POLITECNICO MILANO 1863

DIPARTIMENTO DI ARCHITETTURA, INGEGNERIA DELLE COSTRUZIONI E AMBIENTE COSTRUITO



Unità



SEED[Lab] - Smart Envelope for energy Efficient builDings and Districts [Lab]

Attrezzatura

PERKIN ELMER - Lambda 950

Spettrometro UV-Vis-NIR a doppio raggio, equipaggiato con sfera d'integrazione di 150 mm di diametro che consente la misura della riflettanza e trasmittanza spettrale di materiali regolari e diffondenti fra 250 e 2500 nanometri, oppure con detector 2-D per la caratterizzazione di materiali regolari e liquidi fra 200 e 3300 nanometri.



Localizzazione

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LAMBDA Flex Series UV/Vis, UV/Vis/NIR Systems

Drawing on the long history and unique features of the LAMBDA series high performance spectrophotometer family, PerkinElmer is introducing a new level of flexibility to the already extensive portfolio of LAMBDA high end spectrophotometers.

Offering the most cost-effective solutions possible to support measurements needs, while protecting the ability to change as new projects and requirements arise. The LAMBDA Flex Systems configuration provides a cost-effective solution to any lab or manufacturing site. It allows our customers the unprecedented ability to configure their instrument with the capability needed at the current time, but provide a path to continuously upgrade their system. This ability provides customers a level of flexibility not available in the past or from any other vendor and minimizes their initial capital purchase by allowing them the flexibility to expand the system as needs change.

The LAMBDA Flex Systems include all of the high-performance instrument platforms, LAMBDA 650/750/850/950/1050, in a basic configuration, which excludes the standard detector module.

Performance is never compromised. All instruments are fully aligned and tested with a standard detector module. This ensures every instrument will meet our published specifications based on the standard detector configuration. Upon completing final testing, the standard detector module is removed and the instrument is paired with the selected accessories.

Each sales order will require the selection of one of the various sampling modules from the vast array of techniques currently available. The instrument can be purchased with no detector module. It can be used with a PerkinElmer approved accessory that has a compatible detector configuration, if needed, or utilize an existing detector module. In these cases, additional service is not included, but a quote can be requested from the service team.

There are a few limitations in the configurations that can be selected, which is provided in the System Configuration Matrix. These are due to technical considerations to prevent noncompatible configurations from being selected. This will prevent a configuration from being selected which does not meet requirements.

LAMBDA Series of UV/Vis/NIR Systems: The Customer Advantage

The LAMBDA series instruments provide two sampling areas a primary sample compartment where a wide range of samples can be analyzed, utilizing one of the sample compartment array of accessories available. In addition, the standard detector module is removable allowing it to be replaced with a number of additional sampling accessories, which can be used with the instrument. In many analyses it is convenient or necessary to use both the sample compartment accessory in conjunction with one of the optional detector accessories for a specific analysis.



Figure 1. LAMBDA System with standard sample compartment and open area for accessory additions shown.



System Configuration Matrix

LAMBDA Flex Series Accessory Matrix						
ACCESSORY	PART NO.	LAMBDA 650	LAMBDA 750	LAMBDA 850	LAMBDA 950	LAMBDA 1050
60 mm PbS Sphere	L6020203	Х	Х	Х	Х	Х
60 mm InGaAs Sphere	L6020323	Х	Х	Х	Х	Х
100 mm PbS Sphere	L6020372	Х	Х	Х	Х	Х
100 mm InGaAs Sphere	L6020371	Х	Х	Х	Х	Х
150 mm PbS Sphere	L6020204	Х		Х	Х	Х
150 mm InGaAs Sphere	L6020322	Х		Х	Х	Х
60 mm Collection Sphere	L6020209	Х	Х	Х	Х	Х
270 mm Diffuse Transmission Sphere	L6020370				Х	Х
Large Sample 150 mm Sphere	PELA1002				Х	Х
150 mm PbS Downward Viewing Sphere	PELA1001				Х	Х
150 mm InGaAs Downward Viewing Sphere	L6020370				Х	Х
60 mm Gold PbS Sphere (NIR Only)	PELA1021				Х	Х
UV/Vis URA	L6020209	Х		Х		
UV/Vis/NIR URA	L6020202				Х	
UV/Vis/NIR (1050) URA	L6020358					Х
GPOB, Standard	PELA1003	Х		Х	Х	X
GPOB, InGaAs	L6020238				Х	Х
Automated Reflectance /Transmission Accessory	L6020116				Х	Х
0°/ 45° Diffuse Reflectance Accessory	PELA1016				Х	X
Goniometer Accessory	PELA1032	Х		Х	Х	Х
"X" Indicates a compatible platform						

Interchanging the sampling modules is a simple process. Once a detector unit has been aligned, no additional alignment is typically necessary. Accessories and detector modules use kinematic mounting which provides very good repeatability.

LAMBDA Flex Systems configurations allow more flexibility and help minimize upfront expenses by allowing the exact configuration required at time of purchase. The capability of the LAMBDA system can be enhanced as needed by adding additional measurement capability to meet any sampling challenge necessary at any time.



Figure 2. Changing the sampling module is a simple process and only takes minutes to switch applications.

LAMBDA Flex Systems

The LAMBDA Flex Series of instruments takes advantage of our industry's unique platform concept. This allows the instrument detector module and sample compartment to be removed and be replaced by a wide array of sampling accessories and

detector options. This capability also provides greater expandability to meet measurement challenges as they develop by simply adding the needed functionality. Service installation testing of system, however, is limited by accessory type.

PART NO.	LAMBDA SYSTEM	DESCRIPTION
L6020135	LAMBDA 650 Flex System	Includes a fully tested LAMBDA 650 basic instrument with no detector module. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020137	LAMBDA 750 Flex System	Includes a fully tested LAMBDA 750 basic instrument with no detector module. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020139	LAMBDA 850 Flex System	Includes a fully tested LAMBDA 850 basic instrument with no detector module. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020141	LAMBDA 950 Flex System	Includes a fully tested LAMBDA 950 basic instrument with no detector module. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020143	LAMBDA 1050 Flex system	Includes a fully tested LAMBDA 1050 basic instrument with no detector module. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020144	LAMBDA 650 ES Flex System	Includes a fully tested LAMBDA 650 basic instrument with no detector module and is supplied with the Enhanced Security software to meet the requirements of 21 CFR part 11 compliance. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020145	LAMBDA 750 ES Flex System	Includes a fully tested LAMBDA 750 basic instrument with no detector module and is supplied with the Enhanced Security software to meet the requirements of 21 CFR part 11 compliance. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020146	LAMBDA 850 ES Flex System	Includes a fully tested LAMBDA 850 basic instrument with no detector module and is supplied with the Enhanced Security software to meet the requirements of 21 CFR part 11 compliance. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020147	LAMBDA 950 ES Flex System	Includes a fully tested LAMBDA 950 basic instrument with no detector module and is supplied with the Enhanced Security software to meet the requirements of 21 CFR part 11 compliance. Detector option can be selected at time of purchase or existing detector module may be adapted.
L6020148	LAMBDA 1050 ES Flex System	Includes a fully tested LAMBDA 1050 basic instrument with no detector module and is supplied with the Enhanced Security software to meet the requirements of 21 CFR part 11 compliance. Detector option can be selected at time of purchase or existing detector module may be adapted.

