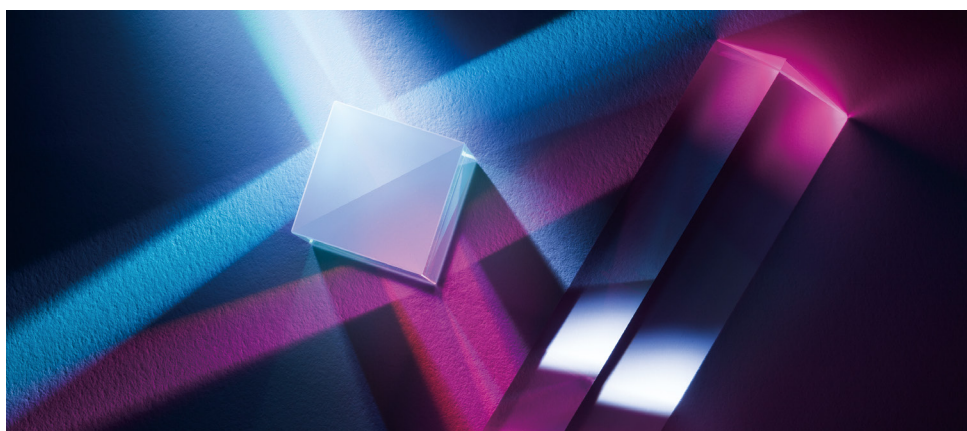


UV

TALK LETTER

Vol. 24



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Introducing Enhanced Functions That Streamline User Operations

Spectroscopy Business Unit, Analytical & Measuring Instruments Division

Yoshiharu Yamada

1. Introduction

We often receive inquiries from spectrophotometer users such as: "We cannot obtain reproducible data even though we followed the procedure," and "We would like to automate instrument operation." Shimadzu's UV-1900i Plus, UV-2600i Plus, and UV-2700i Plus spectrophotometers are equipped with the

functions to support users that help resolve these issues. These features have been developed to streamline research and analysis work, and allow users to spend more of their time on other important tasks. These useful features are described below.

2. Assist Function

Spectrophotometer measurements require preparation before they can provide a stable baseline. Shimadzu has added a feature that verifies at the start of measurement whether this preparation was performed correctly.

To obtain accurate measurement data, baseline correction must be performed with either an empty cell or a cell containing solvent. Shimadzu's systems are equipped with three correction functions for different purposes (Table 1). Each function performs correction to 100%T for transmittance measurements and to 0 Abs for absorbance measurements.

Table 1 Pre-Analysis Corrections and Applications

Name	Description
Baseline correction	A function that performs correction over a specified wavelength range. It performs baseline correction with the parameter file for the measurement loaded.
Auto zero correction	A function that performs correction at a single specified wavelength. It is used when performing measurements at a single wavelength. Use baseline correction if performing measurements at multiple wavelengths. This prevents measurements at wavelengths other than the set single wavelength from shifting.
Cell blank correction	Corrects for differences in absorbance between individual cells, or for wavelength-dependent absorbance characteristics of a specific cell. It is available only when using a multi-cell setup. Cell blank values are stored on a per-cell, per-wavelength basis.

For accurate data, the instrument conditions during correction and measurement must be the same. Accordingly, correction must be repeated whenever the measurement condition parameters are changed or if a long time has passed since the previous use (for example, the next day). If the correction is not performed properly, correct values cannot be obtained. To prevent this problem, Shimadzu has added a setting that issues a notification when the correction is not appropriate. Shimadzu has also added a feature that prevents the user from mistakenly using auto zero correction when measuring

multiple wavelengths. These features allow even first-time or infrequent users of a spectrophotometer to obtain highly reproducible data.

Next, settings related to the warm-up waiting time are described. Warm-up refers to the process in which the instrument interior warms up after power is turned on and the internal temperature stabilizes after a certain period of time. Performing measurement before warm-up is complete leads to baseline shifts as shown in Fig. 1.

