The Influence of the Illuminant on the Luminescent Radiance Factor Spectrum of a Reference Fluorescent Paper

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Abstract: Present ISO standards for the measurement of the Brightness, Whiteness, and Colour of fluorescent papers require adjusting the ratio of UV light to visible light in the illumination to match CIE Illuminant D65 or C. This procedure is shown to be faulty because a true D65 colorimetry of paper requires matching the spectral intensity distribution of the illuminant and not just the net UV content. The detailed shape of the emission spectrum depends on how much the UV spectrum of the illuminant weights the corresponding features of the excitation spectrum. The shape of the excitation spectrum varies among fluorescent white papers. In light of the composite nature of the excitation spectra of fluorescent papers, the only way to perform colorimetry reliably with respect to a standard illuminant is to use a light source with a spectral distribution that matches the spectral distribution of the standard illuminant.

Introduction

A good daylight simulator approximates the relative spectral distribution of light of the target standard illuminant in the ultraviolet range as well as the visible range (CIE, 1981). However, the spectroscopy of fluorescent materials has long been influenced by a simplifying assumption, referred to here as the "singlet conjecture," whereby a given fluorescent moiety will exhibit an excitation and emission band of fixed spectral shape as if it were a single spectral line (Allen, 1973). Within that assumption, only the total quantity of illumination falling within the excitation spectrum is relevant to the total fluorescence and not the precise nature of the spectral distribution of that light. One consequence of the singlet conjecture is an algorithm for separating the luminescent and reflected components of the total radiance factor spectrum from the change in the total radiance spectrum with selective filtering of the excitation source (Allen, 1973). A second consequence is the claim that the colorimetry of a fluorescent material, with respect to any given standard illuminant, can be calculated from spectra

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measured with an arbitrary light source provided that the excitation (ultraviolet) to emission (visible) light intensity ratio can be adjusted (Grum, 1977). By extension, the singlet conjecture was an underlying premise for the calibration procedure devised by ISO/TC6 for paper whiteness.

One challenge to the singlet conjectures lies in the phenomenon of "greening" in which papers with high concentrations of the same fluorescent additive emit relatively more light on the long-wavelength side of the luminescent radiance factor spectrum. One explanation attributes greening to stilbene-stilbene bonds replacing stilbene-cellulose bonds as the coverage exceeds a monolayer (Muller, 1993)]. By this explanation, the chemical moiety changes with additive concentration, but each moiety exhibits a fixed spectrum. An alternative explanation assumes the fluorescence band is a multiplet and that some component lines saturate while other lines continue to grow (Shakespeare, 1999). The multiplet conjecture allows the distribution of light within the excitation band to determine that distribution of light within the emission band. If the shape of the emission spectrum depends on the shape of the illumination spectrum, then this observation supports the multiplet conjecture and undermines the whiteness calibration procedure.

In an article explaining the whiteness calibration, Bristow (1994) shows spectra illustrating the residual difference in the shape of radiance spectra measured on the same fluorescent paper using different reflectometers calibrated to read the same whiteness on a reference paper. The same article also demonstrates that no single filter setting for a filtered Xe source could simultaneously match more than one D65 tristimulus value as calculated from bispectral data. Some years later, Robertson (1998) demonstrated experimentally that the ratio of tint-to-whiteness is sensitive to the spectral distribution of light within the excitation band. This was confirmed by Bristow (1999) but was regarded as an anomaly. A possible explanation is that this effect is the natural result of a multiplet spectrum.

In this note, we use the bispectral luminescent radiance factor data for a fluorescent paper standard calibrated on the reference bispectral reflectometer at the NRCC and calculate the luminescent radiance factor spectra corresponding to various standard illuminants.

Experimental

The same high-whiteness paper used by laboratories authorized by ISO/TC6 for calibration of brightness and whiteness was calibrated in March 2000 using the NRCC's bispectral reflectometer and repeated in October 2000 with the excitation range extended to 250 nm. This process results in a beta matrix of normalized intensities for each combination of input and output wavelength. Each column of the matrix is then weighted by the illuminant at that input

wavelength, and the luminescent radiance factor spectrum is the integral (sum) along each row of these weighted intensities. Since there exists no practical lamp simulation that perfectly matches CIE Illuminant D65, the beta matrix is the most practical and accurate method to determine the colour appearance that a fluorescent paper would exhibit if it were illuminated with a true D65 spectrum.

