

UV Talk Letter

Vol.6 Winter 2011





UV Talk Letter

Light Sources for Spectrophotometers

In this issue, we will describe the light source, an important part of the spectrophotometer that was explained in "The Structure of a Spectrophotometer" in UV Talk Letter Vol.2.

1. Light Source Requirements

The requirements for a spectrophotometer light source include:

- a) bright across a wide wavelength range;
- b) stable over time;
- c) long service life; and
- d) low cost.
- "a) Bright across a wide wavelength range" demands both a high degree of brightness and uniform brightness across the measurement wavelength range (uniform brightness distribution).
- "A high degree of brightness" is a necessary requirement to obtain photometric values with a high S/N ratio. However, as increasing the brightness of the light source generally results in a reduction in condition "c) long service life," the balance between the two must be considered.

As the sensitivity characteristics of the detector are also relevant during actual measurements, a "uniform brightness distribution" is an important condition for acquiring photometric values with a uniform S/N ratio within the measurement wavelength range.

2. Types of Light Source

Many light sources meet some of the requirements above but no light source is able to meet them all. Many spectrophotometers switch between a halogen lamp for the visible range and a deuterium lamp for the ultraviolet range according to the wavelength setting.

This is because of the difficulty in achieving both "a high degree of brightness" and a "uniform brightness distribution" across a wide wavelength range using a single light source. Switching between light sources with different emission wavelength ranges also offers the advantages of reducing the excess incident light into the monochromator and reducing the amount of stray light (Reference 1).

Other instruments use a xenon lamp or xenon flash lamp suitable for the analysis target and aim of the analysis. A low-pressure mercury lamp that produces multiple emission spectra is effective for spectrophotometer wavelength calibration.

Reference 1: What is stray light?

Stray light is defined as the ratio of the total light intensity at wavelengths other than the set wavelength with respect to the light intensity emitted from the wavelength selection device (from JIS K 0115).

For example, assume that 1 % transmittance (2 Abs) was measured at a certain wavelength when monochromatic light containing 0.1 % stray light was incident on the sample. Due to the effect of the stray light, the transmittance is actually 1.1 % (1.959 Abs), such that an error of approximately 2 % occurred.

(1) Halogen Lamps

Similar to a normal incandescent lamp, a halogen lamp filament heats up and emits light when a current flows through it. The tungsten used as the filament material evaporates at high temperatures. Consequently, the bulb containing the filament of a normal incandescent lamp is filled with an inert gas to prevent evaporation of the tungsten.

A halogen lamp contains a halide as well as the inert gas to create the halogen cycle (Reference 2) that returns evaporated tungsten to the filament, resulting in a long lamp life. It also restricts blackening of the tube wall, due to adhering evaporated tungsten, to create a light source that remains bright over long periods.

Fig. 1 shows the light intensity distribution at 3000 K color temperature. The usable wavelength range is 350 nm to 3500 nm, but this is affected by the color temperature.

Halogen lamps are stable over time, offer a long service life (approx. 2000 hours) and are relatively cheap. As such, they many of the conditions required for a spectrophotometer light source.

(2) Deuterium Lamps

A deuterium lamp is a discharge light source with several hundred Pa deuterium sealed in a bulb. As it uses a hot cathode to achieve stable and reliable arc discharge, approximately 10 sec for preheating is required before starting the discharge.

A deuterium lamp requires a large and complex power supply, making it more expensive than a halogen lamp. However, it is one of the few continuous spectrum light sources that is stable in the ultraviolet range.

The deuterium lamp has a short emission wavelength of 400 nm, or less. The window material limits its use at the short wavelength end.

Fig. 2 shows examples using synthetic quartz and UV glass.

The use at the long-wavelength end is limited to about 400 nm. However, the low degree of attenuation toward the long-wavelength end permits use of light above 400 nm. Multiple emission spectra also exist in the range at 400 nm and above. Of these, the spectra at 486.0 nm and 656.1 nm are particularly strong (see Fig. 5) and can be used for wavelength calibration of the spectrophotometer.

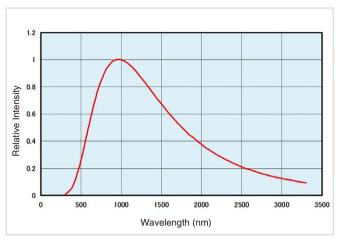


Fig. 1 Emission Intensity Distribution of a Halogen Lamp (3000 K)

Reference 2: What is the halogen cycle?