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Full-Spectrum, Angle-Resolved Reflectance and Transmittance of Optical Coatings Using the LAMBDA 950/1050 UV/VIS/NIR Spectrophotometer with the ARTA Accessory

UV/Vis/NIR Spectroscopy

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Introduction

Optical coatings composed of thin films of dielectric materials have long been commonplace in both the optics and glass industries. For instance, stacks of alternating high- and lowrefractive-index layers are used to form Bragg mirrors in laser cavities, and magnesium fluoride layers are used as antireflection coatings on display screens. In the last two decades, however, the range of available optical coatings has broadened considerably as new materials have emerged to meet new applications. These coatings are not necessarily planar or fully dense—leading to light scattering—and they may be intended to function at nonnormal angles of incidence, for which *s*- and *p*-polarized light behave differently. The solar energy industry provides several nice examples: zinc oxide coatings grown by chemical vapor deposition naturally develop a pyramid surface texture that has been employed to scatter light in thin-film solar cells.¹ Holographic filters, formed by patterning the refractive index of a polymer, split the solar spectrum into beams of distinct colors separated in space (much like



Figure 1. LAMBDA High Performance UV/Vis/NIR Spectrophotometer.

a prism), and photovoltaic cells tuned to each wavelength may be placed at these foci to form a new type of multi-junction solar cell.² A "coating" of silicon nanocylinders on the front of a silicon solar cell acts as a Mie scatterer that has been shown to reduce reflection—thereby increasing absorption in the solar cell—for a wide range of angles of incidence and polarization.³





Figure 2. Rendering and schematic of the proposed curved photovoltaic module. The 3M[®] visible mirror film would make the module appear mirrored at visible wavelengths but black at near-infrared wavelengths.

For all optical coatings—and in particular those that receive light from, or direct light into, non-normal angles—it is vital to characterize the wavelength-, angle-, and polarization-resolved reflectance and transmittance. The PerkinElmer Automated Reflectance/Transmittance Analyzer (ARTA) is a drop-in accessory for the LAMBDATM 950 and LAMBDA 1050 UV/VIS/ NIR spectrophotometers that uses a goniometer to rotate a sample with respect to the beam (varying angle of incidence) and independently rotate an integrating-sphere detector with respect to the sample (varying angle of detection). For any incidence angle/detection angle pairing, spectra may be collected for s- and p-polarized light in the wavelength range of 250–2500 nm.

The ARTA automatically runs a user-specified table of these measurements, allowing users to efficiently answer the question: "Where does all of the incident light go?"

In this note, we investigate the performance of a long-pass optical film ("visible mirror film") manufactured by 3M^{®.4} 3M[®] markets a wide range of these plastic films. They consist of hundreds of layers of transparent polymers of varying thickness and refractive index that together reflect and transmit designated parts of the solar spectrum for applications such as low-emissivity window glass. The visible mirror film chosen for this study absorbs UV light (<350 nm), reflects visible light, and transmits infrared light (>750 nm). We are interested in integrating this film into a curved silicon photovoltaic module, as shown in Figure 2, because the silicon solar cells convert light near their bandgap (700-1100 nm) to electricity with efficiencies exceeding 40%, but shorter wavelengths mostly generate waste heat and are converted with much lower efficiency. By placing the 3M[®] film in front of the solar cells, the infrared wavelengths will be transmitted to the cells while the poorly used shorter wavelengths will be reflected to a focus where another solar collector (photovoltaic, thermal, or chemical) that is tuned to visible light may be placed. The curved photovoltaic module is intended to be placed on a one-axis tracker that will follow the

sun from East to West, but the 3M[®] optical film will still receive sunlight at angles of incidence from 0–60° (in Phoenix, AZ) over the course of the year. Consequently, to determine the annual power output of the entire solar collector, we must first characterize the wavelength-, angle-, and polarization-resolved performance of the 3M[®] optical film.

Experimental

The PerkinElmer LAMBDA 950/1050 UV/VIS/NIR spectrophotometers are dual-beam, dual-monochromator instruments equipped with an optional 150 mm integrating sphere accessory. The Spectralon-coated integrating sphere contains both silicon and InGaAs detectors so that accurate spectra may be collected from 200-2500 nm. The total reflectance, total transmittance, diffuse reflectance, and diffuse transmittance of a film, substrate, or liquid (in a cuvette) may be measured by positioning the sample at either the entrance or exit port of the integrating sphere, and removing the specular port in the case of diffuse measurements. For more detailed analysis of the angular dependence of reflection and transmission for arbitrary angle of incidence, the integrating sphere accessory may be exchanged with the ARTA accessory (Figure 3) in approximately 10 minutes. The ARTA also utilizes a (60 mm) integrating sphere with PMT and InGaAs detectors, but this sphere is mounted on a goniometer so that it may circle 340° around the sample in the horizontal plane, collecting light that falls within its adjustable-width entrance aperture. The sample, which again may be a film, substrate, or liquid, is also mounted on the goniometer and allowed to rotate-independent of the detector-so that a user may choose arbitrary angles of incidence (with respect to the fixed source) and detection. Control of the ARTA is integrated into the UV Winlab software so that a user can specify a run table that will automatically execute.

In the present experiments, total and angular-resolved reflectance and transmittance spectra of a 3M® visible mirror film were collected using a LAMBDA 950 spectrophotometer. For the total reflectance and transmittance spectra, the film was placed at the entrance (0° angle of incidence) or exit (8° angle of incidence) of the 150 mm integrating sphere accessory and spectra were collected over 250–2500 nm using unpolarized light. For the angular-resolved measurements, the film was mounted in the goniometer holder of the ARTA accessory and spectra were collected over 250-2500 nm separately for s- and p-polarized light (Figure 3). In some measurements, the angle of incidence was varied between 5–85° in 5° increments, and the detector movement was coordinated so that the detector position always corresponded to the specular beam (10° increments). In others, the angle of incidence was fixed while the detector swept a full circle around the sample in 1° increments. The latter experiments were done with slits of varying width placed in front of the detector so as to vary the angular resolution of the measurements.



Figure 3. Photograph of the ARTA with the 3M⁶ film (which looks like a mirror since it reflects visible wavelengths) mounted in the sample holder. The detector is shown without a slit aperture, which corresponds to an acceptance angle of 20°.

Results

Before employing the ARTA for in-depth analysis of the 3M[®] film, the total (specular + diffuse) reflectance and transmittance of the free-standing film was measured at nominally normal incidence using the integrating sphere accessory of the LAMBDA 950. The results, shown in Figure 4, reveal that the film has the desired sharp transition from reflecting to transmitting at approximately 750 nm, with a visible reflectance of nearly 100% and an infrared transmittance of approximately 90%. This same film was modeled by 3M[®] using the known thicknesses and refractive indices of the constituent polymer layers, and the simulated spectra match the measured spectra to within 2% at most wavelengths.

