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Fluorescence model for multi-layer papers using conventional spectrophotometers

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KEYWORDS: Whiteness, Kubelka-Munk, Multi-layer, Fluorescence, Fluorescent whitening agents.

SUMMARY: We present an extension of a Kubelka-Munk based fluorescence model in which we introduce an apparent scattering (S_{UV}) and absorption (K_{UV}) coefficient for all wavelengths below 400 nm. We describe a method for modelling the total radiance factor of multi-layer papers and for estimating the optical parameters (S , K and Q) of each layer. Assuming that the fluorescent whitening agent only absorbs below 400 nm, we are able to determine S_{UV} , K_{UV} and the apparent quantum efficiency, $Q(UV, \lambda)$ for $400 \text{ nm} < \lambda < 700 \text{ nm}$, from spectral radiance measurements in the visible part of the electromagnetic spectrum. We test the proposed method on different layered constructions made of three individual pilot paper layers. The proposed method allows the papermaker to determine the illumination independent fluorescence characteristics of single- and multilayer paper layers using a conventional single-monochromator spectrophotometer operating in the visible part of the electromagnetic spectrum, and also to predict the radiance factor of fluorescing layered papers.

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Whiteness is an important quality parameter of paper and a marketing goal for product segments such as office papers. This has led to more bleaching and a substantial increase of the concentration of fluorescent whitening agents (FWA) added in paper. FWA are dyes that absorb ultraviolet (UV) radiation and emit in the blue region of the spectrum, hence increasing the perceived whiteness by both increasing the lightness and the blueness of the paper. FWAs absorb UV radiation and short wavelength visible light, at wavelengths ranging from 240 nm to 420 nm, and emit in the violet-blue, mainly between 380 nm to 500 nm (Shakespeare 2000). The fluorescence efficiency depends on the amount of radiation reaching the FWA molecules, and on the scattering and absorption properties of the furnish at the emitted wavelengths. Measured radiance factors are thus not a direct measure of the intrinsic light (or radiation) absorption and light emission properties of the FWA, since it is affected also by the surrounding of the FWA.

Better understanding of the dependence between fluorescence and FWA concentration is obtained by

separating the fluorescence effects intrinsic to the FWA from scattering and absorption by the furnish. This in turn requires modelling the light scattering process in a fluorescing paper. Light scattering in paper is most frequently modelled with the Kubelka-Munk (1931; 1948) theory (KM). The KM theory relates two reflectance factor measurements to a scattering coefficient, S , and an absorption coefficient, K . Several extensions of the KM theory have been developed over the years to account for fluorescence (Allen 1964; Fukshansky, Kazarinova 1980; Bonham 1986; Shakespeare 2000; Shakespeare and Shakespeare 2003). However, the use of these extensions is limited to either a defined polychromatic illumination or to a semi-infinite layer. More recently, Kokhanovsky (2009; 2010) presented a general analytical solution, where fluorescence in paper can then be modelled within the framework of the KM theory, with spectral scattering (S) and absorption (K) coefficients, thickness (t) and a bi-spectral quantum efficiency (Q) relating the amount of photons emitted at emission wavelength upon absorption at excitation wavelength. Coppel et al. (2012) proposed an extension of the Stokes equations for multilayered media to fluorescence, opening the possibility for modelling of fluorescence in layered papers.

Absorption or radiation by FWA takes place mainly in the UV region of the electromagnetic spectrum. This region is outside the range of conventional spectrophotometers used in the paper industry. Thus, it is not possible to determine the scattering and absorption coefficients at the excitation wavelengths in UV using conventional methods. The radiance factor depends on the illumination and accurate determination of fluorescence and scattering characteristics requires the use of a bispectrophotometer to determine the illumination independent bispectral radiance factor (Coppel et al. 2011a). Previous attempts have been made to estimate the illumination independent fluorescence characteristics using single-monochromator spectrophotometers (Allen 1973; Alman, Billmeyer 1977; Grum, Costa 1977; Löffler, Green 2008) but none of the proposed methods enable the determination of the paper's fluorescence and scattering characteristics in UV.

