C101-E177

SHIMADZU
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UV TALK LETTER

Vol. 22

Photomultiplier Tubes Used in UV-VIS Spectrophotometers

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The wavelength range and sensitivity performance required for UV-VIS spectrophotometers can differ depending on the measurement sample. Therefore, Shimadzu offers a broad product line to ensure the best possible instrument can be offered for given customer objectives. To ensure samples are measured with high sensitivity, mid-level to high-end models are equipped with a photomultiplier tube (PMT) as a detector.

This article focuses on photomultiplier tubes and describes the differences in characteristics and performance of each type.

1. Photomultiplier Tube (PMT) Description

The photomultiplier tube (PMT) is a detector that utilizes an external photoelectric effect to emit photoelectrons when the photoelectric surface is exposed to external light. The photoelectrons (primary electrons) emitted from the photoelectric surface enter a multi-staged dynode (electron multiplier electrode) that repeatedly generates secondary electrons to amplify the original photoelectrons by 10 to 10^8 times (Fig. 1). The ability to significantly amplify light in that way enables high-sensitivity detection of even weak attenuated light after it has passed through a substance with high absorbance, for example.

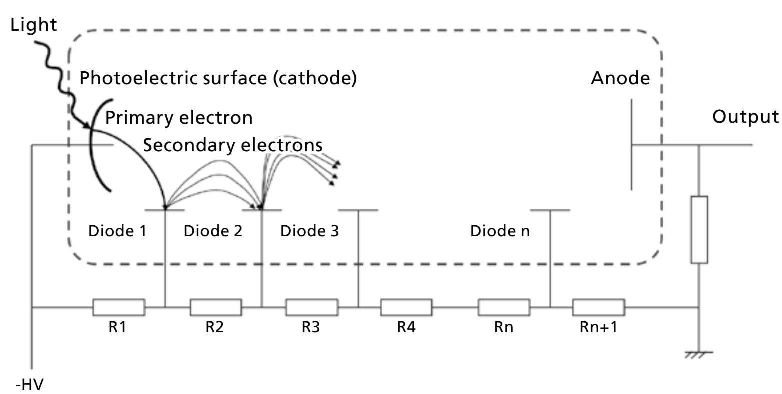


Fig. 1 Operating Principle of PMTs

As of 2021, the following Shimadzu UV-VIS spectrophotometers are equipped with a PMT (Fig. 2).

UV-2600i/2700i

UV-3600i Plus

SolidSpec-3700i

Fig. 2 Shimadzu UV-VIS Spectrophotometers Equipped with a PMT

2. Types of PMTs

There are two main types of PMTs: side-on and head-on (also referred to as end-on).

The Shimadzu UV-VIS spectrophotometers shown in Fig. 2 are equipped standard with side-on PMTs (Fig. 3). In side-on models, the light-receiving surface is located on the side of the detector, resulting in higher amplification and lower cost. Shimadzu UV-VIS spectrophotometers are equipped standard with a model R928 photomultiplier tube (from Hamamatsu Photonics), but customers can also special order a more sensitive option, such as the R5108 or R13456 (both are long-wavelength models from Hamamatsu Photonics).

In head-on PMTs, the light-receiving surface is located at the head of the detector (Fig. 4). Because head-on models have a larger light-receiving surface than side-on models, they can receive more light than side-on models, which enables measurements with less noise. That characteristic is especially beneficial when measuring smaller light quantities. Consequently, Shimadzu uses head-on PMTs for special-order end-on photomultiplier units designed especially for measuring transmittance through suspension, biological, or solid samples. As shown in Fig. 5, end-on photomultiplier units can measure samples accurately by using a diffusion plate and light guide to guide the diffused light that passes through a suspension or other sample onto the large light-receiving surface of the head-on PMTs.

