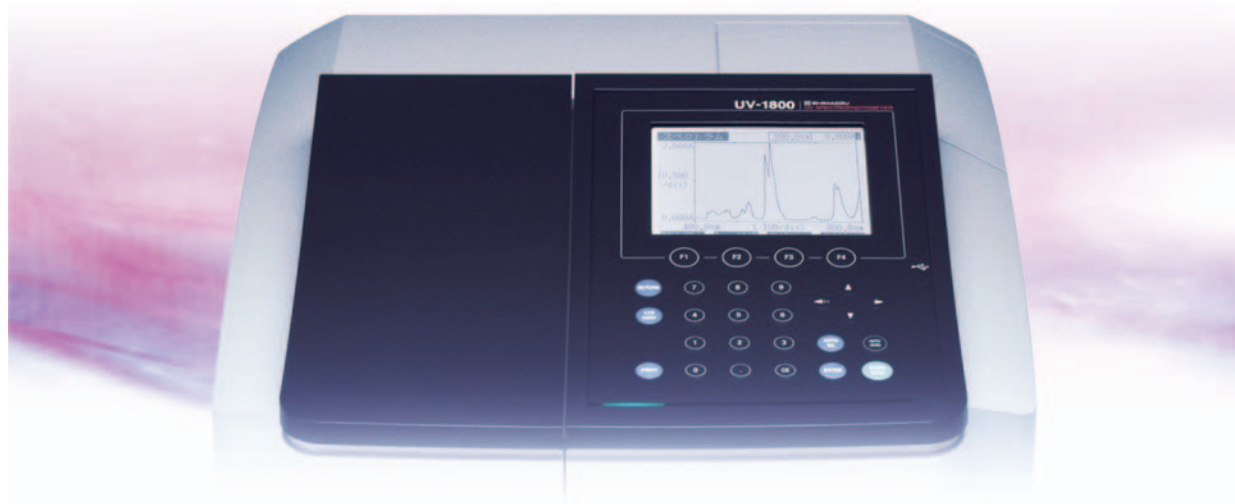


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The streamline-shaped UV-1800 is a compact double-beam UV-VIS spectrophotometer. It uses a fully-fledged Czerny-Turner mount for the monochromator, and boasts the highest level of resolution among instruments of the same class, a bright optical system, and compact dimensions. It can either be used as a stand-alone instrument or controlled from a PC. The main unit is USB-compatible; so measurement data can be saved in highly versatile USB memory, allowing data analysis and printing with a PC.

