

T E C H N I C A L N O T E

a discussion of
optical geometry
and measurement effects



UPF Analysis of Textiles

using the Labsphere

UV-1000F Ultraviolet

Transmittance Analyzer



TABLE OF CONTENTS

This technical note serves to answer questions about the Labsphere UV-1000F Ultraviolet Transmittance Analyzer design, and how it compares to similar measurement instruments. Part One discusses the geometry of the optical system in respect to measuring diffuse transmittance. Part Two discusses the optical design's response to fluorescent fabric additives.

PART 1 DIFFUSE TRANSMITTANCE AND OPTICAL GEOMETRY

1.1 Introduction	2
1.2 Diffuse Transmittance Measurement of Textiles	2
1.3 Reciprocity of Illuminating and Viewing Geometry	2
1.4 Radiometric Advantage of d/0° Geometry	3
1.5 Optical Design of the UV-1000F Ultraviolet Transmittance Analyzer	3
1.6 Summary	4

PART 2 SPECTRAL MEASUREMENT AND SAMPLE FLUORESCENCE

2.1 Introduction	5
2.2 Measurement of Ultraviolet Protection Factor	5
2.3 Fluorescence and Optical Brightening Agents	6
2.4 Spectrophotometers and Fluorescence Materials	6
2.5 Monochromatic Illumination	6
2.6 Polychromatic Illumination	8
2.7 Effects of Optical Brightening Agent (OBA) on Sun Protective Clothing	8
2.8 Measuring Optical Brightening Agent Concentration	9
2.9 Summary	9

PART ONE. DIFFUSE TRANSMITTANCE AND OPTICAL GEOMETRY

1.1 Introduction

The following discussion illustrates diffuse transmittance measurement and the design advantages of employing diffuse illumination for measuring the ultraviolet blocking offered by sun protective fabrics.

The Labsphere UV-1000F Ultraviolet Transmittance Analyzer is designed for measuring the UV transmission of dry textiles as a means of determining their ultraviolet protection factor. The instrument operates by measuring the diffuse transmittance of a fabric sample as a function of wavelength in the ultraviolet spectrum. The UV-1000F satisfies all the requirements of Australian/New Zealand Standard AS/NZ 4399:1996¹

As with many methodology standards, the measuring apparatus details are generalized and subject to interpretation. AS/NZ 4399 does not strictly mandate the use of collimated illumination as some have interpreted. It does mandate the use of an integrating sphere which in practice can be used as either a diffuse light collector or as a diffuse light source, utilizing the principle of optical reciprocity. The AS/NZ standard implies optical reciprocity without being completely explicit. In comparison, methodology standards prepared for the colorimetry of materials are clearly explicit in their endorsement of reciprocal geometries (CIE, ISO, ASTM).

1.2 Diffuse Transmittance Measurements of Textiles

Many textiles are translucent materials which diffuse incident light. A ray of light incident onto a textile sample will be scattered. Light that is not transmitted is reflected or absorbed.

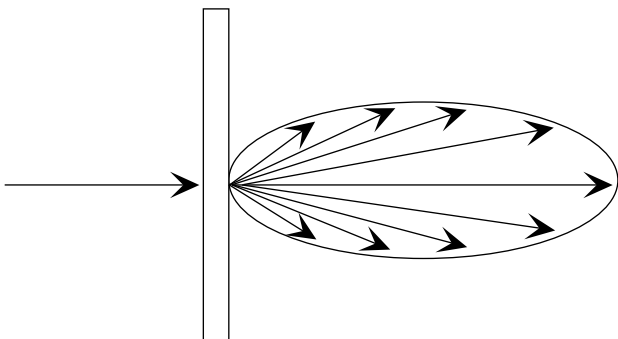


FIGURE 1

For translucent samples, the radiation intensity is strongest in proximity to the regular transmitted direction as shown in Figure 1. More opaque samples will produce an intensity pattern that approaches a uniform, hemispherical distribution. The ratio of the total transmitted light to the total incident light is known as the transmittance, a measurable quantity.

Total hemispherical transmittance is measured by the use of an integrating sphere to collect the light scattered at all angles.