Fig. 3　Side-on PMT

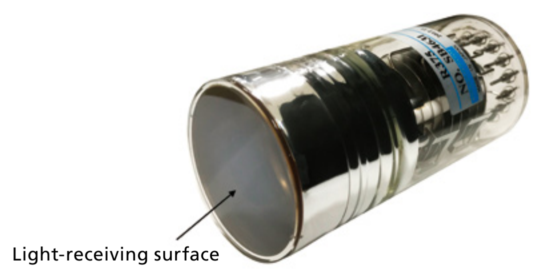


Fig. 4　Head-on PMT

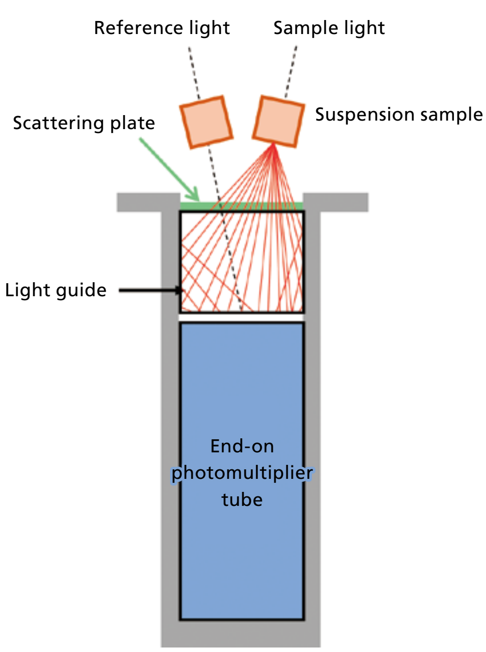


Fig. 5　End-on Photomultiplier Unit

3. Performance Differences between Types

a) Side-on PMTs

Baseline data obtained using the R928 model, included standard in Shimadzu spectrophotometers, and using the R13456 and R5108 high-sensitivity models are shown in Fig. 6. Data was measured using a UV-2700i UV-VIS spectrophotometer.