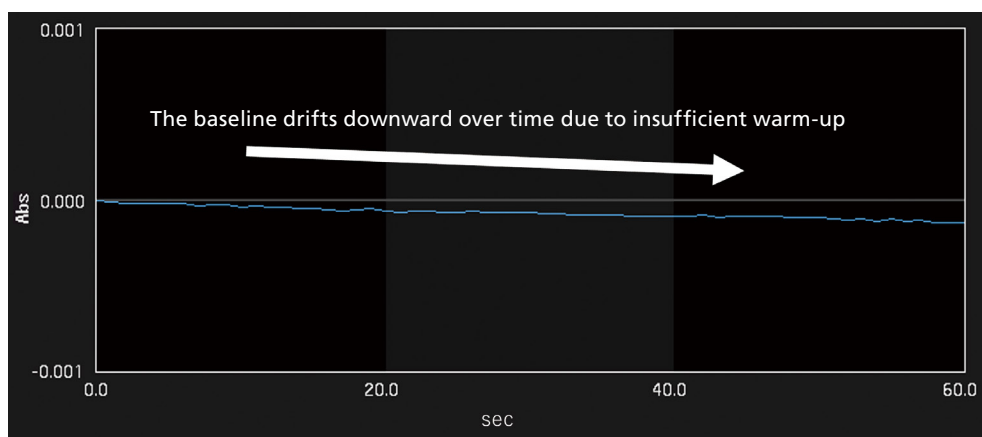


Fig. 1 Baseline Shift Observed Before Warm-Up

To prevent this from occurring, a newly added feature prohibits measurement until the baseline is stable. The typical warm-up time for the UV-1900i Plus, UV-2600i Plus, and UV-2700i Plus is around 30 minutes. The user can select one of three warm-up times: (1) 15 minutes, when warm-up is roughly complete; (2) 30 minutes, as a guideline; or (3) 60 minutes, taking instrument

differences and the environment into account^{*1}. Once configured, the countdown starts after instrument startup or the wakeup described in section 3, and measurement is not possible until the set time has elapsed^{*2}. We strongly recommend this feature for anyone concerned about baseline shift.

*1 When operating from LabSolutions UV-Vis (PC control), warm-up settings can only be configured before the instrument is connected.

*2 During the warm-up wait period, baseline correction cannot be performed.

3. Shutdown Function

The UV-1900i Plus, UV-2600i Plus, and UV-2700i Plus spectrophotometers include a sleep mode^{*3} that reduces energy consumption. By configuring the shutdown function, the system can automatically enter sleep mode (shutdown) and wake up from sleep mode^{*4}.

There are three ways of placing the system in sleep mode: (1) immediate shutdown, (2) shutdown after measurement, and (3) shutdown at a scheduled time. Shimadzu recommends using (1) or (2) when you are certain you are the final user, and using (3) to schedule shutdown^{*5} if others may still use the system.

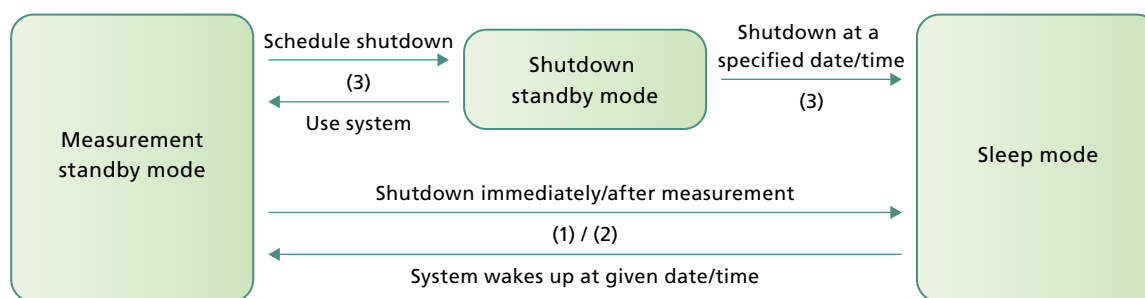


Fig. 2 State Transition of the Shutdown Function

*3 Lamps and motors are turned off while in sleep mode. Sleep mode uses at least 85 % less power than normal operation, roughly equivalent to a single LED bulb in a small room.

*4 After waking from sleep mode, initialization is performed and warm-up is required.

*5 When shutdown scheduling starts, communication between the instrument and LabSolutions UV-Vis software is disconnected, and the instrument enters shutdown standby mode. If the scheduled time is reached without reconnection, the shutdown is executed and the system enters sleep mode. However, if communication is resumed while the instrument is in shutdown standby mode, the schedule is canceled and the system returns to measurement standby mode, meaning shutdown must be scheduled again. The system will not enter sleep mode unexpectedly during measurement or while being operated with LabSolutions UV-Vis.

Using this function can improve the efficiency of routine work. For example, as shown in Fig. 3, combining shutdown after measurement with wakeup the next morning increases the

available measurement time. Automation frees users from waiting for instrument startup and long measurements to finish.