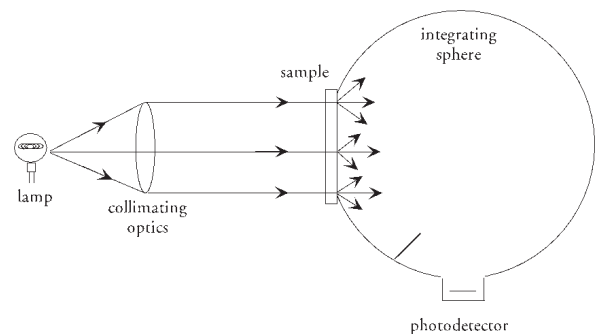


FIGURE 2

The interior walls of the integrating sphere are coated with a white, highly reflective material. In Figure 2, light from an external source is collimated and strikes the sample surface at normal incidence. A photodetector responds proportionally to the internal illumination produced on the sphere wall. A baffle prevents direct illumination of the detector after scattering from the sample. The incident beam flux is recorded initially without the sample in place to determine the measurement baseline.

1.3 Reciprocity of Illuminating and Viewing Geometry

The geometry depicted in Figure 2 is known as normal/hemispherical, which refers to the illuminating/viewing conditions. It is often abbreviated as $0^\circ/h$ or more commonly $0^\circ/d$ (diffuse) geometry.

The Helmholtz Reciprocity Principle^{2,3} states that the loss of light flux within a ray bundle will not be changed if the direction of travel is reversed. As applied to measuring instruments, the results will not change if the geometry of the illuminating and viewing beams are interchanged.⁴ Optical engineers often make full use of this principle in ray tracing calculations.

Consider the light scattering depicted in Figure 1. Instead of an incident ray, consider an observer's field-of-view (FOV). The sample scattering extends the FOV to multiple points in space beyond the sample. The scattered FOV is specific to the sample's scattering profile.

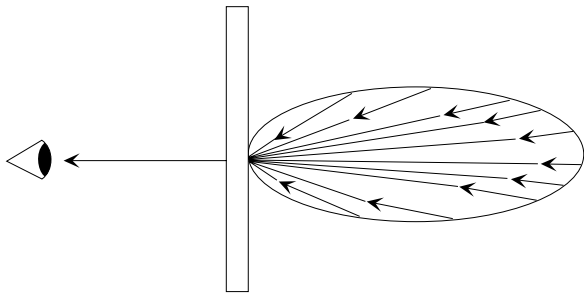


FIGURE 3

In practice, illuminating material samples over the entire hemisphere is the reciprocal method for determining transmittance for a given FOV and any scattering profile. Therefore, the light source and photodetector in Figure 2 can be reversed in order to construct a diffuse/normal ($d/0^\circ$) measuring instrument.

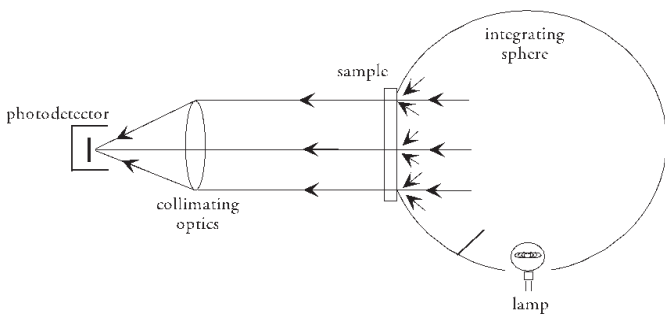


FIGURE 4

It can appear to those not completely familiar with geometrical optics that diffuse illumination will produce a different measurement result than collimated illumination since so many more incident rays and angles are transmitted through the sample. This is not true. The collimated viewing system with hemispherical illumination only accepts the incident rays which are reciprocal to the radiation pattern produced by an identically collimated incident beam.

1.4 Radiometric Advantage of $d/0^\circ$ Geometry

The major advantage of the $d/0^\circ$ system as compared to the $0^\circ/d$ is in radiometric system efficiency. In Figure 2, the amount of light which is collected from the lamp is a function of the f-number ($f/\#$) of the collimating optics. Those familiar with photography understand that $f/\#$ expresses the light gathering power of a camera lens. Lower values of $f/\#$ are required for slower speed film.

