

Spectral Colour Prediction Model for a Transparent Fluorescent Ink on Paper*

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Abstract

A new spectral colour prediction model for a fluorescent ink printed on paper is presented. It is based on our previous work on transparent support⁴ and on a new mathematical formalism which generalizes the Kubelka-Munk theory. The printed paper is modeled by means of three matrices: an interface correction matrix, a matrix exponential modeling the layer which contains the fluorescent ink, and a reflection matrix characterising the substrate. The interface correction matrix allows to take multiple reflections into account by operating the Saunderson correction. These matrices are related to physical properties of ink and paper which must be measured: the transmittance spectra, the quantum yields, the absorption bands and the emission spectra of the fluorescent inks, and the reflection properties of the paper. Our new model can predict the reflection spectra of uniform samples for different ink concentrations and under different illuminants. It is applied successfully to predict the spectra of real samples with an average prediction improvement of about $\Delta E = 17$ in comparison with Beer's law.

Keywords: colour prediction, fluorescence, paper, ink, Kubelka-Munk model, multiple reflections, Saunderson correction.

Introduction

In a previous work,⁴ we proposed a new prediction model for fluorescent inks printed on a transparent substrate which was based on the generalization of the idea of density. The fluorescent substance was modeled by the use of a fluorescence density matrix.

The present study aims at predicting the spectra and the colours of uniform samples produced by printing on paper one fluorescent ink at different concentrations. The method is based on a "two channel" modelization of the phenomenon. This model is used to compute the reflection spectra of uniform colour samples. The proposed prediction model requires measuring the transmittance spectra, the quantum yields, the absorption bands and the emission spectra of the fluorescent inks, and measuring the reflection properties of the paper.

In contrast to existing fluorescence prediction methods,^{5,13,15} our approach enables, without additional measurements, to predict spectra for different ink concentrations and

different light sources. Moreover, the mathematical formalism we have developed can be seen as a generalization of the Kubelka-Munk model. We hereby obtain accurate spectral predictions of uniform colour patches. The study is carried out with transparent inks printed on a high quality paper. This paper is made of fibres or polymer covered by a transparent coating which is an ink-absorbing layer. The inks are only absorbed in this coating, thus avoiding all problems related to ink diffusion in the fibres.

The fluorescence phenomenon

Let us first recall here the basic principles of molecular fluorescence.¹⁴ We consider a theoretical molecule having two electronic energy states, E_0 (ground state) and E_1 (excited state). Each electronic state has several vibrational states (see Figure 1). Incident polychromatic light (photons) excites the molecules which are in state E_0 and makes them temporarily populate the excited vibrational states of E_1 (Figure 1 (a)).

The molecule rapidly loses its vibrational energy and goes down to the electronic energy state E_1 . This relaxation process is non radiative, and it is caused by the collisions with other molecules to which the vibrational energy is transferred. This induces a slight increase of the temperature of the medium. Now, there are two ways for the molecule to give up its excess energy. One of them is called *internal conversion*, a non radiative relaxation whose mechanism is not fully understood. The transition occurs between E_1 and the upper vibrational state of E_0 (Figure 1 (b)), and the lost energy rises the temperature of the medium. The other possible relaxation process is fluorescence. It takes place by emitting a photon of energy corresponding to the transition between E_1 and a vibrational state of E_0 (Figure 1 (c)). The remaining excess energy with respect to E_0 is lost by vibrational relaxation. To quantify the amount of energy emitted by fluorescence, the *quantum yield* is introduced as the rate of absorbed energy which is released by radiative relaxation.

The wavelength band of absorbed radiation which is responsible for the excitation of the molecules is called the *excitation spectrum*. This spectrum consists of lines whose wavelengths correspond to the energy differences between excited vibrational states of E_1 and the ground electronic state E_0 . The *fluorescence emission spectrum* (or fluorescence spectrum) on its part, consists of lines which correspond to the energy differences between the electronic level

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E_1 and the vibrational states of E_0 . The multitude of lines in both spectra is difficult to resolve and makes them look like continuous spectra. Note that the fluorescence spectrum is made up of lines of lower energy than the absorption spectrum. This wavelength shift between the absorption band and the fluorescence band is called the *Stokes shift*. There is a particular case in which the absorbed photon has the same energy as the one re-emitted by fluorescence; it is called the *resonance line*.