As the film is planar with low surface roughness, the total reflectance in Figure 4 should be nearly identical to the specular reflectance measured with the ARTA at the same 8° angle of incidence. The specular reflectance resolved by angle of incidence and polarization is displayed in Figure 5 as a contour plot, and, as expected, a horizontal slice taken just above the x-axis looks like the reflectance in Figure 4. Note that the angle of detection was always twice the angle of incidence-i.e., the detection angle associated with the specular beam-for these measurements. For both polarizations, the reflecting-totransmitting transition remains sharp up to angles of incidence of 50°, but has a slight blue shift. In the intended solar energy conversion application, this will have the effect of shifting over the course of a year the fraction of light coupled to the curved photovoltaic module and to the solar collector at its focusinconvenient but tolerable with proper engineering. However, for angles of incidence above approximately 50°, the transition dissolves for s-polarized light and the film begins to lose its function as a spectrum splitter. A significant consequence of this is that the curved photovoltaic mirror will work poorly during winter or summer months for latitudes greater than approximately [30°].



Figure 4. Total reflectance and transmittance spectra of a $3M^{\circ}$ visible mirror film measured with the 150 mm integrating sphere accessory. Also shown are the simulated spectra calculated by $3M^{\circ}$. The absorbance of the film was calculated as 1-R-T.





After the optical performance of the free-standing film was characterized, film samples were laminated between silicon wafers and glass substrates using various encapsulants to approximate the final, curved, spectrum-splitting photovoltaic module. Figure 6a is a photograph of three such laminates and indicates that the film may either remain planar or become wrinkled to varying degrees during lamination, depending on the details of the process and the encapsulant used. If the curved photovoltaic module is to concentrate the reflected visible light at its focus, the film must remain planar and conformal with the glass surface. The goniometric nature of the ARTA, coupled with the variable acceptance angle of the detector aperture, allows the angular distribution function of scattered light to be guickly measured in transmission or reflection. Figure 6b-d which appear on the next page, displays such data for two laminates-one visibly planar and the other visibly lightly wrinkled—as well as a free-standing film. 600 nm light, which is in the middle of the reflected band, was used for all samples; the free-standing film was also measured at 1100 nm, where the film transmits, for reference (this was not possible with the laminates because the silicon wafer absorbs this light). To perform these measurements, the angle of incidence was held constant at 30° while the detector automatically circled around the sample. The freestanding film and planar laminate show near-unity reflectance at the specular angle, consistent with Figure 5, even when the detector aperture is closed down to a 5° acceptance angle. That is, all light is reflected within a 2.5°-half-angle cone centered



Figure 6. (a) Photograph of three glass/3M^{*} film/silicon wafer laminates with different encapsulants. (b) Reflectance and transmittance of the free-standing 3M^{*} film as a function of the detector angle. In these polar plots, the radial length of the signal corresponds to the intensity; the outermost circle is 100% reflectance or transmittance. In addition, the beam appears to have a wider spread as the detector aperture is increased because for an, e.g., 20° acceptance angle, all of the light is still detected when the detector is <10° from the specular angle. Reflectance of the (c) visibly specular laminate in the middle of the photograph in (a) and the (d) visibly wrinkled laminated in the left of the photograph in (a).

at the specular angle. The wrinkled sample also reflects all light within a 10°-half-angle cone, but only 89% within a 2.5°-halfangle cone; the wrinkles clearly reduce specularity. The scattered light would miss the focus of the curved photovoltaic module, essentially reducing the concentration of light that arrives at the solar collector placed there.

Conclusion

We evaluated a 3M[®] visible mirror film for potential use in a new curved photovoltaic module using a LAMBDA 950 spectrophotometer with an ARTA accessory. In this application, the 3M[®] film must transmit near-infrared photons to the underlying silicon solar cells (where they will be converted directly to electricity) while reflecting visible photons to the focus of the module where they may be absorbed by, for example a wavelength-agnostic thermal absorber used to drive a heat engine. Angle-resolved reflectance and transmittance measurements with the ARTA indicated that the freestanding 3M[®] film is an effective optical filter for both s- and *p*-polarization and angles of incidence of up to approximately 50°. To maintain its efficacy when laminated to the curved glass of the proposed module, the film must be conformally attached to the glass (without wrinkles), and ARTA measurements with a narrow detector aperture revealed the degree to which each evaluated lamination procedure produced the desired result. We are presently using the spectra generated by the ARTA to estimate the annual energy output of a power plant employing these curved modules with thermal receivers at their foci, taking into account the daily and annual movement of the sun and the resulting variation in angle of incidence on the module. We are also pursuing optical filters that reflect both visible and infrared light (while transmitting near-infrared light), and the performance of these is under study with both the integrating sphere and ARTA accessories.

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Linearity Measurements in the Visible Region on a LAMBDA 850/950/1050 Using Hellma Linearity Filters

UV/Vis/NIR Spectroscopy

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Introduction

This note demonstrates the use of Hellma[®] linearity filters to study the linearity of the PerkinElmer[®] high performance LAMBDA[™] instruments (LAMBDA 850, 950 and 1050) in the visible region of the spectrum. Hellma[®] linearity filters are cut from the single block of "black" glass with increasing thickness, and polished to high tolerances, so that the thicknesses increase in equal steps. The glass is selected so that the steps in thickness of the filters (0.25 mm) result in approximately 1 A change in absorbance at 546 nm. Although the steps may not be exactly 1 A, the size of the increase in absorbance should be equal.

Experimental

Wavelength scans are taken on a LAMBDA 950 between 400-700 nm in 2 nm steps, with a slit width of 5 nm and a detector response time of 1 second. When required, signal to noise was optimized by attenuating the reference beam with internal attenuators. The LAMBDA 950 has 1 A and 2 A auto-attenuators which may be augmented by an additional magnetic attenuator on the sample compartment window as necessary. The LAMBDA 1050 features automatic 2 A and 3 A attenuation and can be similarly augmented. For all spectra, 100% and 0% autozero correction scans were taken.

The spectral data collected are displayed in Figure 1. There is no significant noise apparent on the data even for

Results

samples with absorbance greater than 8A. Hellma Linearity Filters



Figure 1. Scan taken with Hellma[®] filters (F1-F7 – See Table 1) between 400 and 700 nm with 2 nm steps, 5 nm slit and 1 second integration time. The attenuation used in the reference beam is shown alongside the filter number.



Table 1. Hellma® filters used.			
Filter number	Absorbance approx.	Thickness	
666.034/1-F1	3 A	0.75 ±0.01 mm	
666.034/1-F2	4 A	1.00 ±0.01 mm	
666.034/1-F3	5 A	1.25 ±0.01 mm	
666.034/1-F4	6 A	1.50 ±0.01 mm	
666.034/1-F5	7 A	1.75 ±0.01 mm	
666.034/1-F6	8 A	2.00 ±0.01 mm	
666.034/1-F7	9 A	2.25 ±0.01 mm	
666.034-F0	-	Blank	

Figure 2 shows the data plotted against filter thickness. A least squares method is used to perform a linear fit to the data. The deviation from the linear fit is small, being <0.04 A. The tolerance on the thickness of the filters (\pm 10 micrometers) is significantly greater than the deviation noted. The fitted line intersects the origin at 0.036 A, this is expected as reflection losses at the two surfaces of the filter are not accounted for in this experiment. The measured reflection loss per surface is 4% T, which is expected for this type of glass.



Figure 2. Measured absorbance of Hellma® filters against filter thickness.

Conclusion

High quality spectral data have been obtained for samples greater than 8 A. The absorbance linearity of the data is very good with only small deviation from the linear fit >0.04 A, and these errors can be attributed to the thickness tolerance of the Hellma[®] linearity filters.