Aim of the present study

The purpose of this work is to determine apparent scattering and absorption coefficients in UV using conventional single-monochromator spectrophotometers operating in the visible spectrum. This allows determining the paper fluorescence and scattering characteristics in the wavelength band where the FWA is active. It is useful for the papermaker to, e.g., determine the effect of different furnishes on the fluorescence efficiency and to predict the radiance factor of layered papers with the UV(C) and UV(D65) UV settings used in

the paper industry. The next section describes the model linking paper optical parameters to radiance factor and whiteness, and the extension of the model to multilayer papers. The section following presents a novel apparent UV fluorescence model. A method to determine the apparent UV content in different spectrophotometer illuminations and the apparent optical properties in UV is then described. The model is finally applied on a set of paper samples and successfully used to predict the whiteness of layered papers from the individual layers' optical properties.

Theoretical background

Measuring fluorescence in paper

The paper industry measures whiteness and fluorescence with a standardised instrument (ISO 2469) using a broad band light source and a UV-adjustment filter controlling the relative UV content in the illumination. The instrument measures the total radiance factor, $\beta_T(\lambda|E)$, at each wavelength λ for a given illumination E . The measured total radiance is the sum of the reflected radiance factor, $\beta_R(\lambda)$, relating the amount of light reflected at λ to the amount of light incident at λ , and the luminescent radiance factor, $\beta_L(\lambda|E)$. The luminescent radiance factor depends on the spectral distribution of the light source and relates the amount of light fluoresced at λ from excitation in UV to the amount of light incident at λ . In single-monochromator spectrophotometers, the UV-content is adjusted to measure the total radiance factor for a given standard illuminant. This calibration follows a standardised procedure involving a hierarchy of standardizing and authorised laboratories (Bristow 1994). It is a pragmatic procedure and a compromise between different factors with the primary goal to ensure the greatest possible statistical reproducibility of the measurements; it is also specific for the type of FWAs used in paper and is in some respects arbitrary (CIE 182, 2007). It is important to recall that the illumination is adjusted to give the same CIE whiteness as if it was illuminated with a D65 (ISO 11475) or C illuminant (ISO 11476), but the actual spectral distribution of the illumination in the corresponding UV(D65) and UV(C) UV settings is not defined.

Model framework

The layered medium that we consider is represented schematically in Fig 1. Each layer is described with a reflectance (R_{xx}^{layer}) and a transmittance (T_{xx}^{layer}) matrix. The subscripts indicate the excitation and emission wavelengths and the superscripts the layer number. When the excitation and emission wavelengths are equal, R_{xx}^{layer} is equivalent to the reflected radiance factor $\beta_R(x)$. The two-dimensional matrix of bispectral radiance factor data R_{xx}^{layer} is known as the Donaldson matrix (Donaldson 1954). These single layer reflectance and transmittance matrices can be measured with a bispectrophotometer or calculated from the layer scattering (S) and absorption (K) coefficients, quantum efficiency (Q) and thickness (t), with a model relating these medium characteristics to

Fig 1. Schematic description of a structure with 3 layers. Each layer is described by bi-spectral reflectance and transmittance matrices that can be calculated from the spectral scattering (S) and absorption (K) coefficients, the thickness (t) and the quantum efficiency (Q) of the layer. The reflectance matrix of the whole 3-layer structure is computed iteratively.

the reflectance and transmittance matrices. The reflectance and transmittance matrix of a layered construction can be calculated iteratively from the individual layer matrices (Coppel et al. 2012).

Fluorescence in Kubelka-Munk

Kokhanovsky (2009; 2010) derived a solution to a generalization of KM theory for the case of monochromatic illumination of a sample by a doublet of lines λ_1 and $\lambda_2 > \lambda_1$ of equal energy. The reflectance (R) and transmittance factor (T) at λ_2 are determined from the scattering and absorption coefficients at both wavelengths, the quantum efficiency Q from λ_1 to λ_2 and the layer thickness (or basis weight) t . The simple but lengthy equations are given in Appendix 1 for clarity.