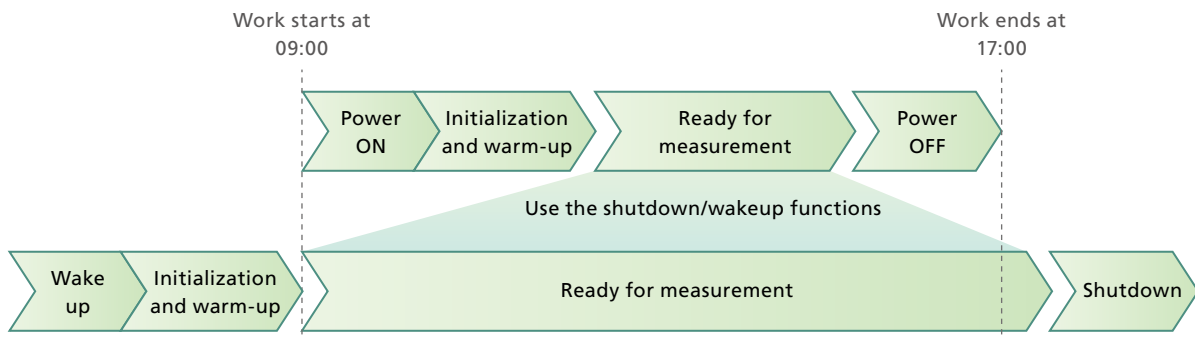


Fig. 3 Example of Using the Shutdown Function

4. Validation Functions and a Startup Validation Function (UV-1900i Plus only)

The UV-1900i Plus includes validation functions that allow the instrument status to be checked. A startup validation function has also been added to run the validation functions automatically at startup or wakeup. (This is a standalone feature that must be configured from the instrument itself, even when using LabSolutions UV-Vis to control the instrument. Once configured, the feature runs automatically.)

First, the usefulness of the validation functions is described. All UV-Vis spectrophotometers currently available from Shimadzu automatically perform initialization on startup that includes a number of checks. These items are mainly operational checks and simple calibrations rather than the performance checks required for instrument performance validation. As a result, deterioration in components such as the light source, circuit board, and detector may be missed, resulting in inaccurate data. In some cases, abnormalities in the measurement data are only noticed later, requiring remeasurement. Shimadzu recommends

performing the performance checks provided by the validation functions on a daily basis.

Next, the startup validation function is described. This function can run the above-mentioned system validation automatically at system startup. Enabling the startup validation function allows the instrument to automatically run performance checks at startup. By combining the above-mentioned wakeup function with the startup validation function, wakeup, initialization, performance checks, and warm-up can be completed before work begins. The startup validation function only supports fully automated checks that do not require inspection jigs. Fig. 4 shows the name of each check and its approximate duration (in brackets), and each item can be selected as needed.

The default settings include reference values specified for periodic inspections and by pharmacopeias. Reference levels and the number of displayed digits can be changed by tapping the  mark on the right of each check item.

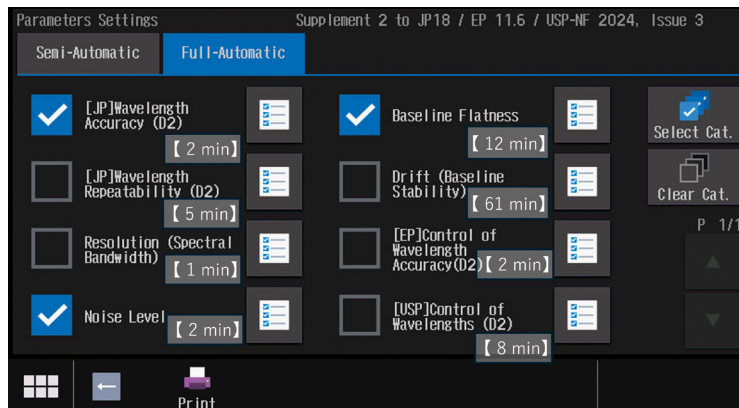


Fig. 4 List of Available Check Items and Approximate Durations

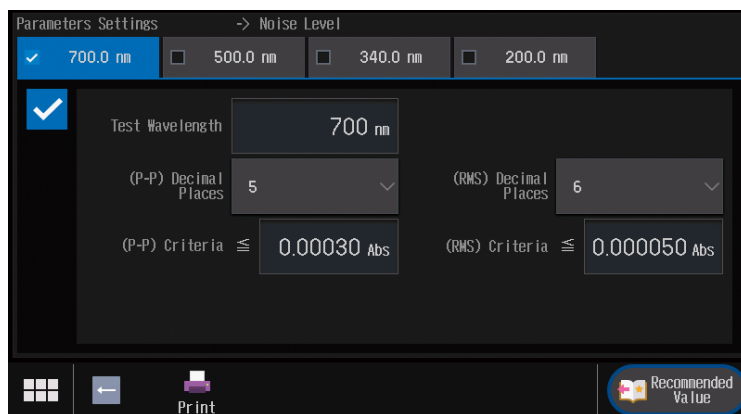


Fig. 5 Changing Check Item Settings (Noise Level)

5. Summary

As labor mobility increases across society, it is becoming more difficult to train and retain skilled users of analytical instruments. For this reason, there is a need for instruments that anyone can easily operate, regardless of skill or experience. An increasing number of workplaces also find themselves unable to meet staffing needs and forced to operate with a reduced workforce. To address these

issues, the UV-1900i Plus, UV-2600i Plus, and UV-2700i Plus spectrophotometers are equipped with the functions to support users that help users unfamiliar with the instrument obtain accurate data and allow them to focus on other tasks through automation. We would be very pleased if the functions to support users described here could be of help to you.