These results were taken with a LAMBDA 950 spectrometer, but equivalent results can be obtained with all instruments in the LAMBDA 850/950/1050 series. The LAMBDA 1050 provides enhanced functionality for high absorbance samples due to its higher light throughput (source doubling mirror) and built-in automated attenuators up to 3 A (LAMBDA 950 up to 2 A). The LAMBDA 1050 can measure samples with attenuation values approaching 8 A without use of additional manual attenuators.

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UV/Vis Spectroscopy

Validating UV/Visible Spectrophotometers



UV/Visible spectrophotometers are widely used by many laboratories – including those found in academia and research as well as industrial quality assurance. The technique is mainly used quantitatively (although some qualitative analysis can also be performed).

For any type of critical determination, whether it be clinical, pharmaceutical or industrial QC, environmental analysis or research, it is essential that the instrument is performing according to specification. In some of these applications, it is important that the instrument performance is monitored regularly and that there is documentary evidence that this is the case.

This will apply to any measurements to do with human or animal health (clinical or pharmaceutical/nutraceutical), food or labs offering an accredited measurement service (e.g. in accordance with ISO 17025). Validation is also a key requirement of Good Laboratory Practice (GLP).

Testing frequency

One common question from laboratories relates to the frequency of testing. There are no regulations, as such, regarding this but for any human health or nutrition related analysis, a testing frequency of at least monthly should be considered. If the instrument is in a high sample throughput environment, then some additional weekly testing (e.g. absorbance and wavelength check) should be performed.

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Testing wavelength accuracy

Wavelength accuracy is normally assessed by using either a sample containing a series of very sharp peaks such as a solution of holmium perchlorate or a holmium oxide and/or didymium doped glass filter or by measuring the emission from a lamp. If the instrument is equipped with a deuterium (D2) lamp as the UV source, this can be used. An external mercury (Hg) lamp can also be used. This is less convenient than using the previously mentioned methods but methodology exists (e.g. in the Ph. Eur. tests) for its use as an alternative to a glass or liquid standard. The advantage of emission lines is that they are inviolate (i.e. the emission wavelengths don't change over time).

Using the deuterium lamp

If the instrument uses a deuterium lamp, it is possible to measure the very sharp emission line at 656.1 nm by switching off the visible lamp and measuring the energy (single beam mode). There is also a weaker emission line at 486.0 nm that can be used. This is not as rigorous as using other wavelength standards (as fewer lines are available) but it does serve as a very convenient and accurate way to assess that the instrument's optics are aligned correctly. Some PerkinElmer instruments (such as the LAMBDA[™] 25/35/45) use the 656.1 nm emission line of D2 upon switch-on to calibrate the monochromator. Others (such as the LAMBDA 800/900 and LAMBDA X50 series) can perform this calibration on demand (and store the values in the instrument firmware). UV WinLab[™] v5 and v6 have methods to check this and produce a report). These methods use the rear beam for the procedure (just in case a sample has been left in the front position by mistake). The 486.0 nm emission line (but not the 656.1 nm line) is one of the possible test points in the Ph. Eur. 5.2 (2005).



Figure 1. Deuterium peak showing peak close to 656.1 nm (smaller peak is due to the heavier tritium).

Using a mercury emission source

The use of a mercury (Hg) emission lamp is another way to check wavelengths. This lamp offers more lines compared to deuterium – particularly in the UV region. The practicalities of using such a lamp are a little more difficult. The mercury lamp needs to be placed in the instrument's lamp compartment. The principal mercury emission lines are shown in Figure 2.

253.7 nm	302.25 nm	313.16 nm	334.15 nm	365.48 nm
404.66 nm	435.83 nm	547.07 nm	576.96 nm	579.07 nm

Figure 2. Wavelengths for mercury emission lamp.

Glass and liquid filters

The most commonly used glass (or quartz) filter is holmium oxide. This provides a guick and easy way to check wavelength accuracy. This standard gives a series of lines in the visible region. It does not provide strong absorption peaks into the UV region and so a solution of holmium oxide in perchloric acid (holmium perchlorate) is recommended by some pharmacopoeias but for general non-pharmacopoeia instrument testing, holmium oxide glass is widely used. Another material that is used is "didymium" - a mixture of praseodymium and neodymium. This is recommended by the U.S. Pharmacopoeia (USP 24) as well as others such as the JP (Japanese Pharmacopoeia). As with holmium oxide, it is also available in solution form. Other wavelength standard solutions commercially available include samarium perchlorate, which gives a range of wavelengths in the UV and visible regions between 230 and 560 nm and "rare earth sulphate" which gives far UV wavelengths between 201 nm and 253 nm.

Holmium oxide quartz	279.2 nm 453.7 nm 637.7 nm	360.9 nm 536.5 nm
Holmium perchlorate solution	241.15 nm 361.5 nm	287.15 nm 536.3 nm
Didymium glass	440.4 nm 513.4 nm 879.3 nm	481.0 nm 684.5 nm





Figure 4. Spectrum of holmium perchlorate solution for wavelength accuracy testing.

Photometric (absorbance) accuracy testing

As with wavelength accuracy testing, either solutions or glass/quartz filters can be used. For general applications neutral density grey glass filters (such as the NIST® 930D set) are a convenient way to test the photometric accuracy of instruments. These offer a number of wavelengths in the visible region. For testing in the UV either "metal on quartz" glass filters or solutions must be used. Metal on quartz filters have a reflective coating applied to a quartz plate. This can cause issues due to the strong back reflection sent back through the instrument's optics so they may not be suitable for all types of instruments. The coating needs to be treated with care as any damage will alter the optical properties.

The most commonly used solution for checking absorbance accuracy is potassium dichromate. The original 1988 Ph. Eur. method tests absorbance at four wavelengths – 235, 257, 313 and 350 nm using between 57.0 and 63.0 mg of potassium dichromate in 0.005 M sulphuric acid diluted to 1000 mL. Since 2005 a second solution has been added to provide an additional test point at 430 nm. This uses the same amount of potassium dichromate but is made up to 100 mL (i.e. it is ten times more concentrated than the original solution). In both cases the A 1%/1 cm value is recorded and checked against the target range.

Nictonic acid (0.1 M hydrocholoric acid) in a range between 6 and 24 mg/L) can be used to assess photometric accuracy in the far UV region (at 213 nm and 261 nm). This is not an official procedure but reference materials are commercially available for this test.

Care has to be taken when preparing the solutions as potassium dichromate is hygroscopic and so it is important that this is dried thoroughly otherwise the weight will be incorrect and this could result in an unnecessary failure.

Double aperture correction for photometric accuracy

No instrument has a perfectly linear detector response and so the observed photometric accuracy will have a greater deviance from the certified values as a result. It is possible to correct for this systematic error by using a technique called double aperture correction. This procedure is only available for instruments at the upper performance range. To correct for this, it is necessary to purchase a double aperture accessory. This accessory consists of a series of shutters either manual or motorized - which are able to measure the top and bottom half of the beam. The mechanism must be highly precise such that there is no overlap between the two measurements. It is then possible to calculate a correction factor that can be used for subsequent measurements. Instrument manufacturers will guote photometric accuracy both with and without double aperture correction as part of their specifications. It will also be used by some national standards

laboratories as part of their determinations but it is very rare to find it used elsewhere due to its complexity and offering a precision that is unnecessary for most measurements.



