Reaching even greater heights

- Unprecedented sensitivity, thanks to a newly developed 3D optical system
- Advanced safety technology
- System configuration evolving to suit the needs of the user

High Performance

- The newly developed 3D optical system is capable of flame: Pb 0.015 ppm detection, and furnace: Pb 0.00005 ppm detection.
- Equipped with the world’s first* 1 vibration sensor, a multimode automatic gas leak check function, and other advanced safety technology.
- Evolving from the basic flame model to suit the needs of the user.
- The dual atomizer system* 2 is the world’s smallest* 1, and a furnace model is also available.

*1 Survey by Shimadzu in November 2008.
*2 The optional auto atomizer changer is required.

Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries. For information about Shimadzu, and to contact your local office, please visit our Web site at www.shimadzu.com
UV Talk Letter
The Structure of a Spectrophotometer

1. The Measurement Principle Used by a Spectrophotometer

The basic measurement principle used by a spectrophotometer is relatively simple and easy to understand. I will explain the principle as it applies to solid samples and solution samples separately.

(1) Solid Samples

As shown in Fig. 1, first the intensity of the measurement light beam, I₀, is measured without the sample cell. Then the sample is set into the path of the measurement light beam, and the intensity of the light beam after it passes through the sample, I₁, is measured.

\[ T = \frac{I_0}{I_1} \]  

(1)

The product of the transmittance, T, and 100 is the percent transmittance (%) of the sample.

(2) Solution Samples

As shown in Fig. 2, a cell containing solvent is set in the path of the measurement light beam, and the intensity of the light beam after it passes through the cell, I₂, is measured.

\[ T = \frac{I_0}{I_2} \]  

(2)

The product of the transmittance, T, and 100 is the percent transmittance (%) of the solution.

2. The Configuration of a Spectrophotometer

You will find from the above explanation that the indispensable elements of a spectrophotometer consist, as shown in Fig. 3, of a light source, a monochrometer, a sample compartment, and a detector. This method is employed in high-speed photometry instruments that are array detectors. In the next sections, I will give an explanation of each element.

3. Light Source

The desirable properties of a light source are as follows:

a) Brightness across a wide wavelength range
b) Spectrally pure

c) A long service life
d) Low cost

Although there are no light sources that have all of these properties, the most commonly used light sources at the moment are the halogen lamp used for the visible and near-infrared regions and the deuterium lamp used for the ultraviolet region. Apart from these, xenon flash lamps are sometimes used.

4. Monochrometer

Spectroscopy is the technique of splitting light into components that correspond to those wavelengths. The element that splits this light is called a dispersive element. Prisms and diffraction gratings are typical dispersive elements. Prisms used to be commonly used as the dispersive elements in spectrophotometers, but recently, grating diffraction gratings have become the most commonly used type of dispersive element. The grating diffraction gratings used in spectrophotometers have several hundred to approximately 2,000 parallel grooves per millimeter cut into a glass plate at an angle of 60°. An example of a glass plate is shown in Fig. 4. If this grating is exposed to white light, because of interference, the white light is dispersed in a direction perpendicular to the grooves, and light components of specific wavelengths are reflected only in specific directions. This is illustrated in Fig. 7 to 9, to represent wavelength. The wavelengths change continuously and so if it is a grating diffraction grating exposed to white light, it appears indiscernible. The way that the clear side of a CD appears to glitter with iridescence when it is exposed to light is based on the same mechanism as the spectroscopy performed with a diffraction grating.

A monochrometer consists of an entrance slit, an exit slit, and a diffraction grating, as well as the mirrors and other parts that come with them. Although various types of monochrometers, which vary according to the arrangement of the elements, have been devised, Fig. 6 shows an example of the standard monochrometer configuration, which uses a concave diffraction grating. Light of varying wavelengths is projected from the exit slit by rotating the concave diffraction grating.

