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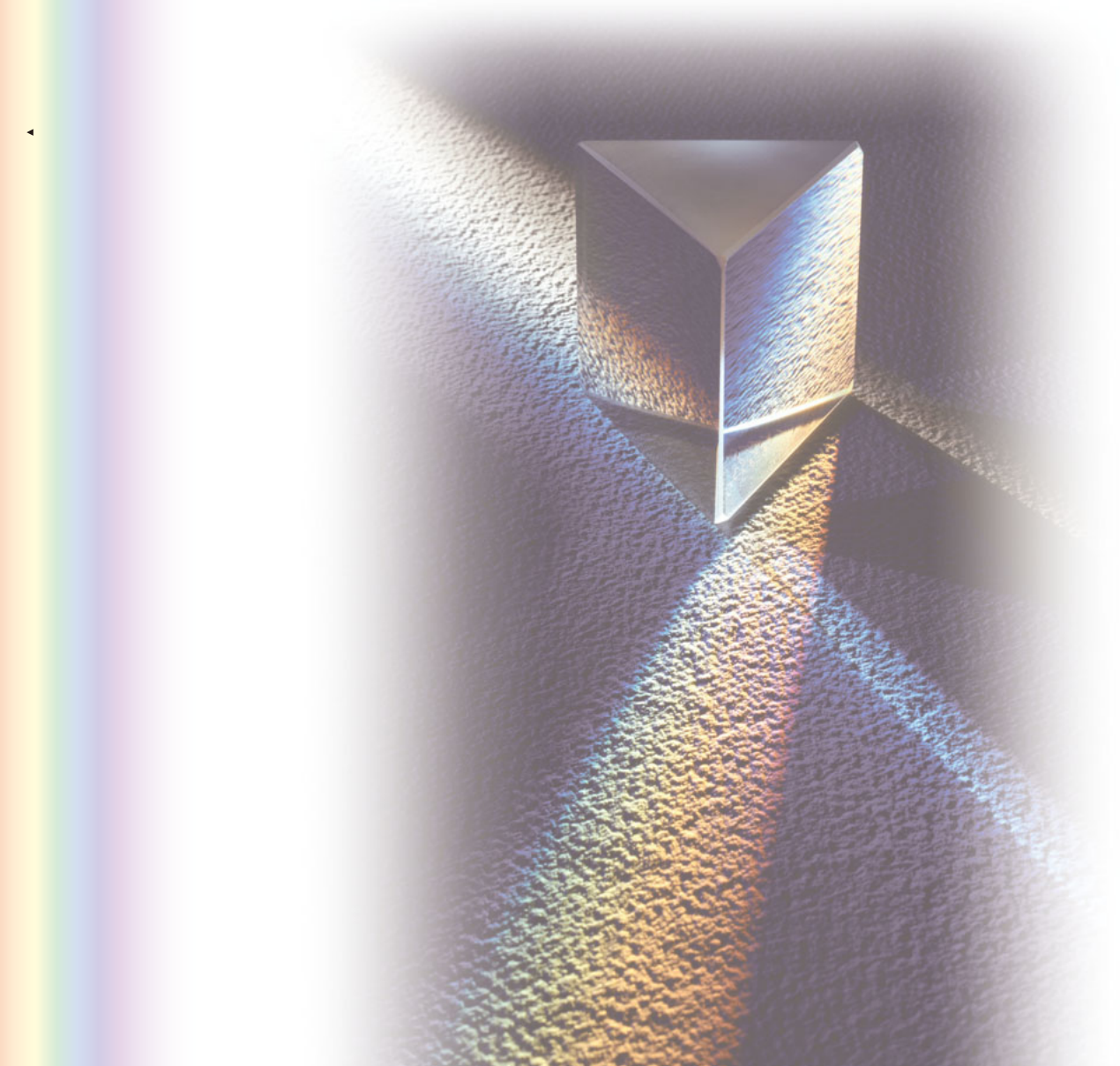
UV Talk Letter

Vol.4 March 2010



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Detectors

In the context of spectrophotometers, the term "detector" refers to a light-receiving element that absorbs the energy of light and consequently induces an electrical change. Types of photoelectric conversion include the external photoelectric effect, a prominent form of which is photoelectric emission from a photoelectric surface into a vacuum, and the internal photoelectric effect, in which photoelectrons are excited into a conduction band. One representative example of a detector based on the former type of photoelectric emission is the photomultiplier tube. Here, of the various aspects of spectrophotometers described in UV Talk Letter Vol. 2, "The Structure of a Spectrophotometer," we will look more closely at these "detectors."