*As of January 2008, according to Shimadzu investigation



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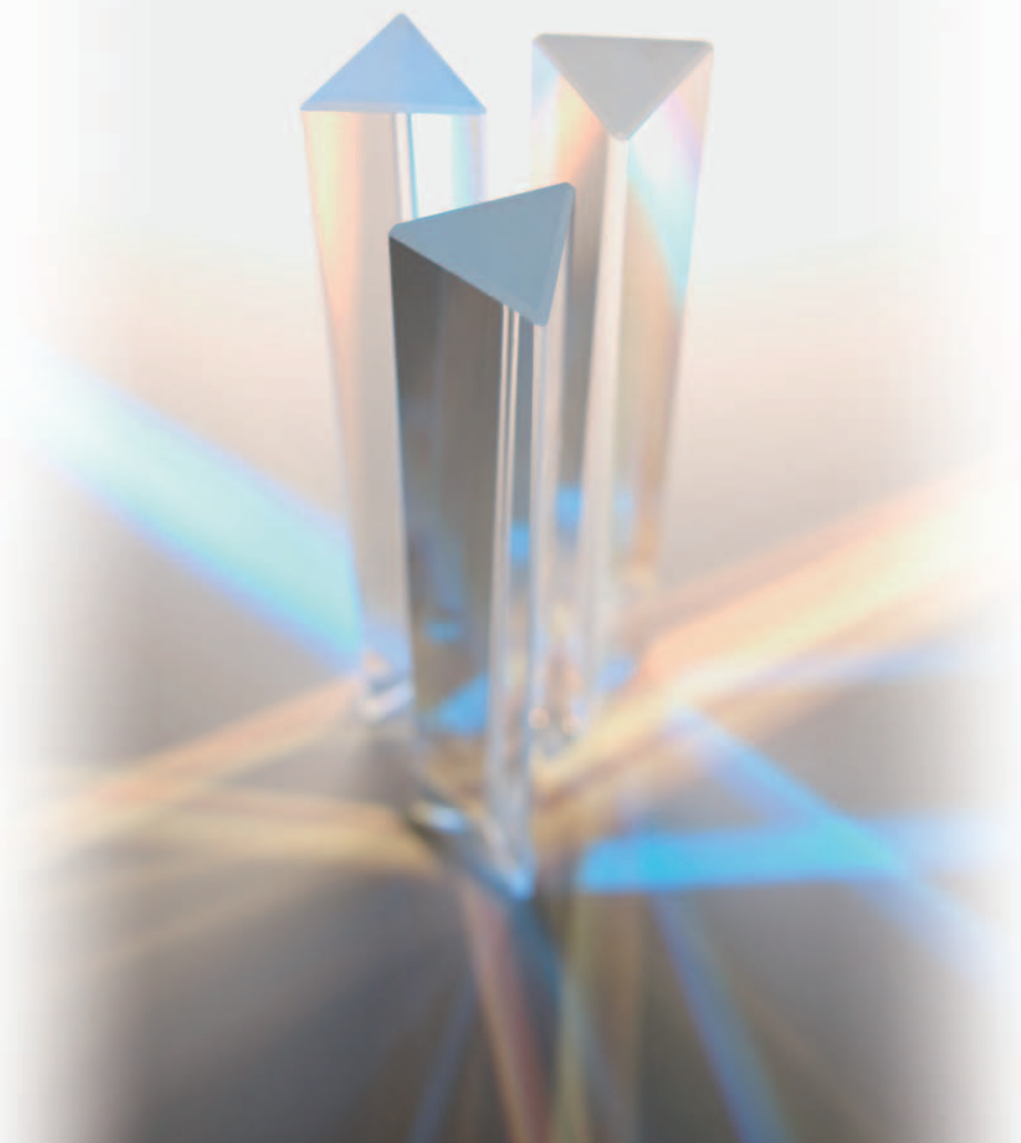
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UV Talk Letter

Vol.1 October 2008

C101-E100



UV Talk Letter On the Occasion of Publication

Thank you for your continued support of our products.

Following on from the publication of information magazines for LC and FTIR, I am pleased to announce the publication of UV Talk Letter, an information magazine for users of UV-VIS spectrophotometers.

The spectrophotometer is one of the oldest types of analytical instruments. Its measurement method of absorption spectroscopy was first implemented by the comparison of colors, as indicated by the fact that it is also called "colorimetry". There is documentation indicating that, even before the advent of instrumental analysis, people would evaluate substances by comparing the colors observed with the naked eye.

Absorption spectroscopy is based on the Lambert-Beer law (Bouguer-Beer law), which relates the concentration of a sample to its absorbance and the optical path length. This law was established during the period spanning from mid-18th century to the mid-19th century. It essentially involves passing light emitted by a light source through a sample and observing the transmitted light. For example, it could be implemented by observing a liquid or a piece of thin film held over something bright. The light that strikes our eyes does not simply consist of transmitted light. It also incorporates light that bounces off the object (reflected light). The fundamental laws of absorption spectroscopy are explained in terms of various types of reflecting and scattering phenomena.