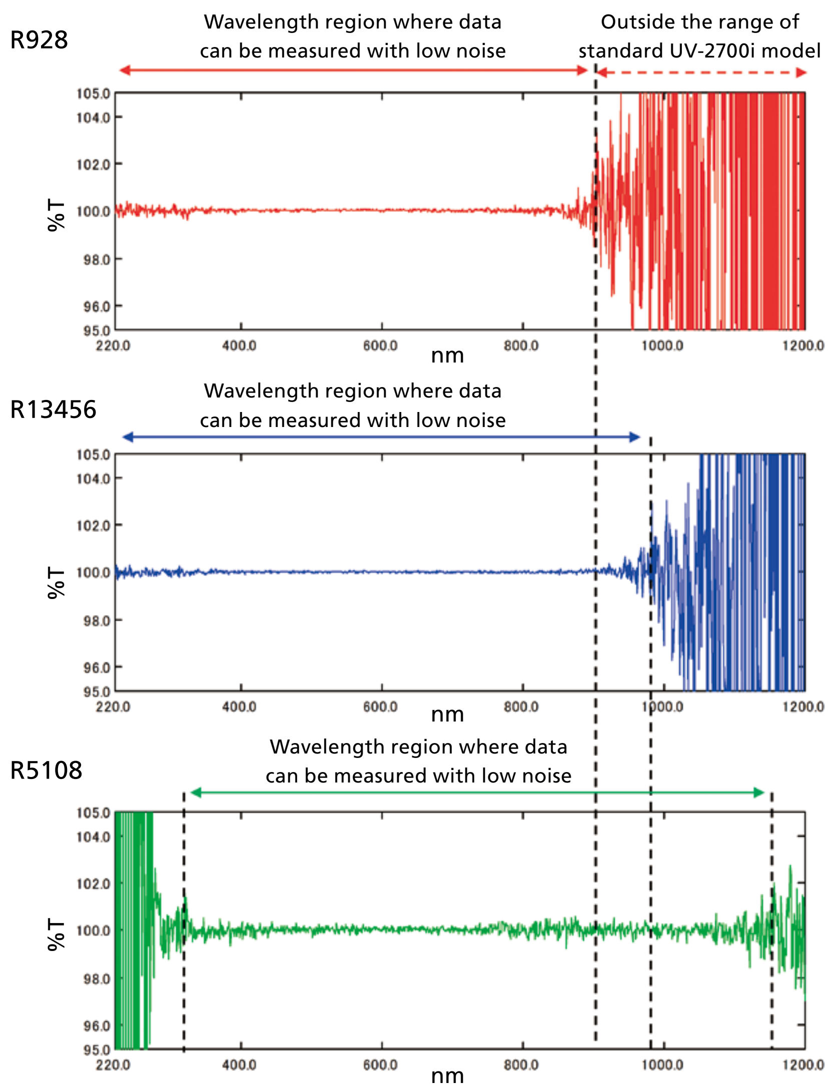


Fig. 6 Comparison of Baseline Data Using R928, R13456, and R5108 Side-on PMTs

The R928 baseline shows large noise at wavelengths longer than about 900 nm, but the R13456 baseline has minimal noise up to about 1,000 nm. If an R5108 is used as the detector, the low-noise region extends even further in the long-wavelength direction, with minimal noise up to about 1,150 nm. Therefore, the optimal detector should be selected based on the position of target peaks for the given substances being measured.

Though each side-on PMT model has wavelength regions where it is particularly well-suited, as described above, they also have regions where they are poorly suited. Table 1 shows results from measuring noise levels (RMS method) at a variety of wavelengths using different side-on PMT models. The blue values indicate the lowest noise value at the corresponding wavelength. The red values indicate the highest noise value at the corresponding wavelength.

Table 1 Comparison of Noise Level at Specific Wavelengths by Different Side-on PMT Models

Units (Abs)	300 nm	500 nm	700 nm	900 nm	1100 nm
	RMS	RMS	RMS	RMS	RMS
R928	0.00006	0.00002	0.00004	0.00079	0.02674
R13456	0.00008	0.00002	0.00002	0.00007	0.00844
R5108	0.00238	0.00009	0.00006	0.00083	0.00113

Blue values: Lowest noise value at that wavelength

Red values: Highest noise value at that wavelength

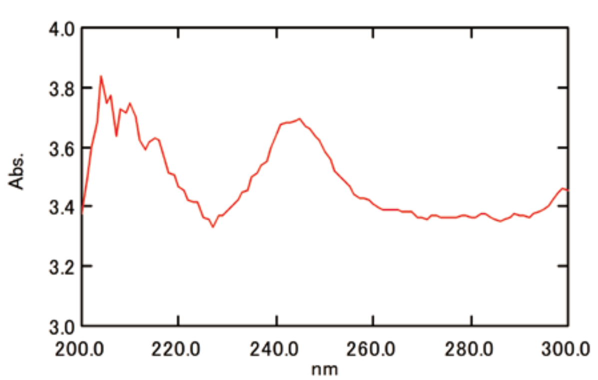
The R5108 offers the lowest noise at a long wavelength of 1,100 nm, whereas it has higher noise than the R928 and R13456 at other wavelengths. Due to such differences in wavelength-specific sensitivity characteristics of respective PMTs, the best PMT model must be selected based on the purpose for using the instrument.

b) Head-on PMTs

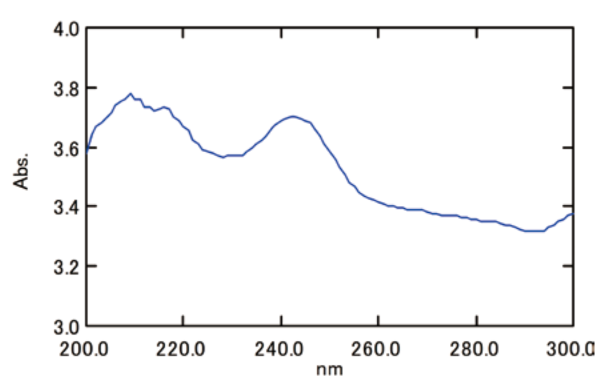
When measuring suspension samples, the light used for measuring is diffused by particles in the sample, resulting in very little light reaching the detector. Consequently, the scattered light cannot be detected by a regular UV-VIS spectrophotometer, which prevents measuring absorbance correctly. Therefore, to provide a method for measuring absorbance of such samples properly, Shimadzu offers an integrating sphere attachment, which is a side-on PMT, and an end-on photomultiplier unit (special order), which is a head-on PMT.

A comparison of absorbance measurement results from an MPC-2600A integrating sphere attachment and from an end-on photomultiplier unit is shown in Fig. 7. The data was obtained using a UV-2600i UV-VIS spectrophotometer. A commercially marketed milk product diluted by 15 times was used as the suspension sample and absorbance was measured using a 10 mm quartz cell.