The reflectance coefficient R_{12}^{layer} is obtained by subtracting the reflectance at λ_2 , R_{22}^{layer} , from the reflectance factor in Eq A1,

$$R_{12}^{\text{layer}} = R(\lambda_2) - R_{22}^{\text{layer}}. \quad [1]$$

In the same manner, the transmittance coefficient, T_{12}^{layer} , is given by

$$T_{12}^{\text{layer}} = T(\lambda_2) - T_{22}^{\text{layer}}. \quad [2]$$

For a semi-infinite layer ($t \rightarrow \infty$) Eq 1 simplifies to (Kokhanovsky, 2009)

$$R_{12}^{\text{layer}} = \frac{K(\lambda_1)Q}{2[\alpha(\lambda_1) + \alpha(\lambda_2)]} \times \left[2 + \frac{K(\lambda_1)}{S(\lambda_1)} - \frac{\alpha(\lambda_1)}{S(\lambda_1)} \right] \left[2 + \frac{K(\lambda_2)}{S(\lambda_2)} - \frac{\alpha(\lambda_2)}{S(\lambda_2)} \right] - , \quad [3]$$

$$R_{22}^{\text{layer}}$$

where $\alpha(\lambda) = \sqrt{\varepsilon(\lambda)^2 - S(\lambda)^2}$ and $\varepsilon(\lambda) = S(\lambda) + K(\lambda)$. The matrix elements R_{11}^{layer} , R_{22}^{layer} , T_{11}^{layer} and T_{11}^{layer} are obtained from KM theory (Kubelka, 1948) according to

$$R_{xx}^{\text{layer}} = \frac{r_{\infty}(\lambda_x) e^{\frac{S(\lambda_x)t}{r_{\infty}(\lambda_x) - r_{\infty}(\lambda_x)}} - r_{\infty}(\lambda_x)}{e^{\frac{S(\lambda_x)t}{r_{\infty}(\lambda_x) - r_{\infty}(\lambda_x)}} - r_{\infty}(\lambda_x)^2} \quad [4]$$

and

$$T_{xx}^{\text{layer}} = \frac{[1 - r_{\infty}(\lambda_x)^2] e^{-\alpha(\lambda_x)}}{1 - r_{\infty}(\lambda_x)^2 e^{-2\alpha(\lambda_x)}}, \quad [5]$$

where

$$r_{\infty}(\lambda) = \frac{S(\lambda)}{\varepsilon(\lambda) + \alpha(\lambda)}. \quad [6]$$

Radiance factor calculation

Generalization to complete excitation and emission spectra with n wavelengths leads to $n \times n$ matrices. For polychromatic illumination, the luminescent radiance factor β_L is computed for any illuminant from the bi-spectral reflectance matrix according to

$$\beta_L(\lambda|E) = \frac{1}{E(\lambda)} \sum_{\mu < \lambda} R_{\mu\lambda} E(\mu), \quad [7]$$

where E is the normalized spectral distribution of the illuminant (Zwinkels, Gauthier 1999). The total radiance factor is then obtained with

$$\beta_T(\lambda|E) = R_{\lambda\lambda} + \beta_L(\lambda|E), \quad [8]$$

from which the chromaticity coordinates (Wyszecki, Stiles 2000) and the CIE whiteness (ISO 11475 2004; ISO 11476 2000) can be calculated for a defined observer (2° for C illuminant and 10° for D65 illuminant).

Fluorescence model for layered constructions

The reflectance and transmittance matrices for a two-layer construction is obtained from the individual layer matrices (Coppel et al. 2012) as

$$R_{12}^{\text{tot}} = \frac{R_{12}^1 + \frac{T_{12}^1 R_{22}^2 T_{22}^1 + T_{11}^1 R_{12}^2 T_{22}^1}{1 - R_{22}^1 R_{22}^2}}{1 - R_{11}^1 R_{11}^2 (1 - R_{22}^1 R_{22}^2)} + \frac{T_{11}^1 R_{11}^2 R_{12}^2 T_{22}^1 + T_{11}^1 R_{11}^2 R_{11}^2 T_{22}^1}{(1 - R_{11}^1 R_{11}^2)(1 - R_{22}^1 R_{22}^2)} \quad [9]$$

