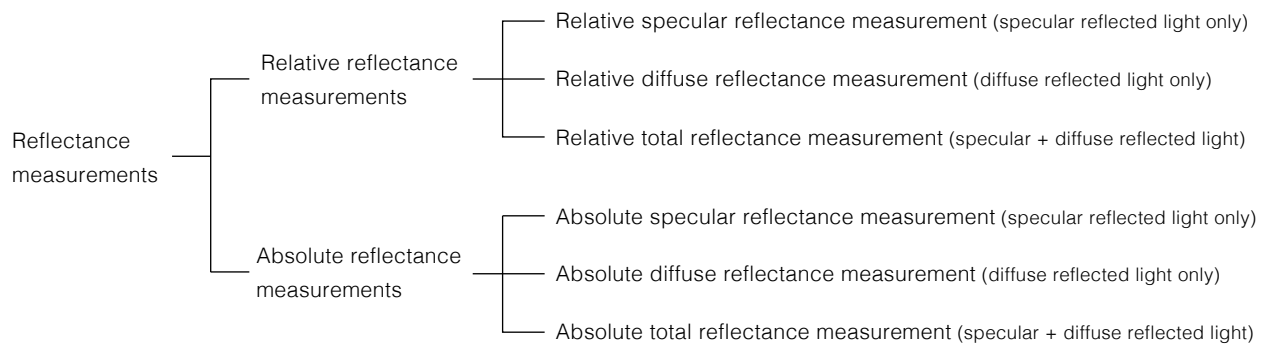


Fig. 2 Types of Reflectance Measurements

2. Relative Specular Reflectance Measurement

Relative specular reflectance measurements involve shining light on the sample, and measuring the specular light reflected at the same angle as the incident light, as shown in Fig. 3-1. Relative specular reflectance measurements are especially useful for measuring thin films on a mirror or metal surface. Fig. 3-2 shows a specular reflectance measurement attachment used to measure relative specular reflectance. The incident angle of this attachment is 5 degrees (the angle represented by θ in Fig. 3-1). The aluminum-coated mirror is typically used as the reference plate for measurements using the specular reflectance measurement attachment. Samples are placed with the measurement surface facing downward.

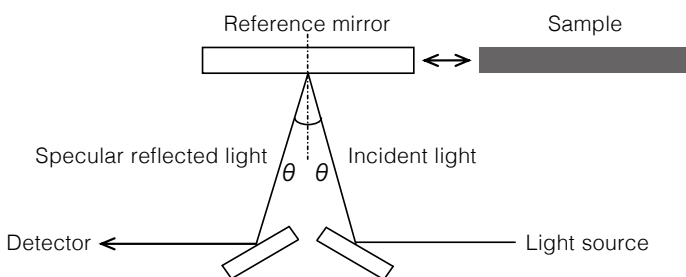


Fig. 3-1 Relative Specular Reflectance Measurement

Fig. 3-3 shows results from measuring a photoresist layer on a wafer using a specular reflectance measurement attachment. This provides the relative reflectance of the sample relative to the aluminum-coated mirror that was used as the reference. However, this specular reflectance measurement attachment cannot be used to measure the diffuse light reflected from samples with a rough surface.

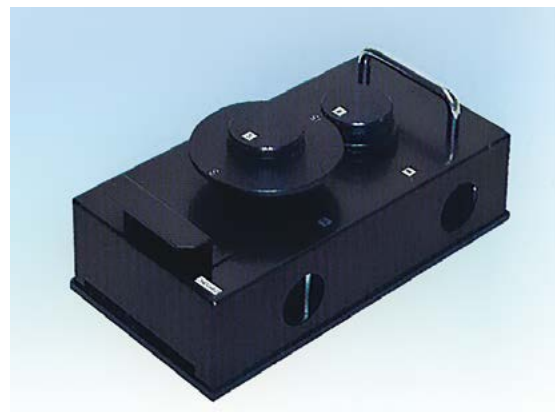


Fig. 3-2 Specular Reflectance Measurement Attachment

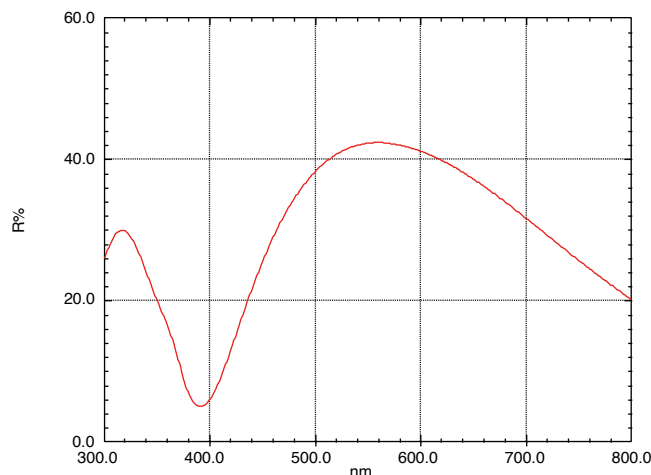


Fig. 3-3 Relative Specular Reflectance Measurement Results from Photoresist Layer

3. Relative Diffuse Reflectance Measurement

Relative diffuse reflectance is measured by using an integrating sphere to measure the diffuse reflected light with specular reflected light excluded, as shown in Fig. 4-1. This is used to measure samples with a rough surface, such as paper.