Figure 5. Double aperture accessory.



Figure 6. Double aperture correction for detector non-linearity.

Stray light testing

Stray light can be defined as the amount of unwanted wavelengths that are present in the sample beam. In a conventional "dispersive" instrument, the monochromator is before the sample and the sample receives one wavelength at a time. After the sample, there is only the detector. This means that any stray light that gets past the monochromator will be seen by the detector. Stray light has a strong impact on the instrument's ability to record accurately at higher absorbances and is a key specification when assessing the guality of a spectrophotometer. For a single monochromator instrument (as found in most chemical and biochemical laboratories) the best achievable stray light value (using ASTM[®] methodology) will be around 0.01%T. This equates to one in every 10,000 photons being due to stray light. This may sound like a small amount but it has to be remembered that absorbance is a logarithmic scale and so 3AU (equivalent to 0.1%T) equates to only one in a thousand photons actually passing through the sample and reaching the detector. If the stray radiation is mainly "far" stray light (i.e. wavelengths some distance from the actual analytical wavelength) then it is unlikely to be absorbed by the sample and thus will cause the linearity to become worse at higher absorbances as the absorbance becomes swamped by the [constant] stray light. If linear performance greater than 3A is required, systems with more than one monochromator must be considered either premonochromator (using a smaller auxiliary

monochromator) or a full double monochromator (two equivalent monochromators). It should, however, be taken into consideration that for most liquid samples, they can be diluted or measured in short pathlength (e.g. 5 mm) cuvettes and so measurement at such a high absorbance value shouldn't be necessary – multiple monochromator systems are usually only necessary for materials and optics analysis where it is not possible to adjust the sample.



Figure 7. Effect of instrumental stray light on absorbance linearity.

Stray light tests should be carried out on the basic instrument and in a configuration specified by the manufacturer for that particular test. If any accessories are fitted (e.g. sippers, integrating spheres, cell changers, etc.) these can have a detrimental effect on the stray light value due to additional light leakage, etc. Clear plastic tubing entering the sample chamber from outside can act as a fiber optic and transfer light from outside to the inside of the instrument. It is recommended to either use black tubing or to shroud the tubing (an outer black tubing sheath works well) for about 5 cm prior to entering the sample area in order to minimize this.

Stray light testing to ASTM® methodology

ASTM[®] stray light testing involves the use of two solutions – 10 g/L sodium iodide (NaI) for 220 nm and 50 g/L sodium nitrite (NaNO₂) for 340 nm and 370 nm. These solutions have a very sharp cut-off in the UV region. This means that if light is detected at a wavelength where the sample is supposed to be completely blocking, this must be due to stray light passing through the transparent part of the sample spectrum. As a further confirmation, it is possible to block the beam (the metal frame of our glass filters inserted "side-ways on" into the instrument makes an ideal beam blocker) and compare the measurement of the stray light solution to the blocked beam – the difference between the two giving the stray light value. A similar test can be performed at 650 nm using a 0.1 g/L methylene blue solution or measuring around the cut-off of pure acetone between 250 and 320 nm.

All tests should be carried out using a 1 cm (10 mm) quartz cuvette.



Figure 8. ASTM $^{\circ}$ stray light test at 220 nm using a 10 g/L sodium iodide (NaI) solution showing stray light to be less than 0.01% T.

Stray light testing for pharmacopoeia

The European Pharmacopoeia (Ph. Eur.) performs the test in absorbance (unlike ASTM[®] where transmittance is used as the ordinate mode) and the recorded value of a 12 g/L aqueous potassium chloride solution at 198 nm should be 2A or greater. This test was revised in 2005 as the test wavelength was moved from 200 nm (which had been used since 1988) to 198 nm. The original 200 nm wavelength was influenced somewhat by the sample temperature and whether or not the solution had been degassed (sealed cuvettes were less prone to this) and so moving the test point down to 198 nm made the test more robust.



Figure 9. Stray light testing according to Ph. Eur. using 12 g/L KCl solution showing the difference in stray light in a premonochromator instrument (LAMBDA 45) compared to a single monochromator instrument (LAMBDA 25/35). It also shows the improvement in the result when using 198 nm as the test point instead of 200 nm.

Some pharmaceutical companies use their own stray light test solutions such as a saturated solution of lithium carbonate (at 227 nm) or sodium chloride (at 205 nm) as part of their in-house procedures but these are not officially recognized by the major pharmacopoeias.

Resolution testing

The European Pharmacopoeia introduced a resolution test as part of the original 1988 methodology. This is based on measuring a solution of 0.02% w/v solution of toluene in hexane, measuring the ratio of the peak (at 269 nm) and the trough (at 266 nm) and measuring the ratio. This ratio should be 1.5 or greater unless prescribed in the monograph. This means that, although it is highly desirable for an instrument to pass this test, it is not essential but most manufacturers regard this to be a part of making an instrument "pharmaceutical compliant" and some carry out the measurement as part of their final test procedure. In practice, an instrument with a bandpass (slit width) of around 1.5 nm should pass this test. For a fixed bandpass instrument, the measurement should give fairly constant results as there is no mechanical movement involved. If the instrument has variable bandpass – particularly if the slits can be varied continuously using a stepper motor "jaw" mechanism, test results may vary more and so the test should be carried out more frequently.



Figure 10. Resolution test using 0.02% w/v toluene in hexane (in this example ratio is approx 1.9).

In 2005 the European Pharmacopoeia introduced a second method involving a solution of toluene in methanol and based on second derivative (D2) spectroscopy. At the time of writing, this test is not widely used.

Additional testing

It may be useful to perform additional tests on the instrument using methodology not contained in pharmacopoeias but using a subset of the manufacturers' own in-house service procedures. These can give an indication of things such as lamp deterioration. Some examples are:

Absorbance stability (drift) – measuring how an absorbance changes (usually in absorbance per hour) under stipulated conditions.

Baseline flatness – the instrument is autozeroed with nothing in the sample compartment across its working range and this is then measured. Some manufacturers specify flatness over a restricted range (e.g. 200-800 nm) which may not be the full working range of the instrument. This is normally the case with photomultiplier based instruments where the photomultiplier suffers a fairly major loss of sensitivity above 800 nm.

Noise – this is measured at a particular wavelength under prescribed conditions. It may be measured at zero absorbance or at a specified absorbance value (e.g. 1A).

Reproducibility (both in terms of wavelength and photometric accuracy).

Testing reflectance

Some laboratories wish to test the accuracy in reflectance. These tend to be the more highly specified instruments and they must be equipped with a suitable reflectance attachment. This is usually an integrating sphere for diffuse and total reflectance and either a relative or absolute attachment for specular reflectance.

For diffuse reflectance, it is possible to purchase diffuse reflectance standards. These are either grey standards where differing amounts of carbon black are added to the white material or color standards where the white material is dyed. For perfectly diffuse materials, Spectralon® is probably the best material. This is a proprietary white sintered PTFE material which is resistant to yellowing and can be cleaned easily. When measuring these standards, it is best to use as large a beam as possible. The standards aren't completely homogenous and so, for very small beams, it is possible to pick up individual "smuts" of carbon which will give an inconsistent result. By measuring the %RSD (Relative Standard Deviation (Figure 16 – Page 9) of these standards, the expected tolerance can be assessed.

