C101-E142

SHIMADZU
Excellence in Science

UV TALK LETTER

Vol. 16

UV Talk Letter

Retrospective of Shimadzu UV-VIS Spectrophotometers—from Initial Release to Today

1. Introduction

UV-VIS spectrophotometers are the most commonly used analytical instrument using light. They are used in a wide variety of fields for applications such as quantitative analysis, colorimetry, measuring the thickness of thin films or coatings, or transmittance or reflectance measurements of optical elements. Historically, it is one of the oldest analytical instruments as well. In the case of Shimadzu, we developed and released our first UV-VIS spectrophotometer using a prism in the early 1950s. This document reviews the history of Shimadzu UV-VIS spectrophotometers, from inception to today.

2. First Shimadzu UV-VIS Spectrophotometer

Before the first UV-VIS spectrophotometer, quantitative analysis was performed using a colorimeter. However, in those days, a glass filter was used to output light of wavelengths corresponding to the sample color and that light was transmitted through containers containing a standard sample and unknown sample. Then the length of the container of (the optical path length of the light beam through) the standard sample (or alternatively the unknown sample) was visually adjusted with the naked eye, so that brightness of both beams was the same, where the concentration of the unknown sample was then determined based on the amount of adjustment. Therefore, there was significant potential for human error occurring in quantitated values.

This situation was swept away in 1945, 70 years ago from now, when the world's first UV-VIS spectrophotometer was released in the United States. That UV-VIS spectrophotometer separated light into its different wavelengths using a prism, like the one illustrated in Fig. 1. The amount of light transmitted through the sample was measured using a photoelectric tube (a vacuum tube that uses the photoelectric effect to convert light energy into electrical energy). Due to its far superior performance than the colorimeter and dramatically higher precision and accuracy than other quantitative methods, the use of UV-VIS spectrophotometers quickly spread throughout the U.S.

UV-VIS spectrophotometers were first imported to Japan immediately after their release in the U.S. Due to the significantly higher quantitative accuracy than the colorimeters commonly used at the time in Japan, the imported UV-VIS spectrophotometers caused a big sensation in the field of analytical chemistry, and Japanese-made UV-VIS spectrophotometers were eagerly waited at the same time. In response to this demand, engineers at Shimadzu used sketches of the U.S.-made UV-VIS spectrophotometer to start developing our own system based on trial and error.

Soon they faced a major problem in the development process. The U.S.-made UV-VIS spectrophotometer used a hydrogen gas discharge tube as a light source for wavelengths below 400 nm, but no one in Japan manufactured hydrogen discharge tubes at the time. Consequently, they asked for help from a sister company in Kyoto city that was manufacturing mercury lamps. Shimadzu obtained the materials needed for manufacturing a hydrogen discharge tube and inspected prototypes, while the sister company designed and manufactured the tubes. With diligent effort by the sister company, we were finally able to create a hydrogen discharge tube that was equivalent to the U.S. product.

The UV-VIS spectrophotometer imported from the U.S. used a photoelectric tube as a detector, but we received information about a photomultiplier tube developed in the U.S. that offered hundreds of times higher sensitivity than the photoelectric tube. Photomultiplier tubes are essentially a photoelectric tube with additional electric current amplification capability and are still used as detectors in UV-VIS spectrophotometers even today. Based on that information, we planned to create Japan's first photomultiplier tube to develop the world's first UV-VIS spectrophotometer equipped with a photomultiplier tube. To develop a Japanese photomultiplier tube, we asked a Japanese manufacturer of photoelectric tubes to jointly develop the tube with us. Thanks to the significant effort by that photoelectric tube manufacturer, we successfully created a photomultiplier tube that rivaled the performance of the U.S. product.

In 1952, we completed Shimadzu's first UV-VIS spectrophotometer system, the QB-50 (Fig. 2). The system used a crystal prism as a spectroscopic element and was the first UV-VIS spectrophotometer in the world with a photomultiplier tube used as the detector. When the performance was compared to the U.S. UV-VIS spectrophotometer at a university in Kyoto city, the QB-50 was not inferior in performance to the U.S. system, but was also able to measure with adequate sensitivity 220 nm light that the American system could not. This system perfectly fit the needs of the times and sold well, becoming one of Shimadzu's leading products.