Applications

Reviewing UV – Solution Measurement –

Solutions COE, Analytical & Measuring Instruments Division

Yoshiyuki Tange

1. Introduction

Starting with this issue, UV TALK LETTER will feature “Reviewing UV,” which covers basic measurement methods and solutions for improving accuracy and efficiency. This article covers solution

measurement, which is a common application for UV-Vis spectrophotometers.

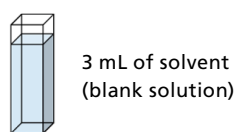
2. Procedures for Solution Measurement

The most common procedure used to measure a solution is shown in Fig. 1. If you want to obtain information on the absorption characteristics of a solute, place about 3 mL of solvent in a 10-mm cell, set it in the sample chamber, and perform a baseline measurement (or auto zero for single-wavelength measurements). Next, rinse the cell with the solution to be measured, fill it with about 3 mL of the solution, set it in the sample chamber, and perform the sample measurement.

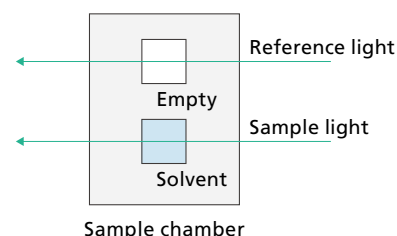
Using the same cell for both baseline and sample measurements reduces the impact of differences in optical properties between cells on the data.

When using a double-beam spectrophotometer, the reference light path is typically located toward the rear of the sample chamber. The main purpose of the reference light is to correct for fluctuations in light source output during baseline and sample measurements. The state of the cell holder on the reference side must always be kept the same during baseline and sample measurements. The reference-side cell may contain solvent or be left empty; in either case, the reference light can still correct fluctuations in light source output, so there is basically no problem.

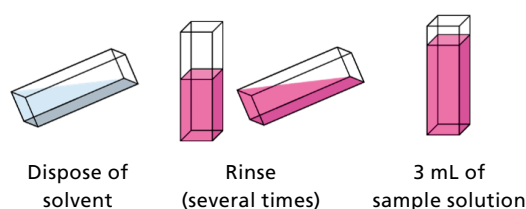
(1) Preparing Blank Solution



(2) Baseline Measurement (Use auto zero when measuring a single wavelength)



(3) Preparing Sample Solution



(4) Sample measurement

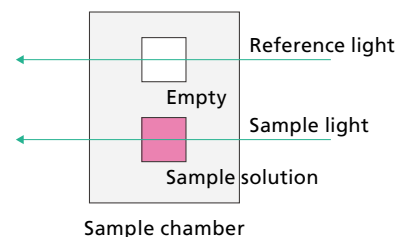
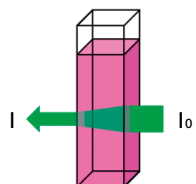


Fig. 1 Procedure for Solution Measurement with a UV-Vis Spectrophotometer

3. Beer-Lambert Law

UV-Vis spectrophotometers can be used to quantify a solute in solution. A key factor in this quantitative analysis is the Beer-Lambert law. As illustrated in Fig. 2, the law defines absorbance as being proportional to optical path length or concentration. Accordingly, by fixing the optical path length, the concentration of a sample can be quantified using absorbance as an indicator. Molar absorptivity is a constant that

differs for each substance. Quantitative analysis can be performed using molar absorptivities reported in the literature, but when an accurate evaluation is required without cell-to-cell or instrument-to-instrument errors, it is preferable to measure a standard substance of known concentration multiple times and create a concentration-absorbance calibration curve.

$$\text{Abs} = \log_{10}(I_0/I) = \epsilon c L$$


ϵ : Molar absorptivity
 c : Concentration
 L : Optical path length

Fig. 2 Beer-Lambert Law

4. Solvent and Cell Selection

The cell material must not absorb light in the measurement wavelength range. Glass and quartz are two of the most common materials used for cells. Disposable cells, which are normally made from polystyrene (PS) or polymethyl methacrylate (PMMA), are also available. The transmission spectrum of each of these cells relative to air is shown in Fig. 3. If a cell has been used since a previous operator's time and it is

unclear whether it is a quartz cell or a glass cell, Shimadzu recommends checking the cell's own absorption characteristics before use.

For reference, Table 1 shows usable wavelength ranges for each cell material.