1.Introduction

The mechanism for sensing light and converting it to signals that we are most familiar with is the human optic nerve. The human eye senses light in a wavelength range of approximately 400 to 700 nm, and sends signals to the brain through nerve tissue. You could say that the eye is the optical detector of visible light that we are most familiar with. The human eye is sensitive to light in the visible region, and is most sensitive to green light with a wavelength of around 550 nm. In the same way, the detectors in spectrophotometers also have a wavelength range that they can be used for, and their sensitivity varies with the wavelength. Representative detectors with sensitivity in the ultraviolet and visible region include the photomultiplier tube and the silicon photodiode. Regarding near-infrared detectors, PbS photoconductive elements were used exclusively in the past, although nowadays there are instruments in which InGaAs photodiodes are used for part of the near-infrared region. Fig. 2 shows the relationship between various detectors and wavelength ranges.

2.Photomultiplier Tube

A photomultiplier tube utilizes the external photoelectric effect, the phenomenon whereby photoelectrons are discharged when light strikes a photoelectric surface. Fig. 3 illustrates the operating principle of a photomultiplier tube. Photoelectrons discharged from a photoelectric surface (i.e., primary electrons) cause the successive emission of secondary electrons from dynodes (electron-multiplier electrodes) arranged in multiple stages, and this cascade ultimately reaches an anode. If one primary electron causes the emission of δ secondary electrons, and this process is repeated n times, then a multiplication factor of δ^n is obtained. Because photomultiplier tubes ultimately produce a large output for a low level of light intensity, their most important feature is that they offer an outstanding level of sensitivity, which cannot be obtained with other optical sensors. δ is referred to as the "secondary emission coefficient." A high voltage (-HV) is applied from outside the tube in order to accelerate the electrons.

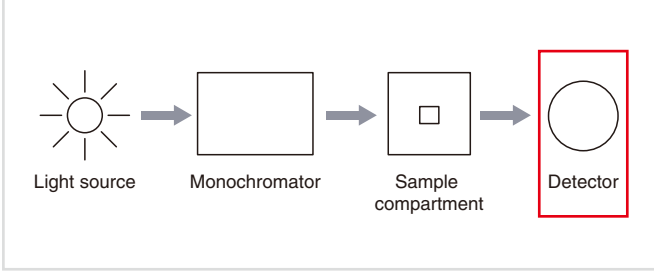

Fig.1 Structure of a Spectrophotometer

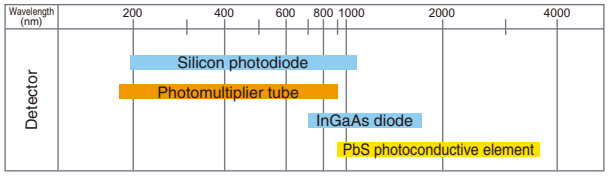

Fig.2 Detectors and Wavelength Ranges

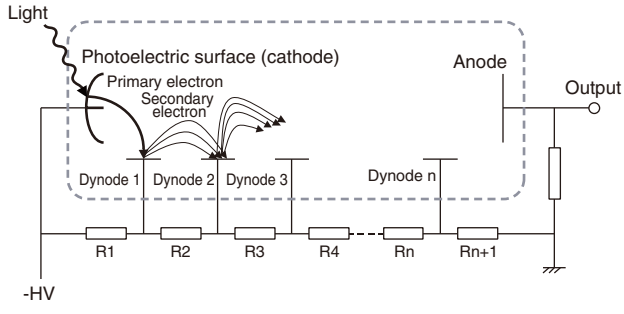

Fig.3 Operating Principle of Photomultiplier Tube

The higher the value of this voltage, the larger the secondary emission coefficient. Another feature of a photomultiplier tube, then, is that the multiplication factor can be adjusted by controlling this high voltage. If there is sufficient light intensity, the voltage is decreased. If the light intensity decreases, the voltage is increased. If the slit is changed, or if accessories that cause significant decreases in light intensity, such as integrating spheres, are used, the advantages offered by this photomultiplier tube become particularly important. For this reason, photomultiplier tubes are used in high-grade instruments.