Tungsten that evaporates at high temperatures binds with halogen near the cool tube wall to form tungsten halide. The suspended tungsten halide moves inside the tube due to convection and separates into halogen and tungsten near the hot filament. The separated tungsten adheres to the filament and the halogen bonds again with evaporated tungsten. This repeated reaction is known as the tungsten cycle.

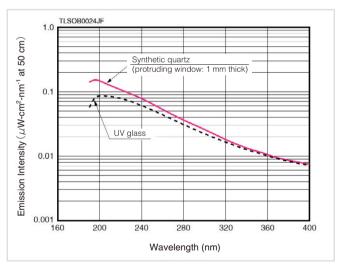


Fig. 2 Emission Intensity Distribution of a Deuterium Lamp 1)

(3) Xenon Lamp (Xenon Arc Lamp)

A xenon lamp is a discharge light source with xenon gas sealed in a bulb. Xenon lamps are categorized as direct-current or alternating-current types, according to the lighting method. If the electrodes become too hot, the tungsten electrode material can evaporate and adhere to the tube wall, resulting in a loss in brightness. As the anode becomes particularly hot, the anode of a direct-current type xenon lamp is made larger than the cathode to increase its thermal capacity. As the electrodes of an alternating-current type electrode alternately become the cathode and anode, both electrodes are the same size. Therefore, the tungsten evaporates more easily than with the direct-current type. However, the alternating-current type permits the use of a compact, low-cost lighting device, as no current rectification is required.

The xenon lamp exhibits a similar spectral distribution to sunlight and produces a continuous spectrum from the ultraviolet to the near-infrared, as shown in Fig. 3. Overall, the xenon lamp is inferior to the halogen lamp and deuterium lamp in terms of cost and output fluctuations. Halogen lamps are often used in general spectrophotometers but xenon lamps are used in cases where a high light intensity is required (such as spectrofluorophotometers), due to their high brightness.

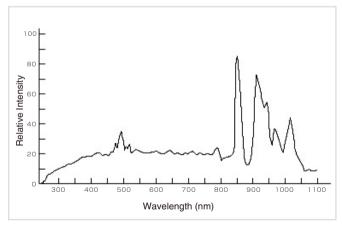


Fig. 3 Emission Intensity Distribution of a Xenon Lamp 2)

(4) Xenon Flash Lamp

This is a compact xenon lamp that generates little heat due to pulsed ignition. Straight and U-tube types are available, depending on the application. The electrodes are sealed in a quartz glass tube (or high-silica glass tube) that is filled with xenon gas.

However, because of its poor reproducibility, a result of larger output fluctuations as compared to an arc lamp, integration of the output data is required to obtain stable data. Therefore, it is used in combination with an array detector in automated instruments (such as colorimeters) to rapidly obtain continuous spectra.

(5) Low-Pressure Mercury Lamp

The low-pressure mercury lamp is a discharge lamp designed to have a low mercury vapor pressure (100 Pa max.) when lit to efficiently emit the mercury resonance lines (254 nm or 185 nm). Fig. 4 shows the spectral distribution of a low-pressure mercury lamp.

Low-pressure mercury lamps are available in versions that use the emitted ultraviolet lights directly, or as so-called fluorescent lamps that use a fluorescent material to convert the wavelength to a different wavelength.

A spectrophotometer uses the mercury emission lines to calibrate the displayed wavelength values. The 254 nm, 365 nm, 436 nm, or 546 nm emission lines can be used for the calibration but care is required with the slit width (spectral bandwidth) used during measurements. For example, as the 365 nm emission line is a triple line (three emission lines in close proximity), the spectral bandwidth must be 0.5 nm max. to accurately measure the respective emission lines.

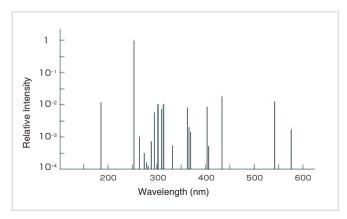


Fig. 4 Spectral Distribution of a Low-Pressure Mercury Lamp 3)

3. Switching Light Sources

As stated above, halogen lamps and deuterium lamps are used in many spectrophotometers.

Fig. 5 shows their respective energy distributions measured by a UV-1800 UV-VIS Spectrophotometer. The light sources are switched near 300 nm to 350 nm, where the emission intensities of the halogen lamp and deuterium lamp are approximately equal.

