Estimating a Donaldson Matrix for Commercial Papers Containing Optical Brightening Agents

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Abstract

A method for estimating a Donaldson matrix from single-monochromator spectral reflectance measurements of optically brightened paper was derived. Optical brightening agents are excited by UV energy and fluoresce in the short-wavelength visible spectrum. Therefore, the spectral reflectance of papers containing optical brightening agents is highly dependent upon the UV content of spectrophotometer source. Fluorescent papers are ideally measured with bispectral spectrophotometers. However, bispectral spectrophotometers are unavailable to most of the graphic arts industry. This method bridges the gap between spectrophotometers and the measurement of fluorescent papers by estimating illuminant independent bispectral radiance factor matrices for fluorescent papers. The method was tested by estimating the Donaldson matrix from spectral reflectances of fifteen papers measured in a Macbeth Color-Eye 7000. In addition, spectral reflectances of the fifteen papers were measured under Incandescent, Daylight, and Cool White sources in a Macbeth Spectralight III light booth. The spectral power distribution of the three sources was imposed upon the estimated Donaldson matrices, and total radiance factors were calculated from each matrix. The mean CIEDE2000s between the measured and estimated total radiances factors for Incandescent, Daylight, and Cool White were 1.38, 1.84, and 0.90, respectively. The estimated Donaldson can be used to predict the spectral reflectance of fluorescent papers under any light source and applied to models predicting the appearance of printed images.

Introduction

When colorimetry was developed in the early 20th century, the reflectance of a white paper was essentially uniform across wavelengths, defined only as a ratio of the sample reflected spectral radiance to spectral radiance of a perfect reflecting diffuser. Within 20 years of the famous 1931 meeting of the CIE, colorimetry was challenged by paper manufacturers who began mixing optical brightening agents (OBAs) into the paper pulping and coating process (Meisser et al., 2005). A paper without these fluorescent OBAs has a maximum reflectance at each wavelength of 1.0. However, OBAs, which absorb ultraviolet (UV) energy, emit light in the visible spectrum between roughly 420 and 550 nm, peaking around 450 nm. The total spectral radiance factor of a paper is dependent on both the reflected spectral radiance and fluorescent radiance. Therefore, total spectral radiance curves for papers containing OBAs can have reflectances greater than zero. It is difficult to separate the emitted energy from reflected energy using standard spectrophotometry. Spectrophotometer sources, such as tungsten and Xenon, contain enough UV energy (below 380 nm) to excite OBAs in paper, but only measure visible energy above 380 nm. Therefore, it is difficult to determine how much energy is emitted as a result of excitation by different bands of UV energy. UV-cut filters are commonly employed in spectrophotometers to measure spectral reflectance independent of OBAs but cannot provide any more than an estimation of the magnitude of total fluorescent emission.

This problem is illustrated when measurements of samples from a spectrophotometer are compared to the appearance of samples in a light booth. Without considering aspects of appearance, as when making critical color comparisons common in many industries, the difference in UV content between the light booth sources and the spectrophotometer source is enough to compromise the comparison. Bispectral spectrophotometry should be used to fully understand and calculate the colorimetric coordinates of fluorescent materials.

Donaldson published a paper describing a new method for measuring fluorescent materials in 1954. His method was based upon the principle of bispectral spectrophotometry. Donaldson was most concerned with the measurement of fluorescent inks. Paper manufacturers had just begun incorporating OBAs into their papers on a mass scale when Donaldson wrote this paper. Bispectral spectrophotometry requires a two-monochromator spectrophotometer. The first monochromator disperses energy from the source, sequentially illuminating the sample with narrow excitation bands. The second monochromator disperses the reflected component. Bispectral measurements, referred to as *bispectral radiance factor,* are stored in an illuminant-independent matrix where each column is a spectral reflectance curve measured from an individual excitation band. Figure 1 illustrates this matrix, known as a *Donaldson matrix.* Each column is an excitation band and each row is an emission band. Summing across the columns results is a measurement of spectral radiance factor, similar to the spectral reflectance measured in single-monochromator devices. The reflected radiance factor is comprised of the diagonal elements where excitation equals emission. The fluorescent radiance factor is comprised of those elements defining the spectral emission of the substrate. Several devices have been developed to measure bispectral radiance factor (Leland et al., 1997; Jablonski et al., 2001; and Zwinkles and Gauthier, 1999).