The total flux collected from the lamp in Figure 2 can be expressed as;

$$\Phi_{0^\circ/d} = I * \frac{\pi}{4f/\#^2} \quad (\text{Watts}) \quad \text{Eq. 1}$$

where I is the intensity of the lamp in units of Watts/sr. The second half of the equation expresses the collected solid angle as a function of $f/\#$ in units of steradians (sr).

If the same lamp is placed inside the integrating sphere, the total flux from the lamp is collected;

$$\Phi_{0^\circ/d} = I * 4\pi \quad (\text{Watts}) \quad \text{Eq. 2}$$

where 4π expresses the solid angle subtended by a sphere.

The ratio of Equation 2 to Equation 1 quantifies the efficiency improvement of the $d/0^\circ$ design. This is equal to:

$$\frac{\Phi_{d/0^\circ}}{\Phi_{0^\circ/d}} = 16 * f/\#^2 \quad \text{Eq. 3}$$

Therefore, even for a highly efficient $f/1$ lens, the $d/0^\circ$ geometry would be 16 times more efficient. When one applies this analysis to diffraction grating spectrophotometers, which are generally $f/3$ and larger, the $d/0^\circ$ system offers greater than two orders of magnitude improvement in radiometric efficiency.

1.5 Optical Design of the UV-1000F

There are several reasons for improving system efficiency by using the $d/0^\circ$ design. One of the most important engineering reasons is known as the signal-to-noise ratio which often determines the dynamic range of a spectrophotometer.

Labsphere's UV-1000F utilizes the efficiency offered by $d/0^\circ$ for several reasons. Improved signal-to-noise ratio is the first. The efficiency of most optics and photodetectors is poor in the ultraviolet spectral region. Although UV rich light

sources are available to compensate for the component efficiency, the amount of UV and thermal exposure on the sample must be minimized. Excessive exposure from the lamp may actively induce unwanted changes in the optical properties being measured.

The optical design of the UV-1000F is depicted in Figure 5 is a side view. The integrating sphere moves up and down for sample insertion. The sample is sandwiched between the sphere port window and the collimating lens. The diameter of the viewing beam is 10 mm.

The lamp used inside the integrating sphere is a xenon flashlamp. The lamp supplies sufficient energy for the instrument's spectral range of 250 nm - 450 nm while minimizing the sample exposure during its microsecond pulse interval.

The instrument utilizes two photodiode array spectrographs for instantaneous spectrum acquisition. One measures the spectral transmittance of the sample while the other references the spectral power distribution of the illuminant to compensate for flash-to-flash variation and the effect of the sample's reflectance on the sphere illumination. A complete spectrum is obtained using three flashes, and data is processed and displayed within five seconds.

1.6 Summary - Part One

Labsphere's UV-1000F Ultraviolet Transmittance Analyzer meets the geometric requirements of AS/NZ 4399 for measuring diffuse transmittance. The $d/0^\circ$ geometry, which uses diffuse illumination, was selected over the reciprocal $0^\circ/d$ geometry in order to maximize system dynamic range while minimizing light exposure on the sample.

Part Two discusses Spectral Measurements and Sample Fluorescence for Sun Protective Fabrics using the UV-1000F Ultraviolet Transmittance Analyzer.