The light sources can be switched by moving the lamps themselves or by rotating a reflector.

Fig. 6 shows the switching method by rotating a reflector. By changing the tilt of the reflector positioned between the halogen lamp and the deuterium lamps, the light beam that enters the monochromator can be switched.

In the UV-1800, the optimal tilt with respect to each light source is automatically adjusted during the initial setup operation after the power is turned on, which eliminates the need for positional adjustment by replacing lamps.

4. Conclusions

This article focuses on the light source, one element of the spectrophotometer. It described typical lamp characteristics and switching mechanisms. The next issue will describe the use of UV-VIS spectrophotometers in the field of life sciences.

- 1) Hamamatsu Photonics K.K. General Lamp Catalog
- 2) Ushio Inc. General Discharge Lamp Catalog
- 3) Ushio Inc. General Discharge Lamp Catalog

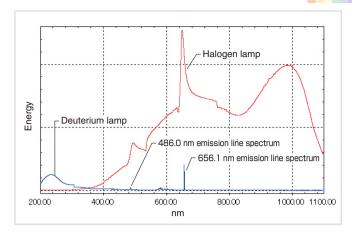


Fig. 5 Light Source Energy Distribution Measured by the UV-1800

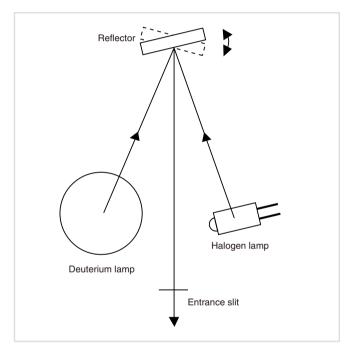


Fig. 6 Method for Switching Light Sources

Measuring Solar Transmittance and Solar Reflectance, Part 2

The previous issue, UV Talk Letter Vol. 5, introduced measurement methods for flat glass, in compliance with JIS R3106 "Testing method on transmittance, reflectance and emittance of flat glasses and evaluation of solar heat gain coefficient." This issue introduces measurement methods for films for glazing used in construction according to JIS A5759 "Adhesive films for glazings," and methods for paint film according to JIS K5602 "Determination of reflectance of solar radiation by paint film."

1. Evaluation of the Optical Performance of Films for Glazing Used in Construction, Conforming to JIS A5759

JIS A5759 prescribes 87 % max. visible light transmittance, 5.9 W/m²K max. heat transfer coefficient, and 3 % max. ultraviolet transmittance for films applied to glazing used in building windows or entrances. The shading coefficient must match the performance, as shown in Table 1. Table 2 provides a description and equation for each item.

Table 1 Shading Coefficients of Window Films

Shading Coefficient	Code
x < 0.40	A
0.40 d x < 0.60	В
0.60 d x < 0.85	С

JIS A5759 prescribes four test items for optical performance: visible light transmittance, shading coefficient, heat transfer coefficient, and ultraviolet transmittance. However, determining the shading coefficient requires the corrected emittance values for the indoor surface and outdoor surface converted from the normal reflectance, in addition to the solar transmittance, solar reflectance, and normal emittance. In addition, the corrected emittance values for the indoor and outdoor surfaces converted from the normal emittance are required to calculate the heat transfer coefficient.

Table 2 JIS A5759 Optical Performance Test Items for Films for Glazing Used in Construction