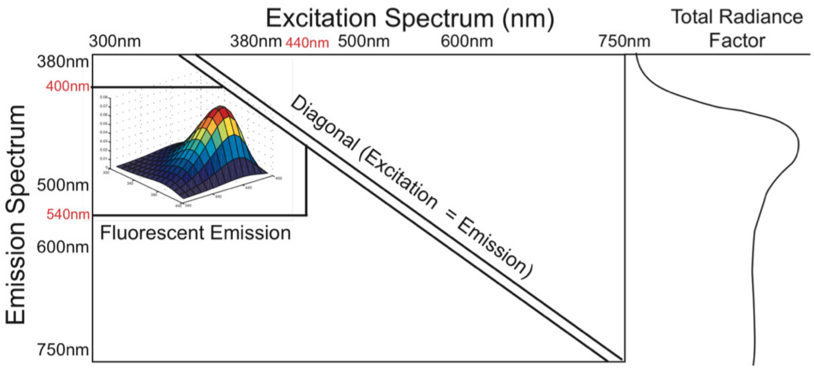

Figure 1. *This figure illustrates the structure of a Donaldson matrix. The region marked "fluorescent emission" represents the bispectral luminescent radiance factor and the "Diagonal" represents the reflected radiance factor. The total radiance factor is calculated by summing across the excitation spectrum.*

Ideally, all measurements of fluorescent materials are made using a bispectral device. However, bispectral spectrophotometers are manufactured by few companies, in small quantities, are not very portable, and are generally very costly. Several methods have been proposed to separate reflected radiance factor from fluorescent radiance factor using single-monochromator spectrophotometers (Allen, 1973; Alman and Billmeyer, 1977; Mohammadi and Berns, 2006; Löffler, 2008; and Mohammadi, 2009). Gill (2003) proposed a simplified method to estimate the reflected radiance factor of a paper containing OBAs whereby a line was drawn through the minimum reflectance between 450 nm and 520 nm, and the maximum reflectance between 650 nm and 700 nm. This line passed beneath the fluorescent radiance factor peak (the region of the total radiance factor curve attributed to fluorescence) and intersected with the spectral curve around 430 nm (depending on the paper). A new spectral curve, estimating the reflectance of the paper with no OBA contribution, was drawn following the line from 730 nm down to where it intersected with the spectral curve below the fluorescent peak, and then continuing on the path of the measured reflectance curve. This had the effect of cutting off the fluorescent emission similar to a UV-cut filter.

The major difficulty when dealing with optically brightened substrates is estimating the total radiance factor under different sources. Most OBA fluorescent excitation occurs below the range of wavelengths commonly measured by single-monochromator spectrophotometers. Therefore, fluorescent emission is due to the UV and short-wavelength visible content of the instrument's source and is less dependent on the illuminants employed in colorimetry. This introduces many problems into the colorimetry workflow. The effect of the illuminant on a non-fluorescent paper is removed during the calibration process in a single-monochromator spectrophotometer. However, these devices do not typically calibrate the UV content of the source. Differences between sources in similar devices can result in fluorescent radiance differences in measurements of the same sample (Shakespeare and Shakespeare, 1999; Connelly, 2003; Jordan and Zwinkles, 2003). The greatest error, however, occurs when comparing spectral radiance of curves measured in devices with two different light sources, for example, tungsten and Xenon. Fluorescent excitation by pulsed Xenon will be much greater than that of tungsten due to the greater quantity of UV energy in pulse Xenon sources.

This paper proposes a new method for incorporating the UV content of a source into spectral radiance measurements from a single-monochromator device. Commonly used OBAs fall within in a small range of fluorescent behavior. Although paper manufacturers apply different concentrations of OBAs to their stock and use different brands, all OBAs are excited by and emit within the same general spectral range. This study attempts to estimate Donaldson matrices for a set of commercial digital press papers using spectral reflectance measurements from a single-monochromator device. The spectral power distribution of any source can be imposed upon the estimated Donaldson to predict the spectral reflectance of a substrate under that particular source. This will enable a direct comparison between the colorimetric coordinates measured by a device to those measured in a light booth or other viewing environment.