$$T_{12}^{\text{tot}} = \frac{T_{12}^1 T_{22}^2}{1 - R_{11}^1 R_{11}^2} + \frac{T_{11}^1 T_{12}^2}{1 - R_{11}^1 R_{11}^2} + \frac{T_{11}^1 R_{12}^2 R_{22}^2 T_{22}^1 + T_{11}^1 R_{11}^2 R_{11}^2 T_{22}^2}{(1 - R_{11}^1 R_{11}^2)(1 - R_{22}^1 R_{22}^2)} \quad [10]$$

The matrix elements R_{11}^{tot} and T_{11}^{tot} are obtained with the Stokes equations (Stokes 1862) giving

$$R_{11}^{\text{tot}} = R_{11}^1 + \frac{(T_{11}^1)^2 R_{11}^2}{1 - R_{11}^1 R_{11}^2} \quad [11]$$

and

$$T_{11}^{\text{tot}} = \frac{T_{11}^1 T_{11}^2}{1 - R_{11}^1 R_{11}^2}. \quad [12]$$

The matrix elements R_{22}^{tot} and T_{22}^{tot} are obtained in the same manner. Eqs 9-12 thus allow calculating the reflectance and transmittance matrices of the two-layer structure from the individual layer matrices. The matrices of a three-layer structure can be obtained by first

computing the matrices of the two first layers, and then compute the matrices of this two-layer structure on top of a third layer. Iterating this n times gives the matrices for n layers.

Apparent UV fluorescence model

FWA absorbs light below 420 nm with peak absorption around 360 nm. We now introduce an (illumination independent) apparent scattering (S_{UV}) and absorption (K_{UV}) coefficient for all excitation wavelengths of the FWA. Assuming that fluorescence only occurs at single excitation wavelength below 400 nm the luminescent radiance factor in Eq 7 simplifies to one summation term and can then be written as

$$\beta_L(\lambda|E) = \frac{R_{UV\lambda} E(UV)}{E(\lambda)} = R_{UV\lambda} E^*(\lambda), \quad [13]$$

where $R_{UV\lambda}$ is the reflectance coefficient from UV to $\lambda \geq 400$, $E(UV)$ is the apparent UV content of the illuminant E , and $E^*(\lambda) = E(UV)/E(\lambda)$.

We notice that the reflectance coefficient $R_{UV\lambda}$, given by Eq 1 for finite thickness or by Eq 3 for a semi-infinite layer, is proportional to the apparent quantum efficiency $Q(UV, \lambda)$. Hence, $\beta_L(\lambda|E)$ is proportional to $Q(UV, \lambda) E^*(\lambda)$. Also, since $R_{UV\lambda}$ is illumination independent, we have

$$\frac{\beta_L(\lambda|E_1)}{\beta_L(\lambda|E_2)} = \frac{E_1^*(\lambda)}{E_2^*(\lambda)}. \quad [14]$$

For the UV(C) and UV(D65) UV settings used in the spectrophotometer we can estimate the ratio $E_{UV(D65)}^*/E_{UV(C)}^*$ from the ratio of the fluorescence component of the radiance factor obtained in the two illuminations. The fluorescence component is obtained by subtracting the radiance factor in UVex(420), i.e. with UV filtered out, from the radiance factor obtained with the UV(D65) or UV(C) UV settings. For an ideal UV filter and $\lambda > 420$ nm, this gives

$$\frac{E_{UV(D65)}^*(\lambda)}{E_{UV(C)}^*(\lambda)} = \frac{\beta_L(\lambda|UV(D65))}{\beta_L(\lambda|UV(C))} = \frac{\beta_T(\lambda|UV(D65)) - \beta_T(\lambda|UVex(420))}{\beta_T(\lambda|UV(C)) - \beta_T(\lambda|UVex(420))} \quad [15]$$

where β_T is the measured radiance factor in the three illuminations with UV(D65), UV(C) and UVex(420) UV settings. Hence, once $Q(UV, \lambda) E_{UV(D65)}^*(\lambda)$ is defined, $Q(UV, \lambda) E_{UV(C)}^*(\lambda)$ can be determined from the radiance factor measured with the three illuminations.