The prism was a triangular pole made of quartz or glass. The prism refracts the white light entering from the light source. The longer the wavelength of light is, the smaller the refractive index will be, and the shorter the wavelength, the larger the refractive index. Consequently, the light is divided into a spectrum of colors in order of wavelength - red, yellow, green, blue, and violet.

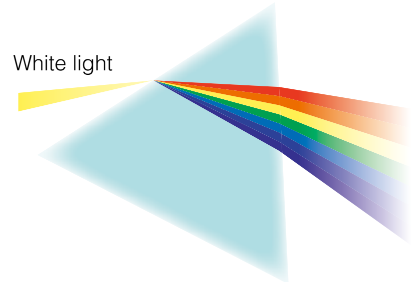

Fig. 1 Light Spectrum from a Prism

Fig. 2 Shimadzu QB-50 UV-Visible Spectrophotometer

3. Development History of Shimadzu UV-Vis Spectrophotometers

Since releasing the QB-50 UV-VIS spectrophotometer, Shimadzu has now developed and released over 70 new models of UV-VIS spectrophotometers so far, as listed in Table 1. Of those, several key models that formed the foundation of Shimadzu's reputation as a leader in manufacturing UV-VIS spectrophotometers are described below.

Table 1 History of Shimadzu UV-VIS Spectrophotometers

Year Released	Model
1952	QB-50
1956	QR-50
1957	RS-20
1958	RS-27
1961	SV-50
1963	QV-50, SG-15, SP-20
1964	MPS-50
1965	MPS-50L, AQV-50
1966	Double-40S/ 40SB/ 40D/ 40DB/ 40R/ 40DF
1968	Coloripet
1970	UV-200
1972	MPS-5000
1973	UV-210, SP-20A
1974	UV-300
1975	UV-140, UV-150
1976	UV-100, UV-110, UV-180, UV-190
1977	UV-220, UV-350, UV-360
1979	UV-365
1980	UV-120, UV-240
1981	UV-250, UV-3000
1982	MPS-2000

Year Released	Model
1983	UV-260
1985	UV-160
1986	UV-265
1987	UV-2100, UV-3100
1989	UV-2200, UV-3100PC
1990	UV-1200
1992	NIR-1500
1993	UV-1200V, UV-2100PC, UV-2200A
1994	UV-1600, UV-1600PC, UV-2400PC, UV-2500PC
1995	BioSpec-1600
1997	MultiSpec-1500, SP-20+
1998	Uvmini-1240, MPS-2400
1999	UV-1650, UV-2450, UV-2550
2000	UV-3150
2001	UV-1700
2004	UV-3600, SolidSpec-3700/3700DUV
2006	BioSpec-mini, MPS-2450
2007	UV-1800
2008	BioSpec-nano
2011	UV-2600, UV-2700
2014	UV-3600 Plus, UV-1280

3-1. History of Double-Beam Spectrophotometers

A system that continuously scans samples with different monochromator wavelengths and automatically records the resulting spectrum on a data recorder is referred to as a recording spectrophotometer. Recording spectrophotometers use a double-beam configuration, where monochromatic light is split into two light beams, a sample light beam and reference light beam, which are alternately transmitted through the sample compartment for measurement. In contrast, the QB-50 used a single-beam configuration, where only one beam was transmitted through the sample compartment. Double-beam recording spectrophotometer were also first developed in the U.S. and imported into Japan. Due to the ability to measure spectra, demand increased for double-beam spectrophotometers, which resulted in releasing the RS-20 in 1957, shown in Fig. 3. The RS-20 monochromator featured a double-beam optical system installed in the same shape housing as the QB-50. The RS-20 represents the starting point for Shimadzu's current line of double-beam spectrophotometers, which is now one of the main product lines at Shimadzu.

In the 1970s, the UV-200 shown in Fig. 4 was released as a smaller and more economical model. The UV-200 features a double-beam optical system with symmetric sample and reference light beams that have identical optical path lengths and an identical number of mirrors reflecting the beams, as shown in Fig 5. Consequently, it offered outstanding baseline flatness, transmittance accuracy, and temporal stability. This configuration is still used today.