Though the integrating sphere attachment is an optional product that is well-suited to measuring suspension samples, the suspension sample in this case had extremely high absorbance levels that resulted in unavoidable overlapping spectral noise (left spectrum in Fig. 7). In contrast, the end-on photomultiplier unit has a very large detection surface that can detect even faint measurement light with good sensitivity, which means it can measure samples with much less noise than when using an integrating sphere attachment (right spectrum in Fig. 7).



MPC-2600A Integrating Sphere Attachment



End-on Photomultiplier Unit

Fig. 7 Comparison of Absorbance Measurement Results from an Integrating Sphere Attachment and End-on Photomultiplier Unit

4. Summary

This article of UV Talk Letter described different types of photomultiplier tubes used as detectors in UV-VIS spectrophotometers and their performance differences. Even for samples that are difficult to measure with a standard detector, it is possible that measurement accuracy could be improved by using the optimal optional product to extend performance capabilities. Therefore, if you are experiencing frustration with day-to-day measurements, feel free to talk to a Shimadzu sales representative.

Applications

Temperature-Controlled Accessories for UV-VIS Spectrophotometers

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A wide variety of accessories are used with UV-VIS spectrophotometers. For example, accessories that can control temperature are used to measure samples for which the spectral shape or absorbance level varies depending on the temperature or for measurements at a constant temperature, such as for pharmaceutical dissolution testing.

This article describes temperature-controlled accessories used for constant-temperature measurements and temperature-controlled accessories with temperature increase/decrease control capability. Examples of analysis using an S-1700 thermoelectrically temperature-controlled single cell holder available from Shimadzu to measure liquid crystals and ink that changes color depending on its temperature are described.

1. Temperature-Controlled Accessories Used for Constant-Temperature Measurements

Temperature-controlled accessories for constant-temperature measurements are used to measure samples maintained at a fixed temperature, such as for measuring biological components or enzyme activity, or for analyzing reaction rates. There are two basic types used. One type controls the temperature by recirculating temperature-controlled water, whereas the other type uses a Peltier element to thermoelectrically heat or cool the accessory. (Electronic temperature control eliminates the need for an external thermostatic water bath or water circulation system for cooling.) Constant-temperature water circulation type accessories offered by Shimadzu include the constant-temperature cell holder (Fig. 1). Thermoelectrically temperature-controlled accessories include the CPS-100/100F 6-cell thermoelectrically temperature-controlled cell positioner (Fig. 2) and the TCC-100 thermoelectrically temperature-controlled cell holder (Fig. 3).

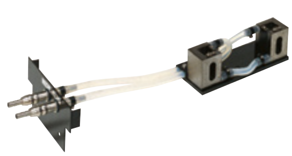

Fig. 1 Constant-Temperature Cell Holder

Fig. 2 CPS-100/100F 6-Cell Thermoelectrically Temperature-Controlled Cell Positioner

Fig. 3 TCC-100 Thermoelectrically Temperature-Controlled Cell Holder

Specifications for the three types of temperature-controlled accessories mentioned above are indicated in Table 1.

Table 1 Temperature-Controlled Accessories Used for Constant-Temperature Measurements

	Constant-Temperature Cell Holder	CPS-100/100F 6-Cell Thermoelectrically Temperature-Controlled Cell Positioner	TCC-100 Thermoelectrically Temperature-Controlled Cell Holder
Number of Cells	Sample side: 1 cell Reference side: 1 cell	Sample side: 6 cells (temperature-controlled) Reference side: 1 cell (not temperature-controlled)	Sample side: 1 cell (temperature-controlled) Reference side: 1 cell (temperature-controlled)
Temperature Control Range	5 to 90 °C (also limited by constant-temperature system used)	16 to 60 °C	7 to 60 °C
Constant-Temperature Water Circulator	Required	Not necessary	Not necessary

Features of the respective temperature-controlled accessories are described below.

Constant-Temperature Cell Holder

This holder can hold one 10 mm standard cell on the sample side and one on the reference side. To hold even more rectangular cells, a four-cell constant-temperature holder is available that can hold four rectangular cells on the sample side and one on the reference side. The single-cell and 4-cell constant-temperature cell holders can be used with an existing constant-temperature water circulator.