Fig. 4-2 shows an integrating sphere attachment used to

measure relative diffuse reflectance. When using an integrating sphere, a material such as barium sulfate or specialized fluorine-based polymer (see Note 1) is used as the reference plate (sometimes referred to as a white reference plate).

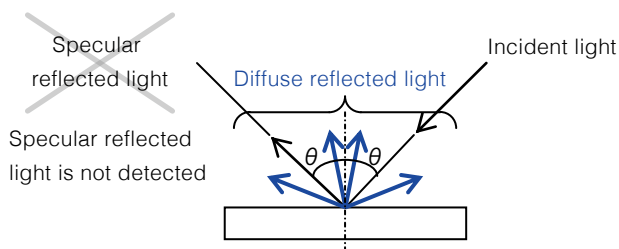


Fig. 4-1 Relative Diffuse Reflectance Measurement

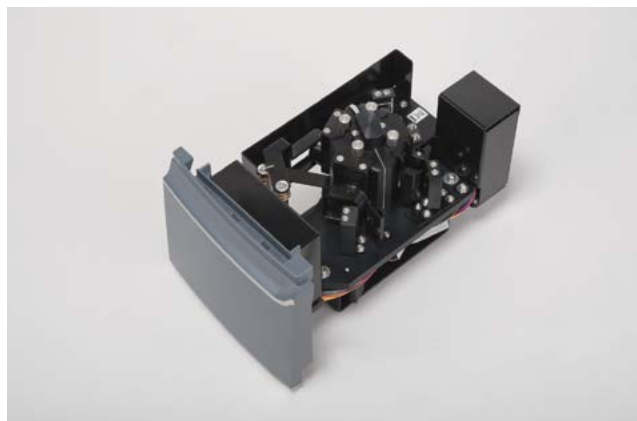


Fig. 4-2 Integrating Sphere Attachment (ISR-2600 Plus)



Fig. 4-3 shows a diagram of the measurement. The measurement procedure is as follows.

1. Attach a barium sulfate or other white reference plate at position (1) in the integrating sphere shown in Fig. 4-3. Perform baseline correction. The sample beam shines on the white reference plate.

2. Remove the white reference plate from position (1) in Fig. 4-3 and attach the measurement sample in its place. Measure the sample to obtain the diffuse reflectance. Specular reflected light is reflected out of the integrating sphere via the sample beam inlet port and, therefore, is not detected (see Note 2).

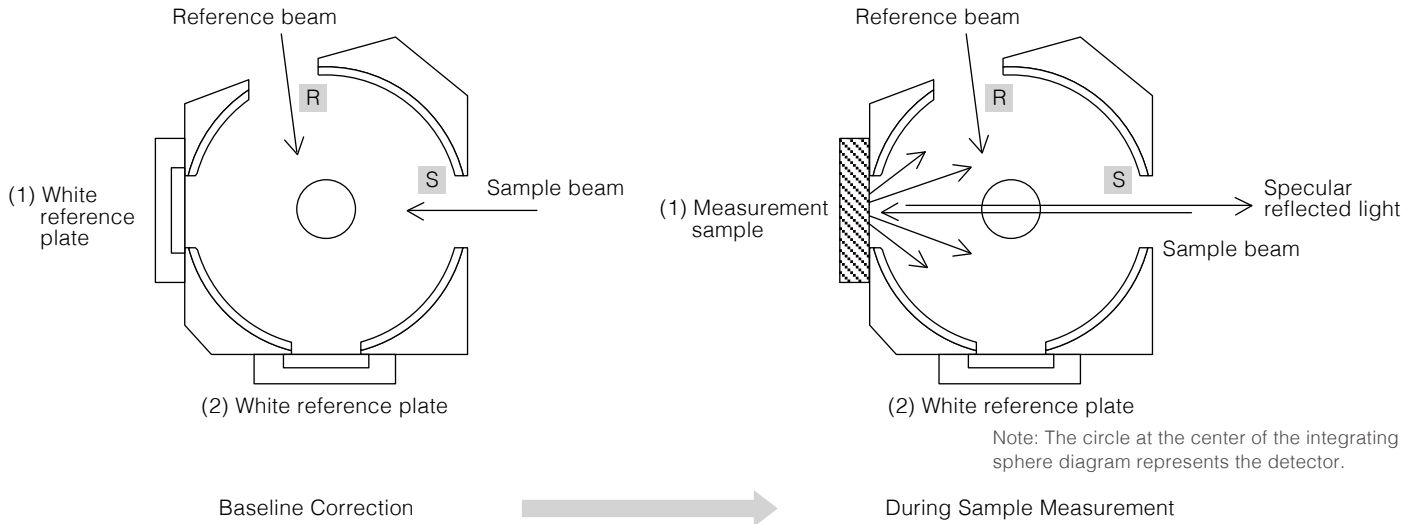


Fig. 4-3 Relative Diffuse Reflectance Measurement

Diffuse reflected light is measured using an integrating sphere according to the procedure indicated above. Fig. 4-4 shows the results from measuring the relative diffuse reflectance from a