5. Sample Compartment

Fig. 9 shows an example of a standard sample compartment. You can see that two light beams (indicated by notches in Fig. 10) pass through the compartment, and that this is therefore the sample compartment of a "double-beam spectrophotometer." The monochromatic light that leaves the spectrometer is split into two beams before it enters the sample compartment. A spectrophotometer in which only one beam passes through the sample compartment is called a "single-beam spectrophotometer." An explanation of the difference between single-beam and double-beam spectrophotometers is given in the Q&A of previous issue of UV Talk Letter. Refer to this explanation if necessary.

In a standard configuration, the sample compartment contains cell holders that, as shown in Fig. 11, hold square cells with optical path lengths of 10 mm. The various accessories are attached by replacing the cell holder units or by replacing the entire sample compartment. Among spectrophotometers of medium or higher grade that use photomultipliers, which will be described later, as detectors, there are models for which large sample compartments are made available in order to allow the analysis of large samples or the attachment of large accessories.
The Measurement Principle Used by a Spectrophotometer

The basic measurement principle used by a spectrophotometer is relatively simple and easy to understand. It explains the principle on which it operates by comparing the light samples and solution samples separately.

(1) Solid Samples

As shown in Fig. 1, the absorbance of the measurement light beam, \( A \), is measured without the sample. Then, the sample is set in the path of the measurement light beam, and the intensity of the light beam after it passes through the sample, \( I_t \), is measured.

The product of the transmittance, \( T \), and 100 is the percent transmittance (%T).

\[ T = \frac{I_s}{I_o} \]  

(2) Solution Samples

As shown in Fig. 3, a cell containing a solution is set in the path of the measurement light beam, and the intensity of the light beam after it passes through the cell, \( I_s \), is measured. The absorbance, \( A_s \), is given by equation (2).

\[ A_s = \log \left( \frac{I_o}{I_s} \right) \]  

Equation (3), which expresses the relationship between the absorbance, \( A_s \), and the sample concentration, \( c \), is called the Lambert-Beer law. There is a proportional relationship between the absorbance and concentration; and this forms the basis of quantitative analysis.

If this diffraction grating is exposed to white light, because of interference, light is divided into a number of parallel, closely spaced fringes at equal intervals. An example of a diffraction grating is shown in Fig. 6.

A monochromator consists of an entrance slit, an exit slit, and a diffraction grating element that splits this light. Prisms and diffraction gratings have become the most commonly used types of dispersive elements.

Spectroscopy is the technique of splitting light that consists of various wavelengths into components that correspond to those wavelengths. The element that splits this light is called a dispersive element. Prisms and diffraction gratings are typical dispersive elements.

A monochromator consists of an entrance slit, an exit slit, and a diffraction grating element that splits this light. The diffraction grating element of a spectrophotometer has several hundred to approximately 2,000 parallel grooves per millimeter cut into it.

Spectrophotometers that use grating elements as the dispersive element are called “grating spectrophotometers” because the dispersed light is monitored with photomultipliers, photodiode array detectors, or similar devices.

The spectrophotometer used in this research system is a grating spectrophotometer. The diffraction grating used in a spectrophotometer is called a “diffraction grating.”

(1) Halogen Lamp

The intensity of light emitted is the same as that for a standard incandescent bulb. Electric current is supplied to a filament, the filament becomes hot, and light is emitted. The bulb is a halogen lamp filled with inert gas and a small amount of a halogen. While the target temperature of the filament is high, the halogen causes the tungsten to return to the filament. This helps create a bright light source with a long-service life. The emission intensity distribution of a halogen lamp can be approximated using Planck’s law of radiation. Fig. 4 shows the emission intensity distribution for a temperature of 3,000 K. A halogen lamp offers superior temporal stability, a service life of 3,000 hours, and a relatively low cost. It has relatively high levels of each of the properties a) to d) mentioned above.