For measuring specular reflectance, the most commonly used material is a front surface coated aluminum mirror as this reflects across the UV/Vis/NIR range. These mirrors are less reliable in the UV range as any surface scratches will contribute to higher scatter in the UV region due to the physics of scatter phenomena. One other issue with these mirrors is that they are often required to be traceable as part of a laboratory gaining accreditation (e.g. ISO 17025). Traceable mirrors often have a poor specification – such as ±1% reflectivity and this may not be good enough for some applications (such as the measurement of laser mirrors where accuracy of 0.1%R is highly desirable). The reason for this wide tolerance is that national standards labs compare their standards with other laboratories and so, the more laboratories are involved, the higher the statistical spread of data which increases the specified uncertainty.

When testing reflectance, there can be some debate about the "correct" result for a particular sample. Most standards are fairly ideal in nature so, for example, Spectralon[®] is almost perfectly diffuse and an aluminum mirror is almost perfectly specular. Actual samples may lie somewhere in between – displaying a mixture of both types of reflectance. In order to address this issue, some industries (e.g. paint manufacturers) sometimes use calibrated ceramic tiles as they have a higher specular component.

When measuring reflectance (unless using an absolute accessory), it is necessary to zero the instrument and accessory using a standard whose reflectance is known. It is then necessary to perform a mathematical correction to remove the contribution of this standard and convert the relative measurement into an absolute one. If this is not done (i.e. the relative value is used) for a set of absolute standards, the results will be invalid.

Testing in the Near Infrared (NIR) region

Some spectrophotometers also have near infrared capability and can measure in excess of 900 nm and so it is necessary to assess performance in this region. There are some test procedures that are applicable in this region. These include:

- Wavelength accuracy of the NIR grating using the second order deuterium emission line at 1312.2 nm or 972 nm (i.e. two times 656.1 nm and 486 nm. respectively).
- Wavelength accuracy using a holmium oxide which gives a peak at 1938 nm.
- Wavelength accuracy using a McCrone standard. This is a composite standard which give additional lines in the NIR from 481 nm to 2326.8 nm (available from the U.K. NPL).
- Stray light using water at 1420 nm chloroform at 2365 nm.

- Photometric accuracy using grey glass standards. Some grey glass standards have test points in the NIR region in addition to the UV/Visible range.
- Reflectance both Spectralon[®] and aluminum mirrors can be used to check reflectance in the NIR region. Spectralon[®] cuts off above 2500 nm.

Validating PerkinElmer UV/Vis and UV/Vis/NIR Spectrophotometers Using UV WinLab software

UV WinLab software (v4 and higher) contains features to aid with the calibration of spectrophotometers.

For medium performance instruments (LAMBDA 20, 25/35, 40/40P and 45), there is the Instrument Performance Verification (IPV) module. This module contains over twenty tests that the user can perform to check performance. Some tests require a standard or an external mercury lamp whereas others do not.

IPVSetup - Winchester	
Certa Prosetup Reporting Tests	Available tests IPV-Wavelength Accuracy Third Party Lamp IPV-Wavelength Accuracy Glass IPV-Wavelength Accuracy Solution IPV-Resolution Benzene IPV-Resolution Toluene IPV-Resolution Toluene IPV-Photometric Accuracy KN03 Solution IPV-Photometric Repeatability Glass IPV-Photometric Accuracy KN03 Solution IPV-Photometric Repeatability Glass IPV-Noise 1 IPV-Noise 1 IPV-Noise 2 IPV-Noise 3 IPV-Absothance Zero Stability IPV-Stray Light Nal 220 nm IPV-Stray Light Nal 220 nm IPV-Stray Light Nal 220 nm IPV-Photometric Accuracy K2Ci207 Solution 430 nm IPV-Photometric Inereativ Green Glass IPV-Photometric Inereativ Green Glass IPV-Photometric Inereativ Green Glass Add >
0	Exit

Figure 11. IPV module – methods list.

Each test can be populated with standard serial number and calibration date information (where applicable) and a testing frequency for each test can also be established. In the ES (Enhanced Security) version of the software, it is possible to set the permissions such that an analyst cannot use the instrument if it has failed the calibration or the calibration is overdue (this can be over-ridden by a system administrator, if required). If any tests are required that are not part of the IPV module, these can be created using standard UV WinLab methods.

Test	Standards Required
Wavelength accuracy – third party lamp	Third party lamp (e.g. mercury)
Wavelength accuracy glass	Calibrated standards set (B0507805). Traceable to German PTB
Wavelength accuracy solution	Pharmacopoeia standards set (B2500100) using holmium perchlorate (Ph. Eur. test)
Wavelength accuracy – D ₂	No standard required – uses instrument's deuterium lamp (486 nm and 656.1 nm)
Wavelength repeatability – D2	No standard required – uses instrument's deuterium lamp (486 nm and 656.1 nm)
Resolution – benzene vapor	Sealed Benzene cell (toluene acceptable substitute)
Resolution – toluene	Pharmacopoeia standards set (B2500100) using toluene in methanol (Ph. Eur. test)
Photometric accuracy glass	Calibrated standards set (B0507805). Traceable to German PTB
Photometric accuracy – K ₂ Cr ₂ 0 ₇	Pharmacopoeia standards set (B2500100) using K ₂ Cr ₂ 07 solution (Ph. Eur. test)
Photometric accuracy – KNO ₃ solution	KNO3 solution
Photometric repeatability glass	Calibrated standards set (B0507805). Traceable to German PTB
Baseline stability (flatness)	No standard required
Noise (three tests)	No standard required
Absorbance zero stability (drift)	No standard required
Stray light KCl solution (1988/2005 Ph. Eur. test)	Stray light standards (B2500099)
Stray light NaI (ASTM®)	Stray light standards (B2500099)
Stray light NaNO ₂ (ASTM®)	Stray light standards (B2500099)
Resolution (toluene in methanol – Ph. Eur. 2005)	Toluene in methanol solution
Photometric accuracy – K ₂ Cr ₂ 0 ₇ at 430 nm (Ph. Eur. 2005)	Solution of K ₂ Cr ₂ 0 ₇

For the high performance instruments, there is a collection of Service Methods. These are similar in nature to the IPV methods but there are more of them (reflecting the additional complexity of these instruments) and they are regular analytical methods arranged into a collection rather than being part of a separate software module. There are also additional service methods for some major accessories such as the integrating spheres and the Universal Reflectance Accessory (URA).

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Figure 12. Service methods for the high performance instruments.

Calibration utility for the high performance LAMBDA instruments

The high performance LAMBDA instruments also have an onboard facility to adjust the instrument's slit and wavelength settings. This calibration utility can be accessed by right-clicking on the instrument icon (in the instruments node of UV WinLab). Unlike other tests described here, it will measure and correct for any wavelength shift detected - it can be regarded as a kind of "autotune" routine. It also calibrates the continuously variable slit mechanism as well as checking the 0%T offset. The wavelength calibration is based on the 656.1 nm deuterium emission line (the 486.0 nm line can be also used optionally). The NIR monochromator can also be checked using the second order 1312.6 nm line. Please note that the photomultiplier is used for all tests (even the NIR wavelength accuracy - due to the fact that it is a second order effect and so the detector is still actually detecting at 656.1 nm). Where possible, it is best to calibrate the instrument using the standard detector rather than with an accessory. This is because very narrow slits are used for the wavelength calibration and so sensitivity is important. For dedicated "S" and "R" versions of the LAMBDA 650 and 750, the calibration routine in v6.0.4 (released in October 2011) has been enhanced in order to allow successful calibration when the sphere or URA are installed in place of the standard detector.