The relationship between the sensitivity of a photoelectric surface and the wavelength of incident light is referred to as the "spectral sensitivity characteristic." It is mainly determined by the material of the photoelectric surface. Fig. 4 shows the spectral sensitivity characteristic of a multi-alkali photoelectric surface that has sensitivity in the ultraviolet and visible region.

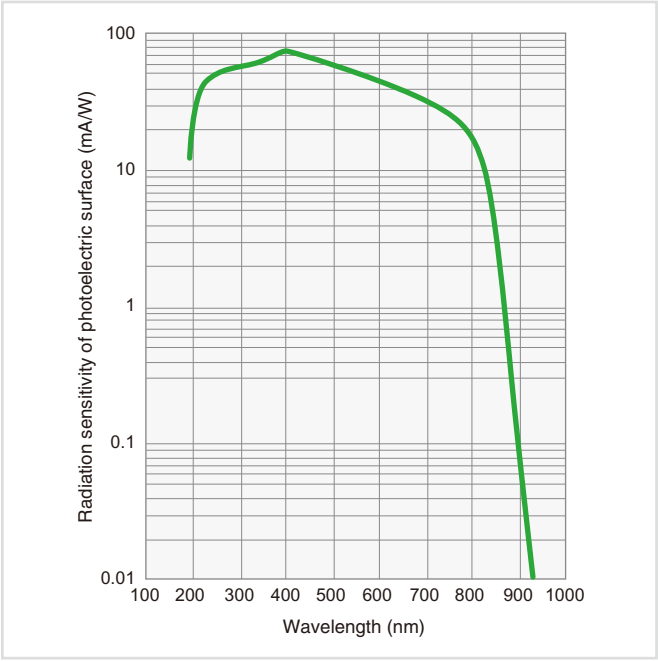

Fig.4 Spectral Sensitivity Characteristic of Photomultiplier Tube[2)]

3.Silicon Photodiode

A silicon photodiode utilizes the internal photoelectric effect, the phenomenon whereby the electrical properties of the detector itself change when light strikes it. As the name suggests, a silicon photodiode is a semiconductor. When light strikes this semiconductor, if the energy of the light is larger than the band gap, electrons in the valence band are excited into the conduction band, and holes are left in the original valence band. As shown in Fig. 5, these electron-hole pairs are created throughout the semiconductor, but in the depletion region, the electric field causes electrons to be accelerated toward the N-region and holes to be accelerated toward the P-region. As a result, electrons accumulate in the N-region and holes accumulate in the P-region, and the two regions become, respectively, negatively and positively charged. If this is connected to a circuit, current flows.

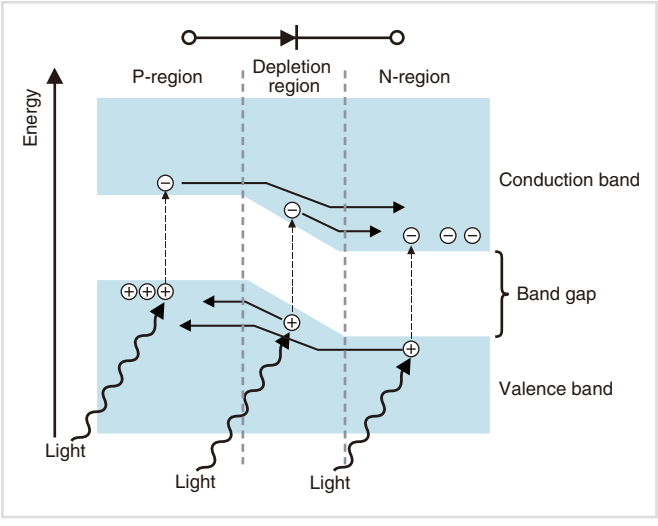

Fig.5 Energy Model of Silicon Photodiode

The band gap of silicon is approximately 1.12 eV, so current flows only for wavelengths that have an optical energy greater than this. This works out to a wavelength upper limit of around 1,100 nm. Fig. 6 shows the spectral sensitivity characteristic of a silicon photodiode.