plastic surface using an integrating sphere with barium sulfate as the white reference plate. For more detailed information on integrating sphere construction, refer to UV TALK LETTER vol. 5.

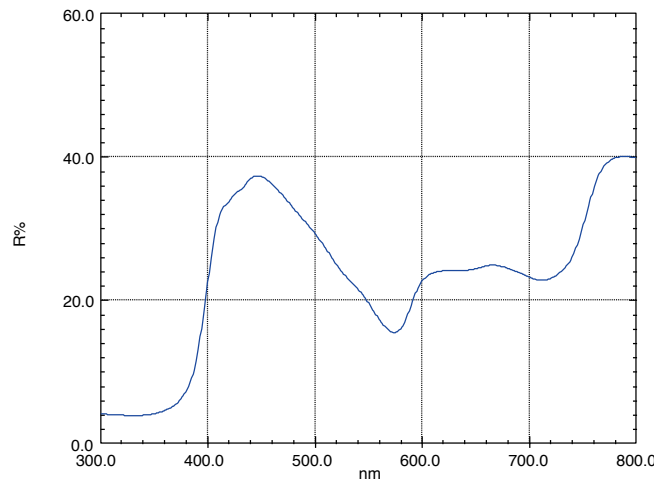


Fig. 4-4 Relative Diffuse Reflectance Measurement of Plastic

Note 1: Due to a small amount of water contained in barium sulfate, using it as the white reference plate for reflectance spectrum measurements in the infrared region may result in effects from water absorption near 1450 nm, 1950 nm, and 2500 nm. In contrast, the special fluoropolymer does not contain any water, so spectra are not affected by water.

Note 2: The purpose of the reference beam indicated in Fig. 4-3 is for correcting light source fluctuations in real time. For more information regarding the role of the reference beam, refer to UV TALK LETTER Vol. 9.

4. Relative Total Reflectance Measurement

Determine relative total reflectance by measuring all the reflected light, including both specular and diffuse reflected light, as shown in Fig. 5-1. This is effective for samples with either rough or shiny surfaces

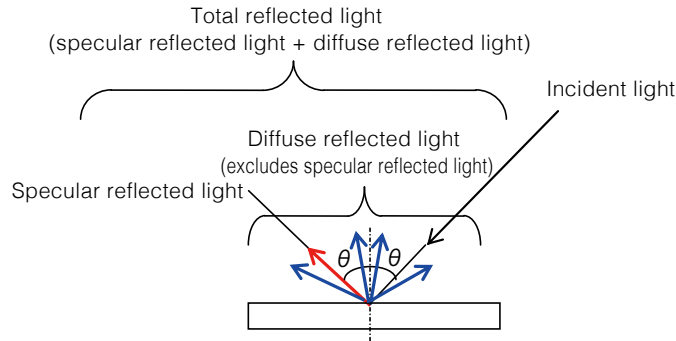


Fig. 5-1 Relative Total Reflectance Measurement

Relative total reflectance is measured using an integrating sphere attachment. Relative total reflectance is measured by shining light on the sample at an incident angle of about 10 degrees or less (8 degrees for Shimadzu integrating spheres) and using an integrating sphere to measure not only the diffuse reflected light, but also the specular reflected light. Typically, a white plate with a rough surface, such as barium sulfate, is used as the reference plate. However, unlike relative diffuse reflectance measurements that do not include specular reflected light, aluminum-coated mirrors are also often used as the reference plate (see also Precautions for the Reference Plate Used for Total Reflectance Measurements).

Fig. 5-2 shows a diagram of the measurement. The measurement procedure is as follows.

1. Reverse the roles of sample and reference beams in measurement parameter settings. In Shimadzu software, this means setting the S/R switching function to reverse.
2. Attach a white reference plate at position (2) of the integrating sphere shown in Fig. 5-2. Perform baseline correction. The sample beam shines on the white reference plate.
3. Remove the white reference plate from position (2) in Fig. 5-2 and attach the measurement sample in its place. For Shimadzu integrating spheres, the beam shines on the sample at an incident angle of 8 degrees.