CPS-100/CPS-100F 6-Cell Thermoelectrically Temperature-Controlled Cell Positioners

These positioners can hold six 10 mm standard cells on the sample side and one on the reference side. They are especially useful for measuring enzyme activity. The CPS-100F is available for holding six flow cells on the sample side for dissolution testing applications. Given that dissolution testing equipment is available from a variety of manufacturers, contact Shimadzu to confirm connectivity with Shimadzu UV-VIS spectrophotometers.

TCC-100 Thermoelectrically Temperature-Controlled Cell Holder

This is also a thermoelectrically temperature-controlled accessory, similar to the CPS-100/100F models. It can only hold one cell each on the sample and reference sides, but it enables measurements at lower temperatures than the CPS-100/100F holders.

2. Temperature-Controlled Accessories with Programmable Temperature Increase/Decrease Control

As mentioned above, accessories with programmable temperature increase/decrease control are especially useful for measuring samples with spectral shapes or absorbance levels that can vary depending on the temperature. For example, the melting temperature (Tm) of drugs needs to be determined during development of nucleic acid drugs anticipated as an innovative therapeutic drug for treating genetic disorders that are otherwise difficult to treat. However, that melting temperature can vary depending on the sample, so measurements need to be performed as the temperature is varied. The temperature-controlled accessories described below offer programmable temperature increase/decrease control capability that is especially useful for developing such nucleic acid drugs. Shimadzu temperature-controlled accessories capable of programmable temperature increase/decrease control include the S-1700 thermoelectrically temperature-controlled single cell holder (Fig. 4) and TMSPC-8 Tm analysis system (Fig. 5).

Fig. 4 S-1700 Thermoelectrically Temperature-Controlled Single Cell Holder

Fig. 5 TMSPC-8 Tm Analysis System

Specifications for the two types of temperature-controlled accessories mentioned above are indicated in Table 2.

Table 2 Temperature-Controlled Accessories with Programmable Temperature Increase/Decrease Control

	S-1700 Thermoelectrically Temperature-Controlled Single Cell Holder	TMSPC-8 Tm Analysis System
Number of Cells	Sample side: 1 cell (temperature-controlled) Reference side: 1 cell (not temperature-controlled)	Sample side: 8-cell multi-cell Reference side: None
Temperature Control Range	0 to 110 °C	0 to 110 °C
Cooling Water	Required	Required

Features of the respective temperature-controlled accessories are described below.

S-1700 Thermoelectrically Temperature-Controlled Single Cell Holder

This holder comes with a stirrer to ensure a uniform temperature distribution is maintained within the cell during measurements. Furthermore, heating rates can be varied between 12 levels so that samples can be heated or cooled quickly or slowly during measurements.

TMSPC-8 Tm Analysis System

This system is designed specifically for analyzing nucleic acid drugs. Configured with an 8-cell thermoelectrically temperature-controlled cell holder, temperature controller, and Tm analysis software, it enables simultaneous measurement of up to eight samples. The Tm analysis software can easily analyze the Tm value of DNA, RNA, or other nucleic acids based on temperature and absorbance curve data.

The Peltier element used to control temperature in both of these temperature-controlled accessories requires a flow of cooling water to maintain proper element performance. Though tap water can be used, a constant-temperature water circulator is recommended for achieving an even broader temperature-control range. For measurements at temperatures of 10 °C or lower, the cell holder must be purged with nitrogen gas to prevent condensation on cell surfaces.

3. Example of Using an S-1700 Thermoelectrically Temperature-Controlled Single Cell Holder to Analyze Ink and Liquid Crystals

For this example, two types of samples that change color in response to changes in temperature were prepared and then the S-1700 holder was used to measure their spectra as the temperature was varied.

Fig. 6 shows thermochromic ink diluted by 400 times with distilled water. (The color changes from blue to pale red at about 40 °C.) Fig. 7 shows a color change in cholesteric liquid crystals as the wavelength of reflected light varies due to variations in the helical structure width in response to heating or cooling. (Reportedly, it is bluish-violet at low temperatures and changes to green, orange, and other colors of the rainbow as it is successively heated.) Measurement and temperature-control conditions are indicated in Tables 3 and 4. The temperature-control program pattern is shown in Fig. 8.