Silicon photodiodes have some advantages over photomultiplier tubes: they are less expensive; there is little unevenness of sensitivity over their light-receiving surfaces; and they do not require a dedicated power supply. Even with respect to sensitivity, if the light intensity is relatively high, they can provide photometric data that is by no means inferior to that obtained with photomultipliers. If the light intensity is relatively low, however, because signals are amplified in the electronic circuit that gives a current, increasing the amplification factor decreases the response speed.

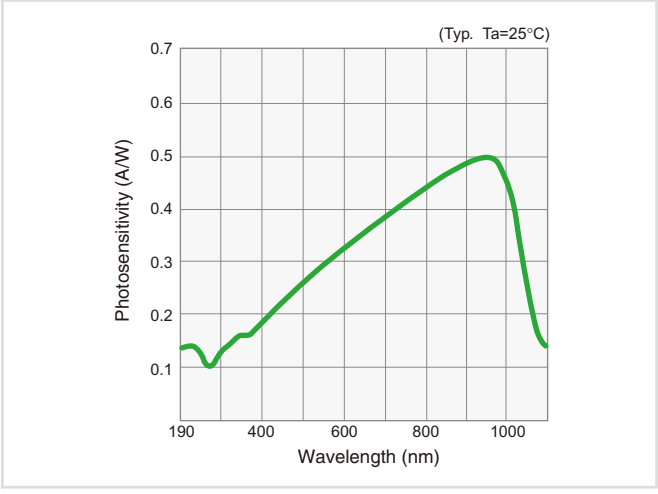

Fig.6 Spectral Sensitivity Characteristic of Silicon Photodiode[3)]

4. InGaAs Photodiode

Indium gallium arsenide (InGaAs) is a compound semiconductor. Like a silicon photodiode, an InGaAs photodiode is a photovoltaic element that has a P-N junction. The band gap energy of InGaAs, however, is smaller than that of silicon, so it absorbs light of longer wavelengths. This means that InGaAs photodiodes are sensitive to wavelengths that exceed the range of silicon photodiodes. Fig. 7 shows the spectral sensitivity characteristic of an InGaAs photodiode.

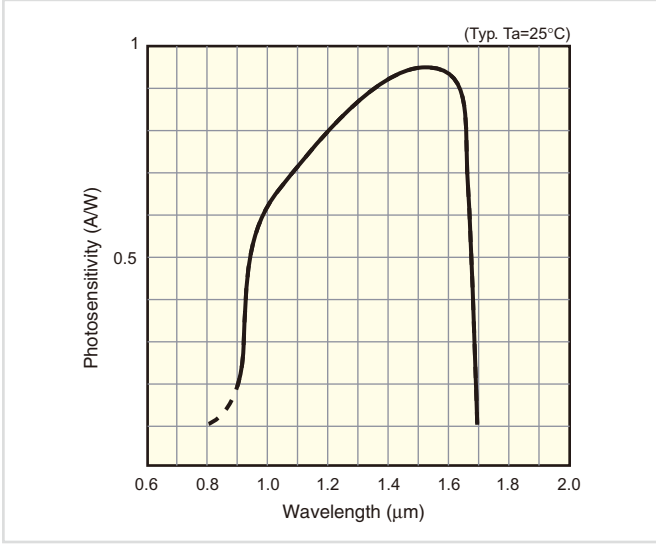

Fig.7 Spectral Sensitivity Characteristic of InGaAs Photodiode[3)]

5. PbS Photoconductive Element

A photoconductive element is a photoelectric conversion element that utilizes the phenomenon of photoconduction, whereby the electrical conductivity (resistance) of a material changes when it is irradiated with light. Fig. 8 illustrates the operating principle. When light of energy greater than the energy gap between the conduction band and the valence band strikes the element, electrons in the valence band are excited into the conduction band, and holes are created in the valence band. With a PbS photoconductive element, the resistance is reduced in accordance with the intensity of incident light, and this is obtained as a signal using an external circuit.