Materials and Methods

In order to test the proposed model a set of papers with a final basis weight of 40 g/m², a basis weight for relatively low opacity with acceptable uniformity, are made at different filler contents to build 3-layer constructions made of the individual layers. The spectral radiance factor of the samples is measured with a conventional spectrophotometer with three different UV settings for one single sheet over a black background, for a pad of n sheets, and for different 3-layer constructions.

The ratio of the measured luminescent radiance factor in UV(D65) and UV(C) UV settings is calculated to determine $E^*(\lambda)$ for the two illuminations. A parameter estimation method is developed to determine the scattering and absorption coefficients and the quantum efficiency of the samples from the measured radiance factors in the visible part of the electromagnetic spectrum. The method allows the determination of the apparent scattering (S_{UV}) and absorption (K_{UV}) coefficients in UV.

The applicability of the proposed model and parameter estimation method are tested by qualitatively comparing the determined coefficients for samples with different filler and FWA concentrations. The predictability of the models is then tested by comparing simulated CIE whiteness values in UV(C) and UV(D65) from the estimated parameters of the individual layers.

Paper samples

Paper samples with a final basis weight of 40 g/m² were produced on the experimental pilot paper machine XPM at MoRe Research, Örnköldsvik, Sweden. The samples were formed from a pulp blend consisting of 75% hardwood and 25% softwood. The samples were sized using a mix of Kemsized (0.04%) and C*bond starch (0.06%) in order to form samples with a target Cobb-value of 25 (varied between 25 and 28). Percol (0.01%) and Bentonit (0.05%) were used as retention agents. No shading dyes were used. The samples were neither surface sized nor calendered. A tetrasulpho FWA, Blankophor P01, was added to the pulp at 3 different concentrations (0, 9, and 18 kg/T fibre). The samples were filled with PCC at three different filler contents (0, 15, and 30%).

Measurements

The samples were measured with a Technidyne ColourTouch d/0° spectrophotometer calibrated in accordance with ISO 2469. The UV amount was adjusted to UV(D65) and UV(C) conditions in accordance with ISO 11475 and ISO 11476 respectively. The spectrophotometer operates in the wavelength range between 380 nm and 740 nm with 10 nm intervals. The measurements were performed on one single sheet over a black background and on a pad of sheets. The maximum number of sheets available were used to make a nearly opaque pad. The number of sheets used differs for the nine different samples and are given in Table 1.

Parameter estimation

Assuming that the FWA only absorbs in UV, we are able to determine S_{UV} , K_{UV} and the apparent quantum efficiency, $Q(UV, \lambda)$ for 400 nm < λ < 700 nm, from spectral radiance measurements in the visible part of the electromagnetic spectrum. This is done in three steps using the radiance factors measured in three different illuminations:

- S and K at 440 nm are determined from measurements in UVex(420) using KM theory. This gives the scattering and absorption coefficient at fluorescence peak (440nm).

- S_{UV} , K_{UV} and $[Q(UV, 440nm)E_{UV(D65)}^*(440nm)]$ are then determined by minimising the error between four simulated and measured radiance factors, i.e. UV(C) and UV(D65) UV settings on both a single sheet and on a pad of samples. Eq 1 is used to simulate $R_{UV\lambda}$ of a single sheet and of a pad of n sheets (the basis weight is multiplied by the number of sheets used for the actual sample). Eqs 13 and 8 are then used to compute the radiance factor in the UV(C) and UV(D65) illuminations.
- Once S_{UV} and K_{UV} are determined, $[Q(UV, \lambda)E_{UV(D65)}^*(\lambda)]$, $S(\lambda)$ and $K(\lambda)$ are determined for λ between 400 and 700 nm with the same fitting procedure.

This method can however not determine S_{UV} and K_{UV} of non fluorescing papers for which Q is equal to zero. S_{UV} and K_{UV} of the sample without FWA are determined by minimising the error between simulated and measured radiance factors in UV(D65) UV setting of two three-layer constructions in which the sample to be determined is in-between or around a fluorescing sample.