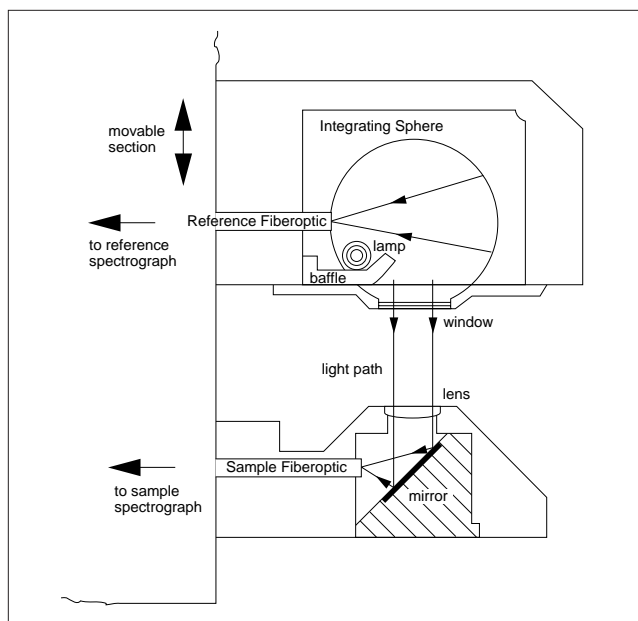


FIGURE 5

PART TWO. SPECTRAL MEASUREMENTS AND SAMPLE FLUORESCENCE

2.1 Introduction

The measurement of the Ultraviolet Protection Factor (UPF) of clothing can be performed by measuring the material's diffuse transmittance in the ultraviolet (UV) spectrum.

A common textile additive known as an optical brightening agent (OBA), enhances a fabric's appearance through the optical effect of fluorescence. A brief overview of the mechanism of fluorescence, as it relates to OBAs, is presented. Ultraviolet spectrophotometers, used to measure spectral transmittance, can exhibit systematic errors when fluorescent samples are introduced.

In addition to geometric requirements, AS/NZ 4399 describes the effect of fluorescent samples on diffuse transmittance measurements for two types of spectrophotometer designs. The discussion is specific to whether the instrument monochromator is placed before or after the sample. In other words, whether the sample illumination is monochromatic or polychromatic.

Instruments like the Labsphere UV-1000F, which use polychromatic illumination, are not effected by fluorescence in determining the UV protection offered by OBA treated fabrics. The UV-1000F has the added ability of quantifying the concentration of OBA in fabrics, supported by the instrument's unique design.

2.2 Measurement of Ultraviolet Protection Factor

AS/NZ 4399 determines the Ultraviolet Protection Factor (UPF) of a clothing material as an *in vitro* test method based on measuring its diffuse spectral transmittance. UPF is analogous to the SPF for a topical sunscreen. However, SPF by definition is determined *in vivo* as the increase in exposure time required to induce erythema, i.e. - SPF 4 means four times longer to induce erythema. UPF is calculated as follows:

$$UPF = \frac{\sum_{290nm}^{400nm} E_{\lambda} \times S_{\lambda} \times \Delta\lambda}{\sum_{290nm}^{400nm} E_{\lambda} \times S_{\lambda} \times T_{\lambda} \times \Delta\lambda} \quad Eq. 4$$

where:

- E_{λ} = CIE erythema spectral effectiveness
- S_{λ} = solar spectral irradiance
- T_{λ} = spectral transmittance of the sample

The two standardized functions, E_{λ} and S_{λ} , are illustrated in Figure 6:

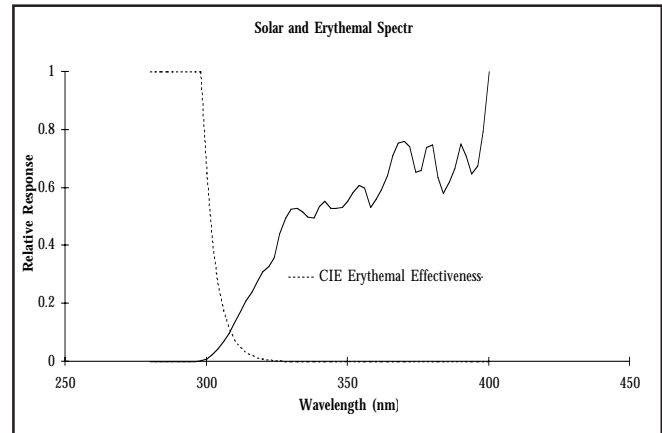


FIGURE 6

The two functions describe the relative sensitivity of erythema to individual wavelengths and the spectral distribution of sunlight as it reaches the earth's surface.

A more revealing plot is the product $E_{\lambda} \times S_{\lambda}$, which appears in both the numerator and denominator of Eq. 4. In Figure 7, the determination of UPF is weighted most heavily by a sample transmittance in the UVB portion of the spectrum, with maximum weighting near 305 nm.