Characteristic Velice	Analytical Instrument Note 1)	Description	Equation	
Characteristic Value	Analytical Instrument ****	Description	Equation	
Visible light transmittance τ_{V}	UV-VIS-NIR	Obtained by measuring the spectral transmittance $\tau(\lambda)$ in the 380 to 780 nm wavelength range, and using Equation (1) that multiplies by the weighting coefficients (D λ , V(λ), $\Delta\lambda$) and takes the weighted average.	$\tau_{V} = \begin{array}{c} \sum_{\lambda} \tau(\lambda) \cdot D\lambda \cdot V(\lambda) \cdot \Delta\lambda \\ \\ \sum_{\lambda} D\lambda \cdot V(\lambda) \cdot \Delta\lambda \end{array} \tag{1} \qquad \begin{array}{c} D\lambda : Spectral distribution at CIE illuminant D65 \\ \\ V(\lambda) : CIE \ standard photopic luminous efficiency \\ \\ \Delta\lambda : Wavelength interval \end{array}$	
Shading coefficient S	UV-VIS-NIR, FTIR	Indicator of solar shading performance. This coefficient expresses the ratio of the transmitted solar radiation incident on 3 mm-thick flat glass with film attached, including the amount initially absorbed and then re-emitted at the face opposite the entrance face, taking the amount transmitted by the glass alone as 1.	$S = \begin{array}{c} \tau_{e} + \text{Ni}(100 - \tau_{e} - \rho_{e}) \\ \hline \tau_{e0} + 0.35(100 - \tau_{e0} - \rho_{e0}) \end{array} \tag{2} \\ \text{Ni} = \begin{array}{c} \tau_{e} : \text{Solar transmittance} \\ \rho_{e} : \text{Solar reflectance} \\ \rho_{e} : \text{Corrected emittance} \\ \text{Outdoor surface (glass surface)} \\ \text{Indoor surface (film surface)} \\ \text{Indoor surface (film surface)} \\ \text{Teo: Solar transmittance} \\ \text{Outdoor surface (film surface)} \\ \text{Teo: Solar transmittance} \\ Teo: Solar tran$	
Solar transmittance Te	UV-VIS-NIR	Obtained by measuring the spectral transmittance $\tau(\lambda)$ in the 300 to 2500 nm wavelength range, and using Equation (4) that multiplies by the weighting coefficients (E λ , $\Delta\lambda$) and takes the weighted average.	$\tau_{e} = \begin{array}{c} \displaystyle \sum_{\lambda} \tau(\lambda) \cdot E\lambda \cdot \Delta\lambda \\ \displaystyle \sum_{\lambda} E\lambda \cdot \Delta\lambda \end{array} \tag{4}$ $\underbrace{E\lambda: \text{Solar relative spectral distribution}}_{\Delta\lambda: \text{ Wavelength interval}}$	
Solar reflectance Pe	UV-VIS-NIR	Obtained by measuring the spectral reflectance $p(\lambda)$ in the 300 to 2500 nm wavelength range, and using Equation (5) that multiplies by the weighting coefficients (E λ , $\Delta\lambda$) and takes the weighted average.	$\rho_{\text{e}} = \begin{array}{c} \displaystyle \sum_{\lambda} \rho \left(\lambda \right) \cdot E \lambda \cdot \Delta \lambda \\ \displaystyle \sum_{\lambda} E \lambda \cdot \Delta \lambda \end{array} \tag{5}$ $\begin{array}{c} E \lambda : \text{Solar relative spectral distribution} \\ \Delta \lambda : \text{Wavelength interval} \end{array}$	
Normal emittance £n	FTIR	Calculated from the equation shown using spectral reflectance $p_n(\lambda)$ obtained by specular reflection measurements using an infrared spectrophotometer.	$\epsilon n = \ 1 - \rho n$ $\rho n = \frac{1}{30} \sum_{i=1}^{30} \ \rho n (\lambda_i)$ Refer to JIS R3106 for details.	
Corrected emittance ɛ̂e;Coutdoor surface (glass surface) ɛ̂i;Outdoor surface (film surface)	FTIR	Normal emittance value corrected using the coefficients prescribed in JIS A5759.	Refer to JIS A5759 for details.	
Heat transfer coefficient U [W/m²K]	FTIR	Expresses the thermal insulation performance. The value expresses the amount of heat that flows in unit time through 1 $\rm m^2$ of 3 mm-thick flat glass with film attached that has a 1 °c difference in air temperature on each side.	$\begin{split} \frac{1}{U} &= \frac{1}{4.9\epsilon_{e} + 16.3} + 0.003 + \frac{1}{5.4\epsilon_{i} + 4.1} \\ \epsilon_{e:} & \text{Corrected emittance} & \text{Outdoor surface (glass surface)} \\ \epsilon_{i:} & \text{Corrected emittance} & \text{Indoor surface (film surface)} \end{split}$	
Ultraviolet transmittance TUV	UV-VIS-NIR	Obtained by measuring the spectral transmittance $f(\lambda)$ in the 300 to 380 nm wavelength range, and using Equation (6) that multiplies by the weighting coefficients (U λ , $\Delta\lambda$)) and takes the weighted average.	$\tau_{\text{UV}} = \begin{array}{c} \displaystyle \sum_{\lambda} \tau(\lambda) \cdot \text{U}\lambda \cdot \Delta\lambda \\ \displaystyle \sum_{\lambda} \text{U}\lambda \cdot \Delta\lambda \end{array} \text{(6)} \qquad \begin{array}{c} \text{U}\lambda\text{: UV relative spectral distribution} \\ \Delta\lambda\text{: Wavelength interval} \end{array}$	