A filtered Xe source is not a standard illuminant, but is the source used by most of the reflectometers for measuring paper whiteness. To see how it corresponds to the standard illuminants, we took another pad of the same paper and measured it repeatedly on an Elrepho 2000 abridged reflectance spectrophotometer. We set the UV filter to maximum and calibrated the reflectance with a non-fluorescent Spectralon 99 tablet. We then measured in sequence a second Spectralon 99, a pad of the standard fluorescent paper, and three Everwhite opal tiles. The UV filter was then set to minimum, recalibrated with Spectralon 99 and the same samples were remeasured. The sequence was repeated 60 times, 30 each at high and low ultraviolet settings. The mean and standard deviation for the 30 high and 30 low repeats were calculated along with the standard deviation of the means.

As a separate survey of the range of absorption spectra associated with the fluorescent moieties, we calculated the Kubelka-Munk remission function (k/s) from the reflectance of a collection of fluorescent papers between 260 nm and 400 nm. A Cary 3 reflectometer equipped with a Labsphere reflectance attachment was used with a U-330 filter sandwiched between the sphere aperture and the paper pad. This filter passes light with wavelength between 260 nm and 400 nm, but prevents fluorescent emissions of visible light from entering the sphere and interfering with the reflectance measurement.

The excitation and emission spectra of these same papers were also measured on Spex Model-F112 spectrofluorometer equipped with a 450 W Xenon light source, a single grating excitation and a double grating emission monochromator. A front face mode with an angle of 22.5° from the excitation beam for detecting emission was employed. Spectra were corrected for incident light intensity and detector response by using the Rhodamine-B internal reference. The two excitation and two emission slits were set to 0.25 mm. After a λ-2 weighting function was applied to the recorded intensity, the Spex output closely matched the bispectral intensities from the NRCC.

The Influence of the Illuminant's Spectrum on the Emitted Radiance of a Fluorescent Paper

Figure 1 shows the excitation spectra from the beta matrix associated with the emission at 410 nm, 430 nm, and 450 nm. Differences are apparent in the range between 375 nm and 410 nm. This dependence of the excitation spectra on the emission wavelength, and vice versa, suggests a complex fluorophor system. In

such a case, it is expected that the shape of the net luminescent radiance factor spectrum will depend not only on the total number of photons absorbed in the excitation range but also on the precise spectral power distribution of the excitation source. A small change in the spectral selectivity of the source, e.g. due to aging, could produce large variations in the shape of the fluorescent radiance factor curve, such as the presence or absence of shoulders due to selective excitation of different fluors. The figure indicates a rising sensitivity below 310 nm and suggests that light with wavelength below 300 nm would also excite fluorescence in this range. This is confirmed below when the data range is extended to 250 nm. However, the standard illuminants lack intensity below 300 nm and would not be capable of exciting a lower wavelength peak. So for now we will focus on the range above 300 nm relevant to standard illuminants.

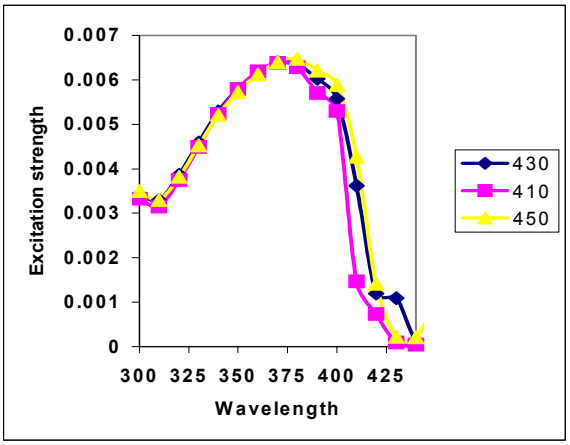

Figure 1. Excitation spectra corresponding to three different emission wavelengths of the fluorescent paper sample.