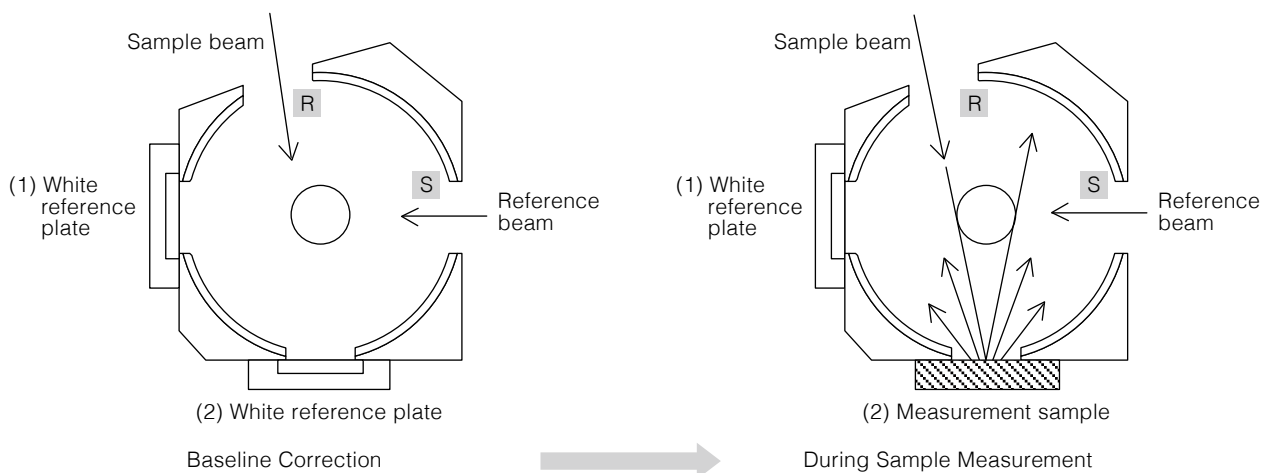


Fig. 5-2 Relative Total Reflectance Measurement

Fig. 5-3 shows the results from using a barium sulfate reference plate to measure the relative total reflectance of the plastic measured in 3. Relative Diffuse Reflectance Measurement. Fig. 5-4 shows a comparison of the relative diffuse reflectance

spectrum and relative total reflectance spectrum. Because the relative total reflectance includes the specular reflectance components, the reflectance level is higher than the relative diffuse reflectance.

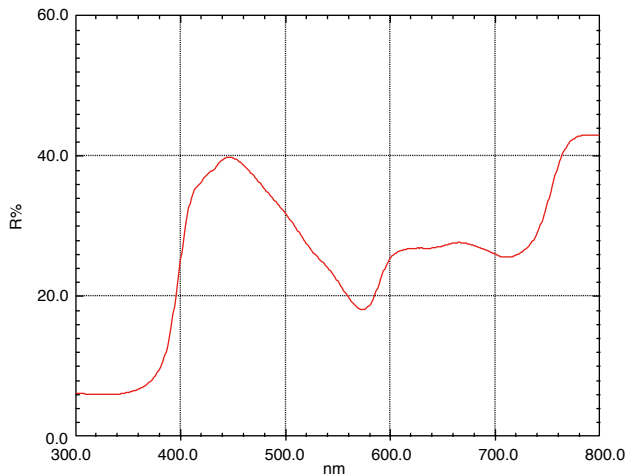


Fig. 5-3 Relative Total Reflectance Measurement of Plastic

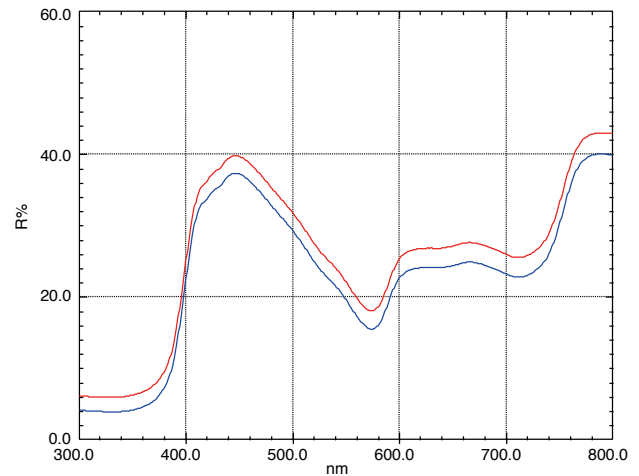


Fig. 5-4 Comparison of Relative Diffuse (Blue Line) and Relative Total (Red Line) Reflectance Measurements

Precautions for the Reference Plate Used for Total Reflectance Measurements

To match the light scattering status in the integrating sphere during sample measurements and baseline correction as closely as possible, use a reference plate with a shiny surface, such as an aluminum-coated mirror, to measure samples with predominantly specular reflectance. To measure samples with predominantly diffuse reflectance, use a reference plate with a rough surface, such as barium sulfate.