2. Examples of Film Measurements

The spectral transmittance is obtained by measuring the transmittance of 3 mm-thick glass with film attached to one face. For these tests, we determined the visible light transmittance, UV transmittance, solar transmittance, solar reflectance, and shading coefficients for four types of film adhered to glass. The measurements were performed on light incident from the glass surface using a UV-VIS-NIR spectrophotometer with an integrating sphere accessory under the conditions shown in Table 3. Fig. 1 shows the transmission spectra in the ultraviolet, visible, and near-infrared regions. Fig. 2 shows the reflection spectra. Data measured by a Fourier transform infrared spectrophotometer was used to calculate the shading coefficients, but details of the measurement method and conditions are omitted here.

Solar transmittance measurement software was used to calculate the performance test items. This software supports the calculation of visible light transmittance, UV transmittance, solar transmittance, and solar reflectance for flat glass according to JIS R3106. For these tests, the calculations prescribed in JIS A5759 were performed in the user-defined mode by entering the weighting coefficients. Fig. 3 shows a sample screen to set the calculation items for the solar transmittance measurement software. Fig. 4 shows sample calculated results for the visible light transmittance, UV transmittance, and solar transmittance.

Table 3 Measurement Conditions for Glass with Film Attached

Measuring instrument	UV-3600 UV-VIS-NIR spectrophotometer, ISR-3100 integrating sphere attachment
Measurement wavelength range	300nm~2500nm
Scan speed	Medium
Sampling pitch	2.0nm
Slit width	(20)nm
Light source switching wavelength	310nm
Grating switching wavelength	720nm
Detector switching wavelength	830nm

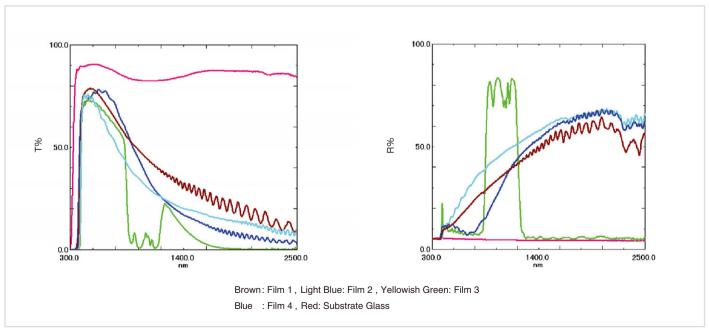


Fig. 1 Transmission Spectra in Ultraviolet, Visible, and Near-Infrared Regions

Fig. 2 Reflection Spectra in Ultraviolet, Visible, and Near-Infrared Regions

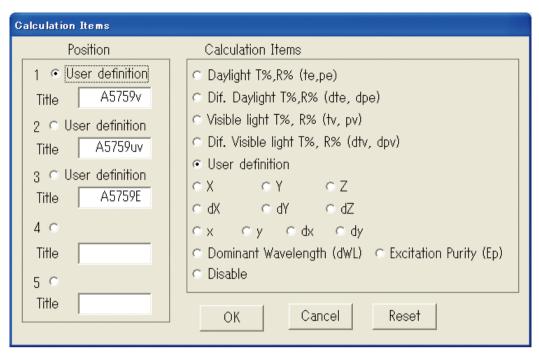


Fig. 3 Setting Screen for Solar Transmittance Measurement Software Calculation Items

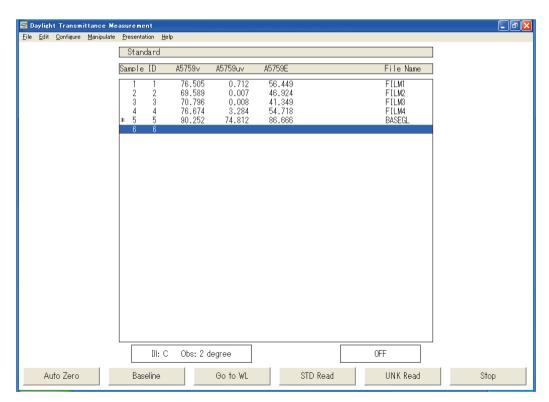


Fig. 4 Sample Calculated Results for Films

Table 4 shows the calculated results for each sample. Film 1 exhibits a high value for solar transmittance. Films 2 and 3 allow almost no transmittance of ultraviolet. Film 4 offers the best transmittance of visible light and ultraviolet and exhibits the highest shading coefficient value.