In 1980, the UV-240 was released with separate control and measurement units, as shown in Fig. 6. That innovative model was acclaimed for being the first UV-VIS spectrophotometer system available with the operator interface separated from the measurement unit. The control unit featured a graphic recorder that could print spectra, measurement conditions, quantitative analysis calculation results, and so on, on chart paper. It also featured a holographic grating as the device used to disperse light. Holographic gratings are diffraction gratings made by using laser holographic interference fringes to form parallel grooves and then using an ion beam to etch the grooves. Compared to conventional mechanically machined diffraction gratings, holographic gratings provide superior diffraction efficiency and lower stray light levels. The UV-240 was one of our best sellers at the time, with over 3600 units sold worldwide.

Around 1990, the cost of personal computers had decreased sufficiently and the demand increased for computer-controlled UV-VIS spectrophotometers. Consequently, we released the UV-2100PC in 1993 and the UV-2400PC and UV-2500PC models in 1994. Currently, we are selling the successors to those models, the UV-2600 and UV-2700.

In 1985, we released the UV-160, shown in Fig. 7, which was an all-in-one double-beam spectrophotometer that included a CRT screen, keypad, printer, and other functionality all integrated in a single unit. Due to its low price and high performance, we sold over 20,000 units worldwide, which contributed significantly to the widespread use of UV-VIS spectrophotometers. The UV-1800 currently being sold features a similar configuration to that system.

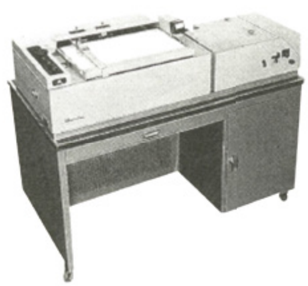

Fig. 3 Shimadzu RS-20 UV-VIS Spectrophotometer

(Excerpted from p. 275 of "Shimadzu Analytical Instruments 'People & Stories' from Pioneers to Leaders in 60 Years" planned & compiled by Hideki Makabe, Published by Shimadzu Corporation, 2006)

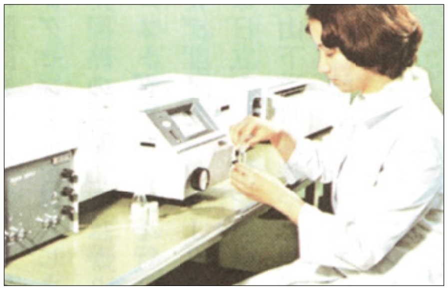

Fig. 4 Shimadzu UV-200 UV-VIS Spectrophotometer

(Excerpted from p. 289 of "Shimadzu Analytical Instruments 'People & Stories' from Pioneers to Leaders in 60 Years" planned & compiled by Hideki Makabe, Published by Shimadzu Corporation, 2006)

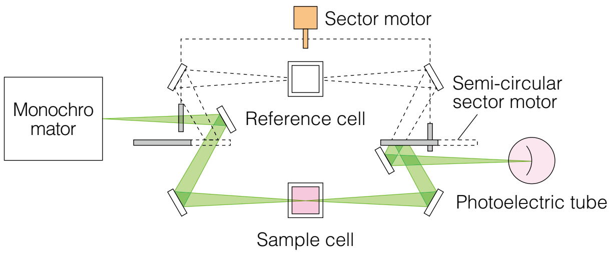

Fig. 5 Optical System in Symmetric Double-Beam Spectrophotometer

(Excerpted from p. 289 of "Shimadzu Analytical Instruments 'People & Stories' from Pioneers to Leaders in 60 Years" planned & compiled by Hideki Makabe, Published by Shimadzu Corporation, 2006)