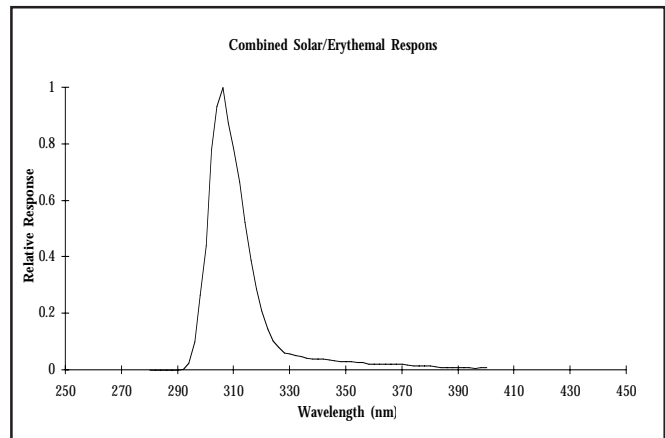


FIGURE 7

2.3 Fluorescence and Optical Brightening Agents

Fluorescence is one type of photoluminescence, the physiochemical phenomenon in which the absorption of a photon within a material species induces the emission of a photon of a longer wavelength, being in excess of that due to thermal emission. It is accurately defined as "photoluminescence in which the emitted optical radiation results from direct transitions from the photoexcited energy level to a lower level, these transitions taking place generally within 10 nanoseconds after the excitation."⁵ From chemistry, we know that these are generally p^*p transitions, involving p orbitals from either conjugated aromatic compounds (organic) or inorganic transition metals or rare earth metal compounds and complexes.

In the case of fabrics, the typical fluorescent material is an optical brightening agent. An OBA is used to give an enhanced appearance in the blue region of the visible spectrum. A decrease in the blue reflectance of a natural white material will make it appear more yellow and less appealing, therefore, many new white fabrics are treated. OBAs are typically highly conjugated derivatives of stilbene or benzimidazole which have been derivatized to give them water solubility or polar characteristics to make them attracted to the fabric substrate on which they will be used. Different OBAs are used for substrates such as cotton, polyester and nylon.

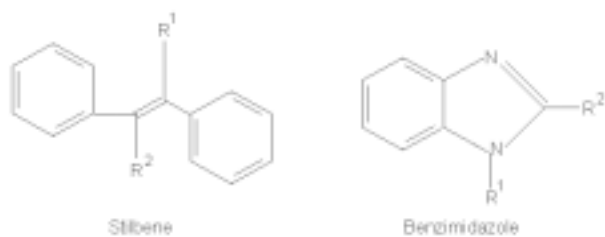


FIGURE 8

Optical brighteners and whiteners are also used in laundry detergents to suppress the yellowing that can accompany the repeated laundering of white garments. Most OBAs have excitation maxima in the very near UV or at the lower end of the visible scale, wavelengths in the range from 340 nm to 400 nm. Emissions typically peak at blue wavelengths around 435 nm - 440 nm. Typical excitation and emission spectra are illustrated in Figure 9.

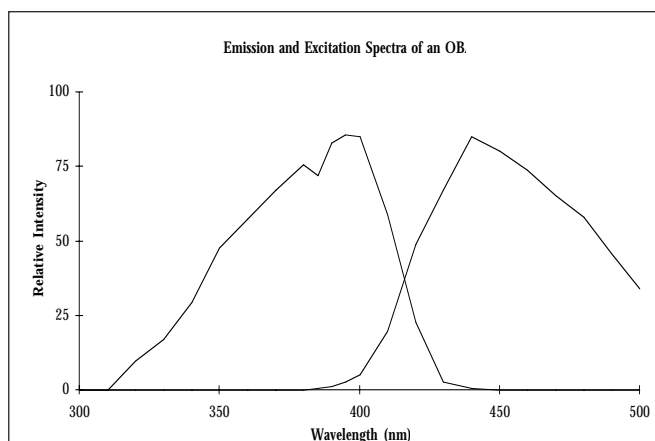


FIGURE 9

2.4 Spectrophotometers and Fluorescent Materials

A spectrophotometer is an analytical instrument used to determine the optical transmittance, reflectance or absorbance of a material as a function of wavelength. The essential components of a spectrophotometer are a light source, a monochromator to separate the wavelengths of light, and a photodetector. As discussed in Part One - Optical Geometry, an integrating sphere is required for diffuse transmittance measurement. It can be used in conjunction with either the illumination or collection sub-system.