Other methods have been proposed to make colorimetric calculations of fluorescent substrates while accounting for changes in the spectral power of a source. Lee, Shen, and Chen (2001) measured fluorescent substrates with seven sources (three of which were used in their initial calculations) using a single-monochromator device. They used Fourier analysis and regression to determine fluorescent radiance factor and reflected radiance factor. Although mathematically elegant, their method accounted for changes resulting from different illuminants but did not consider spectral data below 380 nm. Imura (2007) proposed a method for measuring the effective bispectral fluorescent radiance factor of a printed sample. He incorporated Donaldson matrices in to his calculations and was able to estimate the spectral reflectance of a substrate excited by a standard illuminant. However, this method requires a Donaldson matrix as an input. Imura suggested obtaining a Donaldson matrix measured for a similar substrate. This method extends Gill's work, addresses the problem of estimating the illuminant-independent properties of fluorescent papers, and improves upon the prediction of fluorescent paper under different sources from the other previous work.

Method

Fifteen digital press papers were collected with assistance from the RIT Printing Applications Laboratory and Neenah Paper. The samples included 15 substrates divided among six manufacturers varying in properties such as color, weight, and OBA concentration. The measured sample from each substrate was a square, approximately 3x3-in., made opaque by layering six sheets of the substrate. The samples were measured using a Macbeth Color-Eye 7000 (CE7000). The CE7000 has a Xenon source, an integrating sphere, and was operated in UV-included mode. The spectral power of the Xenon source was measured using an Ocean Optics USB2000 from 300 nm to 780 nm. The spectral radiance of each sample was then measured in a Macbeth Spectralight III using a Photo Research 650 (PR650) with approximately 0/45 measurement geometry. The spectral radiance of all samples was measured under Incandescent, Cool White, and Daylight sources. The relative spectral power distribution of each source was measured using the Ocean Optics USB2000.

The goal of this method was to transform measurements from a single-monochromator spectrophotometer into device-independent Donaldson matrices. The design of the estimated Donaldson matrices was based upon Donaldson matrices measured with a Labsphere Bispectral Fluorescence Colorimeter 450 (BFC). Each of the 15 samples was measured by the BFC, and the position of the fluorescent radiance peak was surveyed in each of the BFC Donaldson matrices. However, those matrices were not used in the fitting of the model parameters. It was determined that the optimal position for the fluorescent radiance peak in the Donaldson matrix was from excitation wavelengths 300 nm to 440 nm and emission wavelengths 400 nm to 540 nm (see the region of the illustration in Figure 1, “Fluorescent Emission”).

The first step in implementing this model required removing the fluorescent radiance peak from the spectral reflectance curves measured by the CE7000 and the PR650 (calibrated with a PTFE chip). The spectral reflectance curve without the fluorescent radiance peak is an estimation of the paper’s spectral curve after the removal of OBAs. The new curve served as the Diagonal of the model Donaldson matrix. A line was fit through the spectral reflectance points at 570 nm and 620 nm. The line was substituted into the original spectral curve from the point at which the line intersected the spectral curve in the short-wavelength region, to 570 nm (Figure 2).

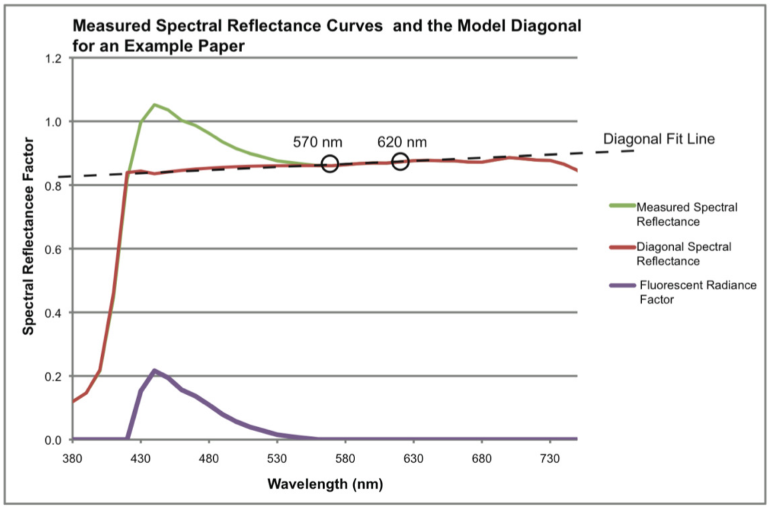

Figure 2. *The Diagonal (reflected radiance factor) is estimated by removing the fluorescent peak from the measured spectral reflectance curve. A straight line is fit between reflectances at 570 nm and 620 nm. The line is substituted into the measured curve between it's intersection with the curve at short wavelengths and 570 nm.*