Fig. 6 Shimadzu UV-240 UV-VIS Spectrophotometer

Fig. 7 Shimadzu UV-160 UV-VIS Spectrophotometer

3-2. History of Double-Monochromator and UV-VIS-NIR Spectrophotometers

Double-monochromator spectrophotometers reduce stray light by monochromating the light from the light source in two consecutive stages. Shimadzu's first double-monochromator spectrophotometer was the Double-40 series, released in 1966. Double-40 series double-monochromator spectrophotometers included both a prism and diffraction grating and were available in either single-beam or double-beam configuration. In 1981, Shimadzu released the UV-250, the double-monochromator version of the UV-240 mentioned above. UV-2500PC, UV-2550PC, and UV-2700 models, mentioned above, were also released as part of the same series. The UV-2700 model currently being sold, features a diffraction grating that achieves ultra low stray light levels, which expands the measurement range to 8 Abs and accurately determines transmittances to 0.000001 % (1 part in 100 million). Spectrophotometers capable of measuring light in the ultraviolet, visible, and near infrared regions are called UV-VIS-NIR spectrophotometers. In 1958, the RS-27 was released as a version of the RS-20 mentioned above with an extended measurement range that includes the near infrared region. It was Shimadzu's first UV-VIS-NIR spectrophotometer. The RS-27 was a single-monochromator design with a prism-based monochromator. In 1977, Shimadzu released the UV-360, Shimadzu's first double-monochromator UV-VIS-NIR spectrophotometer, which was equipped with both prism and diffraction grating-based monochromators. Its successor model, the UV-365, was released in 1979, shown in Fig 8. It was the first UV-VIS(-NIR) spectrophotometer equipped with a microprocessor, which were gaining widespread popularity at the time. The UV-3600 Plus and SolidSpec-3700 models, which feature three detectors (a photomultiplier tube, InGaAs detector, and cooled PbS detector) and higher sensitivity in all measurement wavelength regions, are currently Shimadzu's top-of-the-line UV-VIS spectrophotometer models that have both flowed from the original RS-27 model.

Fig. 8 Shimadzu UV-365 UV-VIS-NIR Spectrophotometer

4. Unique UV-VIS Spectrophotometers

Around 1960, a university in Tokyo asked Shimadzu to develop a UV-VIS spectrophotometer capable of measuring spectra from semi-transparent samples with turbidity. That resulted in developing a unique unprecedented instrument. To increase the detection efficiency of scattered light emitted from the samples, the instrument used an end-on photomultiplier tube detector with a light-receiving surface on the measuring head, as shown in Fig. 9. Due to its ability to measure transparent, semi-transparent, or opaque samples (reflectance was measured for opaque samples), the instrument was released in 1964 with the model name MPS-50 (based on an acronym for "multipurpose system"). It caused a major response from academic institutions and companies involved in biochemistry. The MPS-50 still used vacuum tubes, but transistors and integrated circuit devices were used for the MPS-5000 successor model (Fig. 10) released in 1972, which was smaller and offered higher performance.

Another unique UV-VIS spectrophotometer model was the UV-300 released in 1974. Referred to as a dual-wavelength double-beam recording spectrophotometer, the UV-300 featured two built-in monochromators connected in parallel, which allowed using one monochromator to measure the absorbance spectrum, as usual, while the other measured absorbance at a specific fixed wavelength, so that the difference in absorbance measured at the two wavelengths could be recorded as a spectrum. That allowed measurement of spectra without being affected by turbidity. In 1981, a successor model was released, the UV-3000 shown in Fig. 11, which featured improved functionality using a microprocessor and a measurement wavelength range from 190 nm to 900 nm.
Both the MPS series and UV-300 series were unique UV-VIS spectrophotometers, but sales were discontinued after demand decreased.

Fig. 9 End-On Photomultiplier Tube

(Excerpted from p. 282 of "Shimadzu Analytical Instruments 'People & Stories' from Pioneers to Leaders in 60 Years" planned & compiled by Hideki Makabe, Published by Shimadzu Corporation, 2006)

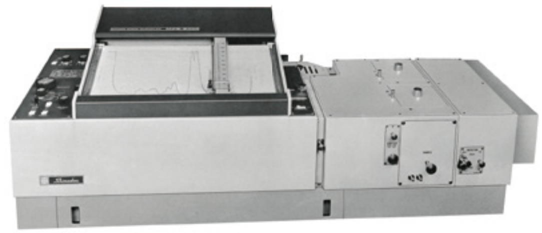

Fig. 10 Shimadzu MPS-5000 Multipurpose Recording Spectrophotometer

Fig. 11 Shimadzu UV-3000 Dual-Wavelength Double-Beam Recording Spectrophotometer

5. Summary

Shimadzu has sold about 190,000 UV-VIS spectrophotometers around the world, starting with the QB-50 released in 1952. Today, UV-VIS spectrophotometers have become an essential analytical instrument for quantitative analysis or for determining the optical properties of substances. Consequently, Shimadzu will continue to offer improved systems that better meet the needs of various users.