There are basically two types of spectrophotometers which differ by position of the monochromator with respect to the sample. Sample illumination is either monochromatic or polychromatic. Each has its own characteristic response to fluorescent materials. Measurement data from both types of spectrophotometers are presented in this report. The ideal type of instrument for fluorescent samples would use both monochromatic illumination and monochromatic detection. The design is difficult to realize in practice, especially with respect to diffuse transmittance measurements and integrating spheres.

2.5 Monochromatic Illumination

In most commercial spectrophotometers, the monochromator precedes the sample, illuminating sequentially with single wavelengths. This type of instrument is intended for non-fluorescent materials. A distinct systematic error occurs when a fluorescent sample is introduced as depicted in Figure 10.

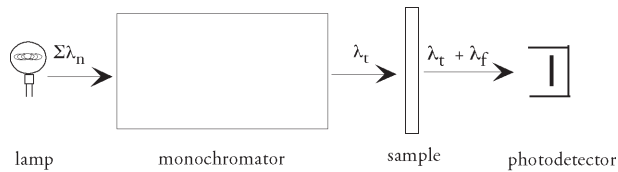


FIGURE 10

The instrument is set to measure the transmittance at wavelength λ_t . However, if λ_t also corresponds to an excitation wavelength for that material, it will emit an associated fluorescent wavelength λ_f . The photodetector in this instrument is capable of responding to both λ_t and λ_f but incapable of distinguishing between the two. The instrument would display an erroneously high transmittance value for λ_t since it adds the signal generated by photons emitted with wavelength λ_f .

The systematic error can be eliminated by using an optical filter that effectively removes the fluorescent component before it reaches the photodetector as depicted in Figure 11.

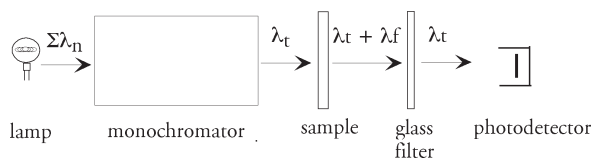


FIGURE 11

Practical application of this method and proper filter selection presumes a foreknowledge of the excitation and emission spectra. Fortunately, this can be applied to measuring the ultraviolet transmittance of fabrics containing OBAs.

Since OBAs excite below 400 nm and emit above 400 nm, AS/NZ 4399 recommends the use of Schott UG-11 filter glass for monochromatic illumination. Its spectral transmittance is shown in Figure 12.

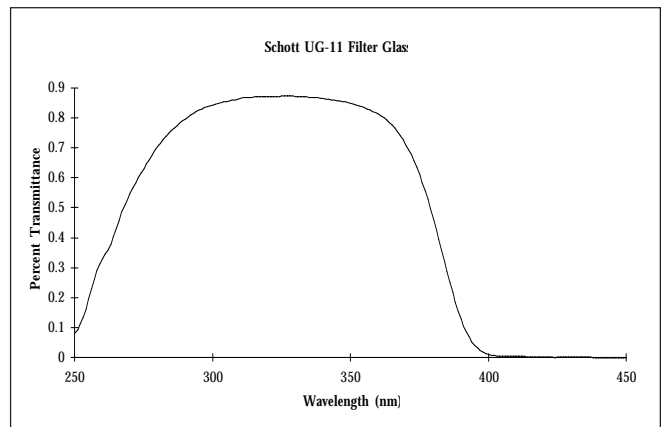


FIGURE 12

The measurement error associated with monochromatic illumination can be quite substantial in determining UPF if the fluorescent emission is not removed. A white fabric containing an OBA was measured on this type of spectrophotometer with and without a UG-11 filter. The results are shown in Figure 13 below.