Table 1. Sample number, FWA concentration, filler concentration and number of sheets used for radiance factor measurements of a pad of sheets.

Sample	FWA kg/T	Filler (%)	Nr. sheets
1	0	0	25
2	9	0	27
3	18	0	25
4	0	15	24
5	9	15	50
6	18	15	28
7	0	30	27
8	9	30	30
9	18	30	28

Results

Determination of $E(UV)/E(\lambda)$

Fig 2 shows the measured ratio of the fluorescence component in UV(D65) and UV(C) UV settings for the six samples with FWA. According to Eq 15 this ratio is equivalent to the ratio of luminescent radiance factor and to the ratio of apparent relative UV content in the illumination. In the region above 500 nm the signal is noisy because the effect of the fluorescence component decreases to zero. We can see that the ratio of the luminescent radiance factors is approximately constant with wavelength. This is due to the fact that the same illumination is actually used for the UV(C) and UV(D65) UV settings making thus $E(\lambda)$ in the visible region of the electromagnetic spectrum equal in both illuminations. The spectral distributions of the two illuminations differ only in the UV region. It is worth noting that the ratio of luminescent radiance factors is dependent on the basis weight. This means that the samples respond differently to a change of illumination at different basis weight. Further investigation of this phenomenon is not within the scope of this work. On the other hand, the ratio varies only between 2 for relatively thin papers (40 g/m²) and

Fig 2. Measured ratio of the luminescent radiance factor for UV(D65) and UV(C) UV settings. $E_{UV(D65)}^*/E_{UV(C)}^*$ is constant with wavelength, but surprisingly dependent on basis weight. The signal is noisy above 500 nm where Q becomes small.

2.2 for nearly opaque pads of papers. Henceforth $E_{UV(C)}^* = E_{UV(D65)}^*/2.1$ is therefore used for all measurement configurations.

Parameter estimation

Fig 3 shows the estimated KM scattering coefficients for the nine 40 g/m² samples with different FWA and filler concentrations. In line with previous research, the KM scattering coefficient decreases with increasing absorption coefficient (Rundlöf, Bristow 1997; Koukoulas, Jordan 1997). This means that S depends on the FWA concentration. The product of the apparent quantum efficiency with apparent UV content in the UV(D65) UV setting illumination [$Q(UV, \lambda)E_{UV(D65)}^*(\lambda)$] is shown in Fig 4. The apparent quantum efficiency depends also on the FWA concentration because of the absorption of UV light from the non fluorescing furnish (Coppel et al. 2011b). Since part of the UV radiation is absorbed by the non fluorescing fibres and fillers, the apparent quantum efficiency is lower at lower FWA concentration than at higher FWA concentration where the absorption by the furnish becomes negligible in comparison to the absorption by the FWA. The estimated absorption coefficients are shown in Fig 5. The absorption coefficient is larger in UV than in the visible part of the electromagnetic spectrum even for the samples without FWA. This shows that a significant part of the UV radiation is indeed absorbed by the furnish without leading to fluorescence. Moreover, it should be noted that the apparent absorption coefficient K_{UV} of the samples without FWA increases significantly with increasing filler amount. This can be interpreted as fillers being UV-thief since they decrease absorption of UV by the FWA.

Fig 6 shows the results of the fitting of the simulated radiance factor of sample 6 in the two illuminations for one single sheet over a black background and for an opaque pad. Similar results are obtained for all six samples with FWA. Fig 7 shows the results of the fitting of the simulated radiance factor of the 3-layer stacks used for determination of S_{UV} and K_{UV} in the layers without FWA (samples 1, 4 and 7) where e.g. 121

Fig 3. Estimated scattering coefficient (S) for the 9 samples.

Fig. 4 Estimated product of quantum efficiency with apparent UV amount in UV(D65) UV setting [$Q(UV, \lambda)E_{UV(D65)}^*(\lambda)$] for the 6 samples with FWA.