Gill originally proposed a method, discussed in the introduction, for estimating such a curve. However, two weaknesses were noticed in the latter method. Gill proposed the first point of the fitted line be the minimum reflectance between 450 nm and 520 nm. Papers, such as the example paper in Figure 2, fluoresce at wavelengths longer than 520 nm. If the line were fit to 520 nm, for example, then the estimated reflected radiance beneath the fluorescent radiance peak would be too high. Gill proposed the second point of the fitted line be the maximum reflectance between 650 nm and 700 nm. Gill operated under the assumption that the reflectance of white papers is relatively flat at longer wavelengths. This assumption is acceptable for a general analysis. However, the reflectance of some papers increases at long wavelengths. Therefore, reflectances at middle wavelengths, 570 nm and 620 nm, were chosen to avoid the fluorescent emission peak and minimize the effect of increasing reflectance at long wavelengths. A comparison between the Gamm and Gill methods is shown in Figure 3.

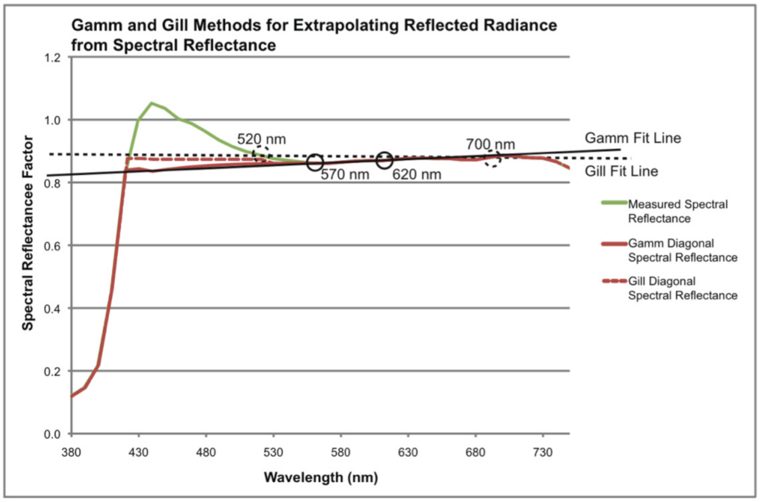

Figure 3. *Gamm's and Gill's (2003) methods for extrapolating the diagonal spectral reflectance curve from a spectral reflectance measurement are shown. The line fit by Gamm (black solid line) is shown passing through points in the solid circles, and the line fit by Gill (black dotted line) is shown passing through the dotted circles. The solid red diagonal spectral reflectance is fit using Gamm's method and the dotted red diagonal spectral reflectance is fit using Gill's method.*

The second step was to determine a function of approximately the same shape as the fluorescent radiance factor. The shape of a gamma distribution closely resembles the shape of the fluorescent radiance peak. A two-dimensional function was needed to model the Donaldson matrix. Equation 1 shows the function chosen to model the bispectral fluorescent radiance,

$$\beta_{\mu,\lambda} = A(\mu - \mu_\circ)^{\alpha_\mu}(\lambda - \lambda_\circ)^{\alpha_\lambda} e^{-\gamma_\mu(\mu-\mu_\circ)-\gamma_\lambda(\lambda-\lambda_\circ)} \tag{1}$$

where $\beta_{\mu,\lambda}$ is the bispectral fluorescent radiance; *A* is a scaling factor, α_μ, α_λ, γ_μ, and γ_μ are exponential shape factors (for excitation, μ, and emission, λ); μ and λ are the excitation and emission wavelengths; and μ_0 and λ_0 are offsets. The general shape of the function is illustrated in Figure 4.