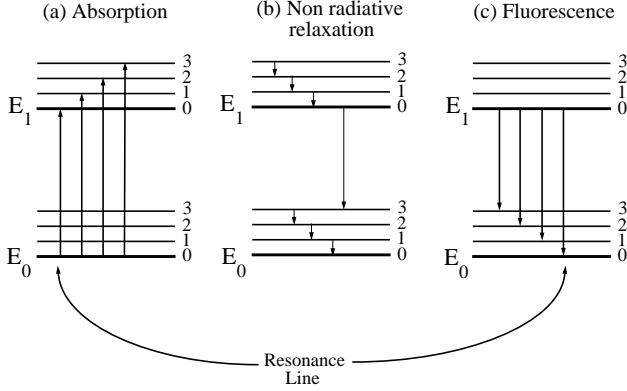


Figure 1. Energy level diagram of (a) absorption, (b) non radiative relaxation and (c) fluorescent emission. Note that for the resonance line, absorbed and emitted photons have the same energy.

The shape of the fluorescence emission spectrum does not depend on the spectrum of the exciting light, but on the probability of the transition between the excited state E_1 and the vibrational states of E_0 . Often, the fluorescence spectrum looks like a mirror image of the excitation spectrum;¹² this is due to the fact that the differences between vibrational states are about the same in ground and excited states. We denote by $f(\lambda)$ the normalized fluorescence spectrum whose integral equals 1.

At high concentrations the behaviour of the fluorescent substance is no longer linear. The absorption is too large and no light can pass through to cause excitation. Temperature, dissolved oxygen and impurities reduce the quantum yield, too, and therefore they also reduce the fluorescence; this phenomenon is called *quenching*. In our study we will suppose that no quenching occurs.

Infinitely thin transparent layer

In this section we give a short reminder of the mathematical tools developed in our previous study.⁴ These tools will be extensively used in the next sections. In order to establish a mathematical formula that predicts the behaviour of a transparent medium containing fluorescent molecules, we consider a slice of thickness dx . We denote by $\epsilon(\lambda)$ the extinction coefficient of the fluorescent molecules, by c the ink concentration and by Q their quantum yield in this medium. In the model for transparent media,⁴ only the positive direction of propagation is taken into account (see Figure 2).

The intensity variation $d\phi$ of the light emerging in the

positive direction has two components. The first, $d\phi_1(\lambda)$, is

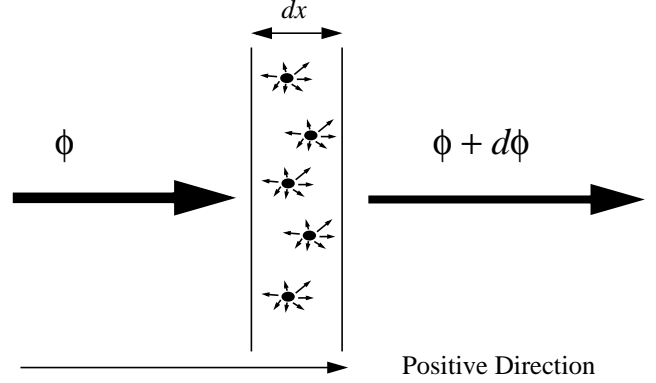


Figure 2. Absorption and emission in an infinitely thin fluorescent layer when irradiated by a diffuse light flux ϕ .

due to the light which has been absorbed. For diffuse light, this absorption is twice⁸ the value given by Beer's law:

$$d\phi_1(\lambda, x) = -2 \ln 10 \ c \epsilon(\lambda) \phi(\lambda, x) dx \quad (1)$$