Film	Visible Light Transmittance Tv [%]	UV Transmittance Tuv [%]	Solar Transmittance Te [%]	Solar Reflectance pe [%]	Shading Coefficient S
1	76.51	0.71	56.45	25.65	0.68
2	69.59	0.01	46.92	33.03	0.60
3	70.80	0.01	41.35	21.58	0.60
4	76.67	3.28	54.72	21.10	0.70
Substrate glass	90.25	74.81	86.67	4.87	

Table 4 Calculated Results for Films

3. Determination of Solar Reflectance of Paint Film According to JIS K5602

Solar reflectance measurements in accordance with JIS K5602 use the integrating sphere accessory, 300 to 2500 nm wavelength measurement range, and an angle of incidence of light onto the sample not exceeding 15 degrees. The specular reflectance of the sample is determined at each wavelength, based on 100 % spectral reflectance for a standard white sheet calibrated by a public organization. The solar reflectance is obtained using Equation (7) to multiply by the weighting coefficient for the spectral irradiance distribution of standard sunlight and take the weighted average. The solar reflectance is determined individually in three wavelength ranges: near-ultraviolet/visible (300 to 780 nm), near-infrared (780 to 2500 nm), and full wavelength (300 to 2500 nm).

$$\rho_{e} = \frac{\sum_{\lambda} [(E\lambda \times \Delta\lambda) \times \rho(\lambda)]}{\sum_{\lambda} (E\lambda \times \Delta\lambda)}$$
 (7)

ρ_e:Solar reflectance

 $\rho(\lambda)$: Spectral reflectance (%)

Eλ×Δλ: Weighting coefficient for standard sunlight (W/m²)

λ:Wavelength (nm)

4. Examples of Paint Film Measurements

Spectral reflectance measurements were performed on three types of paint applied to contrast ratio test paper (Paint Films 1, 2, 3). Measurements were made using a UV-3600 UV-VIS-NIR spectrophotometer with an ISR-3100 integrating sphere attachment under the conditions listed in Table 5. The sample was positioned against the integrating sphere, as shown in Fig. 5. The measured results are shown in Fig. 6. Paint Film 1 has lower reflectance than the other two paint films across the full wavelength range. Paint Film 2 offers equivalent reflectance to Paint Film 3 in the near-infrared range above 1200 nm but has lower reflectance than Paint Film 3 in the near-infrared to visible range below 1200 nm. Paint Film 3 offers the highest reflectance across the full wavelength range.

The solar reflectance of each paint film was then calculated using the measured spectral reflectance values and Equation (7). Table 6 shows the solar reflectance in each wavelength range. An Excel macro developed to calculate the solar reflectance of paint films was used to perform these calculations in accordance with JIS K5602. This macro reads the measured spectral reflectance data and automatically calculates the solar reflectance in each wavelength range using Excel^{® Note 2)}. It also displays the spectral reflectance spectra.

Note 2) Excel is a registered trademark of Microsoft Corporation.



Fig. 5 Sample Positioned Against Integrating Sphere

Measurement Conditions for Paint Films Table 5

Measuring instrument	UV-3600 UV-VIS-NIR spectrophotometer, ISR-3100 integrating sphere attachment
Angle of incidence	8°
Measurement wavelength range	300nm~2500nm
Scan speed	Medium
Sampling pitch	0.5nm
Slit width	(20)nm
Light source switching wavelength	290nm
Grating switching wavelength	720nm
Detector switching wavelength	870nm