If the element is cooled, the spectral sensitivity characteristic shifts to the long-wavelength end; as a result, the element becomes more sensitive to longer wavelengths. At the same time, however, the response speed decreases. Although PbS photoconductive elements can, unlike some other near-infrared detection elements, be used at room temperature, they are still delicate elements for which the sensitivity, response speed, and dark resistance change according to the temperature. Fig. 9 shows the spectral sensitivity characteristic of a PbS photoconductive element.

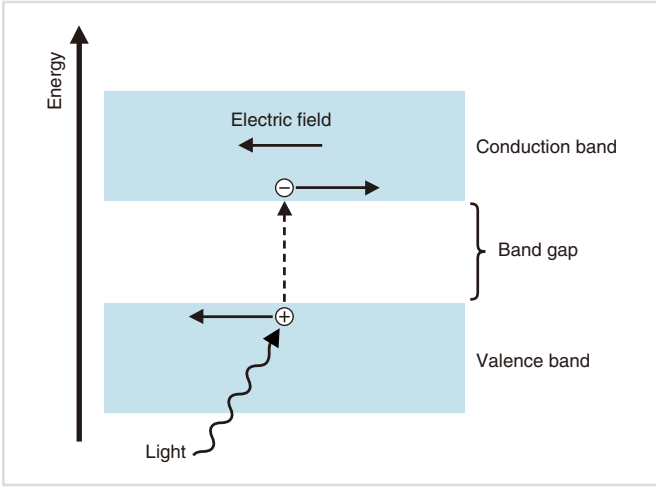

Fig.8 Operating Principle of Photoconductive Element

6. Summary

Here, we have looked at detectors that convert light to electrical signals.
Although it does not require consideration in the analysis of solution samples, when performing transmission measurement for solid samples of a certain thickness, such as glass plates and lenses, the form of the light beam that strikes the detector may vary according to whether or not the sample is present. In this case, unevenness of sensitivity over the detecting surface of the detector can cause measurement errors. An accessory called an "integrating sphere" allows measurement to be performed without being influenced by this unevenness of detector sensitivity.

In the next issue, we plan to provide a more detailed explanation of this integrating sphere, which can be described as part of the detector. I look forward to your continued interest.

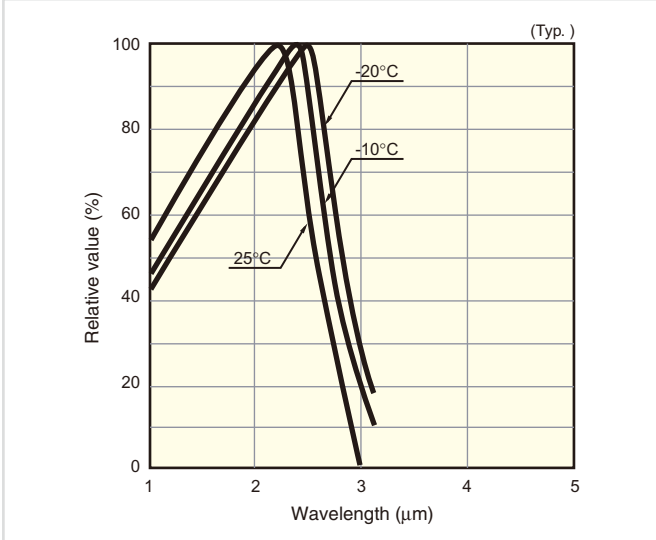

Fig.9 Spectral Sensitivity Characteristic of PbS Photoconductive Element[3)]

1) Lecture text from Shimadzu course on absorption spectrometry:
"Operating Principles, Structure, and Applications of Spectrophotometer" (Shimadzu Corporation)
2) Hamamatsu Photonics Photomultiplier Brochure
3) Hamamatsu Photonics Opto-Semiconductor Element Brochure

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Cell Types and Their Selection

The analysis of solutions is a common application of measurement performed using ultraviolet-visible spectrophotometers. There are many types of cells used for solution analysis. Depending on the material, optical path length, and volume of a cell, its application and purpose vary, as do the points that need to be observed in their use. Here, we look at the features of the various types of cells as well as some of the points to consider in their use.