For example, if an aluminum-coated mirror is used as the reference plate for measuring the total reflectance of paper, the reflected light first hits in a different location inside the integrating sphere during sample measurement compared to during baseline correction. The light scattering status during sample measurement remains different from the status during baseline correction throughout the measurement, and this difference is added to measurement values. (These effects are due to differences in the status of scattered light and the fact that the internal surfaces of the integrating sphere are not completely

uniform.) Therefore, measurement results include a certain error factor. When using systems that switch between different detectors, this can cause a discontinuity in measurement data at the wavelength where the detectors are switched.

In contrast, if the paper is measured using barium sulfate as the reference plate, the reflected light initially hits about the same position inside the integrating sphere during both sample measurement and baseline correction. Consequently, correct relative reflectance values are obtained.

For the same reason, a mirror surface, such as an aluminum-coated mirror, must be used as the reference plate for measuring the relative total reflectance of films and coatings on a predominantly mirror-like (shiny) surface, such as metal substrates

That is the reason that reference plates with shiny surfaces are used to measure shiny samples and reference plates with diffuse surfaces are used to measure diffuse samples.

5. Summary

This issue describes the measurement principle, measuring method, and precautions mainly for relative reflectance measurements. The reflectance measurement method used differs depending on the sample surface status and objectives. Hopefully this explanation will provide a helpful reference. When measuring reflectance, absolute reflectance measurements are also very important, and these will be introduced in the next issue.

Application – How to Choose Integrating Spheres and White Reference Plates –

Sections 3 and 4 of the previous chapter discussed the measurement of relative reflectance using an integrating sphere. When using an integrating sphere, measurement values can vary depending on the inner wall material of the integrating sphere and the white reference plate. Therefore, this chapter describes some actual examples and discusses how to choose the inner wall material of the integrating sphere and the white reference plate.

1. Inner Wall Material of the Integrating Sphere

For diffuse transmitted light and diffuse reflected light measurements, a coating or plastic material with almost 100 % reflectance is used on the inner walls of integrating spheres. Primarily either barium sulfate paint ("BaSO₄ paint" below) or a special fluoropolymer are used for these materials.

Fig. 1 shows the absolute reflectance of BaSO₄ paint and a special fluoropolymer. The reflectance of these materials differs significantly in the near infrared region. For BaSO₄ paint, reflectance in the visible light region is over 90 %, but drops to about 80 % in the near infrared region. In contrast, the reflectance for the special fluoropolymer is over 95 % in the visible light region and over 90 % even in the near infrared region. Therefore, if only using the integrating sphere for measurements in the visible light region, then BaSO₄ paint should provide more than adequate performance, but an integrating sphere with a

special fluoropolymer interior would be more useful if performing precision measurements in the near infrared region.

However, the problem with using the special fluoropolymer is that the interior wall thickness needs to be 8 to 9 mm to obtain adequate reflectance levels. This forms a ledge where the sample meets the integrating sphere's inner wall, as shown in Fig. 2, which can affect measurements.

Note that the downward peaks in the BaSO₄ spectrum in Fig. 1 near 1450 nm, 1950 nm, and 2500 nm are due to the absorption by water contained in BaSO₄.

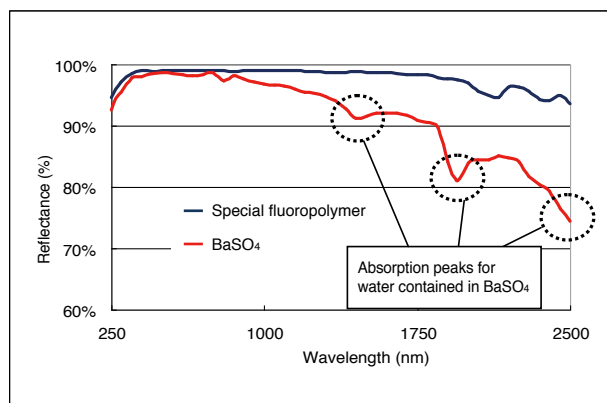


Fig. 1 Reflectance of Barium Sulfate Paint and Special Fluoropolymer

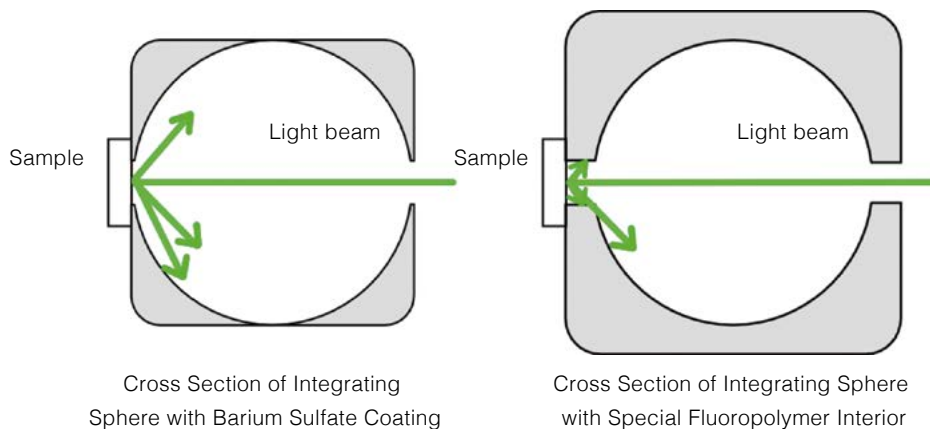


Fig. 2 Differences in Inner Wall Status Due to Differences in Integrating Sphere Material