This article was based on "Shimadzu Analytical Instruments 'People & Stories' from Pioneers to Leaders in 60 Years," planned and compiled by Hideki Makabe, published by Shimadzu Corporation in 2006.

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Takahiro Tajima

Expertise for Measuring Transmittance in Solid Samples and Corresponding Examples

In UV Talk Letter Volume 11, we explained the principle of measuring transmittance. However, it is not unusual for actual measurements to result in unexpected discontinuities in spectra or other problems. Therefore, this article provides three points of practical expert advice useful for actual transmittance measurements.

1. Technique for Minimizing Discontinuities in Spectrum Data— Measuring the Transmittance Through Thick Transparent Samples

Spectral measurements can sometimes result in jumps (discontinuities) in the spectra at wavelengths where the system switches between different detectors or diffraction gratings. This can occur particularly when measuring transmittance through thick (2 mm or more) transparent samples (such as glass or plastic plates) in the standard sample compartment. In such cases, they must be measured using an integrating sphere attachment.
Fig. 1 shows a comparison of results from measuring a 5 mm thick clear glass plate in the standard sample compartment versus using an integrating sphere. Fig. 2 shows the sample placed in the standard sample and Fig. 3 in the integrating sphere. Fig. 1 shows how using an integrating sphere reduces the size of discontinuities. In the case of thin transparent sample less than 2 mm thick, discontinuities are smaller even when using the standard sample compartment. However, measuring cloudy samples require detecting diffused light, which means they must be measured in an integrating sphere regardless of thickness.

<Causes of Spectrum Discontinuities and Reason Why Using an Integrating Sphere Makes Them Smaller>

The following explains why discontinuities occur in spectra and why using an integrating sphere reduces their size.
The measurement procedure involves first correcting the baseline based on measurement without any sample in the sample compartment, before measuring the sample. During baseline correction, the light hits the blue and green areas on the light-receiving surface of the detector, as shown in Fig. 4. Next, if a thick sample is measured, the light refracts as it passes through the sample and hits the blue area on the light-receiving surface. Consequently, the region (or area size) where the light hits the detector input surface is different from during baseline correction (blue plus green), which changes the detector output. Furthermore, the detector sensitivity varies depending on where the light hits on the light-receiving surface (uneven sensitivity), which can also affect the output. If the light hits a different region or different size area of the light-receiving surface of the detector during baseline correction from it does during sample measurement, then the measurement will not be accurate. If spectra are measured in ranges involving multiple detectors, then non-uniformities in the sensitivity of the each detector can affect data, which tends to create a discontinuity at the wavelength where the system switches between the different detector ranges. However, even if measuring samples within the wavelength range of a single detector, switching between different gratings can change the shape of the light beam. Thus, a spectrum discontinuity occurs as a result of light refraction by the sample, with the data affected by sensitivity non-uniformities on the detector input surface during baseline correction and sample measurement.
On the other hand, if an integrating sphere is used for measurements, then the light hits the entire light-receiving surface of the detector uniformly, which eliminates effects from uneven sensitivity. Consequently, that reduces the size of discontinuities. For more details about the construction of integrating spheres, refer to UV Talk Letter Volume 5.