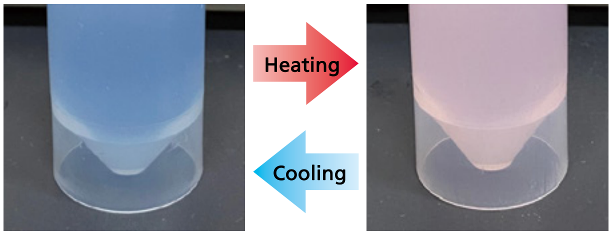

Fig. 6 Change in Thermochromic Ink Color in Response to Changes in Temperature (at 25 °C on the left and 40 °C on the right)

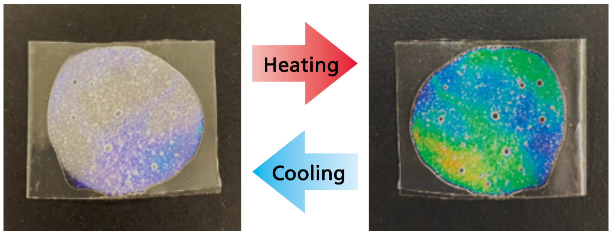

Fig. 7 Change in Cholesteric Liquid Crystal Color in Response to Changes in Temperature (at 5 °C on the left and 25 °C on the right)

Table 3 Measurement Conditions

Instrument	UV-1900i
Measurement Wavelength Range	350-900 nm
Data Intervals	1.0 nm
Scan Speed	High speed
Slit Width	1 nm
Cycle Count	15 cycles for ink and 7 cycles for liquid crystals
Interval between Cycles	180 sec.

Table 4 Temperature Control Conditions

Sample	Thermochromic Ink	Cholesteric Liquid Crystals
Instrument	S-1700 thermoelectrically temperature-controlled single cell holder	
Starting Temperature	30.0 °C	5.0 °C
Retention Time at Starting Temperature	60 sec.	
Temperature Change Rate	1.0 °C/min	5.0 °C/min
Wait Time before Measurement	120 sec.	
Cycles	14 cycles	6 cycles

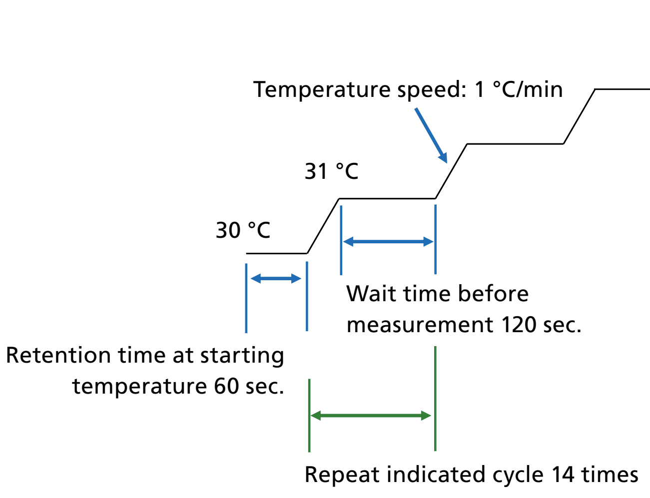

Fig. 8 Diagram of Temperature Program

3-1 Example of Analyzing Thermochromic Ink

The absorption spectra of thermochromic ink at each temperature are shown in Fig. 9.

Fig. 9 does not show any spectral changes in the 600 to 900 nm wavelength region below 35 °C. However, when the temperature reaches 36 to 37 °C, the absorbance value suddenly drops and then gradually decreases at successively higher temperatures above 38 °C.