The second component, $d\phi_2(\lambda, x)$, is the light emitted by fluorescence. The fluorescent molecules emit a fraction Q of the energy absorbed in the excitation spectrum Δ and spread it over the whole emission band defined by the normalized fluorescence spectrum $f(\lambda)$. Due to the fact that fluorescent emission is made in all directions of space, only one half of the energy goes into the positive direction. Hence, the quantum yield must be divided by two. The second component $d\phi_2(\lambda, x)$ is therefore given by:

$$d\phi_2(\lambda, x) = 2 \ln 10 \ c \frac{Q}{2} \cdot f(\lambda) \left[\int_{\Delta} \epsilon(\mu) \phi(\mu, x) d\mu \right] dx \quad (2)$$

The integral between square brackets multiplied by dx equals the amount of absorbed energy. Equation (2) leads to the following differential form which is an extension of Beer's law for diffuse light and fluorescent media:

$$d\phi(\lambda, x) = -2 \ln 10 \ c \epsilon(\lambda) \phi(\lambda, x) dx + 2 \ln 10 \ c \frac{Q}{2} \cdot f(\lambda) \left[\int_{\Delta} \epsilon(\mu) \phi(\mu, x) d\mu \right] dx \quad (3)$$

This can be simplified due to the fact that we work with a finite number of wavelength bands whose widths are $\Delta\lambda$, so that the integral is replaced by a finite sum. The new relation is given in equation (4) where the index i runs through the wavelength bands.

$$d\phi(\lambda_i, x) = -2 \ln 10 \ c \ \epsilon(\lambda_i) \phi(\lambda_i, x) dx + 2 \ln 10 \ c \ \frac{Q}{2} \cdot f(\lambda_i) \left[\sum_{j \in \Delta} \epsilon(\lambda_j) \phi(\lambda_j, x) \Delta\lambda \right] dx \quad (4)$$

Writing equation (4) for each of the bands leads to a system of linear differential equations with constant coefficients which can be put into a matrix form. If we denote $K_{i,j} = -\epsilon(\lambda_j) f(\lambda_j) \Delta\lambda Q / 2$ we obtain equation (5).

$$\begin{pmatrix} \frac{d\phi(\lambda_1, x)}{dx} \\ \vdots \\ \frac{d\phi(\lambda_i, x)}{dx} \\ \vdots \\ \frac{d\phi(\lambda_n, x)}{dx} \end{pmatrix} = -2c \ln 10 \begin{pmatrix} \varepsilon(\lambda_1) & 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ K_{2,1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ K_{i,1} & \cdot & K_{i,j} & \cdot & \varepsilon(\lambda_i) & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ K_{n,1} & \cdot & K_{n,j} & \cdot & \cdot & \cdot & \cdot & \cdot & K_{n,n-1} & \varepsilon(\lambda_n) \end{pmatrix} \begin{pmatrix} \phi(\lambda_1, x) \\ \cdot \\ \cdot \\ \phi(\lambda_j, x) \\ \cdot \\ \cdot \\ 0 \\ \phi(\lambda_n, x) \end{pmatrix} \quad (5)$$

The fact that an emitted photon has less energy than the absorbed one implies that $K_{i,j} = 0$ for $\lambda_j \geq \lambda_i$; hence the matrix is triangular.

The solution of equations such as (5) has already been investigated by mathematicians.¹ Systems of differential equations whose general expression is $d\Phi/dx = -cM \cdot \Phi$ (where M is the constant square matrix of equation (5) and Φ is the column vector containing $\phi(\lambda_1, x), \dots, \phi(\lambda_n, x)$) admit as solution, when x is integrated between 0 and d :

$$\Phi(d) = \exp(Mcd) \cdot \Phi(0) \quad (6)$$

The vector $\Phi(0)$ is the spectrum of the incident light (light source) and $\Phi(d)$ is the spectrum of the light emerging from a slice of thickness d of the fluorescent medium. The exponential of the matrix Mcd is defined as follows:

$$\exp(Mcd) = \sum_{i=0}^{\infty} \frac{(Mcd)^i}{i!} \quad (7)$$

where:

$$\frac{-M}{2 \ln 10} = \begin{pmatrix} \varepsilon(\lambda_1) & 0 & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ K_{2,1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ K_{i,1} & \cdot & K_{i,j} & \cdot & \varepsilon(\lambda_i) & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 0 \\ K_{n,1} & \cdot & K_{n,j} & \cdot & \cdot & \cdot & \cdot & \cdot & K_{n,n-1} & \varepsilon(\lambda_n) \end{pmatrix} \quad (8)$$