Regarding the instruments used, several types of colorimeters emerged at the end of the 19th century and the beginning of the 20th century. The photoelectric spectrophotometer, a close relative of the modern spectrophotometer, was first produced around 1950. Shortly after that, Japanese companies started making spectrophotometers, with Shimadzu producing the QB-50 model, and photoelectric spectrophotometers became commercially available. These events were followed by the switch from using prisms to using diffraction gratings in spectrophotometers, the appearance of instruments based on microcomputer control, and the emergence, as the predominant type of instrument, of automatic-recording-type spectrophotometers that produce the kind of spectra that we are familiar with today.

The "UV" used in the title of this magazine is now used in the names of products to indicate that they are UV-VIS spectrophotometers. With previous products, however, letters such as "S" and "SP" were used to indicate the spectrum, and the letters "Q" and "G" were used to indicate, respectively, the use of quartz prisms and diffraction gratings. According to documentation, the first Shimadzu spectrophotometer to bear the letters "UV" was the "UV-200", which went on sale in 1970.

A review of the Japanese Industrial Standards (JIS) reveals that, in November 1964, standards were established for absorption spectroscopy before other spectroscopic methods. Since then, several amendments have been made, standard substances have been adopted, and several accessories that keep technically evolving and quantitative applications for the field of biochemistry have been added. Regarding the target samples, in addition to the analysis of liquid samples focusing mainly on quantitative analysis, this field has expanded to include colorimetry and the study of the physical properties of solids. Additionally, this field includes the use of various optical components with characteristics related to permeability and reflectivity, and which thereby give these components added value. Regarding wavelength regions, looking at the analysis of the physical properties of semiconductors as an example, we see that this field has broadened beyond the visible light region and into the near-infrared region to encompass the evaluation of band gaps. Further, in accordance with the use of shorter wavelengths for lasers used in semiconductor manufacturing equipment, these applications go beyond the ultraviolet region to observe characteristics of even shorter waves in the deep ultraviolet region. In addition to the spectrophotometer-specific applications, these devices are also used as detectors for chromatographs and automatic measuring devices. Additionally, in terms of technology and instrumentation, they form a substantial part of the platform on which analytical chemistry is performed.

We will make every effort to ensure that this UV Talk Letter provides useful information to all those involved in spectroscopy, a field set to further its application range, and hope that it may be of some help to you in your work. We look forward to your continued patronage.

Takashi Hine, Analytical Applications Department,
Analytical & Measuring Instruments Division

What Is Light?

The question of whether light is wave or particle, throughout history, been the subject of much debate. It is well known that various theories developed from Newton's assertion that light is particle and Huygen's assertion that light is wave. In modern physics, it is now known that; while light has the wave nature, it also has particle-like properties. In this article, we will describe the dual nature of light and the relationship between matter and light absorbance.

1.The Dual Nature of Light

(1) Wave-Like Properties of Light

Although light is generally said to be a wave, unlike the waves that occur at the surface of a body of water, it does not require a medium. As shown in Fig.1, light consists of an electric field and a magnetic field that intersect each other at a right angle as they move through a vacuum. The distance between successive peaks of either the electric field or the magnetic field is the wavelength.

When handling light, one encounters phenomena that are particular to waves, such as interference and diffraction. The experiment in which Young discovered the interference of light and concluded that light was a waveform is well known. As shown in Fig.2, the monochromatic light emitted from a light source, L, passes through a single slit, and then passes through two more slits, S1 and S2. As a result, interference fringes are observed on the screen at the back as a pattern of alternating strips of brightness and darkness. This can be explained by thinking of S1 and S2 as light sources in phase with each other. Waves travel from these light sources to the screen at the back. At points where the waves are in phase, they reinforce each other, whereas at points where the waves are out of phase, they cancel each other out. If one thinks of the surface of this paper as the surface of a body of water, and the slits as partitions with holes in them, then waves moving from left to right would behave in the same way. In this sense, Young's experiment demonstrates the wave-like nature of light in an intuitive way. Incidentally, the diffraction grating used in a UV-VIS spectrophotometer creates monochromatic light using the wave nature that light diffracts and causes interference.