Routine	Description	Last Calbrated	Enable
Siles	Calbrates sits	04 October 2011 14:05	
UWis Wavelength	Calbrates the UV/Vis wavelength range	04 October 2011 14:06	2
NIR Wavelength	Calbrates the NIR wavelength range	04 October 2011 14:10	
Zero Percent 1	Calbrates the electronic offsets	04 October 2011 14:13	×
ssages librating 0% T, please wak T calibration successful	Settings	Colixete	
T calbration saved te: 2011/10/04 14:13:19 sample 1933;1940,1942;15 reference 1941;1943;1948	45,1951,1963 1957,1977,2015		
ady	AUGU 110		

Figure 13. Calibration utility screenshot.





Setting tolerances

When devising a validation test, it is necessary to set realistic tolerances for the test, otherwise it will fail unnecessarily. The tolerance should comprise of three parts which should be added together. These are:

- The uncertainty of measurement given on the standard certificate (or published emission wavelength if using a source emission line).
- The manufacturer's specification for the instrument that relates to that particular standard (e.g. a wavelength accuracy test will be influenced by the instrument's wavelength accuracy specification as well as the tolerance of the standard).
- Any influence to the measurement coming from the operator or other parts of the system.

Validating assays

So far, the instrument validation itself has been discussed. An instrument may be working perfectly but may still not be fit for purpose of a particular assay. This may be because the instrument has unsuitable specifications for that particular determination. As a trivial example, a perfectly functional instrument covering the range 190 to 900 nm would be unsuitable for measuring absorbance at 1000 nm.

Cuvette validation

Testing of the type of cuvette chosen for a particular assay should also be included in any validation of the assay. This should be in terms of design (macro, semi-micro, micro, ultra-micro, whether the walls are blackened, etc.), construction material (quartz, fused silica, NIR silica, glass, etc.) and the manufacturing tolerance of the nominal pathlength (usually to German norm DIN 58963-1/2).

Validating solvents

Water is a commonly used solvent in UV/Visible absorption spectroscopy. It is a near perfect material offering transparency over of the UV/Visible range (but having stronger absorption bands in the NIR region) and ideal for the wide range of water-soluble analytes.

Some materials (e.g. organic species) will not dissolve in water and others (mainly biological compounds) may require other substances to be present in order to stabilize the material (e.g. buffer solutions).

It is necessary, therefore, to check that the analysis is being conducted at a wavelength where the solvent is sufficiently transparent for the assay to be stable and reproducible. This can be done by assessing the cut-off point of the solvent. The most commonly used definition is the point at which the solvent has a transmittance of 10% (1 Absorbance) in a 1 cm cuvette. This can be ascertained quite easily by scanning the solvent or buffer on its own in a 1 cm quartz cuvette (using air as the autozero) and observing the point at which the spectrum reaches 1 absorbance.

Beyond the cut-off point, the solvent becomes completely opaque and the instrument will try as best it can to continue measuring (particularly if solvent is in both sample and reference beams) but what is observed is not useful analytically and routine methods should be constructed in such a way that they don't collect data where the solvent is beyond its cut-off point as it will only cause confusion in trying to interpret meaningless results. Measuring the sample in energy (single beam) mode will give a clearer picture of what the instrument's detector is observing. Solvent manufacturers offer different purity grades of solvents and the UV cut-off point will normally be stated on the bottle. Some approximate cut-off points of common solvents are shown in the table below.

Solvent	Cut-off (nm) (>1 AU in 1 cm cuvette)
Water	190
Cyclohexane	200
Acetonitrile	200
Methanol	205
Isopropanol	210
Dichloromethane	233
Ethyl Acetate	256
Toluene	254
Acetone	330

Using statistics to evaluate the data

Statistical analysis techniques provide a useful "toolkit" in the assessment of validation data – both in terms of the instrument calibration and also with respect to a particular assay.

It is also necessary to determine the robustness of a calibration or assay in terms of its accuracy and precision. The diagram below gives a good visual representation of these two terms.



Figure 15. Pictorial representation of accuracy and precision.

Assessing precision is useful when dealing with autosamplers – either "sippers" or carousel type devices. These devices rely on pumping the sample through a flowcell and are, therefore, prone to carryover. Although it is possible to devise operating parameters that will avoid this (e.g. minimum pumping times), they will be affected by things such as sample viscosity, temperature, etc.

Statistical assessment of the measurement result

The following statistical formulas are useful in assessing precision and accuracy:

Mean Value

$$\overline{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

The arithmetic mean value of a set of data points.

Standard Deviation

$$s_x = \sqrt{\frac{1}{n-1}} \cdot \sum_{i=1}^n (x_i - \overline{x})^2$$

Relative Standard Deviation (%RSD)

$$RSD(\%) = \frac{S_X \cdot 100}{\overline{X}}$$

Residual Error (of linearity data or a calibration curve)

$$s_y = \sqrt{\frac{1}{df}} \sum_{j=1}^{H} (y^*_i - y_j)^2$$

Variance

$$s_x^2 = \frac{1}{(n-1)} \sum_{j=1}^n (x_j - \bar{x})^2$$

Where:

- n Number of data points.
- x_i The analytical value of the data point (e.g. concentration).
- y_i The ordinate value of the data point (e.g. absorbance).
- y^{*} Corresponding point on the calibration curve.
- df Number of degrees of freedom (linear curve without intercept = 1, linear curve plus intercept term = 2, quadratic curve without intercept = 2, quadratic curve with intercept = 3).

Error assessment

Random errors

Random errors are caused by unavoidable deviations of the analytical results obtained with *n* determinations of the same sample from the related value (mean value of unknown samples, known value with reference samples). A measure for the random error is the repeatability, estimated from measurement values of completely independently repeated measurements. Each repeated measurement must be carried out as if it were a separate unknown sample.

Systematic errors, bias

Systematic errors (bias) are the deviations of the mean value obtained from *n* repeated measurements (expectation) from the related value (true or conventional true value). If there are systematic errors, this difference is bigger than the range of confidence of the mean value. The respective range of confidence is calculated from the standard deviation according to the given statistical accuracy. The systematic deviations are also characterized by the term **trueness**.

Shewhart Charts

Shewhart Charts (or Means Control Charts) are a useful tool to trend data – either within a particular analytical batch (if there are a statistically significant number of samples) or over a time period. They are useful for trending both analytical data and the results from calibrations so that any change in instrument performance can be monitored and the result of any change in the measurement system (such as a lamp change) can be assessed. UV WinLab uses a database as the primary repository for data and so it is possible to query this database using a combination of search criteria such as user, date range, instrument, keywords in either the method or task (data) name in order to select data that fits the search criteria.

In the example shown, the deviation from the deuterium emission line at 656.1 nm is trended to show the mean deviation is approximately 0.016 nm (specification is 0.08 nm for this particular instrument – a LAMBDA 1050 UV/Vis/NIR spectrophotometer). Statistical limits (based on 2 and 3 standard deviations – 2σ and 3σ) are also shown on the diagram.