(Deuterium Lamp)

A deuterium lamp is a discharge light source in which the bulb is filled with deuterium (D2) at a pressure of several hundred pascals. Fig. 5 shows the emission intensity distribution for a deuterium lamp. Although 400 nm is, in general, an approximate usage limit at the long wavelength end because the degree of attenuation at this end is quite low, light of wavelengths greater than 400 nm is used. In the region beyond 400 nm, there are also large numbers of bright line spectra. Among these, the bright line spectra at 466.0 nm and 464.1 nm are particularly intense, and can be used for the wavelength calibration of spectrophotometers. The usage limit at the short wavelength end is determined by the transmittance of the window material. In Fig. 5, the graphs for cases where synthetic silica and UV glass are used are given as examples.

4. Monochromator

Spectroscopy is the technique of splitting light that consists of various wavelengths into components that correspond to those wavelengths. The element that splits this light is called a dispersive element. Prisms and diffraction gratings are typical dispersive elements.

A spectrophotometer consists of a light source, a monochromator, a sample compartment, and a detector. Although various types of monochromators, which vary according to the arrangement of the elements, have been devised, Fig. 6 shows an example of the simplest monochromator configuration, which uses a concave diffraction grating. Light of varying wavelength is projected from the output slit by rotating the concave diffraction grating.

A monochromator consists of an entrance slit, an exit slit, and a diffraction grating. As well as the mirrors and other parts that come with it. Although various different monochromator types are available, they are made available in order to allow the analysis of large samples or the attachment of large accessories.

5. Sample Compartment

Fig. 9 shows an example of a standard sample compartment. You can see that two light beams (indicated by notches in Fig. 9) pass through the compartment, and that this is therefore the sample compartment of a “double-beam spectrophotometer.” The monochromatic light that leaves the spectrophotometer is split into two beams before it enters the sample compartment. A spectrophotometer that has only one beam pass through the sample compartment is called a “single-beam spectrophotometer.” An explanation of the differences between single-beam and double-beam spectrophotometers is given in the Q&A of previous issue of UV Talk Letter. Refer to this explanation if necessary.

In a standard configuration, the sample compartment contains cell holders, as shown in Fig. 9. Hold square cells with optical path lengths of 10 mm. The various accessories are attached by replacing these cell holder units or by replacing the entire sample compartment. Among spectrophotometers of medium or higher grade that use photomultipliers, which will be described later, as detectors, there are models for which large sample compartments are available in order to allow the analysis of large samples or the attachment of large accessories.
6. Detector

The light beams that pass through the sample compartment enter the detector, which is the last element in the spectrophotometer. Photomultipliers and silicon photodiodes are typical detectors used with spectrophotometers for the ultraviolet and visible regions. For the near-infrared region, PIG photodiodes have always been used. However, for spectrophotometers incorporating InGaAs photodiodes, which have been used in the visible region, a special power supply is not required. Even regarding sensitivity, if compared with photomultipliers, silicon photodiodes offer advantages such as relatively small light intensity. The most important feature of a photomultiplier is that it achieves a significantly high level of sensitivity that cannot be obtained with other optical sensors, if there is sufficient light intensity. This feature becomes increasingly useful. For this reason, photomultipliers are used in high-grade instruments. The spectral sensitivity characteristics of a photomultiplier are mainly determined by the material of the photodiode surface. Fig. 10 shows an example of the spectral sensitivity characteristics of a multi-alkali photoelectric surface, a type of surface that is often used in spectrophotometers.

(2) Silicon Photodiode

A silicon photodiode is a detector that uses the fact that photocurrent is emitted from a photoelectric surface when it is exposed to light. Unlike a photomultiplier, the photocurrent emitted from the photoelectric surface is proportional to the incident light intensity. Moreover, since it is not necessary to use a special power supply, it has the advantage that it is easier to use. A silicon photodiode is often used in the visible region and near-infrared region.