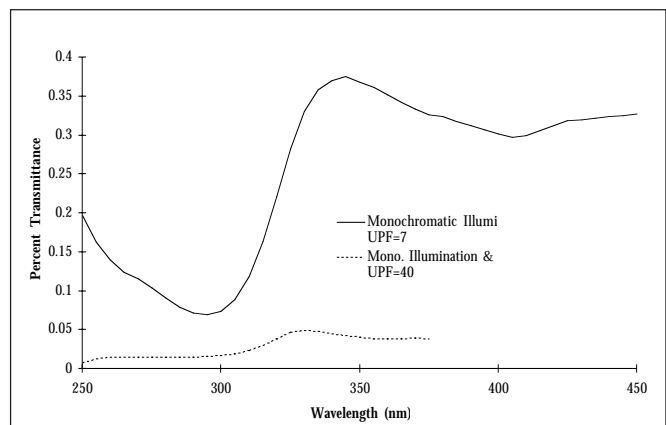


FIGURE 13

The data without the filter reveals that the OBA is excited by virtually all of the incident wavelengths. The dramatic error most adversely affects the calculation of UPF. Without correcting for the systematic error due to fluorescence, this fabric would seem to offer a UPF of only seven. However, the true effect of the OBA absorption provides a UPF of 40, revealed when the UG-11 filter is utilized. Incidentally, the instrument fitted with the UG-11 filter did not produce useful data for wavelengths above 380 nm due to the filter's sharp cutoff in transmittance.

2.6 Polychromatic Illumination

The second type of spectrophotometer design uses polychromatic illumination of the sample and monochromatic detection. Placing the monochromator after the sample separates both λ_t and λ_f before they are detected. The division of wavelengths can be distributed spatially as depicted in Figure 14.

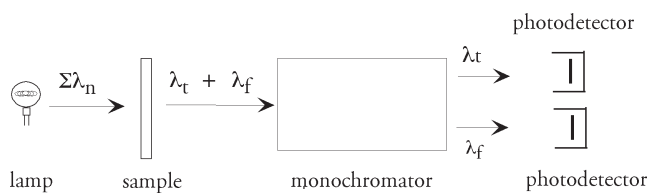


FIGURE 14

Labsphere's UV-1000F Ultraviolet Transmittance Analyzer employs a 256 element photodiode array spectrograph to separate and simultaneously capture as many wavelengths over the instrument's 250 nm to 450 nm spectral range. The wavelengths can also be separated in time through the use of a sequential step scanning monochromator.

The measured spectrum correctly displays the transmittance for wavelength λ_t . However, the result for λ_f combines the material's transmittance and fluorescent emission at that wavelength. The combined result at λ_f also depends on the UV content of the instrument's light source, i.e. - the measurement result will change for a different lamp type.

Spectrophotometers which use polychromatic illumination reveal the effect of OBAs on a measured spectrum. The use of OBAs is to enhance the blue reflectance of white fabrics. This type of instrument in a reflectance geometry is used for measuring the whiteness of textiles containing OBAs⁶. Commercial instruments that characterize fluorescent whiteness must also use light sources filtered to provide a standardized UV content⁷.

Since fluorescence is diffuse by nature, the emitted component is both reflected and transmitted. White cotton fabrics measured in the transmittance geometry of the UV-1000F Analyzer will also display the effect of OBA additives as illustrated in Figure 15.

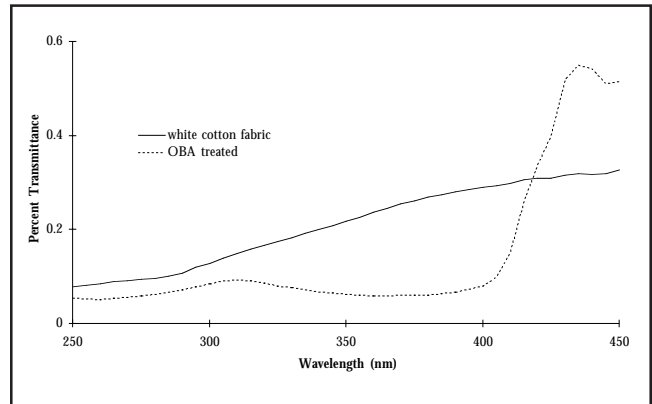


FIGURE 15

The xenon flashlamp in the UV-1000F contains sufficient UV content to excite the fluorophores. The effect of the OBA is clear. The emission spectrum appears at visible blue wavelengths, beyond 400 nm with a peak at 435 nm.