Each illuminant weights the ultraviolet excitations differently. Figure 2 illustrates the weighting of four illuminants normalized to unity at 370 nm, where the fluorescent excitation is greatest. Illuminants C and A place relatively more weight at longer wavelength. Daylight illuminants D65, D50, and C vanish below 300 nm because the ionosphere absorbs shorter wavelength ultraviolet light. The incandescent lamp (Illuminant A) and the Xenon lamp both emit some light with wavelength shorter than 300 nm, and light from a Xenon lamp is particularly strong at the shorter wavelengths.

Figure 3 shows the luminescent radiance factor spectra for the fluorescent paper sample calculated for four illuminant conditions, and Figure 4 shows these same spectra normalized to the same maximum peak height.

Note that the spectra associated with Illuminant A and with Illuminant C cross very near the nominal wavelength of brightness, 457 nm.

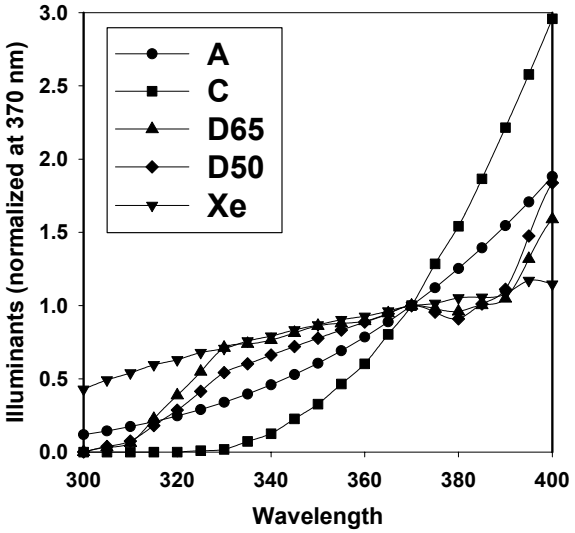

Figure 2. The relative excitation weights for four illuminants and a Xenon lamp normalized to unity at 370 nm.

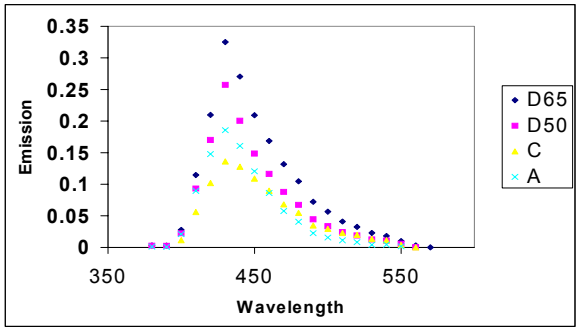

Figure 3. Luminescent radiance factor spectra calculated for four CIE illuminant conditions.

Difference spectra from the Elrepho 2000 were used to compare the standard illuminants (D65 and C) with the common Xe source, as shown in Figure 5. The technique was first verified using non-fluorescent Spectralon 99. After averaging 30 repeats, the expected error (95% level) on the Elrepho 2000 spectra was on the order of 0.02%. Difference spectra double that error.

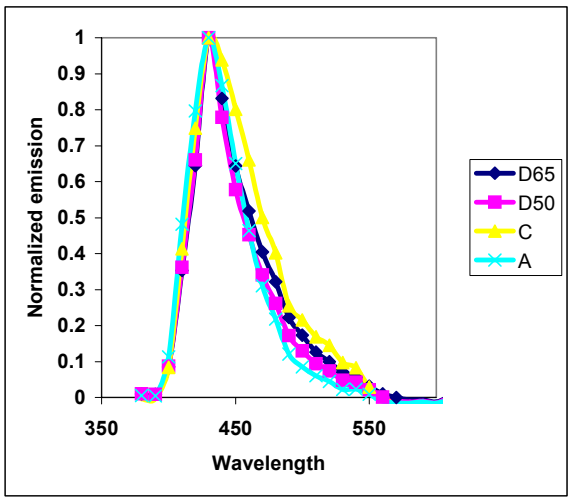

Figure 4. Normalized luminescent radiance factor spectra for different illuminant conditions to show line shape differences.