Light consists of certain types of electromagnetic waves. Electromagnetic waves are referred to by different names in accordance with their wavelength, as shown in Fig.3. "Light" usually refers to electromagnetic waves in the range spanning infrared radiation and ultraviolet radiation, but in some cases it refers only to visible light. Light with wavelengths in a range of approximately 400 to 800 nm is referred to as "visible light", and is the light that we humans can see with the naked eye. For example, light with a wavelength of 470 nm is blue, light with a wavelength of 540 nm is green, and light with a wavelength of 650 nm is red. Visible light could be described as the kind of light that we humans are familiar with because of our ability to actually see it.

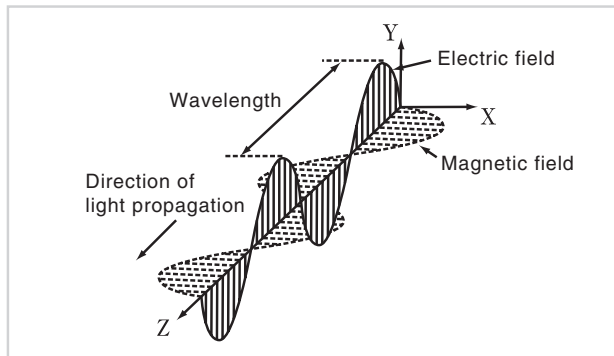


Fig.1 Electric Field and Magnetic Field in Light⁽¹⁾

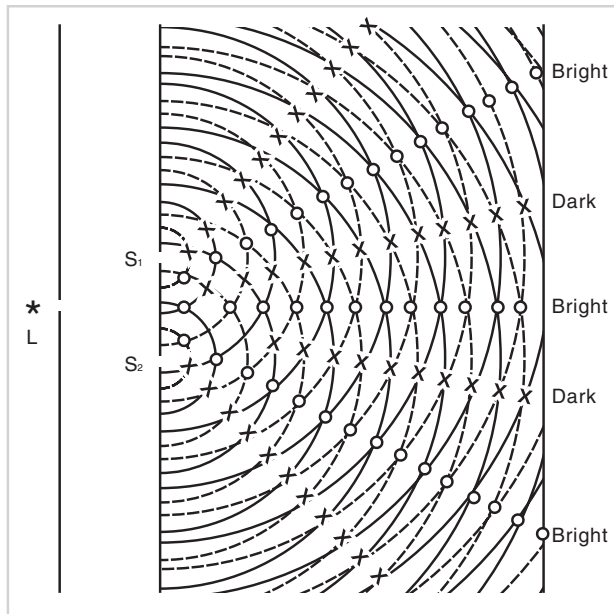


Fig.2 Young's Experiment⁽²⁾

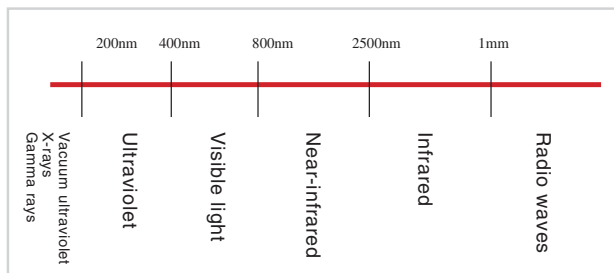


Fig.3 Classification of Light According to Wavelength

(2) Particle-Like Properties of Light

Next, let us look at the particle-like behavior of light. Among the developments that helped identify this behavior was a series of experiments on the photoelectric effect that were conducted in the late 19th century and the early 20th century. The results of these experiments could not be explained by considering light as a wave, but they could be explained by considering it as a particle. When emphasizing the particle-like aspects of light, the term "photon" is used.