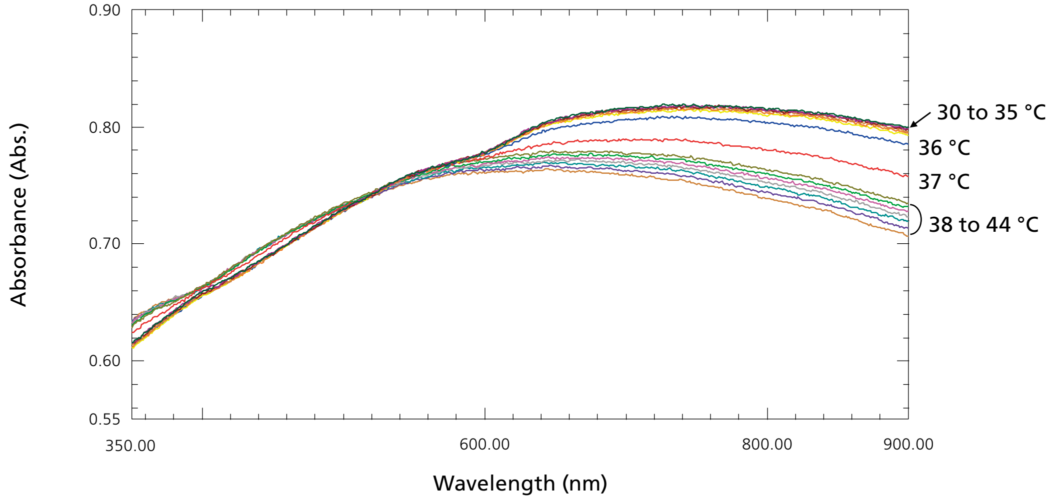

Fig. 9 Absorption Spectra of Thermochromic Ink at Respective Temperatures

3-2 Example of Analyzing Cholesteric Liquid Crystals

In this example, cholesteric liquid crystals, such as those used in heat-sensitive films, were measured. The sample could not be measured directly because it was in paste form, so it was sandwiched between plastic films and measured while held in the cell-type sample holder shown in Fig. 10. The S-1700 thermoelectrically temperature-controlled single cell holder is designed for temperature-controlled measurements of liquid samples, but using it in combination with a cell-type sample holder, it can be used for temperature-controlled measurements of samples not only in liquid form but also in paste or film form.

Measurement and temperature-control conditions are indicated in Tables 3 and 4. Samples were measured at 5 °C increments from 5 to 35 °C. (For measurements at 5 and 10 °C, the sample compartment was purged with nitrogen gas to prevent condensation on cell surfaces.)

Fig. 10 Cell-Type Sample Holder

The transmittance spectra from cholesteric liquid crystals are shown in Fig. 11. As mentioned above, the wavelength of light reflected from cholesteric liquid crystals varies depending on the temperature, resulting in a color change. Therefore, transmittance is plotted on the vertical axis.

Fig. 11 shows that as the temperature increases, the region where light is transmitted gradually shifts in the long-wavelength direction. In this case, the reflected light presumably shifted, in response to heating, in the short-wavelength direction[1], which resulted in the transmittance region in the transmittance spectra shifting in the long-wavelength direction.

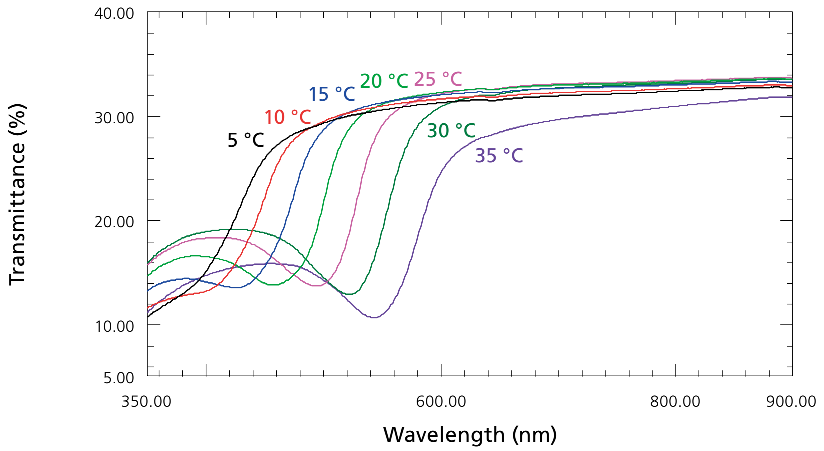

Fig. 11 Transmittance Spectra of Cholesteric Liquid Crystals

4. Summary

This article described various temperature-controlled accessories used with UV-VIS spectrophotometers. Hopefully, this will provide a reference for selecting the best accessory for the given measurement objectives.