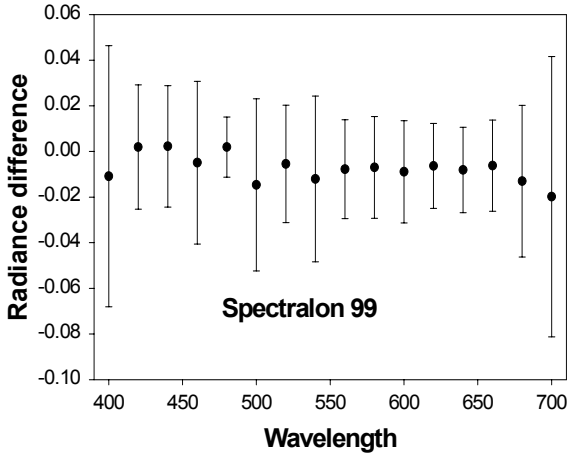

Figure 5. Shows the radiance difference spectra for the Spectralon 99, confirming that the Spectralon is non-fluorescent.

The spectrum associated with Illuminant C is the broadest and that associated with Illuminant A is narrower and more peaked. Figure 6 shows the spectra associated with C and D65 with the spectrum measured in the Elrepho 2000 superimposed. The filtered Xe lamp seems to be more compatible with D65 than

C. The data point at 400 nm does not show on the graph because it is slightly negative. The radiance difference method has problems near the wavelength (395 nm) where the ultraviolet light is being filtered if the excitation spectrum overlaps that wavelength.

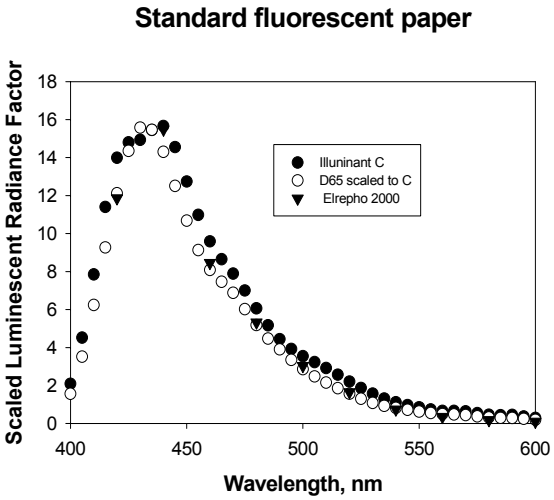

Figure 6. Superposition of spectra corresponding to D65, C, and filtered Xe.

Short Wavelength Ultraviolet Light

The emphasis in this note has been on subtle variations in the total radiance factor brought about by the way different illuminants weight the long-wavelength or short-wavelength sides of the main excitation peak centered at 370 nm. A somewhat different issue arises when we consider excitation of fluorescence below 300 nm. If paper has significant excitation below 300 nm, then this fluorescence will be excited by the Xenon lamp in a reflectometer but will not be excited by indoor or outdoor end-use lighting. Hence, such fluorescence would spuriously enhance the measured total radiance factor and cause the calibration filter to de-emphasize the excitation of the main 370 nm. As long as the short-wavelength excitation is just a wing of the same excitation band as the main peak a single calibration will address both wings. Independent variation of two excitation bands may call for separate controls.

A closer look at the excitation and emission spectra of the standard paper helps to put the issue into perspective. Figure 7 shows the excitation spectra corresponding to emission at the indicated wavelengths. In this case, the excitation spectrum is extended to 250 nm. The spectra are normalized to match at 370 nm. Most of the fluorescence emitted at any particular wavelength is

excited at shorter wavelength (higher energy). So the excitation spectrum of light emitted at 400 nm falls sharply just below 400 nm, and the other excitation spectra fall sharply below their respective emission wavelengths. Light emitted in the 400 nm to 420 nm range is relatively more dependent on excitation by 280 nm light than by light in the 370 nm peak. This is evident as well in the corresponding emission spectra shown in Figure 8.