Fig 5. Estimated absorption coefficient (K) for the 9 samples.

stands for one sample 1 over one sample 2 over one sample 1.

Prediction of layered paper whiteness

As shown in Fig 8 the predicted radiance factors of two three-layered constructions agree well with measurements. This holds for all the layered constructions tested, as shown in Fig 9 for simulated and predicted CIE whiteness, where e.g. 121 stands for one sample 1 over one sample 2 over one sample 1.

Fig 6. Measured (lines) and simulated (markers) radiance factor in UV(C) and UV(D65) illuminations for sample 6 (single sheet and nearly opaque pad used for parameter estimation)

Fig 7. Measured (lines) and simulated (markers) radiance factor in UV(D65) illumination for the 3-layer constructions used to determine S_{UV} and K_{UV} of the samples without FWA. "212" stands for sample 2 over sample 1 over sample 2.

Fig 8. Measured (lines) and simulated (markers) radiance factor in UV(C) and UV(D65) illumination for stacks of samples 5/4/5 and 6/4/6.

Discussion

The main feature of the proposed apparent UV fluorescence model is the representation of the optical properties in UV at one single apparent excitation wavelength λ_{UV} . This reduces the number of parameters in the UV to one apparent scattering (S_{UV}) and absorption coefficient (K_{UV}) and one spectral apparent quantum efficiency [$Q_{UV(\lambda)}$] that can be determined by fitting simulated radiance factors to six measured radiance factors obtained with standardised spectro-photometer. These measurements, i.e. radiance factor from a single sheet and radiance factor from a pad of sheets using the UVex(420), UV(D65) and UV(C) UV settings, are today performed on a routine basis in the paper industry. The actual spectral distribution of the illumination in these different UV settings is generally not known. However, since the same lamp is used for both UV(C) and UV(D65) UV settings, we can assume that the two illuminations only differ in UV due to different levels of UV filtering. Moreover, only the ratio of the UV content of the two illuminations is needed for the parameter estimation. This ratio is here set to a constant

Fig 9. Measured and simulated CIE whiteness for all stacks of samples. Stacks marked in grey are optimised to determine S_{UV} and K_{UV} in the layers without FWA.

for simplicity but can be estimated individually for each measured sample, and a different ratio could be used for the single sheet than for the pad of sheets. The proposed method enables not only determining apparent S and K in UV but also between 400 and 420 nm, a region previously inaccessible due to the cut-off filter at 420 nm used in the UVex(420) UV setting. The determined parameters show the same characteristics as those determined with a bispectrophotometer (Coppel et al. 2011a) and the results show that the proposed method can be used to characterise the effect of absorption by the furnish on fluorescence.

It should be noted that the model neglects fluorescence excitation in the visible part of the electromagnetic spectrum, between 400 nm and 420 nm for common FWA (Coppel et al. 2011b), and that the estimated parameters are apparent parameters valid only within the model. Thus, the proposed method does not remove the need for bispectrophotometric measurements to accurately and objectively characterise fluorescence from paper. Nonetheless, it is of practical use for fast and inexpensive characterisation as well as for simulation and optimisation.

Conclusion

We present an apparent UV fluorescence model and a parameter estimation method for characterising the illumination independent fluorescence characteristics from paper with conventional measurement techniques. The model can be used to study the effect of UV scattering and absorption from furnish and FWA, and to predict the radiance factor of layered papers. This allows improved characterisation using conventional measurement techniques and simulating the fluorescence response in layered papers.

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Appendix 1: Kokhanovsky single layer fluorescence model