7. Summary

Here, I have given an overview of the structure of UV-VIS spectrophotometers. Due to space limitations, I have only described the detector, which is the last element in the spectrophotometer. Photomultipliers and silicon photodiodes are typical detectors used with spectrophotometers for the ultraviolet and visible regions. For the near-infrared region, PIG photodiodes have always been used. However, for spectrophotometers incorporating InGaAs photodiodes, which have been used in the visible region, a special power supply is not required. Even regarding sensitivity, if compared with photomultipliers, silicon photodiodes offer advantages such as relatively small light intensity. The most important feature of a photomultiplier is that it achieves a significantly high level of sensitivity that cannot be obtained with other optical sensors, if there is sufficient light intensity. This feature becomes increasingly useful. For this reason, photomultipliers are used in high-grade instruments. The spectral sensitivity characteristics of a photomultiplier are mainly determined by the material of the photodiode surface. Fig. 10 shows an example of the spectral sensitivity characteristics of a multi-alkali photoelectric surface, a type of surface that is often used in spectrophotometers.

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A silicon photodiode is a detector that uses the fact that electrical properties of a detector change when it is exposed to light. Unlike a photomultiplier, the photocurrent emitted from the photoelectric surface is proportional to the incident light intensity. Moreover, since it is not necessary to use a special power supply, it has the advantage that it is easier to use. A silicon photodiode is often used in the visible region and near-infrared region.

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6. Detector
The light beams that pass through the sample compartment enter the detector, which is the last element in the spectrophotometer. Photomultipliers and silicon photodiodes are typical detectors used with spectrophotometers for the ultraviolet and visible regions. For the near-infrared region, FDS photoconductors have been used in the past, but recently, instruments incorporating indium-arsenic photodiodes have been sold. Silicon photodiode array detectors are used in combination with the back spectroscopy method, for high-speed photometry instruments. Photomultipliers and silicon photodiodes are described below.

(1) Photomultiplier
A photomultiplier is a detector that uses the fact that photoelectrons are discharged from a photoelectric surface when it is subjected to light (i.e., the external photoelectric effect). The photoelectrons emitted from the photoelectric surface repeatedly cause secondary electron emission in sequentially arranged dynodes, ultimately producing a large output for a relatively small light intensity. The most important feature of a photomultiplier is that it achieves a significantly high level of sensitivity that cannot be obtained with other optical sensors, and there is sufficient light intensity, this feature is not particularly relevant. But as the light intensity decreases, this feature becomes increasingly useful. For this reason, photomultipliers are used in high-grade instruments. The spectral sensitivity characteristics of a photomultiplier are mainly determined by the material of the photoelectric surface. Fig. 10 shows an example of the spectral sensitivity characteristics of a multi-alkali photoelectric surface, a type of surface that is often used in spectrophotometers.

(2) Silicon Photodiode
A silicon photodiode is a detector that uses the fact that the electrical properties of a detector change when it is exposed to light (i.e., the internal photoelectric effect). Solar cells, which have attracted much attention recently, use the same structure and principle as silicon photodiodes. In comparison with photomultipliers, silicon photodiodes offer advantages such as low cost, little locality of sensitivity in the light-receiving surface, and the fact that a special power supply is not required. Even regarding sensitivity, if the light intensity is relatively large, they can obtain photometric data that is no inferior to that obtained with photomultipliers. Fig. 11 shows an example of the spectral sensitivity characteristics of a silicon photodiode.

7. Summary
Here, I have given an overview of the structure of UV-VIS spectrophotometers. Due to space limitations, I have only described the basics. In the future, I plan to give more detailed explanations about specialized topics. I look forward to your continued interest.

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References
2. Hamamatsu Photonics (2014). New Coccine and Brilliant Blue FCF.

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The Relationship Between UV-VIS Absorption and Structure of Organic Compounds

There are many colored organic compounds, such as dyes and pigments. How is it that these colors come about? There is a close relationship between the color of an organic compound and its structure. Here, I will explain this relationship using absorption spectra of organic compounds obtained with Shimadzu’s UV-2550 UV-VIS spectrophotometer.