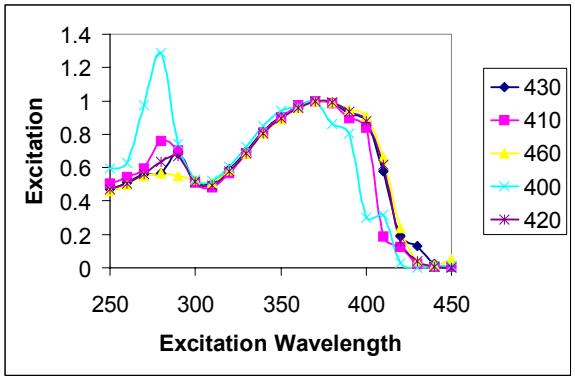

Figure 7. The excitation spectra of the fluorescence calibration paper corresponding to emission at the indicated wavelengths. The spectra are normalized to match at 370 nm.

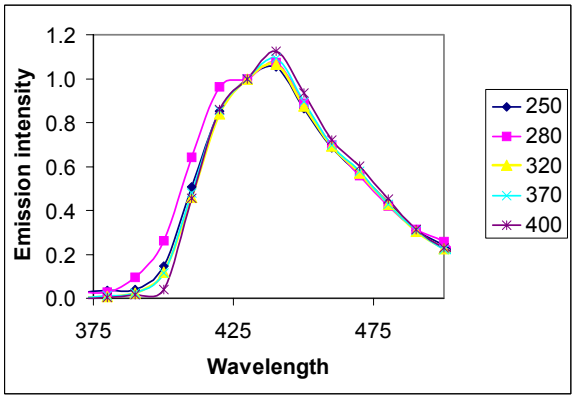

Figure 8. The emission spectra of the fluorescence calibration paper corresponding to the indicated excitation wavelengths. The spectra are normalized to match at 430 nm.

Here we show the spectral distribution of emitted light that was excited at the indicated wavelengths. The spectra were normalized to the same intensity at 430 nm. The emission spectra exhibit a main peak near 440 nm with shoulders near 420 nm and 470 nm. The shorter wavelength shoulder appears to be particularly dependent on excitation by 280 nm light. For this paper, at least, the amount of UV illumination available at 280 nm compared to the illumination at 370 nm controls the relative strength of the short wavelength shoulder in the fluorescent emission spectrum.

Spectral Differences Among Fluorescent Fine Papers

We measured the Kubelka-Munk remission function between 260 nm and 400 nm on 25 fluorescent papers that were purchased in office supply stores on a given day in Pointe-Claire, Quebec. As shown in Figure 9, the ultraviolet absorption spectrum clearly exhibits separate bands centered at 280 nm and 370 nm. All these papers are classified as wood-free fine papers, and were analyzed to contain 1% or less mechanical pulp. The 280 nm peak is absent in the non-fluorescent paper in this study. Clearly, the relative strengths of the two absorption peaks are not constant, as shown in Figure 10. Furthermore, Figures 11 and 12 show a cusp in the fluorescent excitation at 310 nm followed by the rise toward a second peak below 300 nm. Nevertheless, the excitation of fluorescence associated with the two absorption peaks may not be in the same ratio as the absorption itself.

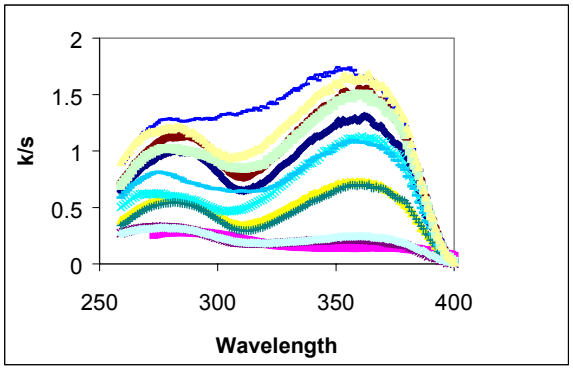

Figure 9. The Kubelka-Munk remission function (k/s) ultraviolet absorption spectra of a sampling of fluorescent papers.

The excitation spectra show the same features as the absorption spectra, but with somewhat different peak shape. Figure 11 shows the excitation spectra of these papers as measured on the Spex fluorescence spectrometer for light emitted at 440 nm.