1. Cell Material

The material of the cell must have no absorption at the measurement wavelength. Two materials often used for cells are glass and quartz. Polystyrene (PS) and polymethylmethacrylate (PMMA) are mainly used for disposable cells. Table 1 indicates the wavelengths for which the different types of cells can be used.

Cell Type	Measurement Wavelength Range
Glass cell (G cell)	320 to 2,500 nm
Quartz cell (S cell)	190 to 2,500 nm
Quartz cell (IR cell)	220 to 3,200 nm
Disposable PS cell	340 to 750 nm
Disposable PMMA cell	285 to 750 nm

Table 1 Measurement Wavelength Ranges for Cells of Different Materials

In this way, the measurable wavelength range varies according to the cell material. Fig. 1 shows the transmission spectra obtained for different types of cells using air as the object of measurement. It can be seen that there is no absorption by the cells in the measurement wavelength ranges given in Table 1.

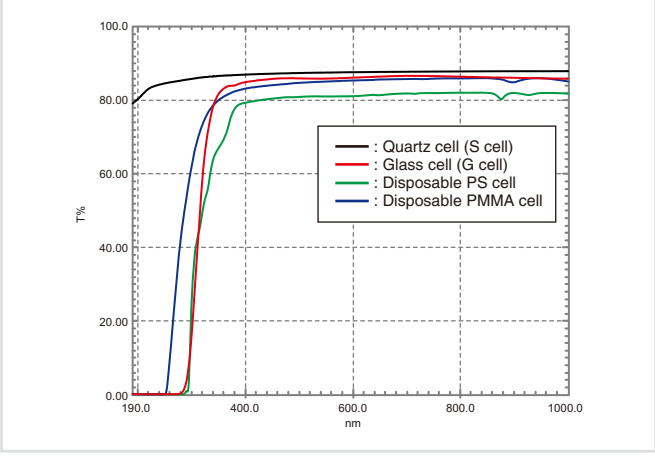

Fig.1 Transmittance of Different Types of Cells

In addition to measurement wavelength, there is also the issue of chemical resistance. Except for use with strongly alkaline solutions, glass and quartz have extremely good chemical resistance. With resin cells, however, the chemical resistance varies with the material, so care is required when selecting the cell used for measurement.
Another point to be noted is that there are small differences in the optical path lengths of individual disposable cells, which are generally discarded after use. This may lead to errors in quantitative values.

First, the cell type (material) is selected in accordance with the measurement wavelength and the solvent used.

2. Analysis of Low-Concentration and High-Concentration Samples

Cells with an optical path length of 10 mm are used in many different types of solution analyses. If the sample concentration is low, however, it may not be possible to obtain sufficient absorbance with a cell of this size. Although concentrating such samples allows the use of 10-mm cells, concentration is difficult in cases where the sample vaporizes or undergoes a chemical change during the concentration process. In such cases, measurement using a "long-path cell" is effective. There are long-path cells with optical path lengths of 20 mm, 50 mm, and 100 mm. The absorbance increases in proportion to the optical path length of the cell. Fig. 2 shows the results obtained by analyzing a 10-mg/L potassium permanganate solution with a 10-mm cell and a 100-mm cell. It can be seen that the absorbance of the 100-mm cell is ten times that of the 10-mm cell.

A well-known application of analysis using a long-path cell is the turbidity measurement of water. 50-mm and 100-mm cells are often used to analyze samples with a low turbidity.