Figure 16. Shewhart chart showing deviation from deuterium emission line at 656.1 nm.

Standards Available from PerkinElmer

The following standards materials are available from PerkinElmer:

Part Number	Description	Traceability
B0507805	Photometric and Wavelength Accuracy Reference Material Set Set of secondary reference materials traceable to NIST [®] to verify the ordinate and abscissa (wavelength) accuracy of UV/Vis and UV/Vis/NIR spectrometers. The set comprises four glass filters mounted in precision aluminum spring mounts. They are designed for use with the standard 10 mm cuvette holders of most UV/Vis and UV/Vis/ NIR spectrometers. The set is provided in a robust aluminum container. There are three neutral density glass filters for checking the ordinate accuracy and a holmium oxide glass filter for checking the wavelength accuracy of a spectrometer. Each filter has a unique identification number. The certified ordinate and abscissa values and tolerances of each filter are quoted in the accompanying Certificate of Calibration. Measured wavelengths for the three neutral density filters are 440.0, 546.1, 635.0, 1700, and 2300 nm. The glass filters are chosen to provide nominal absorbance values of 0.3 A (50%), 0.5 A (30%) and 1 A (10%).	German PTB
N1010545	Holmium Oxide Glass Filter Holmium oxide glass filter for checking the wavelength accuracy of a UV/Vis or UV/ Vis/NIR spectrometer. The filter is mounted in precision aluminum spring mount and is provided in a robust aluminum container, with a Certificate of Calibration.	U.S. National Institute of Standards and Technology (NIST®)
B2500099	Stray Light Solutions Reference Material Set Set comprising four solutions in sealed cuvettes – one reference solution and three test solutions. The cuvettes are designed for use with the standard 10 mm cuvette holders of most UV/Vis and UV/Vis/NIR spectrometers. The test solutions comprising sodium iodide, sodium nitrite and potassium chloride, which act as high-pass filters with very precise cut-off wavelengths. Potassium Chloride (KCL) for measuring stray at 200 nm, Sodium Iodide (NaI) for measuring stray light at 220 nm, and Sodium Nitrite (NaNO ₂) for measuring stray light at 340 and 370 nm. The set is provided in a robust aluminum container, with a Certificate of Calibration.	Instrument calibrated using NIST [®] 930D standards

Standards Available from PerkinElmer, continued

Part Number	Description	Traceability
B2500100	 Pharmacopoeia Reference Material Set Set comprising six solutions in sealed cuvettes – two reference solutions and four test solutions to verify calibration in accordance with pharmacopoeia monographs: Ordinate (photometric) accuracy; potassium dichromate. Measured wavelengths are 235, 257, 313 and 350 nm 	Instrument calibrated using NIST® 930D standards
	Abscissa (wavelength) accuracy; holmium perchlorate	
	Level of stray radiation; potassium chloride for measuring stray radiation at 200 nm Resolution; toluone in havene	
	The cuvettes are designed for use with the standard 10 mm cuvette holders of most UV/Vis and UV/Vis/NIR spectrometers. The set is provided in two robust aluminum containers with Certificates of Calibration.	
PELA9057 (1.25" dia.)	Calibrated Spectralon [®] Diffuse Reflectance Standard 250 - 2500 nm, reported every 50 nm. CD-ROM provided with data every 1 nm.	U.S. National Institute of Standards and Technology (NIST®)
PELA9058 (2" dia.)		
PELA9010 (1.25" dia.)	Spectralon[®] UV/Vis/NIR Diffuse Reflectance Reference Materials Spectralon [®] diffuse reflectance reference material sets consist of a diffuse white reference	U.S. National Institute of Standards and Technology (NIST®)
PELA9011 (2" dia.)	 material and a selection of three diffuse gray reference materials. Each reference material in the set is supplied with complete diffuse reflectance data from 250 nm to 2500 nm, and is mounted in an anodized aluminum frame. The set is packed in an airtight storage case. Durable, chemically inert 	
	Reflectance values – 99%, 75%, 50% and 2%Washable	
PELA9012 (1.25" dia.) PELA9013 (2" dia.)	 Spectralon[®] UV/Vis/NIR Diffuse Reflectance Reference Materials Spectralon[®] diffuse reflectance reference material sets consist of a diffuse white reference material and a selection of seven diffuse gray reference materials. Each reference material in the set is supplied with complete diffuse reflectance data from 250 nm to 2500 nm, and is mounted in an anodized aluminum frame. The set is packed in an airtight storage case. Durable, chemically inert Reflectance values – 99%, 80%, 60%, 40%, 20%, 10%, 5% and 2% Washable 	U.S. National Institute of Standards and Technology (NIST®)
PELA9018 (1.25" dia.) PELA9019 (2" d	Set of Four Color Standards (Red, Green, Blue, and Yellow) ia.)	U.S. National Institute of Standards and Technology (NIST®)
PELA9020	Set of Four Color and Four Grey 2" Standards (Red, Green, Blue, Yellow, Plus Four Greys) (99%, 50%, 20%, 2%)	U.S. National Institute of Standards and Technology (NIST®)
PELA9021	Set of Eight Color 2" Standards (Red, Green, Blue, Yellow, Orange, Cyan, Violet and Purple)	U.S. National Institute of Standards and Technology (NIST®)
L6310204	 UV/Vis/NIR Second Surface Reference Mirror Metal-dielectric multi-layer second surface reference mirror design optimized for stability and maximum reflectance in the UV/Vis/NIR range from 200 nm – 2,600 nm for checking the accuracy of absolute and to correct the spectra of non-absolute specular reflectance accessories. Easy to clean, protective 2 mm silica front plate Smooth reflectance curve without water related absorption bands in the NIR range Size 50 mm x 100 mm Calibration at 8 degrees incidence in the wavelength range 200 nm - 2,500 nm, calibration uncertainty typical < 0.25% Delivered in a lightweight protector case, accompanied by the calibration report and a 	Manufactured by OMT Solutions, Eindhoven, Netherlands This is not traceable to a national standard as it offers greater accuracy than any traceable material commonly available standard material.
	CD-ROM with the calibration data in different Excel® formats.	

Standards Available from PerkinElmer, continued

Part Number	Description	Traceability
N1010504	Disposable Reference Mirror for Reflectance Spectroscopy This mirror is necessary to check the accuracy of absolute and to correct the spectra of non-absolute specular reflectance accessories. The mirror is a secondary reference material and is calibrated according to GLP regulations, wavelength range 250 to 2,500 nm.	U.S. National Institute of Standards and Technology (NIST®)

Recalibration of standards

Most standards can be recalibrated. In some cases (e.g. aluminum mirror), the standard itself is an inexpensive material and also gets scratched over time and so it is not practical to have it recalibrated. It is, therefore, referred to as "disposable".

Some liquid standards can present issues with couriers/ airlines when being sent back for recalibration due to the materials (albeit only a trace) that they contain.

Further reading

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Standard method of estimating stray radiant energy (E387-72), in Analytical Methods of Spectroscopy, Philadelphia, PA: American Society of Testing Materials Committee E-13, Annual Book of ASTM[®] Standards, 1974, pp 291-302.

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