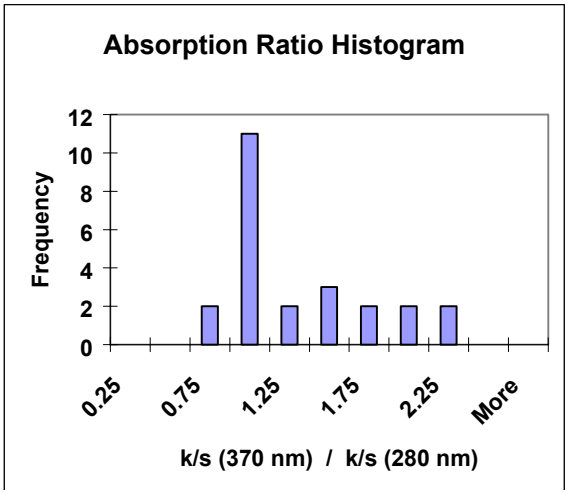

Figure 10. Histogram of the ratio of the light absorption strength in the short-wavelength peak (280 nm) and long-wavelength peak (370 nm).

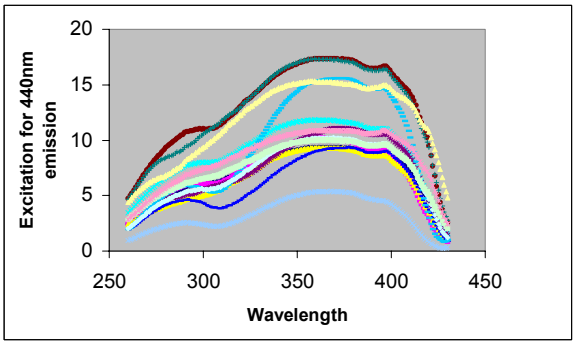

Figure 11. Excitation spectra of various fine papers corresponding to emission at 440 nm.

To better illustrate the spectral shapes, these excitations are shown in Figure 12 normalized to the same maximum intensity. Different fine papers clearly differ in their relative sensitivity to shorter wavelength and longer wavelength ultraviolet light. We can distinguish several ranges in the excitation: Low Peak (I) contains the 280 nm peak and covers wavelengths from 250 nm through 300 nm; The Gap (II) covers the trough between excitation peaks between 300 nm and 320 nm; Low Wing (III) spans from 320 nm to 350 nm; Main Peak (IV) contains the peak at 370nm and ranges from 350 nm to 400 nm; and lastly, the

High Wing (V) between 400 nm and 430 nm. As illustrated above, the Low Peak exerts more influence on the low-wavelength (410 nm) shoulder of the emission, and the High Wing influences the high-wavelength (470 nm) shoulder in the emission. The Main Peak in the excitation influences the whole of the emission spectrum. The Gap and Low Wing vary substantially among the papers. The excitation propensity in the Gap at 310 nm is proportional to the Low Peak propensity at 280 nm (R2 = 0.91), but the relationship between the Main Peak strength and the other spectral features is less fixed. Figure 13 illustrates this relationship.

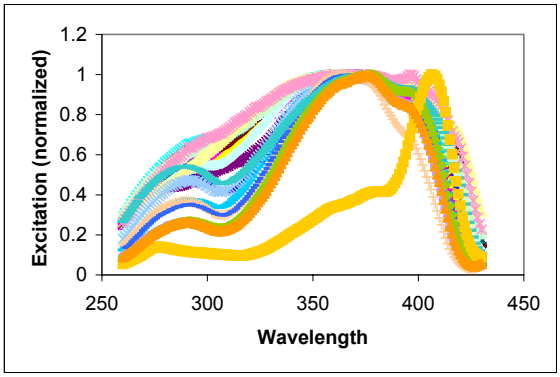

Figure 12. Excitation spectra of various fine papers corresponding to emission at 440 nm, normalized to the same maximum intensity.