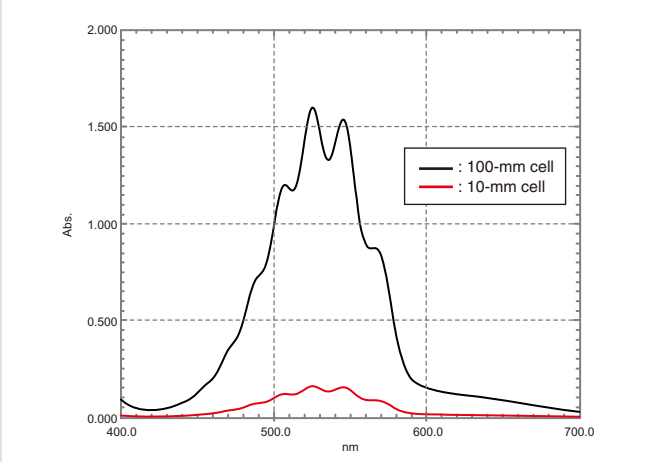

Fig.2 Absorption Spectra of Potassium Permanganate (Optical Path Lengths: 100 mm and 10 mm)

In the case of high-concentration samples, diluting the sample allows measurement with a 10-mm cell. There are samples, however, that cannot be diluted easily. For example, due to interaction with the solvent, diluting a sample may cause a change in the absorbance (i.e., a shift in the peak wavelengths).

In cases where the absorbance is high and dilution is difficult, measurement using a "short-path cell" is effective. There are short-path cells with optical path lengths of 1 mm, 2 mm, and 5 mm. Fig. 3 shows the results obtained by analyzing toluene with a 1-mm cell and a 10-mm cell. It can be seen that there is much less absorption saturation (i.e., 0 % transmittance) with the 1-mm cell than there is with the 10-mm cell.

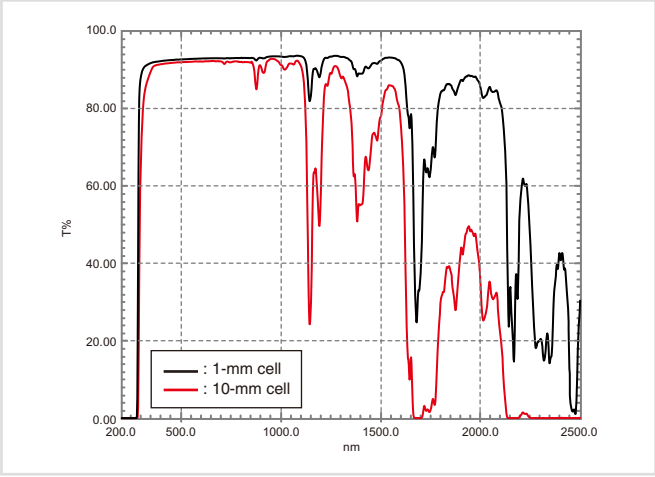

Fig. 3 Absorption Spectra of Toluene
(Optical Path Lengths: 1 mm and 10 mm)

A well-known application of measurement using a short-path cell is solution analysis in the near-infrared region. If a 10-mm cell is used for measurement in the near-infrared region, saturation often occurs due to absorption by the solvent, making it impossible to ascertain the absorption of the sample. A short-path cell is used to prevent absorption saturation due to the solvent.

With low- and high-concentration samples, the optical path length of the cell is selected in accordance with the size of the absorbance or transmittance.

3. Analysis of Micro-Volume Samples

In cases where the volume of sample required for measurement with a 10-mm cell (i.e., 3 mL) is not available, using a cell that is specifically designed for the analysis of micro-volume samples is effective. Such cells include "semi-micro cells" (required volume: 1 mL), "micro cells" (required volume: 400 µL), and "supermicro cells" (required volume: 50 to 100 µL). Although it depends on the size of the light beam obtained with the instrument used, in order to prevent the measurement beam striking parts other than the sample itself, a specialized cell holder is used with these kinds of cells. Fig. 4 shows the measurement results obtained for a sample using a supermicro cell (sample volume: 50 µL). With micro-volume cells, the intensity of the light that irradiates the sample is reduced and so the amount of noise increases somewhat. Nevertheless, it can be seen that good results are obtained.