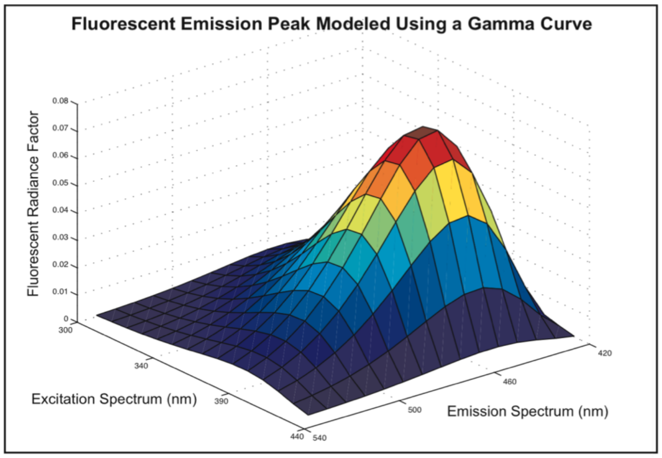

Figure 4. *This is a representation of the 2-D curve, calculated from Equation 1, optimized to fit the bispectral fluorescent radiance factor in the estimated Donaldson matrix.*

It is important to note that this model does not attempt to model the total fluorescent excitation, calculated by summing across the rows of the Donaldson matrix. Total fluorescent excitation describes the energy radiant from the sample as a function of incident wavelength. The total excitation spectrum was modeled to resemble the shape of the average total excitation curves calculated from the BFC-450 Donaldson matrices initially measured before modeling began.

The modeling process is as follows:

1. The spectral reflectance of a sample is measured using a single-monochromator spectrophotometer, and the spectrophotometer's source emission is measured with a spectroradiometer down to at least 300 nm.

2. The fluorescent radiance factor peak is removed from the spectral reflectance curve.

3. The new spectral reflectance curve is placed into the Donaldson matrix as the Diagonal.

4. The parameters α, γ, and x from Equation 1 are optimized such that the RMS between total spectral radiance factor of the model Donaldson matrix and the measured spectral reflectance curve is minimized when the device source is imposed upon the model Donaldson matrix.

The total spectral radiance factor of a Donaldson matrix is calculated using Equation 2,

$$\beta_T(\lambda) = \frac{\sum_\mu \beta(\mu, \lambda)S(\mu)}{S(\lambda)} \tag{2}$$

where $\beta(\mu,\lambda)$ is the spectral radiance factor matrix (Donaldson matrix), $S(\mu)$ is the source spectral power distribution as a function of excitation, and $S(\lambda)$ is the source. The diagonal is calculated using Equation 3,

$$\beta_R(\lambda) = \sum_\lambda \beta(\lambda, \lambda)S(\lambda) \tag{3}$$

where $\beta(\lambda,\lambda)$ is the total spectral reflectance where excitation wavelength equals emission wavelength. An example total spectral radiance model curve and the spectral reflectance curve from which it was optimized are shown in Figure 5.

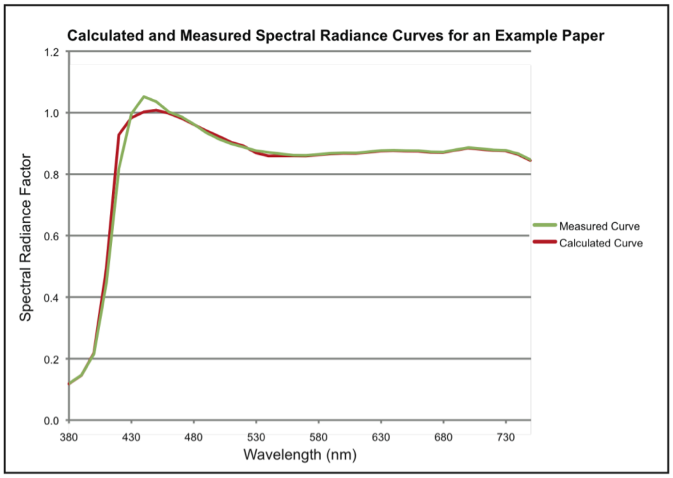

Figure 5. *The total radiance factor calculated from an estimated Donaldson matrix for an example paper (red), optimized to match the measured spectral reflectance (green).*

Three sources were used to evaluate the model Donaldson matrix for the 15 papers. Spectral radiances measured with Ocean Optics for the Daylight, Cool White, and Incandescent sources were imposed upon the model Donaldson matrices (Equation 2). The effectiveness of the model was evaluated by computing the CIEDE2000 color differences between the total spectral radiance factor curves of the model Donaldson with each of the three sources imposed upon it, and the spectral reflectances calculated under each source by the PR-650. Figure 6 illustrates the optimization process and the comparison between the modeled total spectral radiance curves and spectral reflectance curves measured under the light booth.