Fig.4 illustrates the basic concept of the photoelectric effect, a phenomenon in which electrons are emitted from a metal surface when light strikes it. The emitted electrons are called "photoelectrons". Even though no electrons are emitted when intense light strikes the surface, electrons are emitted when light of a shorter wavelength strikes the surface. If the wavelength of the light striking the surface is decreased, the number of electrons emitted does not change, but the energy of the electrons increases. If the light striking the surface is intensified, the number of emitted electrons increases, but the energy of the electrons stays the same. These phenomena cannot be explained by considering light as a wave, but they can be explained by considering it as a particle, with electrons being knocked out by these particles when they strike the metal. In combination with results of experiments on the Compton effect and other experiments, the particle-like properties were recognized. Incidentally, the photomultiplier tube that is used as the detector in UV-VIS spectrophotometers detects light using the photoelectric effect.

We have looked at the dual nature of light, with its mixture of wave-like and particle-like properties. The fact that light has these two opposing characteristics may seem strange, but this is the way light is modeled in modern physics.

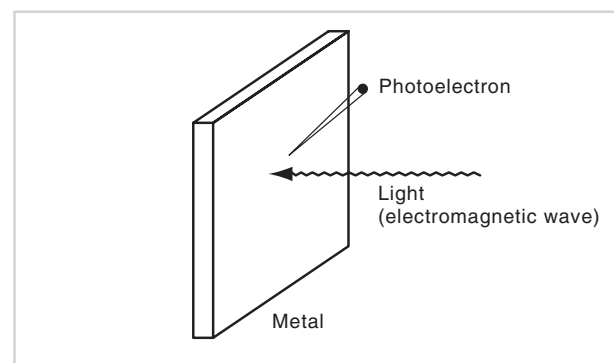


Fig.4 Concept of Photoelectric Effect³⁾

2.Absorption of Light by Matter

A wide variety of information about a substance can be obtained by irradiating it with light. With a UV-VIS spectrophotometer, irradiating a substance with ultraviolet and visible light makes it possible to obtain information about the electrons in that substance, and it is even possible to measure its quantity.

Let us consider the absorption of light by matter. This is closely related to quantum mechanics. The theory of quantum mechanics was developed in the early 20th century, and forms part of the basis of modern physics. Quantum mechanics can be easily understood by comparing it to Newtonian mechanics. Broadly speaking, Newtonian mechanics is a theory that relates to the motion of large particles, whereas quantum mechanics is a theory that relates to the motion of small particles (e.g., atoms and molecules). Newtonian mechanics handles the motion of particles as a continuous entity, whereas quantum mechanics asserts that small particles exist in discrete states of motion (energies). At the time when Newtonian mechanics was the dominant theory, the concept of quantum mechanics was difficult for people to accept. Over time, however, its validity was demonstrated.

Solving the equations of quantum mechanics that relate to the electrons in an atom gives a model, like that shown in Fig.5, in which the electrons have discrete energy states. E_0 is called the "ground state" and E_1 , E_2 , etc., are called "excited states". In order for an electron to switch from E_0 to E_1 , light with an energy of $(E_1 - E_0)$ must strike the electron. This is the "absorption" of light. Electrons have particular energy levels, and rays of ultraviolet and visible light have the energy to change the energy states of the electrons.

Because the higher energy state, E_1 , is unstable, the electron soon returns to the ground state, E_0 . The energy discharged when the electron returns from E_1 to E_0 ($E_1 - E_0$) is converted to heat. If, for some reason, it is not converted to heat, the energy is discharged as light. The phenomenon of light emission is well known as fluorescence or phosphorescence.

In relation to quantitative measurement performed with spectroscopy, the consequence of this phenomenon is that there is a large amount of absorption if a large number of target molecules exist in a solution, and only a small amount of absorption if there is only a small number of target molecules. Obtaining the quantity, and thereby the concentration, of a substance from the degree of absorption is the fundamental principle behind quantitative measurement.