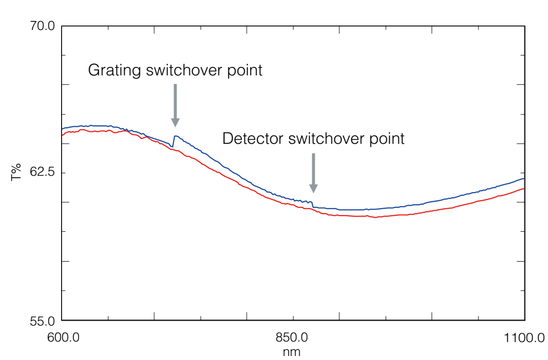

Fig. 1 Transmittance Spectra of 5 mm Thick Glass Plate
(standard sample compartment used for blue line and integrating sphere for red line)

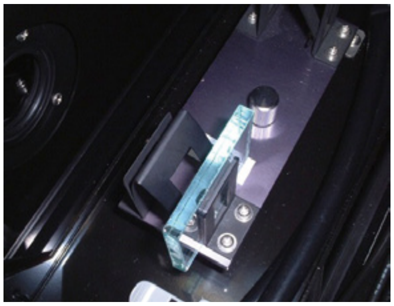

Fig. 2 5 mm Thick Glass Plate Placed in Standard Sample Compartment (film holder)

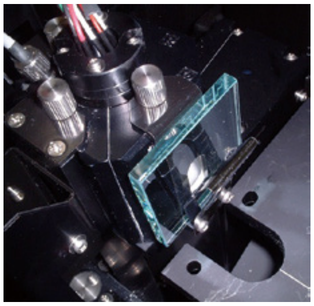

Fig. 3 5 mm Thick Glass Plate Placed in Integrating Sphere

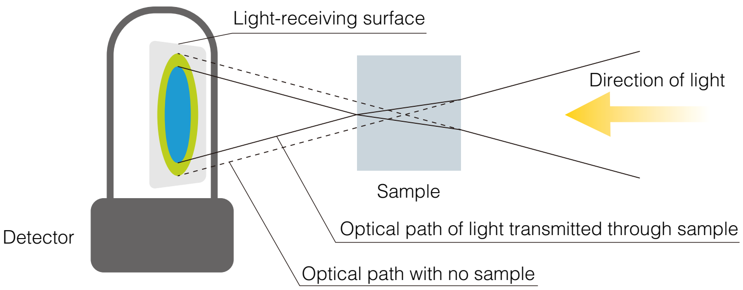

Fig. 4 Incident Light on Light-Receiving Surface of the Detector

2. Technique for Reducing Noise—Measuring Samples with Low Transmittance

If a spectrum includes significant noise levels, there are generally two ways to reduce the noise level, either use a slower scan speed or smaller sampling pitch (interval between measurements). A slower scan speed reduces noise by increasing the number of integrations, whereas a smaller sampling pitch increases the moving average. In general, a combination of these two methods is used to reduce noise. However, if samples with especially low transmittance is used, the photometric balance between the sample light and reference light levels is deteriorated, which makes it even more likely for noise to occur than normal. In such cases, a separate technique can be used to reduce noise, in addition to the two methods above. That technique is to use a mesh filter. Mesh filters consist of wire mesh formed in a grid pattern that reduces the amount of light passing through the filter. A photograph of a mesh filter is shown in Fig. 5. To measure a sample with low transmittance, the mesh filter is inserted into the path of the reference light beam, which reduces the noise by decreasing the amount of reference light so that it is well-balanced with the sample light. For more information about the role of reference light, refer to UV Talk Letter Volume 9.

Containers made of PET (polyethylene terephthalate) have low transmittance in the UV region of less than about 1 %. In this example, the UV transmittance of a square sample cut out from the container, a few centimeters long on each side, was measured in an integrating sphere. Results that compare transmittance with and without using a mesh filter are shown in Fig. 6. A photograph of the measurement setup is shown in Fig. 7. The results show that using a mesh filter provides lower noise.