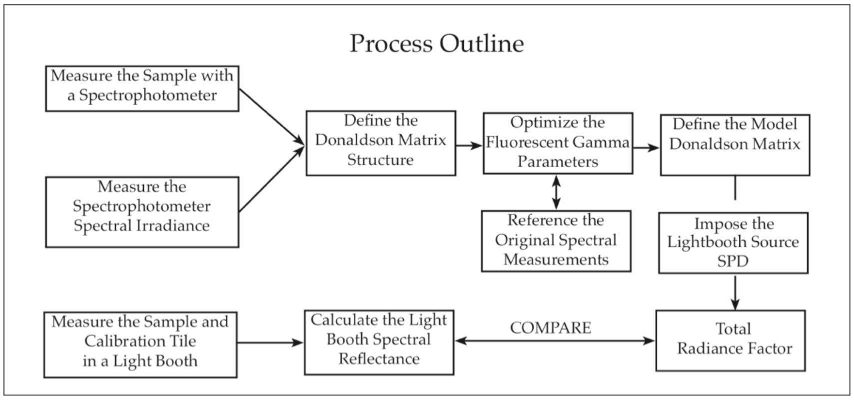

Figure 6. *The flow chart diagrams the process for estimating the total radiance factor of a fluorescent paper. First, the sample is measured in a spectrophotometer and the light source of the spectrophotometer is measured with a spectroradiometer. Next, the structure of the Donaldson matrix is defined (Figure 1). The gamma-curve parameters in Equation 1 are optimized to the original spectral reflectance measurements. A light-booth source is imposed upon the estimated Donaldson matrix, and a calculated total radiance factor is compared to the spectral reflectance of the sample measured under the same source.*

The spectral reflectance measurements made by the PR650 in the light booth were normalized to the modeled spectral radiance curve to which they were compared at 580 nm. Fluorescent emission does not occur in the long wavelength region of paper white spectral reflectance curves. Therefore, it is reasonable to assume that the spectral curves of a white paper under different sources are equal at wavelengths where fluorescent emission does not occur. Due to system noise and small calibration inconsistencies, the light booth PR650 long wavelength spectral reflectances differed from the model spectral radiance factor curve by a multiplicative factor. Therefore, for the purposes of comparison in this research, the PR650 spectral reflectances were scaled to account for calibration differences.

Results and Discussion

Modeled total spectral radiance curves for paper samples under each of the three sources were compared to the spectral reflectance curves of each sample measured with the PR650 using CIEDE2000. Figure 7a shows the mean

CIEDE2000 for each source averaged across all papers. Figure 7b shows the mean ΔL*, ΔC*, and ΔH* for each source average across papers.

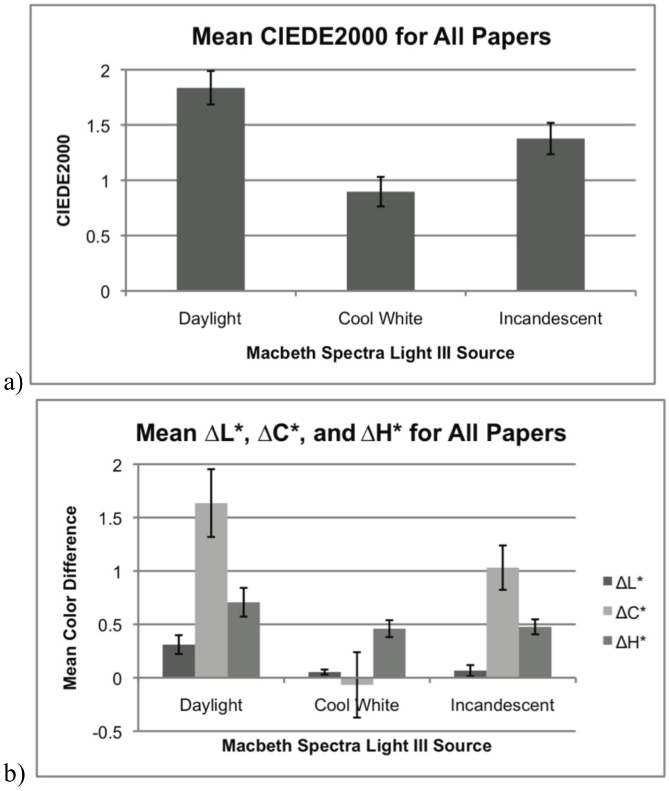

Figure 7. *The mean CIEDE2000 color differences, averaged over all samples, were calculated for three sources in the Macbeth Spectralight III light booth (a). The mean color difference components, ΔL*, ΔC*, and ΔH*, averaged over all samples, were calculated as well (b). Standard error bars are overlaid on each bar.*