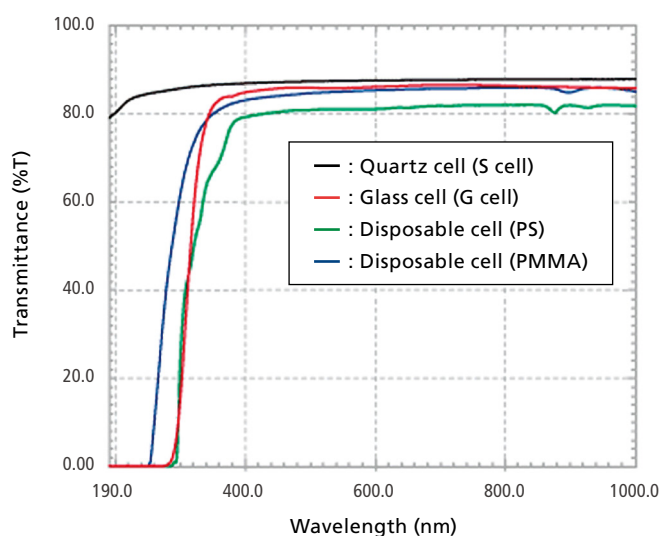


Fig. 3 Transmittance of Each Cell Type

Table 1 Usable Wavelength Ranges by Cell Type

Cell Type	Usable Wavelength Range
Glass cell (G cell)	320 to 2500 nm
Quartz cell (S cell)	190 to 2500 nm
Quartz cell (IR cell)	220 to 3200 nm
Disposable cell (PS)	340 to 750 nm
Disposable cell (PMMA)	285 to 750 nm

The usable wavelength range is also affected by the solvent. Even transparent solvents may absorb light in the ultraviolet (UV) and near-IR regions, making measurement difficult.

Fig. 4 shows compatible wavelength ranges for a variety of solvents in the UV region. As illustrated, aqueous solvents allow

measurements down to the UV region. By contrast, many organic solvents absorb UV light, and organic solvents with double bonds, such as benzene and acetone, are unsuitable for measurements below 300 nm.

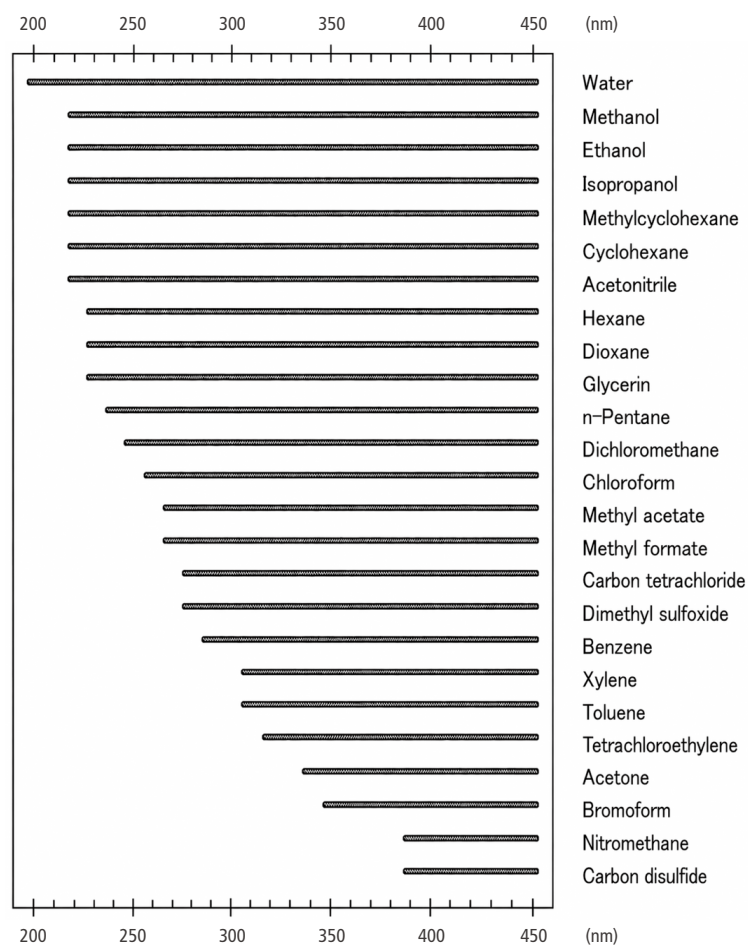


Fig. 4 Compatible Ultraviolet Wavelength Ranges for Various Solvents

Fig. 5 shows compatible wavelength ranges for a variety of solvents in the near-IR region. In the near-IR region, water also has strong absorption, so operators need to consider using an organic solvent depending on the wavelength of interest. When

selecting a solvent, operators should consider not only compatibility with the solute and polarity or non-polarity, but also the transmittance of the solvent in the measurement wavelength range.