2. White Reference Plate Materials

Typically, the material used for white reference plates is BaSO₄ powder that has been pressed into a solid, but special fluoropolymer material is used for measurements that require high sensitivity in the near infrared region. Characteristics and

procurement sources for the BaSO₄ powder and special fluoropolymer are listed in Table 1. The following describes differences between the materials and how to use them.

Table 1 Comparison of White Reference Plates

	BaSO ₄ Powder	Special Fluoropolymer
Price	◎ : Low price (a few thousand yen per bottle)	○ : About 100,000 yen per white reference plate
Reflectance Characteristics	○ : Lower reflectance in the near infrared region and includes absorption peaks from water	◎ : High reflectance characteristics throughout a wide range, from UV to NIR regions
Attachment of Absolute Reflectance Data	× : Absolute reflectance data is not included with products, so measurement values cannot be converted to absolute reflectance values.	○ : Absolute reflectance data is included with products, so relative reflectance values can be converted to absolute reflectance values.* ¹
Maintenance	○ : Refill if BaSO ₄ becomes dirty	× : If the properties of the plastic change, the original reflectance values can no longer be obtained, so the reflective surfaces must be re-polished or replaced.
Representative Products	Generic BaSO ₄ powder reagent	Spectralon® from Labsphere* ²
Procurement Source (for reference)	Wako Pure Chemical Industries, Ltd.	Systems Engineering Inc.

*¹ Confirm with the manufacturer whether or not absolute reflectance data is included before purchasing.

*² Spectralon® is a registered trademark for a special fluoropolymer manufactured by Labsphere.

3. Effect of White Reference Plates on Reflectance Measurements

Reflectance measurements using an integrating sphere are relative reflectance measurements. Therefore, if the white reference plate changes, it changes the measurement values as well. To indicate such changes, reflectance measurement values are compared using tracing paper as a diffuse reflection sample and using BaSO₄ and special fluoropolymer as the white reference plate. These results are shown in Fig. 3. The results confirm that the measurement values differ and the difference in measurement values is particularly prominent in the near infrared region, where the difference in reflectance from the white reference plate is especially large.

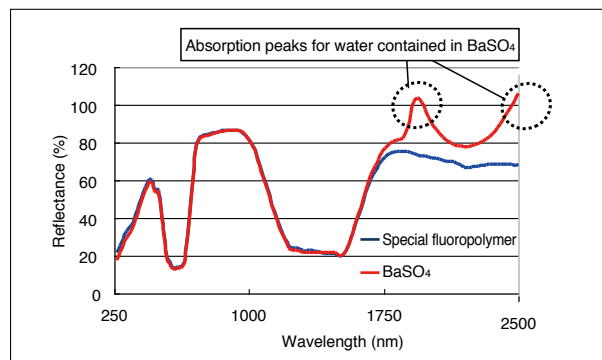


Fig. 3 Measurement of Tracing Paper Reflectance Using Different White Reference Plates

Relative reflectance is expressed by the following formula, which gives values that are affected by the reflectance of the white reference plate.

$$\text{Relative Reflectance (\%)} = \frac{\text{Amount of Light Reflected from the Sample}}{\text{Amount of Light Reflected from the White Reference Plate}} \times 100$$

Fig. 4 shows results for measuring relative reflectance of two BaSO₄ powder products used as white reference plates using a special fluoropolymer as the white reference plate. This indicates that differences in reflectance values can even occur for the same BaSO₄ powder, due to how the powder was packed. Similarly, reflectance values can change for an identical white reference plate if the reflection surface becomes contaminated or deteriorates over time.

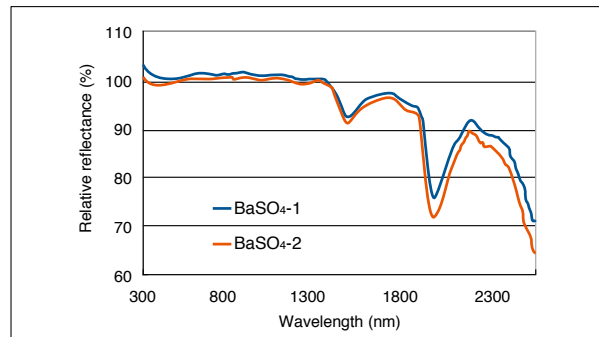


Fig. 4 Measurement of Reflectance Using Two BaSO₄ White Reference Plates

4. Effect of White Reference Plates on Transmittance Measurements

For clear samples that do not diffuse transmitted light, transmittance measurements determine the absolute transmittance. However, if measuring samples with some cloudiness that diffuses transmitted light, deviation from the absolute transmittance can be quite significant if the materials used for the inner walls of the integrating sphere and white reference plate differ. Therefore, it is necessary to use material in the integrating sphere and white reference plate