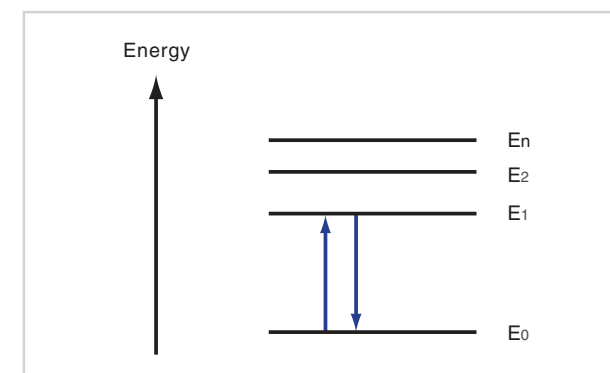


Fig.5 Energy Levels

The graph obtained by using the horizontal axis to represent the wavelength and the vertical axis to represent the degree of absorption is called an "absorption spectrum". The degree of absorption is expressed in terms of the unit "absorbance" (Abs). Fig.6 shows an absorption spectrum of β -carotene solution obtained with the Shimadzu UV-2550 UV-VIS spectrophotometer (Fig.7). β -carotene is the principle substance in carrots that gives them their color. As shown in Fig. 6, mainly blue and purple light of wavelengths in the range of 400 to 500 nm is absorbed. Because the visible light that reaches the eye of the observer consists of a mixture of the green and red components that are left over, carrots, which contain a large amount of β -carotene, appear to have a yellow-red coloring.

3.Summary

Here, we have looked at the properties of light and the way that it is absorbed, two fundamental aspects of the operation of a UV-VIS spectrophotometer. In the field of spectroscopy, in addition to UV-VIS spectrophotometers, there are various other types of spectroscopic measurement devices, such as infrared spectrophotometers, atomic absorption photometers, Raman spectrophotometers, and fluorescence spectrophotometers, all of which perform distinctive types of analysis. Using these devices selectively makes it possible to obtain various types of information about samples from different perspectives. In the next volume, we will describe the structure of a UV-VIS spectrophotometer.

- 1) Kanji Kihone: Measuring Light, Chapter 10
(Edited by the Illuminating Engineering Institute of Japan, Published by Nippon Riko Shuppankai, 1993), p. 172
- 2) Akira Harajima: Elementary Quantum Mechanics
(Shokabo, 1987), p. 3
- 3) Ryuzo Abe: Introduction to Quantum Mechanics
(Iwanami Shoten, Publishers, 1987), p. 31

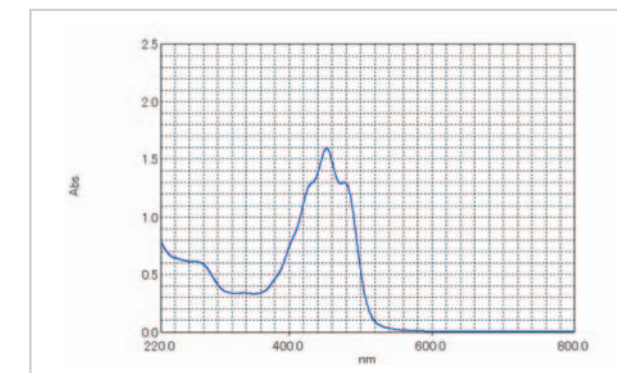


Fig.6 Absorption Spectrum of β -carotene



Fig.7 Shimadzu UV-2550 UV-VIS Spectrophotometer

Film-Thickness Measurement

The thickness of a single-layer film can be measured easily using a spectrophotometer. Note, however, that this is possible only for film thickness in a range of approximately 0.3 to 60 µm, and that the refractive index of the film material is required for measurement.