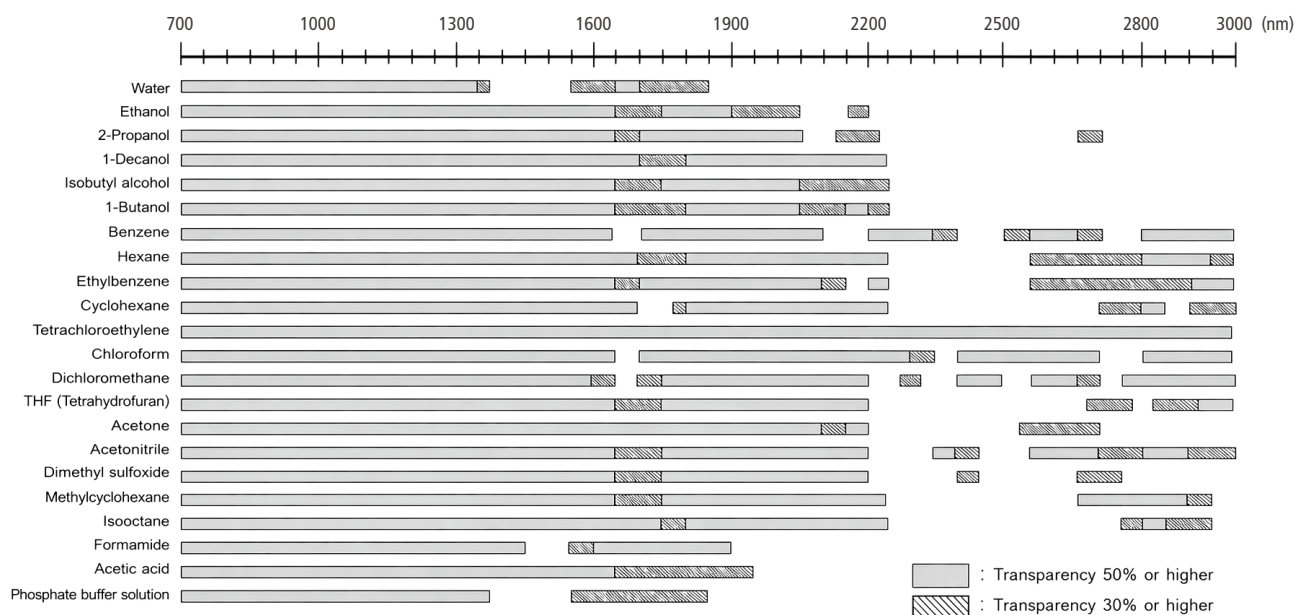


Fig. 5 Compatible Near-IR Wavelength Ranges for Various Solvents

5. Optical Path Length

Cells with a 10-mm optical path length are commonly used, but changing the optical path length makes it possible to measure high- or low-concentration solutions without diluting or concentrating the sample. For example, using a cell with an optical path length of 100 mm yields 10 times the absorbance of a 10-mm cell, as shown in Fig. 6. This is an effective method when quantitative analysis of lower-concentration samples is required. Similarly, a cell with a 1-mm optical path length yields one-tenth the absorbance of a 10-mm cell.

Short optical path cells are commonly used for solution

measurements in the near-IR region. Often, if a 10-mm cell is used for measurements in the near-IR region, solvent absorption becomes saturated and the sample signal cannot be obtained. Short path cells are used to prevent saturation caused by solvent absorption.

Cells with ultra-short path lengths below 1 mm are sometimes used to evaluate materials such as sunblock creams. Demountable cells (Fig. 7) are slightly more difficult than standard cells in terms of path length reproducibility, but they are easy to clean and convenient to use.

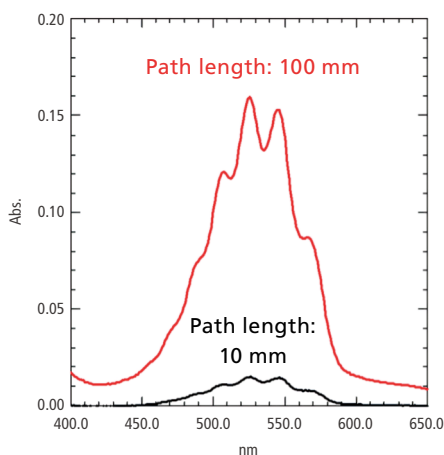


Fig. 6 Potassium Permanganate Solution Absorption Spectra



Fig. 7 Demountable Cells (Path Length: 0.01 mm)

6. Turbidity Measurements and the Impact of Light Diffusion

Caution is recommended when analyzing solutions with light-diffusing properties. In a direct-detection optical system commonly used for solution measurements (one that does not use an integrating sphere*), measuring a light-diffusing sample can cause the measurement light to extend beyond the detector's light-receiving surface, lowering transmittance (and increasing absorbance).

The impact of this light scattering varies depending on the relative distances between the light source, sample, and detector, which can cause differences in measurement results between instruments.