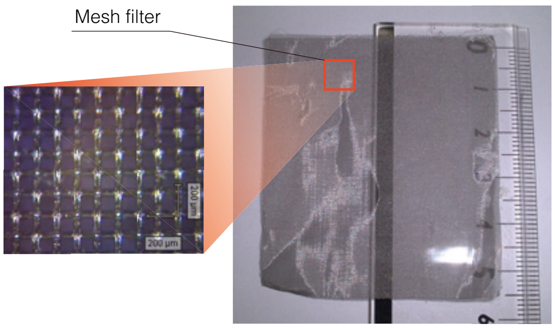

Fig. 5 Mesh Filter

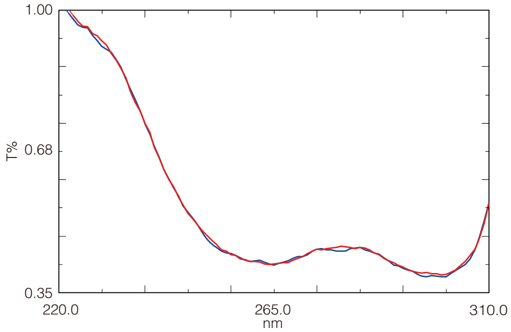

Fig. 6 Transmittance Spectra of PET Container
(Transmittance using a mesh filter is shown in red and without a mesh filter in blue)

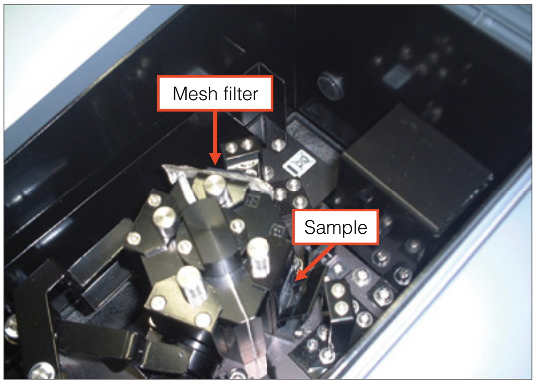

Fig. 7 Sample (PET Container) Measurement Setup

Note:
The mesh filter used is available from Shimadzu by ordering the following part numbers.

- Vertical/horizontal wire mesh (one sheet) P/N: 204-04694-01
- Diagonal wire mesh (one sheet) P/N: 204-04694-02

To increase the amount of light reduction, stack multiple mesh filters by alternating between vertical/horizontal and diagonal mesh filters. Mesh filters for use in the standard sample compartment are indicated below.

- Mesh filter assembly (three each of vertical/horizontal and diagonal mesh filters)
  P/N: 206-82299-91

3. Technique for Reducing Interference Waveforms — Measuring Film

When measuring the transmittance through film, results often have a jagged interference waveform, as shown in Fig. 8. This phenomenon occurs when internally reflected light exits the film in the same direction as the transmitted light and causes interference patterns with the transmitted light. The interference waveform causes alternating peaks and valleys, which makes it difficult to accurately determine the transmittance values at specific wavelengths. In such cases, the interference waveform pattern can be reduced by increasing slit width. Fig. 8 shows a transmittance spectrum measured from a 46 μm thick transparent film sample placed in the standard sample compartment (in the film holder), with a 1.0 mm slit width. Results measured after changing the slit width to 5.0 nm are shown in Fig. 9. This resulted in a smooth spectrum with most of the interference pattern gone. Increasing the slit width decreases the interference waveform because it reduces the ability to resolve small changes in spectrum and, therefore, provides more averaged data. It can be difficult to eliminate the interference pattern if the wavelength intervals between peaks and valleys are large, but if they are closely spaced, as in this example, then changing the slit width is usually sufficient for resolving the problem.

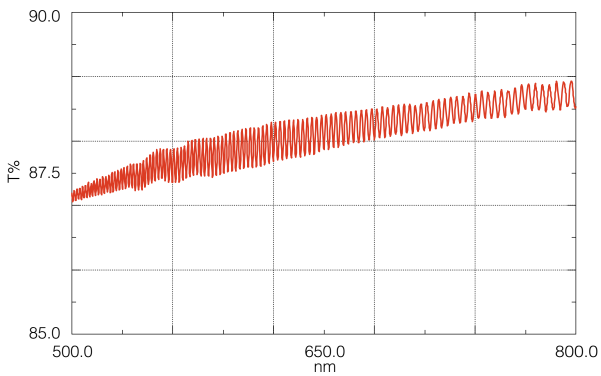

Fig. 8 Transmittance Spectrum of Film (Slit width: 1.0 nm)