First, I will explain the principle of film-thickness measurement relative to reflection measurement. When light strikes the film at a certain angle, there is interference between light reflected from the incident surface (A) and light reflected from the opposite surface (B), as shown in Fig.1, and the undulating interference spectrum shown in Fig.2 is created. Counting the number of peaks (or valleys) in the interference spectrum within a certain wavelength range makes it possible to calculate the film thickness using expression (1).

$$d = \frac{\Delta m}{2\sqrt{n^2 - \sin^2 \theta}} \times \frac{1}{\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)} \quad (1)$$

Here, "d" is the film thickness, "Δm" is the number of peaks in the wavelength range used for calculation, "n" is the refractive index, "θ" is the angle of incidence with respect to the sample, and "λ₁" and "λ₂" are the start and end wavelengths in the wavelength range used for calculation.

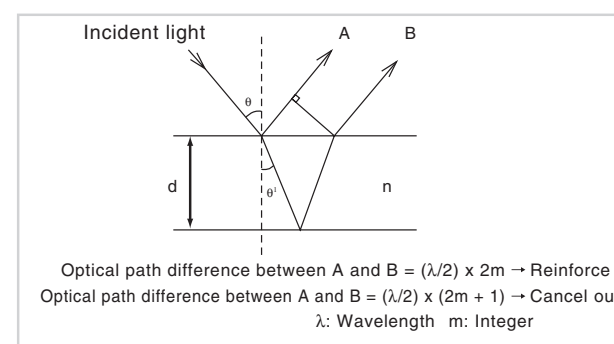


Fig.1 Principle of Interference

If film-thickness measurement software, which is sold as an option, is used, simply setting the wavelength range used for calculation and the refractive index makes it easy to calculate the film thickness, as shown in Fig.2. The "peak SD" value shown in Fig.2 is an indicator of the accuracy of the film-thickness calculation, and the calculation range is determined in accordance with this value.

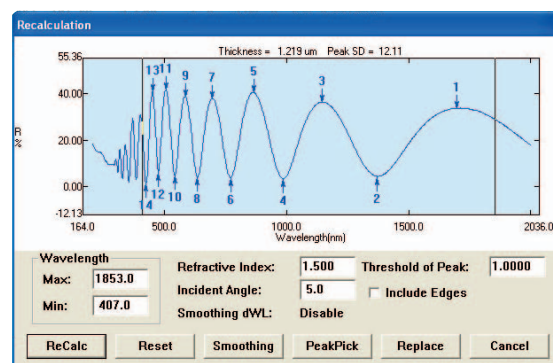


Fig.2 Recalculation Window of Shimadzu Film-Thickness Software

As shown in Fig.3 and Fig.4, the pitch of the waveform is longer for thinner films and shorter for thicker films.

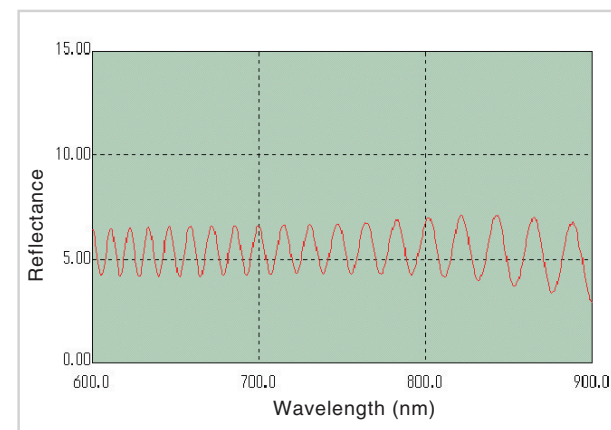


Fig.3 Film Thickness: 10 µm (Polyvinylidene Chloride Film)