For reference, Fig. 8 shows a schematic illustration of the impact of detector position when analyzing a light-diffusing sample. If the sample does not scatter light, the measured values do not change between positions A and B; however, for a sample that does scatter light, the amount of light received differs depending on the detector position. While the increase in absorbance caused by scattering is sometimes used for turbidity measurement, the measured values differ between instruments. Therefore, the common practice is to create a calibration curve using a formazin standard solution or a kaolin standard solution for turbidity measurement.

* An integrating sphere is an optical component that diffuses scattered light across its spherical inner surface and uniformly directs it to a detector. It is used when measuring to reduce the effects of scattering.

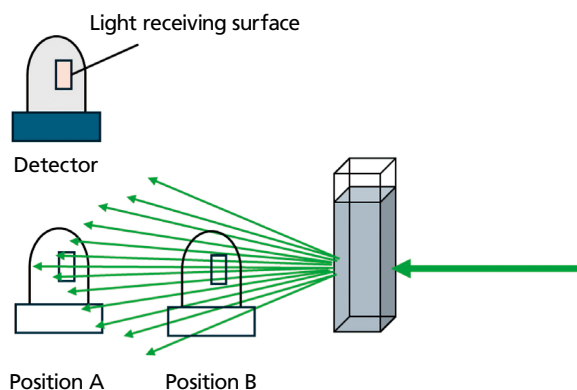


Fig. 8 Effect of Detector Position when Measuring a Light-Diffusing Sample
(If the sample scatters the measurement light, the amount of light reaching the detector's light-receiving surface differs between positions A and B)

7. Summary

This article has covered the procedures and precautions for solution measurement using a UV-Vis spectrophotometer. Topics covered include the fact that different cells and solvents have different usable wavelength ranges, and the need to select an appropriate optical path length according to the target

concentration. Although solution measurement is a widely used application of UV-Vis spectrophotometers, we hope that reviewing these points will lead to more accurate measurements and new ways to use the instrument.

Q&A

When I create a calibration curve for measuring a solution quantitatively, the curve becomes non-linear in the high-concentration region. Is there a way to address this without changing the quantitative concentration range?

Using the spectrum-based quantitative analysis feature*¹, you can measure and review the spectra of standard samples, then create a calibration curve at any selected wavelength.

When measuring high-concentration samples, absorbance saturation may occur, causing the measured value to be lower than the true absorbance. If absorption saturation occurs during quantitative measurement, the linearity of the calibration curve decreases*².

When creating a calibration curve in Quantitative mode, only the absorbance at the specified wavelength is measured, whereas the spectrum-based quantitative analysis feature measures the spectra of standard samples in Spectrum mode. Then, by selecting multiple spectra for calibration and specifying a wavelength, you can create a calibration curve. Fig. 1 shows spectra recorded from ten standard samples and the calibration curves prepared from these spectra at wavelengths A and B. At wavelength A, absorption saturation is observed in the high-absorbance region of the calibration curve, and the square of the correlation coefficient is 0.99498. At wavelength B, there is no visible absorption saturation in the calibration curve, and the square of the correlation coefficient is 0.99997, demonstrating that this calibration curve exhibits better linearity than the curve prepared at wavelength A.

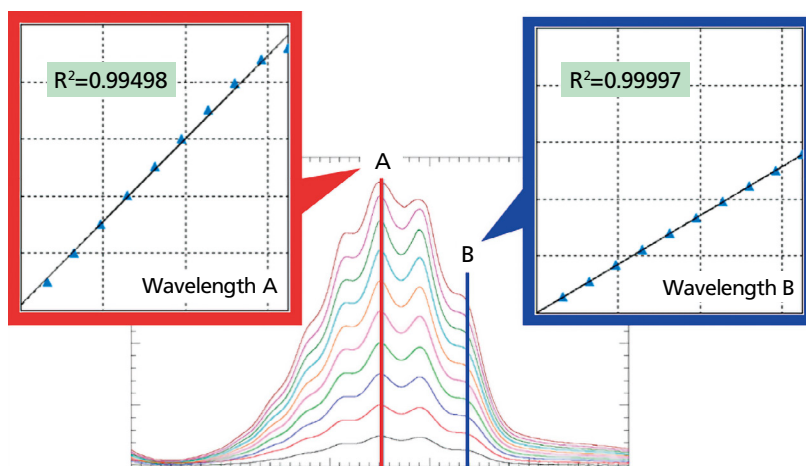


Fig. 1 Spectra of Standard Samples and Calibration Curves at Wavelengths A and B

As shown above, by using the spectrum-based quantitative analysis feature, you can review the data obtained after spectral measurement and then select the optimal wavelength to create a calibration curve. Further details and examples of using the spectrum-based quantitative analysis feature can be found in Application News No. 01-00842-EN.