We will call M the *fluorescence density matrix*. The spectrum resulting from the combined action of fluorescence and absorption can be computed for each wavelength λ using the expression $\phi(\lambda, d)/\phi(\lambda, 0)$ where $\phi(\lambda, d)$ and $\phi(\lambda, 0)$ are respectively components of $\Phi(d)$ and $\Phi(0)$.

The solution given by equation (6) is a generalization of Beer's law: for a purely absorbing substance when no fluorescence is present, the matrix M consists of the terms $2 \ln 10 \cdot \varepsilon(\lambda_j)$ on the diagonal and of zeros anywhere else. This allows us to simplify equation (6) and leads to the absorption

equation for diffuse light.⁸

From a one flux to a two flux model for paper

In the present study, we consider high quality paper consisting of an ink-absorbing layer in optical contact with the substrate which is a diffuse white reflector. This reflector is supposed to be Lambertian⁹ and is never in contact with the inks. Like in the Kubelka-Munk analysis, we consider an upward flux j and a downward flux i going through an infinitely thin layer of the transparent coating which contains a fluorescent ink at concentration c (see Figure 3). The positive direction of the variable x is oriented upwards, and its origin is at the bottom of the transparent layer. In order to simplify the equations used in this section, let us introduce the column vector \mathbf{j} whose components are the intensities of the upward flux at various wavelength, and the column vector \mathbf{i} whose components are the intensities of the downward flux. We also write the fluorescence density matrix M of the ink as the sum of a diagonal matrix A representing the absorption, and a strictly lower triangular matrix F representing the fluorescent emission:

$$M = A + F \quad (9)$$

$$\begin{aligned} &= -2 \ln 10 \left[\begin{pmatrix} \varepsilon(\lambda_1) & 0 \\ \cdot & \cdot \\ 0 & \varepsilon(\lambda_n) \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ \cdot & \cdot \\ K_{i,j} & 0 \end{pmatrix} \right] \\ &= -2 \ln 10 \begin{pmatrix} \varepsilon(\lambda_1) & 0 \\ \cdot & \cdot \\ K_{i,j} & \varepsilon(\lambda_n) \end{pmatrix} \end{aligned}$$

Considering first the vector of upward flux \mathbf{j} , its variation $\frac{d}{dx} \mathbf{j}(x)$ has two components. The first one is the absorption and fluorescent emission caused by the upward flux which is, according to the results of the previous section, $cM\mathbf{j}(x)$. The second component is the fluorescence caused by the downward flux \mathbf{i} which is emitted in the upward direc-

tion: $c\mathbf{F}\mathbf{i}(x)$. Hence, the change of \mathbf{j} is:

$$\frac{1}{c} \cdot \frac{d}{dx} \mathbf{j}(x) = \mathbf{F}\mathbf{i}(x) + \mathbf{M}\mathbf{j}(x) \quad (10)$$

The same reasoning is applied to the downward flux and leads to a similar equation. Note that the downward orientation of \mathbf{i} introduces a change of sign. By combining the equations obtained for \mathbf{j} and \mathbf{i} , we get a system of differential equations whose matrix form is:

$$\frac{1}{c} \cdot \frac{d}{dx} \begin{pmatrix} \mathbf{i}(x) \\ \mathbf{j}(x) \end{pmatrix} = \begin{pmatrix} -\mathbf{M} & -\mathbf{F} \\ \mathbf{F} & \mathbf{M} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{i}(x) \\ \mathbf{j}(x) \end{pmatrix} \quad (11)$$