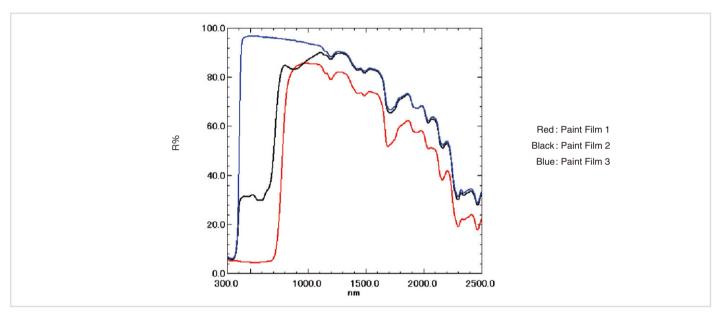


Fig. 6 Spectral Reflectance Measurement Results for Paint Films

Table 6 Solar Reflectance Calculation Results for Each Paint Film

Sample	Near-Ultraviolet/Visible Range 300 to 780nm	Near-Infrared Range 780 to 2500nm	Full Wavelength Range 300 to 2500nm
Paint Film 1	7.72%	74.67%	36.78%
Paint Film 2	37.51%	81.80%	56.48%
Paint Film 3	89.07%	87.13%	88.12%

5. Conclusions

JIS standards relating to solar measurements include JIS A5759, which covers films for glazing used in construction, JIS K5602, which covers paint films, and JIS R3106, which covers flat glass. This article describes the measurements of films for glazing used in construction and of paint films. Refer to the previous issue, UV Talk Letter Vol. 5, for measurement methods for flat glass.

Further information is given in the following issues of Shimadzu Application News.

- No. A404 "Glass Plate Analysis in Accordance with JIS R3106"
- No. A412 "Analysis of Adhesive Films for Glazings Conducted in Accordance with JIS A5759"
- No. A424 "Determination of Solar Reflectance of Paint Film in Accordance with JIS K5602"

Acknowledgement: Samples for paint film measurements were kindly supplied by the Marketing Group, Architectural Coating Department, General Coating Division, Dai Nippon Toryo Co., Ltd.



How is the minimum limit of quantitation determined?



It is important to know the minimum limit of quantitation when measuring the concentration of a solution. The minimum limit of quantitation is the lowest limit of concentration that can be measured. It is determined from the calibration curve equation as the concentration corresponding to the absorbance equivalent to ten times the discrepancy. The discrepancy is determined as the standard deviation of repeated measured values on a blank solution (or a low-concentration sample solution).

An example of determining the minimum limit of quantitation in a caffeine solution is described below.

Fig. 1 shows the absorption spectra of aqueous solutions of caffeine corresponding to 2 mg/L, 4 mg/L, 10 mg/L, 20 mg/L, and 40 mg/L caffeine concentrations. Fig. 2 shows the calibration curve created from the absorbance at a peak wavelength of 273 nm. The calibration curve equation was determined as:

Absorbance (Abs) = $0.05191 \times \text{concentration (mg/L)} \dots (1)$

Table 1 shows ten repeated measured values for a blank solution (pure water) at 273 nm and the standard deviation σ . 10 σ was determined to be 0.002624 Abs. The concentration corresponding to the 10 σ absorbance, that is, the minimum limit of quantitation, can be determined from Equation (1), as follows:

Minimum limit of quantitation = 0.002624/0.05191 = 0.051 mg/L

The minimum limit of quantitation for caffeine was determined in this example. However, note that the minimum limit of quantitation differs according to the substance, as the amount of absorbed light (absorption coefficient) differs from substance to substance.

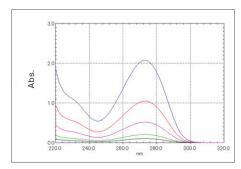


Fig. 1 Absorption Spectra of Aqueous Solutions of Caffeine (Black: 2 mg/L, Green: 4 mg/L, Purple: 10 mg/L, Red: 20 mg/L, Blue: 40 mg/L)

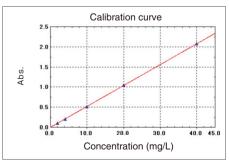


Fig. 2 Calibration Curve for Aqueous Solutions of Caffeine

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00037
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00018
00024
00021
00029
02624

Table 1 Ten Repeated Measurements on a Blank Solution and Standard Deviation σ

References

¹⁾ Chapter 7, Genba de Yakudatsu Kagakubunseki no Kiso (Fundamentals of Chemical Analysis to Assist Onsite) (2006), edited by The Japan Society for Analytical Chemistry, Supervising Editor Shoji Hirai (published by Ohmsha, Ltd.)

NEW PRODUCTS





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Shimadzu Spectrophotometer for Life Sciences

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Furthermore, dedicated software simplifies operation. Just click buttons on the toolbar to conduct basic operations, such as measurement, report printing, and exporting data.

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