Kokhanovsky derived a solution to a generalization of KMT for the case of monochromatic illumination of a sample by a doublet of lines λ_1 and λ_2 of equal intensity. The reflectance $R(\lambda_2)$ and transmittance $T(\lambda_2)$ coefficients at the emission wavelength λ_2 are determined from the scattering and absorption coefficients at excitation wavelength ($S(\lambda_1)$ and $K(\lambda_1)$), the scattering and absorption coefficients at emission wavelength ($S(\lambda_2)$ and $K(\lambda_2)$), the quantum efficiency Q from λ_1 to λ_2 , and the layer thickness t , with the following set of equations:

$$R(\lambda_2) = c_1 + c_2 + \frac{A+B}{\alpha(\lambda_1)^2 - \alpha(\lambda_2)^2}, \quad [A1]$$

$$T(\lambda_2) = D_1 e^{-\alpha(\lambda_2)t} + D_2 e^{\alpha(\lambda_2)t} + D_3 e^{-\alpha(\lambda_1)t} + D_4 e^{\alpha(\lambda_1)t}, \quad [A2]$$

where $\alpha(\lambda) = \sqrt{\varepsilon(\lambda)^2 - S(\lambda)^2}$, $\varepsilon(\lambda) = S(\lambda) + K(\lambda)$ and

$$A = -\frac{a}{2} K(\lambda_1) Q [\varepsilon(\lambda_2) + S(\lambda_2) - \alpha(\lambda_1)], \quad [A3]$$

$$B = -\frac{b}{2} K(\lambda_1) Q [\varepsilon(\lambda_2) + S(\lambda_2) + \alpha(\lambda_1)], \quad [A4]$$

$$D_1 = \frac{[\varepsilon(\lambda_2) + \alpha(\lambda_2)]c_1}{S(\lambda_2)}, \quad D_2 = \frac{[\varepsilon(\lambda_2) - \alpha(\lambda_2)]c_2}{S(\lambda_2)}, \quad [A5]$$

$$D_3 = \frac{[\varepsilon(\lambda_2) + \alpha(\lambda_1)]A}{[\alpha(\lambda_1)^2 - \alpha(\lambda_2)^2]S(\lambda_2)} - \frac{K(\lambda_1)Qa}{2S(\lambda_2)}, \quad [A6]$$

$$D_4 = \frac{[\varepsilon(\lambda_2) - \alpha(\lambda_1)]B}{[\alpha(\lambda_1)^2 - \alpha(\lambda_2)^2]S(\lambda_2)} - \frac{K(\lambda_1)Qb}{2S(\lambda_2)}, \quad [A7]$$

$$c_1 = \frac{q_1 + [\varepsilon(\lambda_2) + \alpha(\lambda_2)]c_2}{\varepsilon(\lambda_2) + \alpha(\lambda_2)}, \quad [A8]$$

$$c_2 = \frac{q_1 + [\varepsilon(\lambda_2) + \alpha(\lambda_2)]^{-1} e^{-2\alpha(\lambda_2)t} - q_2 e^{-\alpha(\lambda_2)t}}{1 - [\varepsilon(\lambda_2) - \alpha(\lambda_2)][\varepsilon(\lambda_2) + \alpha(\lambda_2)]^{-1} e^{-2\alpha(\lambda_2)t}}, \quad [A9]$$

$$q_1 = \frac{A[\varepsilon(\lambda_2) + \alpha(\lambda_1)] + B[\varepsilon(\lambda_2) - \alpha(\lambda_2)]}{\alpha(\lambda_1)^2 - \alpha(\lambda_2)^2} - \frac{1}{2} K(\lambda_1) Q (a + b) - S(\lambda_2), \quad [A10]$$

$$q_2 = \frac{A e^{-\alpha(\lambda_1)t} + B e^{\alpha(\lambda_1)t}}{\alpha(\lambda_1)^2 - \alpha(\lambda_2)^2}, \quad [A11]$$

$$a = \frac{1 + r_\infty(\lambda_1)}{1 - r_\infty(\lambda_1)^2 e^{-2\alpha(\lambda_1)t}}, \quad [A12]$$

$$b = \frac{[1 + r_\infty(\lambda_1)]r_\infty(\lambda_1) e^{-2\alpha(\lambda_1)t}}{1 - r_\infty(\lambda_1)^2 e^{-2\alpha(\lambda_1)t}}, \quad [A13]$$

where $r_\infty(\lambda)$ is the reflectance of a semi-infinite layer at λ given by KM theory (Kubelka, 1948):

$$r_\infty = \frac{S}{\varepsilon + \alpha}. \quad [A14]$$