that is as similar as possible. Fig. 5 shows total transmittance spectra (sum of diffuse and linear transmittance) for tracing paper as the diffuse transmittance sample measured using BaSO₄ and a special fluoropolymer as the white reference plate material on the reflection surfaces inside the integrating sphere. It shows how differences in the white reference plate result in differences in spectra from a diffuse transmittance sample.

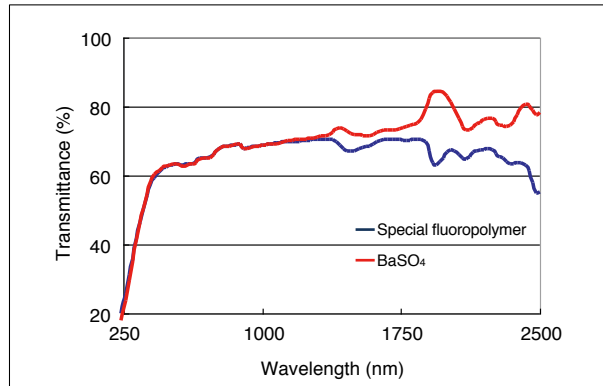


Fig. 5 Transmittance of Diffuse Sample with Different White Reference Plates

The causes of these differences in transmittance is detailed in Fig. 6. During baseline correction, the light beam travels straight so that the entire beam hits the white reference plate surface. In contrast, the light beam transmitted through the diffuse transmittance sample is diffused and hits a wide area

inside the integrating sphere. Consequently, differences in reflectance levels of the white reference plate and the integrating sphere wall are included in measurement values and prevent obtaining absolute transmittance values.

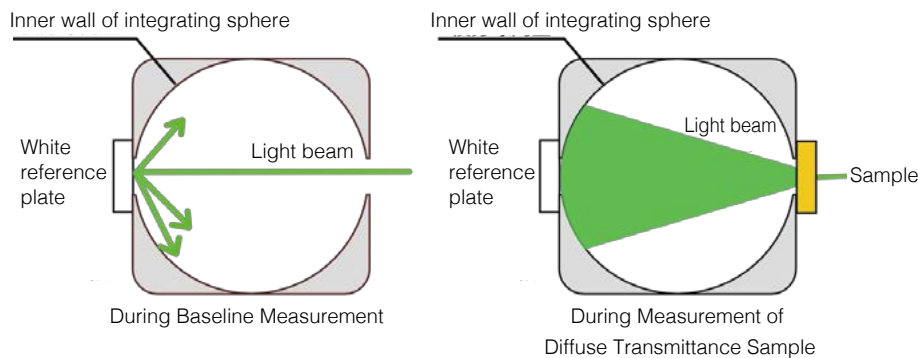


Fig. 6 Status of Light During Measurement of Diffuse Transmittance Sample

Typically, integrating spheres include a port for measuring reflected light on the opposite side of the sphere as the port for incident light, so that they can measure both transmittance and reflectance. However, to prevent differences when

measuring diffuse transmittance samples, integrating sphere models are also available without the port for reflection (hole where the white reference plate is installed), as shown in Fig. 7.

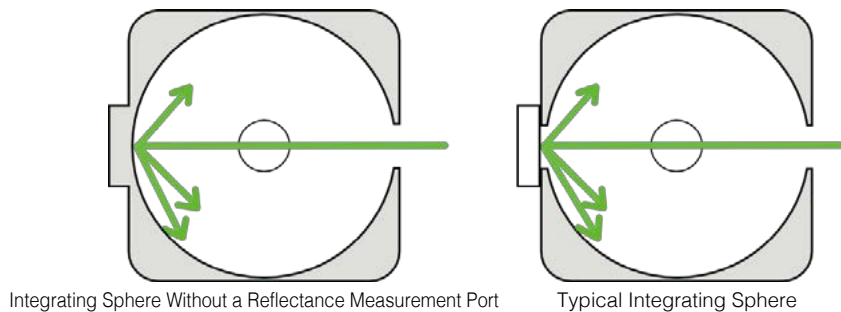


Fig. 7 An Integrating Sphere Without a Reflectance Measurement Port and a Typical Integrating Sphere

Furthermore, reflectance differs slightly even between models using packed BaSO₄ powder and models painted with BaSO₄. Fig. 8 shows an example of the difference in reflectance for

these two types of reference plates. Therefore, to measure transmittance with higher precision, we recommend using an integrating sphere without the reflectance measurement port.