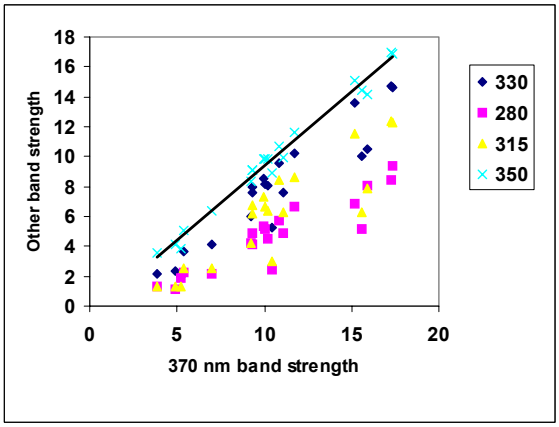

Figure 13. The relative strength of other features in the excitation spectrum to the Main Peak at 370 nm.

Although highly fluorescent papers tend to be strong in both the Main Peak and the Low Peak, their peak strengths are linear but not proportional as seen in Figure 14. The ratio of these peaks is highly nonlinear. Figure 10 displays a histogram of the peak intensity ratio for all 25 papers.

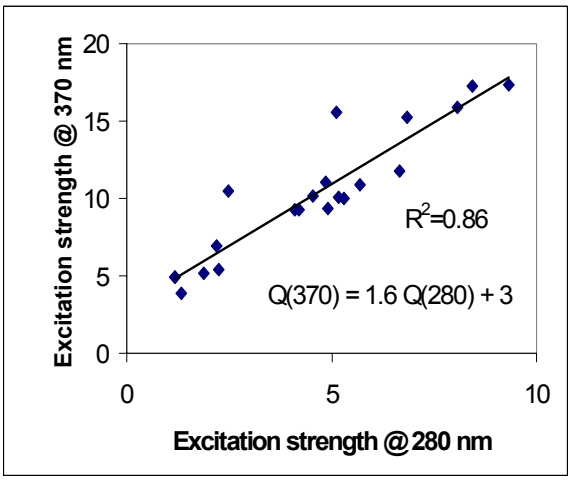

Figure 14. The strength of the Low Peak at 280 nm compared to the strength of the Main Peak at 370 nm.

Robertson (1998) and Bristow (1999) altered the illumination spectrum by filtering the lamps in their reflectometer to remove light with wavelengths shorter than 320 nm. Their filters removed the fluorescence from the short-wavelength excitation peak that would be excited in the reflectometer and not in end-use. As shown in Figure 6, the two peaks can have very different strengths.

Discussion and Conclusions

In order to measure the colour of a fluorescent paper with respect to CIE Illuminant D65, does our illumination have to match the spectral distribution of D65 or just contain the equivalent total UV content? The equivalent total UV content is much easier to achieve and both common practice and standard practice are premised on that option. Procedures based on that premise have proven enough practical value, that we would expect its premise to be valid to a good approximation. Four conditions would make it valid:

1. If all parts of the emission band share a common excitation spectrum, and
2. If all parts of the excitation band evoke the same emission band, and
3. If the excitation spectrum weighted by different illuminants produces a total radiance spectrum with the same shape, or

4. If all features in the excitation spectrum appear in the same proportion in all papers.

The first three equivalent conditions are needed for accurate D65 colorimetry and the fourth condition permits inaccurate but still consistent colorimetry.

Figure 1 confirms a general agreement with the first condition (a common excitation spectrum), while exhibiting subtle discrepancies. Figures 3 and 4 show subtle but significant violations of the third condition that weighting with different illuminants should produce the same shape to the emission spectrum.

In Figure 6 we go beyond the standard illuminants to the commonly used Xenon lamp. The emission excited by the Xenon lamp is richer at 400 nm than the emission produced by the standard illuminants. Noting that illumination from a Xenon lamp itself is particularly strong below 300 nm as implied in Figure 2, we turn our attention in Figure 7 and Figure 8 to the effect of light in the 250 nm through 300 nm range. We see that light at 280 nm seems to exert a strong influence on the 410 nm shoulder in the emission band. Figure 7 and Figure 8 show strong contradiction of the first two conditions for relying solely on control of the total UV content in the illumination. Thus, the short-wavelength ultraviolet light from a Xenon lamp excites fluorescence beyond the reach of the daylight illuminants, and that very fluorescence complicates the validity of our standard procedures for fluorescence colorimetry.