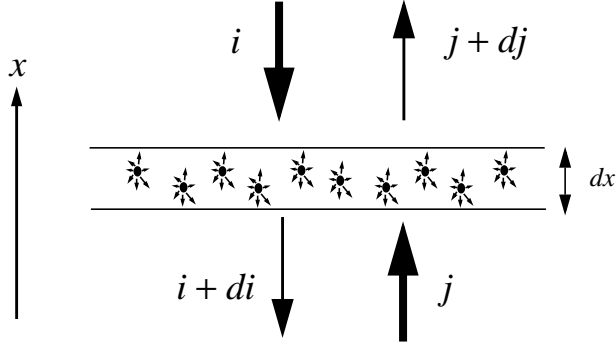


Figure 3. Absorption and emission in an infinitely thin layer of the transparent coating containing a fluorescent ink.

Equation (11) is a linear differential equation of the first order with constant coefficients. When x is integrated between 0 and d , it admits a solution¹ which is given by the matrix exponential:

$$\begin{pmatrix} \mathbf{i}(d) \\ \mathbf{j}(d) \end{pmatrix} = \exp \left[\begin{pmatrix} -\mathbf{M} & -\mathbf{F} \\ \mathbf{F} & \mathbf{M} \end{pmatrix} cd \right] \cdot \begin{pmatrix} \mathbf{i}(0) \\ \mathbf{j}(0) \end{pmatrix} \quad (12)$$

where $\mathbf{i}(d)$ and $\mathbf{j}(d)$ are respectively the spectra of the downward and of the upward flux at vertical location d . The matrix exponential is defined as follows:

$$\exp \left[\begin{pmatrix} -\mathbf{M} & -\mathbf{F} \\ \mathbf{F} & \mathbf{M} \end{pmatrix} cd \right] = \sum_{i=0}^{\infty} \frac{\left[\begin{pmatrix} -\mathbf{M} & -\mathbf{F} \\ \mathbf{F} & \mathbf{M} \end{pmatrix} cd \right]^i}{i!} \quad (13)$$

At the bottom of the transparent layer, the spectrum of the upward flux $\mathbf{j}(0)$ is linked with the spectrum of the downward flux $\mathbf{i}(0)$ by the relation:

$$\mathbf{j}(0) = \mathbf{R}_g \cdot \mathbf{i}(0) \quad (14)$$

where \mathbf{R}_g is the reflection matrix of the substrate. For pure reflectors, this matrix is diagonal and the coefficients on the diagonal are the reflection coefficients. If the substrate contains fluorescent substances (optical brighteners), the matrix \mathbf{R}_g is triangular.

Multiple internal reflections

The high quality paper is made of an ink-absorbing layer which is in optical contact with the substrate of diffuse reflection \mathbf{R}_g . Since the transparent coating has a refractive index n different from that of air, multiple internal reflections occur⁷ as shown in Figure 4. This phenomenon significantly increases the optical density of the ink containing layer. Traditionally, this is taken into account by applying the Saunderson correction¹⁰ to the computed spectrum. In this section, we write the Saunderson correction in matrix form, to be applied to equation (12).

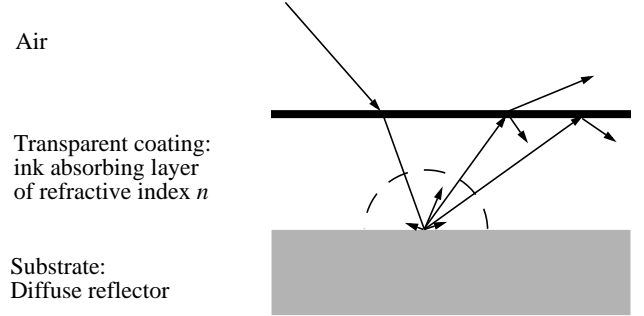


Figure 4. Multiple internal reflections caused by the interface between air and the ink-coating.