AS/NZ 4399 recommends that the polychromatic illumination should conform to the requirements of a solar simulator, i.e. - in UV spectral distribution. However, as revealed by Figure 15, this would only be relevant to quantifying the emission spectrum or whiteness of the sample. The source spectrum does not impose on the UV absorption measurement.

2.7 The Effect of OBAs on Sun Protective Clothing

As seen in Figure 15, the OBA has increased the UV absorption of the fabric. This is a desired effect in the manufacture of sun protective clothing. The OBA fluorescence emission measured by the UV-1000F has no bearing on evaluating a fabric's UV protection.

The UV-1000F correctly measures the UPF 40 sample used for Figure 13 despite the obvious sensitivity to the fluorescent emission at blue wavelengths. Measurement results for both instrument types are compared in Figure 16.

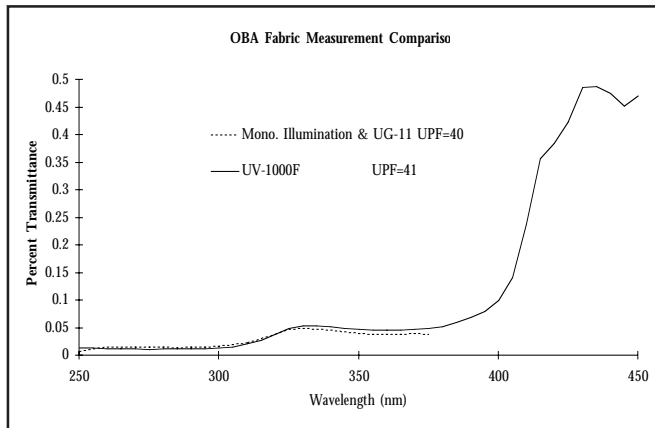


FIGURE 16

The measured transmittance data for the cotton samples from Figure 15 can also be converted to UPF values:

SAMPLE	UPF	UVA blocking	UVB blocking
White Cotton	6.5	77%	88%
OBA Treated	11.4	93%	92%

The increase in UPF offered by the OBA additive is apparent from Table 1. The same advantage applies to the total blocking (100%-T%) for either UVA (315 nm - 400 nm) or UVB (280 nm - 315 nm). The OBA treated fabric offers improved sun protection.

2.8 Measuring OBA Concentration

The emission spectrum in Figure 15 was isolated by the measured difference between the treated and untreated fabrics. The increased absorption at UV wavelengths is also evident. The relative strengths of both the absorption and the emission spectra are proportional to the concentration of the OBA.

Quantitative analysis is possible by devising a calibration curve using a sample set of known OBA concentration. The application is uniquely supported by the design of the UV-1000F due to its use of polychromatic illumination, diffuse transmittance geometry, and spectral range of 250 nm to 450 nm.

2.9 Summary- Part Two

Optical brightening agents are often applied to enhance the whiteness of textiles by inducing fluorescence by UV excitation and visible blue emission. OBAs have the added benefit of increasing the UV absorption and hence a textile's sun protective ability.

UV spectrophotometers exhibit systematic errors when fluorescent samples are introduced. Labsphere's UV-1000F, which use polychromatic illumination, is not effected by the fluorescence in determining the UPF of OBA treated fabrics. The UV-1000F can also be used to quantify the concentration of OBA in fabrics, supported by the instrument's geometry and spectral range.

REFERENCES

1. Australian/New Zealand Standard AS/NZ 4399:1996, "Sun protective clothing - Evaluation and classification," Published jointly by Standards Australia and Standards New Zealand.
2. Helmholtz, H. von, *Handbuch der Physiologischen Optik*, 3rd ed., 198-199, 1909.
3. "Selection of Geometric Conditions for Measurement of Reflection and Transmission Properties of Materials," ASTM E 179-91a.
4. *The Helmholtz relationship also considers the state of polarization for incident and emergent fluxes.*
5. Gundlach, D. and Terstiege H., "Problems in Measurement of Fluorescent Materials," *Color Research and Application*, 19, 6, 427-436 (1994).
6. AATCC 10, "Whiteness of Textiles."
7. CIE Publication 51, "A Method of Assessing the Quality of Daylight Simulators for Colorimetry."