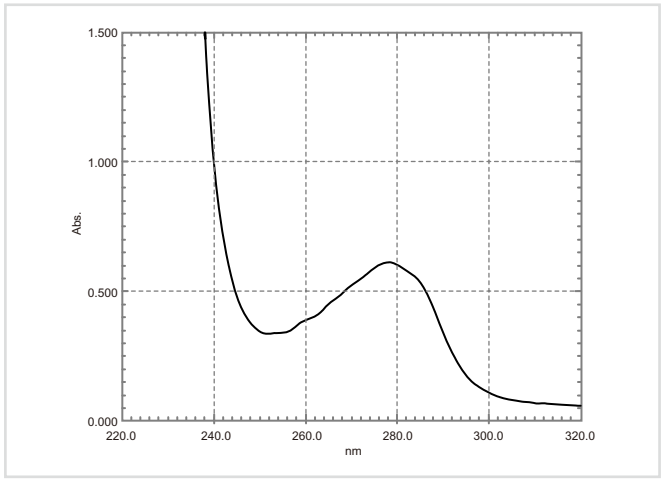

Fig. 4 Absorption Spectrum of Bovine Serum Albumin
(Supermicro Cell; Sample Volume: 50 µL)

In addition to these cells, there is a "3-µL capillary cell set for ultramicro volume measurement." The sample is put in an extremely narrow glass tube giving an optical path length of around 0.5 mm. This enables measurement with a sample volume of only 3 µL.

Well-known applications of analysis using micro-volume cells include the analysis of nonionic surfactants in water and the quantitation of protein extracts and DNA.

When only a small volume of sample is available, the cell is selected in accordance with this volume.

4. Analysis of Volatile Samples

If the type of cell typically used for solution analysis is used to analyze a highly volatile sample, the sample or solvent may vaporize during measurement, and the concentration may change as a result. A "cell with a stopper" is effective for the analysis of such volatile samples. Closing the cell with a stopper after adding the sample prevents vaporization of the sample and enables accurate measurement.

5. Summary

Here, focusing on cells that are commonly used, we have looked at the features of these cells as well as some points to note in their use. In addition to these, various other types of cells are commercially available, including an assembly-type cell with an extremely short optical path length of 0.05 mm (50 µm) and a cell that allows measurement with an optical path length of 10 mm to be performed with a sample volume of only 10 µL. Using a cell that is suitable for the application enables simple and accurate measurement.

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Analytical & Measuring Instruments Division

Q

I often hear the word "validation." What does it mean exactly?

A

What Is Validation?

Validation consists of "(a) verification that the buildings and facilities of a manufacturing site and procedures, processes, and other production control and quality control methods achieve the expected result; and (b) documentation of this."*1

More specifically, in relation to ultraviolet-visible spectrophotometers, it consists of the following: (1) documentation of the procedures used for inspection and maintenance; (2) inspection and maintenance of equipment (including configuration) in accordance with documented procedures; (3) periodic inspection; and (4) recording of inspection results. JIS K0115 and the Japanese Pharmacopoeia provide guidance on specific inspection methods. As JIS does not provide specific values (i.e., for acceptability criteria), many pharmaceutical manufacturers refer to the Japanese Pharmacopoeia.

The nine items covered by JIS and the four items covered by the Japanese Pharmacopoeia are given below. Although JIS specifies nine items, it is sufficient to perform inspections only for required items in accordance with the application actually used.

"Wavelength accuracy" and "photometric accuracy" are particularly important for ultraviolet-visible spectrophotometers. The wavelength accuracy can be checked by using an optical filter*2 for wavelength calibration, or measuring the bright line spectra of a deuterium lamp installed in a spectrophotometer as a light source. The photometric accuracy can be checked with a certified optical filter*2 using the difference between calibration standard value and actual measurements.

JIS K0115 (The asterisks indicate the four items covered by the Japanese Pharmacopoeia.)

(1) *Wavelength accuracy
(2) *Wavelength setting repeatability
(3) Resolution
(4) Stray light
(5) *Photometric accuracy
(6) *Photometric repeatability
(7) Baseline stability
(8) Baseline flatness
(9) Noise level

Reference

*1) Item 4, Article 1 (Definition), Revised GMP for Pharmaceuticals, Notification Dated 27 January 1994, Ministry of Health, Labour and Welfare Ordinance No. 3
*2) Provided by organizations such as the National Institute of Standards and Technology (NIST) and the Japan Quality Assurance Organization (JQA).

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*Survey by Shimadzu in January 2009.

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