Let us denote by i the incident flux on the external surface of the paper and by j the flux emerging from the paper. Let r_s be the fraction of diffuse light reflected by the air-coating interface (external surface of the paper), and let r be the fraction of diffuse light reflected by the air-coating interface (internal surface of paper). The values of r_s and r depend only on the refractive index of the transparent coating. Judd⁶ has computed their numerical values for a range of refractive indexes.

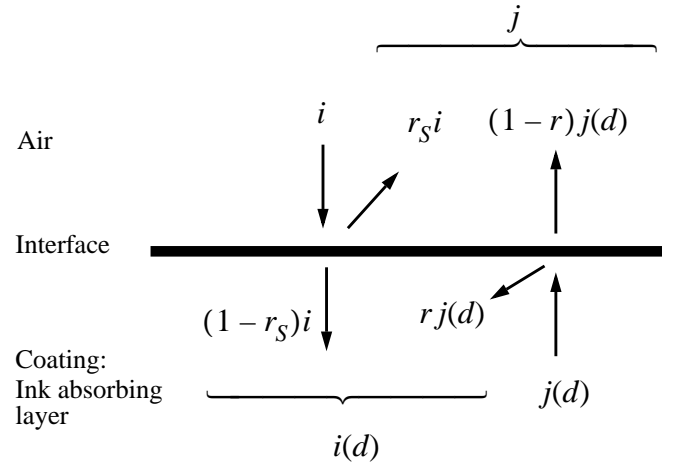


Figure 5. External and internal reflections of the upward and downward fluxes on the air-coating interface.

The balance of the fluxes at the air-coating interface, as shown in Figure 5, leads to the following system of equations

for $i(d)$, the incident flux below the air-coating interface and for j , the emerging flux above the air-coating interface:

$$\begin{aligned} i(d) &= (1 - r_S)i + rj(d) \\ j &= r_S i + (1 - r)j(d) \end{aligned} \quad (15)$$

Assuming that the refractive index of the coating is constant over the whole visible range, r_S and r are also constant. Hence, equation (15) can be written in the following matrix form:

$$\begin{pmatrix} \mathbf{i} \\ \mathbf{j} \end{pmatrix} = \begin{pmatrix} \frac{1}{1-r_S}\mathbf{I} & \frac{-r}{1-r_S}\mathbf{I} \\ \frac{r_S}{1-r_S}\mathbf{I} & \left(1-r-\frac{rr_S}{1-r_S}\right)\mathbf{I} \end{pmatrix} \begin{pmatrix} \mathbf{i}(d) \\ \mathbf{j}(d) \end{pmatrix} \quad (16)$$

where \mathbf{I} is the identity matrix which has the same dimension as \mathbf{M} . Hence, the Saunderson correction is made by combining the interface correction matrix of equation (16) and equation (12), as will be shown in the next section.

Spectral prediction

The high quality paper made of a diffusely reflecting substrate with an ink-absorbing coating is modeled by means of three matrices: the interface correction matrix (equation (16)), the matrix exponential (equation (12)) which modelizes the transparent layer, and the reflection matrix \mathbf{R}_g of the substrate (equation (14)).

By multiplying the interface correction matrix with the matrix exponential, we get the following relation:

$$\begin{aligned} \begin{pmatrix} \mathbf{i} \\ \mathbf{j} \end{pmatrix} &= \begin{pmatrix} \frac{1}{1-r_S}\mathbf{I} & \frac{-r}{1-r_S}\mathbf{I} \\ \frac{r_S}{1-r_S}\mathbf{I} & \left(1-r-\frac{rr_S}{1-r_S}\right)\mathbf{I} \end{pmatrix} \cdot \exp \left[\begin{pmatrix} -\mathbf{M} & -\mathbf{F} \\ \mathbf{F} & \mathbf{M} \end{pmatrix} cd \right] \cdot \begin{pmatrix} \mathbf{i}(0) \\ \mathbf{j}(0) \end{pmatrix} \\ &= \begin{pmatrix} \mathbf{T} & \mathbf{U} \\ \mathbf{V} & \mathbf{W} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{i}(0) \\ \mathbf{j}(0) \end{pmatrix} \end{aligned} \quad (17)$$