*¹ This feature is compatible with LabSolutions UV-Vis Ver. 1.20 and higher.

*² The absorbance range over which calibration curves remain linear differs by instrument. Instruments with less stray light can maintain linearity at higher absorbances.

UV-Vis Spectrophotometer

UV-1900i Plus

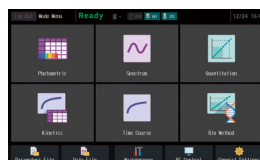
The UV-1900i Plus is a double-beam UV-Vis spectrophotometer using Shimadzu's original LO-RAY-LIGH diffraction grating technology. In addition to its high optical performance, the UV-1900i Plus features high resolution, low stray light, high reproducibility, and an ultra-fast scan function. It also has an easy-to-use interface on a color touchscreen display. The system also features a faster response speed by adopting a new CPU.

Measurement wavelength range	190 to 1,100 nm
Spectral bandwidth	1 nm
Wavelength scanning speed	29,000 nm/min maximum speed
Stray light	0.02 % or less (220 nm, NaI)

Brochure No. C101-E181

Refined User-Friendliness

The UV-1900i Plus on-screen user interface includes large, easy-to-see icons deployed on a black background, so the instrument settings are evident at a glance. These icons also improve intuitive understanding, which enables users to quickly become familiar with the operations. Furthermore, the user interface is designed to minimize transitions between windows, so users do not get confused during the operations.



Startup Validation Function

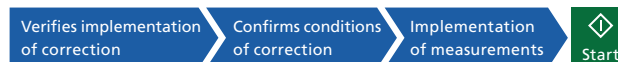
Instrument performance checks can be performed automatically when the instrument is turned ON. This enables even more reliable instrument operation. It can also be implemented in combination with the Wakeup function.



Assist Function*



The instrument assists the user to ensure that measurements are performed using the correct procedure.



Checks whether or not baseline correction, auto zero correction or cell blank correction has been performed and informs the user if it has not been.

Informs the user if the last correction performed is not appropriate for the planned measurement.

Informs the user if the UV-1900i Plus is not ready to begin measurement and when starting measurements and 100 %T (0 Abs) corrections.

* This function is also standard on the UV-2600i Plus/2700i Plus.

Automatic Spectral Evaluation, Shutdown/Wakeup Functions

The automatic spectral evaluation function can be used by controlling the UV-1900i Plus with a PC. Shutdown/wakeup functions are also available for stand-alone models.

UV-Vis Spectrophotometer

UV-2600i Plus

UV-2700i Plus

The UV-2600i Plus is a single monochromator system with 0.005 % low stray light and the UV-2700i Plus is a double monochromator system with 0.00005 % low stray light (220 nm, NaI).

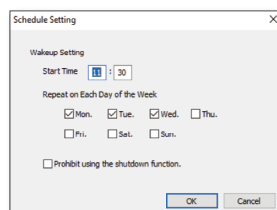
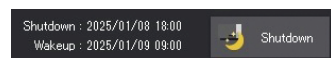
By installing an optional ISR-2600Plus Integrating Sphere Attachment with the UV-2600i Plus, the measurement wavelength range can be extended to include the near-infrared region. The UV-2700i Plus can measure high absorbance levels up to 8 Abs, which means it can measure low transmittance levels in highly concentrated samples, films, or other samples with low transmittance characteristics.

Measurement wavelength range	185 to 900 nm (220 to 1,400 nm with the UV-2600i Plus when the ISR-2600Plus is used)
Spectral bandwidth	0.1 to 5 nm
Stray light	UV-2600i Plus: 0.005 % max. or less (220 nm, NaI) UV-2700i Plus: 0.00005 % max. or less (220 nm, NaI)

Brochure No. C101-E184

Shutdown/Wakeup Functions

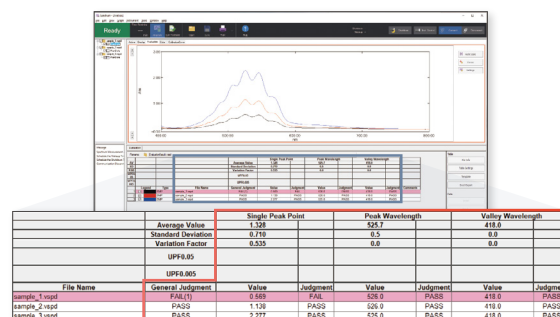
The instrument can be automatically shut down and put into sleep mode at a set time to limit power consumption and help preserve the lamp. It can also automatically wake up the equipment at a specified time, contributing to effective use of time.



Automatic Spectral Evaluation



By specifying various evaluation criteria for measurement results, spectra judgments can be made automatically. In the report creation window, reports can either be prepared based on a previously specified report format or freely laid out based on various parameters, data, or other elements.



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