As seen in Figure 7a, the CIEDE2000 varies between source; however, the results are promising. It was stated in the method that the excitation shape and offset parameters in Equation 1 were standardized prior to optimization based upon the general shape of the total excitation curve from BFC-450. However, the excitation characteristics of OBAs are variable in both shape and scale. The variability of total excitation is supported by the physical properties of OBAs, including the increase in emission intensity proportional to excitation, greening of OBAs as the concentration approaches saturation point, and fluorescent cascades as the concentration exceeds the saturation point (Shakespeare and

Shakespeare, 1999; Roick and Hunke, 2004). Even these complex physical properties are characterized by bispectral spectrophotometers.

One technique common in commercial laboratories is the use of a UV-cut filter to adjust the UV content of the device source. A variety of UV-cut filters are used in instrumentation. Handheld devices often use plastic UV-cut filters transmitting a reduced portion of the short-wavelength visible spectrum, cutting out UV energy completely below 380 nm. Tabletop devices, such as the Macbeth Color-Eye 7000 may incorporate glass UV-cut filters with sharp reductions in UV transmission at specific application-dependent wavelengths, e.g., 400 nm. All varieties of UV-cut filters serve the purpose of reducing the intensity of UV energy exciting the sample, thus reducing or nullifying the fluorescent emission of OBAs. Löffler (2008) recently proposed a method for classifying papers based upon the difference in total fluorescent radiance factor between measurements made with UV-included and UV-excluded. In addition, she characterized the fluorescent absorption and emission of offset papers through an analysis of Donaldson matrices measured at the German Federal Institute for Materials Testing and Research (BAM). She scaled the magnitude of the fluorescent radiance factor by the difference between UV-included and UV-cut emission.

Unlike the methods mentioned above and in the introduction, the method proposed in this paper estimates a Donaldson matrix without direct use of data from a bispectral device. The only data requirement, besides the spectral reflectance measurement, is the spectral power distribution of the device source. However, it may not be necessary to measure the spectral power distribution of every device with which this model is implemented. For example, the Xenon source of one Macbeth Color-Eye 7000 may be reasonably expected to have a similar spectral power distribution of all Color-Eye 7000 devices, assuming the device is maintained and the source has not degraded with age. Nevertheless, Connelly (2003) cites significant color difference due to inter-instrument agreement error.

The variation between color differences under the three illuminants can most likely be attributed to the differences in the peak wavelength region of their spectral power distributions. Daylight has more energy in the OBA excitation region than Incandescent and Cool White fluorescent sources. Therefore, any inaccuracy in the total excitation curve used in the model is accentuated when Daylight is imposed upon the model Donaldson matrix. Further investigation is needed to determine the exact reason why the color differences vary from one source to another. Nevertheless, the authors are confident that the parameters used in Equation 1 to generate the excitation curve can be optimized to reduce the color differences listed above. Optimizing the excitation parameters requires a reduction of excitation curve variability, such as is obtained from principle components analysis. In future work, Donaldson matrices will be measured for additional paper samples to allow further study of excitation curves. With these data, methods such as used by Allen (1973), Alman and Billmeyer (1977), and Mohammadi and Berns (2006) and described in Mohammadi (2009) or variations on such methods, can be incorporated to optimize the excitation parameters in Equation 1. Nevertheless, the model presented in this paper provides the foundation for a method can be used to bridge the gap between spectrophotometer and light booth when comparing papers containing OBAs.

Conclusion

A method for estimating a Donaldson matrix from standard spectral reflectance curves was presented. The Donaldson matrix can also be implemented in models where the spectral radiance factor of printed samples is estimated. It can also be used to enable paper manufacturers, printers, and photographers to estimate the appearance of the paper in a light booth, art gallery, or other environment. This paper presents the foundation for bridging the gap between spectrophotometry and the bispectral measurement of fluorescent papers.

Acknowledgments

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