Reference

[1] Hiroyuki Sugimoto, Thermal Printing on a Rewritable Full-Color Recording Material of a Medium-Molecular-Weight Cholesteric Liquid Crystal. Ricoh (2000)

Q&A

When I measured transmittance of a film, the spectrum exhibited a regularly-spaced wave pattern. Why is that?

The pattern occurred due to an interference pattern between two light wavelengths. Fig. 1 illustrates how the interference pattern occurs.

During film transmittance measurements, when light that is reflected inside the film (red line in Fig. 1, which is sometimes referred to as internal reflection) propagates in the direction of transmittance again, it generates interference with light transmitted directly through the film (black line in Fig. 1).

A similar phenomenon can occur during reflectance measurements as well. When measuring the reflectance of coating samples on a substrate, light reflected from the sample surface (black line in Fig. 2) can interfere with light that was reflected from the substrate after passing directly through the sample (red line in Fig. 2).

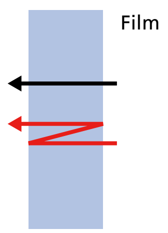

Fig. 1 Light Interference during Film Transmittance Measurements

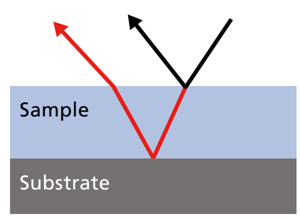

Fig. 2 Light Interference during Reflectance Measurements of Sample Coatings on a Substrate

To reduce interference, samples can be tilted or irregularities added to their surface, for example, but it requires particular care to prevent affecting vertical axis values of a spectrum, such as by changing the optical path length or increasing reflected stray light components. To reduce interference without affecting vertical axis values, changing the slit width used for measurements is recommended.

Fig. 3 shows a transmittance spectrum from food wrap measured using three different slit widths. (The inset is an enlargement of the 350 to 500 nm range.)

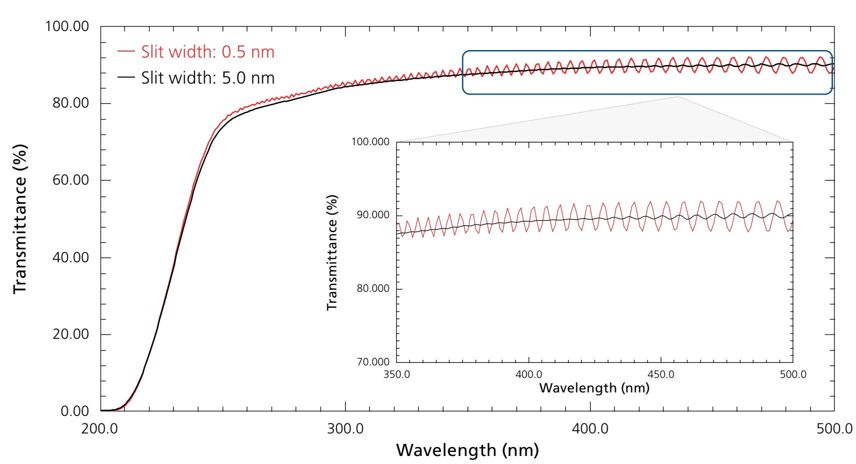

Fig. 3 Transmittance Spectrum of Food Wrapping Film

A slit width of 0.5 nm resulted in a large interference pattern, whereas a wider slit resulted in a smoothing effect that reduced the interference pattern. By using the interference pattern, the thickness of the food wrap film can be calculated. For more details, refer to Application News A614.

Link to Application News A614

— To Customers Using Shimadzu UV-VIS Spectrophotometers —

Supply of Spare Parts for UV-1600/1650/1700 and UV-2400/2500 Series Has Ended

Thank you for your continued use and enjoyment of Shimadzu spectrophotometers.
Shimadzu has strived daily to supply spare parts for the UV-1600(PC)/1650/1700 and UV-2400/2450/2500/2550 models even after ending production of these models, but continuing to supply these spare parts has become impractical. This may cause circumstances where repair is impossible and may have a significant bearing on your analysis work. Please consider upgrading to a new UV-VIS Spectrophotometer.

Consider Upgrading to the Latest Models!

UV-1900i

UV-2600i/2700i

UV-1600

UV-1650

UV-1700

UV-2400/2450/2500/2550

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