If the three conditions of accurate D65 colorimetry are compromised, what about the fourth condition for consistent colorimetry? Since the 280 nm excitation by Xenon light is particularly problematic, its significance would still be reduced if the excitation spectra of all papers had the same ratio between the 280 nm peak and the 370 nm peak. Figures 9 through 14 demonstrate substantial variation among fluorescent fine papers in the strengths of different features in their excitation spectra. Although Figure 14 shows a linear relationship between the strength of the 280 nm feature and the 370 nm feature, the relationship is not a proportionality.

This explains why Robertson (1998) and Bristow (1999) found that filtering out the shorter-wavelength UV light from their Xenon lamps caused the radiance spectra of some papers to change more than others.

Does this mean that the common practice of attenuating light from a Xenon lamp with a filter at 395 nm is incapable of making an effective match to Illuminant D65 or Illuminant C for fluorescent colorimetry? This is what present ISO standards for the paper industry require. Is it achievable? Bristow's finding (Bristow, 1994) that no one setting of the attenuation filter could simultaneously calibrate more than one tristimulus value to a D65 target suggests that no filter

position produces an adequate match to D65. Figure 15 frames the question differently.

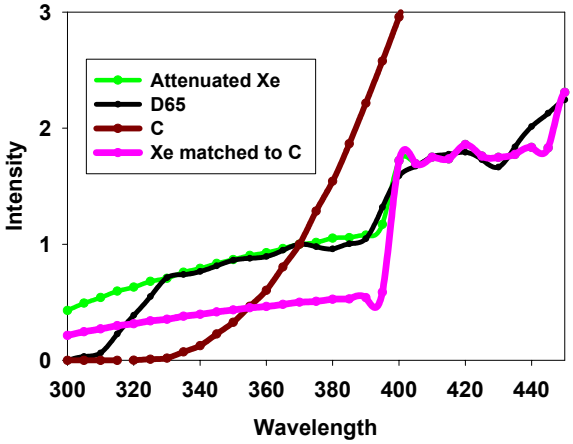

Figure 15. The spectral distributions of Illuminant D65 and Illuminant C and the spectra of Xenon light attenuated at 395 nm to match the illuminants.

We see that a filter at 395 nm permits the output of a Xenon lamp to conform to the shape of D65 in the important range between 320 nm and 430 nm. If no fluorescence were excited below 320 nm, then the current practice of adjusting the filter's attenuation to the point where the measured whiteness matches the calculated true D65 whiteness should realize the match shown in Figure 15. However, in current practice, the calculated whiteness comes largely from the 370 nm peak and the measured whiteness includes contributions from both the 370 nm peak and the 280 nm peak. This results in a deeper attenuation than the one shown in Figure 15, and a poorer approximation to the shape of the D65 spectrum. Figure 15 also demonstrates how badly Xenon lamps attenuated at 395 nm approximate the shape of Illuminant C.

Conclusions and Recommendations

Several standards under ISO TC6 for the Brightness, Whiteness, or Colour of fluorescent paper purport to measure the colour as if the specimen were illuminated with a source matching CIE Illuminant D65 or CIE Illuminant C. This claim is unjustified. It may have been justified for the colorimetry of other materials if their excitation band responds to light as a monolithic unit – what we term a singlet. The excitation spectra of fluorescent white papers appear to be composed of a composite of separate features that appear with different weights in different papers. These separate features express different influences

on the shape of the corresponding emission spectra, so each emission spectrum depends on how much weight the illuminant gives to each feature in the corresponding excitation spectrum.

In light of the composite nature of the excitation spectra of fluorescent papers, the only way to perform colorimetry reliably with respect to a standard illuminant is to use a light source with a spectral distribution that matches the spectral distribution of the standard illuminant. This could be done physically with a combination of lamps and filters, or analytically from bispectral data. It is particularly important to exclude fluorescence from wavelengths like 280 nm that are beyond the range of the standard illuminant.

We recommend that the relevant ISO standards be reviewed and redrafted with reference to realizable illuminants.

Acknowledgments

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