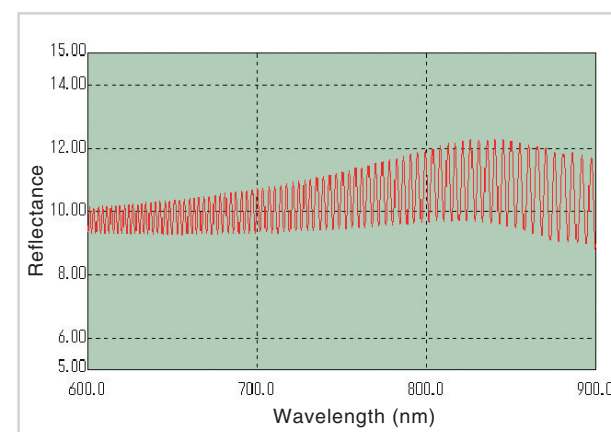


Fig.4 Film Thickness: 46 µm (Polycarbonate Film)

If the film is on an opaque substrate, such as a wafer, reflection measurement is used to measure its thickness. If the film is on a transparent substrate, or if only the film itself is subjected to analysis, transmission measurement can be used to measure its thickness. In film-thickness measurement, it is necessary that the surface of the film is clean and has a mirror finish. Measurement is not possible for samples with rough surfaces. Refer to Shimadzu Application News, No. A292, for details.

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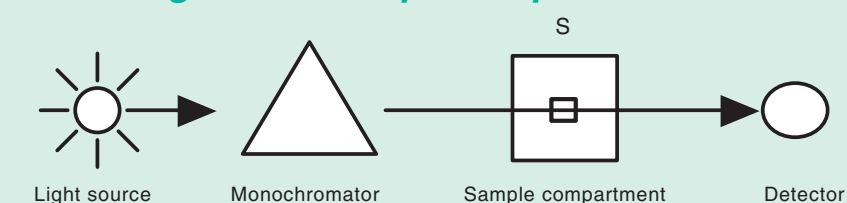
Q

What is the difference between a single-beam spectrophotometer and a double-beam spectrophotometer?

A

Spectrophotometers in which a single beam passes through the sample compartment are called "single-beam" and those with two beams are called "double-beam". As shown in the figure below, in a single-beam spectrophotometer, the monochromatic beam emitted from the monochromator is guided directly to the detector (i.e., there is only a sample beam), whereas in a double-beam spectrophotometer, the light emitted from the monochromator is divided into a sample beam and a reference beam before being guided to the detector. Single-beam spectrophotometers have a simpler configuration and are less expensive. In a spectrophotometer, the intensity of the light source and the sensitivity of the detector fluctuate over time. In configurations where only the sample beam is detected, if the intensity of the light source or the sensitivity of the detector changes between the time of baseline measurement and the time of sample measurement, errors will occur in measurement values. The reference beam performs the role of continuously monitoring these fluctuations and correcting for any influence they may have. With a double-beam spectrophotometer, then, stable measurement is possible even if the intensity of the light source or the sensitivity of the detector changes. On the other hand, single-beam spectrophotometers are directly affected by such changes. As a result, when using a single-beam spectrophotometer, steps must be taken to minimize the influence of these changes. This may consist of waiting for the light source and detector to stabilize after turning ON the power or frequently executing baseline and auto-zero corrections.

Single-Beam Spectrophotometer



Double-Beam Spectrophotometer

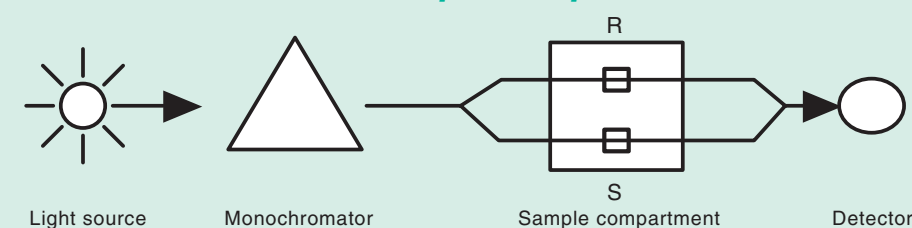


Fig. Basic Configurations of Single-Beam and Double-Beam Spectrophotometers