1. The Relationship Between Conjugated Double Bond Systems and Absorption Peaks

There are many organic compounds that have conjugated double bond systems (hereafter referred to as “conjugated systems”), in which every other bond is a double bond. These conjugated systems have a large influence on peak wavelengths and absorption intensities.

Fig. 1 shows the structures of benzene, naphthalene, and anthracene. Fig. 2 shows the absorption spectra obtained by dissolving these compounds in ethanol and analyzing the resulting solutions. The concentrations were adjusted so that the absorption intensities of the components were roughly the same. It can be seen in Fig. 2 that peak wavelengths tend to be shifted toward the long wavelength region as the conjugated system gets larger. Table 1 gives the peak wavelengths and the molar absorption coefficients of various organic compounds. The molar absorption coefficient is a measurement of how strongly a substance absorbs light. The larger its value, the greater the absorption. With larger conjugated systems, the absorption peak wavelengths tend to be shifted toward the long wavelength region and the absorption peaks tend to be larger.

2. Absorption Spectra of Food Dyes with Large Conjugated Systems

Fig. 3 shows the structures of food dyes New Coccine (Red No. 102) and Brilliant Blue FCF (Blue No. 1). and Fig. 4 shows their absorption spectra. Food dyes tend to have large conjugated systems, like those shown in Fig. 3, and therefore their peak wavelengths tend to be shifted toward the long wavelength region, with peaks appearing in the visible region (450 to 700 nm). This is why they are recognized as colors. Incidentally, the color that we see is the color that is not absorbed by the substance (which is called the “complementary color”). As shown in Fig. 4, New Coccine absorbs blue and green light in the range 450 to 550 nm, and so the complementary color, red, is seen by the human eye. Brilliant Blue FCF absorbs yellow light in the range 560 to 650 nm and so blue is seen by the human eye.

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Table 1: Absorption Peaks and Molar Absorption Coefficients of Various Organic Substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Absorption Peak (nm)</th>
<th>Molar Absorption Coefficient (M Abs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>247</td>
<td>6000</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>300</td>
<td>11000</td>
</tr>
<tr>
<td>Anthracene</td>
<td>353</td>
<td>15000</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>267</td>
<td>16000</td>
</tr>
<tr>
<td>β-carotene</td>
<td>445</td>
<td>14000</td>
</tr>
<tr>
<td>Vitamin A</td>
<td>356</td>
<td>1800</td>
</tr>
<tr>
<td>Anthracene</td>
<td>400</td>
<td>180</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>365</td>
<td>1400</td>
</tr>
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</tr>
</tbody>
</table>

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Fig. 1 Structures of Benzene, Naphthalene, and Anthracene

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Fig. 2 Absorption Spectra of Benzene, Naphthalene, and Anthracene

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Fig. 3 Structures of New Coccine and Brilliant Blue FCF

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Fig. 4 Absorption Spectra of Food Dyes New Coccine and Brilliant Blue FCF
3. The Influence of Functional Groups
Absorption peaks are also influenced by functional groups. Fig. 5 shows the absorption spectra of benzene, phenol, which consists of a hydroxyl group bonded to a benzene ring, and p-nitrophenol, which consists of a hydroxyl group and a nitro group bonded to a benzene ring. The functional groups influence the conjugated systems, causing the absorption peaks to appear at longer wavelengths than the peak wavelength of benzene, although they do not go beyond 400 nm and enter the visible region. The color of organic compounds, then, is influenced more strongly by the size of the conjugated system.

4. Absorption Spectra of Compounds with a Large Molecular Framework and a Small Conjugated System
Fig. 7 shows the absorption spectra of prednisolone, which is used as a pharmaceutical, and benzene. Although prednisolone has a large molecular framework, its conjugated system is small and so its peak wavelengths are not shifted greatly toward the long wavelength region, and its peaks appear at roughly the same position as those of benzene.