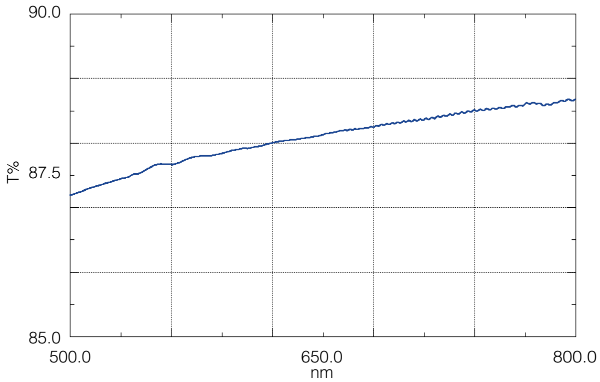

Fig. 9 Transmittance Spectrum of Film (Slit width: 5.0 nm)

4. Summary

This article described three useful techniques for measuring transmittance. Discontinuities, noise, and interference waveforms are common problems with even routine measurements. If they are encountered, try the techniques described above. In future articles, we plan to describe expert advice for reflectance measurements.

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Q How soon can samples be measured after switching the UV-VIS spectrophotometer power ON?

A

1 Single-Beam UV-VIS Spectrophotometers (UVmini-1240)

In single-beam UV-VIS spectrophotometers, any variations in the light source brightness directly affect measurement data. (The basic configuration of single-beam spectrophotometers is illustrated in Fig. 1.) Therefore, wait until the brightness of the light source stabilizes sufficiently before measuring, usually about one hour after switching the power ON.

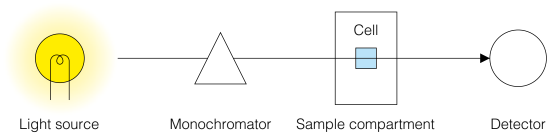

Fig. 1 Configuration of Single-Beam Spectrophotometers

2 Double-Beam Monitoring UV-VIS Spectrophotometers (UV-1280)

In UV-VIS spectrophotometers with double-beam monitoring, variations in light source brightness tend not to affect measurement data, because, unlike single-beam systems, double-beam systems use a separate detector to monitor the light level from the light source. (Fig. 2 illustrates the basic configuration of double-beam monitoring UV-VIS spectrophotometers.) However, the brighter the light source, the lower the noise level in measurement data. Consequently, it is preferable to wait a while after switching the light source ON before measuring. In addition, considering instrument temperature changes and electrical circuit stabilization time after switching the light source ON, wait about 30 minutes after switching the power ON before measuring samples.

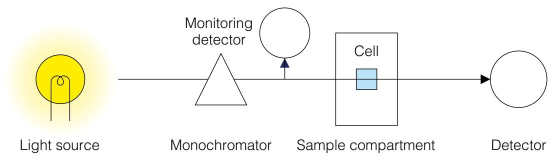

Fig. 2 Configuration of Monitoring Double-Beam Spectrophotometers

3 Double-Beam UV-VIS Spectrophotometers (UV-1800, UV-2600, UV-2700, UV-3600 Plus, and SolidSpec-3700)

Double-beam UV-VIS spectrophotometers are designed to prevent variations in light source brightness from affecting measurement data by monitoring the light level of the reference light. (Fig. 3 illustrates the basic configuration of double-beam UV-VIS spectrophotometers.) Furthermore, double-beam monitoring also can reduce the effects from absorption by solvents. However, just like the other configurations, the brighter the light source, the lower the noise level in measurement data. Consequently, it is preferable to wait a while after switching the light source ON before measuring. Considering instrument temperature changes and electrical circuit stabilization time after switching the light source ON, wait about 30 minutes after switching the power ON before measuring samples.

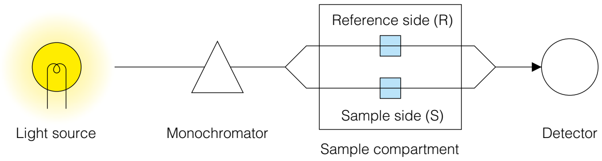

Fig. 3 Configuration of Double-Beam Spectrophotometers

For a more detailed description of the differences between single and double-beam configurations, refer to UV Talk Letter Volume 9.