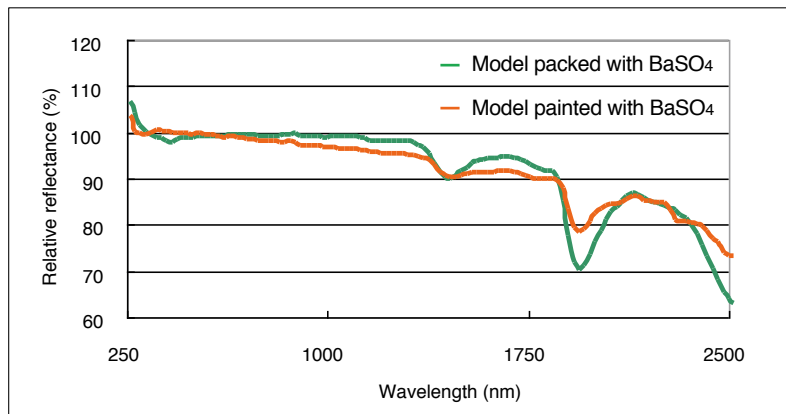


Fig. 8 Differences in Reflectance for Models Packed with BaSO₄ Powder and Painted with BaSO₄

5. Summary

This issue discusses characteristics of reflectance and transmittance measured using an integrating sphere and factors that can cause a margin of error in those measurements.

An important point to consider when measuring reflectance using an integrating sphere is that sample reflectance values are relative values compared to the reflectance of a white reference plate. Therefore, they can vary depending on

variations in the material and status of the white reference plate.

If unexpected reflectance values are obtained from a sample that is the same as usually measured, then double-check that the white reference plate is not dirty or has somehow changed. Also, if measuring the diffuse transmittance of a sample with high diffusion levels, using an integrating sphere model without a reflectance measurement port is recommended.



Sometimes when using a 10 mm cell to measure the transmittance in the near infrared region, the peaks cannot be confirmed due to saturation. What should I do?



Complicated combinations of overtone peaks can appear in the near infrared region, such as from second and third overtones of the fundamental frequencies of the -OH or other functional groups. The intensity of absorption from second overtones and other combined tones at wavelengths longer than about 1300 nm is relatively high. Therefore, using a 10 mm cell can prevent confirming the absorption peaks of target substances due to the higher absorption levels.

In this example, the transmittance spectrum of water was measured using quartz cells with optical path lengths of 1 mm and 10 mm. The baseline was corrected with air for both cells. Table 1 shows other analytical conditions.

Fig. 1 is a transmittance spectrum of water measured using a quartz cell with an optical path length of 10 mm, which is commonly used for measurements with UV-VIS spectrophotometers. The absorption of water is stronger at wavelengths longer than about 1300 nm, with transmittance falling to about 0 % without any identifiable absorption peaks.

In contrast, Fig. 2 is a transmittance spectrum of water measured using a quartz cell with an optical path length of 1 mm. Using a shorter optical path length inhibits the absorption of water to allow confirming other absorption peaks.

Therefore, if peaks are saturated in transmittance measurements in the near infrared region, it is important to consider changing the cell's optical path length.

Table 1 Analytical Conditions

Instrumentation Used	Shimadzu UV-3600 UV-VIS-NIR spectrophotometer
Measurement Wavelength Range	900 to 2600 nm
Scan Speed	Medium
Sampling Pitch	1.0 nm
Measurement Value	Transmittance
Slit Width	5 nm

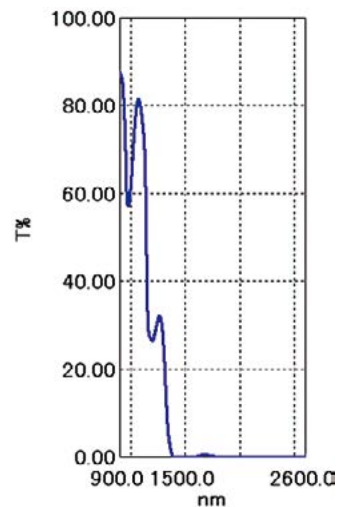


Fig. 1 Absorption Spectrum of Water (using a 10 mm cell)

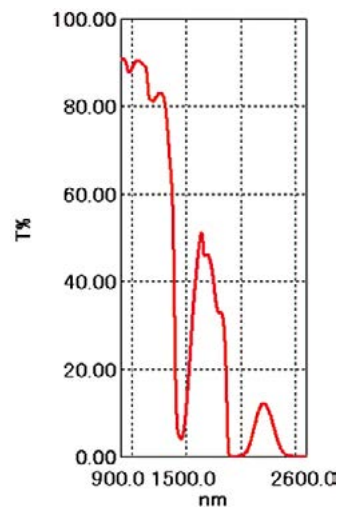


Fig. 2 Absorption Spectrum of Water (using a 1 mm cell)