5. The Reason for the Shift Toward the Long Wavelength Region
I have shown the relationship between molecular structure and absorption spectra. Why, then, does the peak wavelength tend to appear in regions where \( \lambda \) is large, i.e., the long wavelength region? Let us consider the relationship between the energy of light and the movement of electrons.

Light exhibits properties of both waves and particles (photons). The energy of one photon is expressed as \( hc/\lambda \), where \( h \) is Planck’s constant, \( c \) is the speed of light, and \( \lambda \) is the wavelength.

Absorption in the ultraviolet and visible regions is related to the transition of electrons. “Transition” refers to the switching of an electron from one state of motion to another. The state of motion of the \( \pi \) electrons in the conjugated system changes more easily than that of the \( \sigma \) electrons that form the molecular frameworks. If a photon collides with a \( \pi \) electron, that \( \pi \) electron readily changes to a different state of motion. This is true even if the photon has only a small amount of energy. The \( \pi \) electrons in relatively large conjugated systems are more easily affected by low-energy photons. Transition expresses the way that the energy of photons is absorbed by electrons. If a photon has a relatively small amount of energy, the value of \( hc/\lambda \) for that photon is relatively small, and therefore the value of \( \lambda \) is relatively large. \( \lambda \) is observed as the absorption wavelength and so, if there is a conjugated system, peaks tend to appear in regions where \( \lambda \) is large, i.e., the long wavelength region.

References

Mikio Sugisaka
Applications Development Center, Analytical Applications Department, Analytical & Measuring Instruments Division

The term “stray light” appears in product brochures. What is this exactly?

“Stray light” is light of any wavelength contained in the light used in a spectrophotometer that differs from the set target wavelength. It is expressed as the ratio (%) of the total amount of light of wavelengths other than the target wavelength to the amount of light of the target wavelength. Fig. 1 shows the graphic illustration of stray light. In Fig. 1, the blue section corresponds to the target wavelength and the gray section corresponds to stray light. Checks for stray light are performed using filters (e.g., NaI solution filter and NaNO₃ solution filter) that do not allow light of specific wavelengths to pass through. The measurement wavelength is set to the wavelength that should be completely absorbed by the filter, the actual transmittance is measured, and from this the amount of stray light is calculated.

Stray light is a problem because it influences the linearity of the calibration curves used for quantitative analysis. This influence is hardly observed at all in low-absorbance regions, but if there is a lot of stray light in high-absorbance, high-concentration regions, the calibration curve is prone to bend. (See Fig. 2.) The wavelength of stray light differs from the target wavelength and so it is not absorbed by the sample. Light of wavelengths other than the target wavelength passes through the sample without being absorbed and so, in accordance with the Lambert-Beer law, the measured absorbance is less than the true value. Even if the calibration curve is bent, quantitative analysis is still possible using quadratic expressions. However, because the sizes of changes in absorbance with respect to the sizes of changes in sample concentration decrease, the quantitative error increases.

In general, the level of stray light is lower with double-monochromator instruments than it is with single-monochromator instruments.
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References

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Q&A
What Is Stray Light?

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Fig. 5 Absorption Spectra of Benzene, Phenol, and p-Nitrophenol

Fig. 6 Structures of Phenol and p-Nitrophenol

Fig. 7 Absorption Spectra of Prednisolone and Benzene

Fig. 8 Structures of Prednisolone and Benzene

Fig. 1 Graphic Illustration of Stray Light

Fig. 2 Change in Calibration Curve due to Stray Light
AA-7000 Series
Shimadzu Atomic Absorption Spectrophotometers

Reaching even greater heights
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- Advanced safety technology
- System configuration evolving to suit the needs of the user

High Performance
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Founded in 1875, Shimadzu Corporation, a leader in the development of advanced technologies, has a distinguished history of innovation built on the foundation of contributing to society through science and technology. We maintain a global network of sales, service, technical support and applications centers on six continents, and have established long-term relationships with a host of highly trained distributors located in over 100 countries. For information about Shimadzu, and to contact your local office, please visit our Web site at www.shimadzu.com