where \mathbf{T} , \mathbf{U} , \mathbf{V} and \mathbf{W} are matrices. Thanks to relation (14), it is possible to express the vector \mathbf{j} as a function of \mathbf{i} :

$$\mathbf{j} = (\mathbf{V} + \mathbf{W} \cdot \mathbf{R}_g) \cdot (\mathbf{T} + \mathbf{U} \cdot \mathbf{R}_g)^{-1} \cdot \mathbf{i} \quad (18)$$

Since the multiplication of matrices is not commutative, the order of the terms in equation (18) must be respected. This corresponds to the fact that superposed fluorescent layers don't commute.

If the paper is illuminated by a diffuse light source of spectrum \mathbf{i} , the spectrum of the diffuse reflected light is \mathbf{j} . The reflection spectrum is computed by dividing the components of \mathbf{j} by the components of \mathbf{i} : $R(\lambda) = j(\lambda)/i(\lambda)$.

Measuring the parameters of the model

To compute the fluorescence density matrix \mathbf{M} , four elements have to be determined: the excitation spectrum, the extinction coefficient $\epsilon(\lambda)$, the normalized fluorescence function $f(\lambda)$ and the quantum yield Q . (Note that \mathbf{M} contains discrete values of the functions $\epsilon(\lambda)$ and $f(\lambda)$). The measuring techniques for these parameters are described in our previous work.⁴

Since the refractive index of the coating is known from the literature,² the internal and external reflections coefficients r and r_S can be computed using Judd's⁶ method. The reflection matrix of the substrate \mathbf{R}_g is measured using the two monochromator method described by Donaldson,³ using barium sulphate (BaSO_4) as white reference. Note that this measurement must be performed on an identical sample without ink-absorbing coating.

Results of the spectral and colorimetric predictions

The model was applied to predict the spectra of several fluorescent samples which were made by printing a uniform fluorescent ink layer on a high quality paper. Orange, yellow and magenta inks from fluorescent markers were used. They were printed on two kinds of supports: a white paper without optical brighteners from MPA¹¹ and a white cardboard with optical brighteners. Their reflection spectra were measured using the two monochromator method.³ The reflection spectrum of the substrate of the MPA paper is given in Figure 6. The refractive index of the coating (poly vinyl alcohol) is about $n = 1.5$, and therefore, according to Judd,⁶ we must take $r = 0.59$ and $r_S = 0.09$. The samples were illuminated by a tungsten light source from Light Source, and their spectra were measured with a radiometer INSTASPEC II from Oriel combined with an integrating sphere. The spectrum of the light source, which is given in Figure 7, was measured by mounting the radiometer at the position of the sample holder. Note that the influence of the optical brighteners in the white cardboard is negligible because the light source does not emit much energy under 400 nm, i.e. in the excitation band of the optical brighteners.

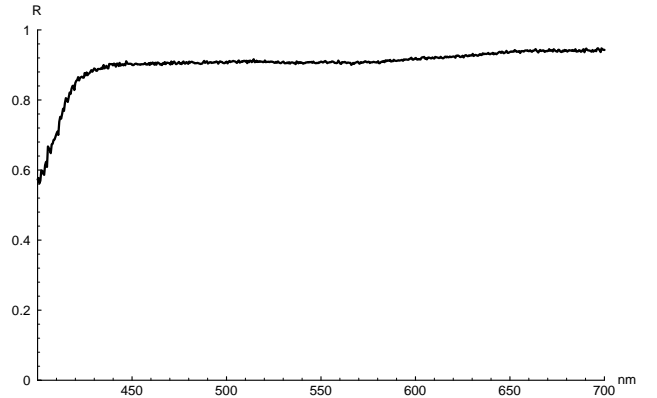


Figure 6. Reflectance of the MPA paper without optical brighteners.

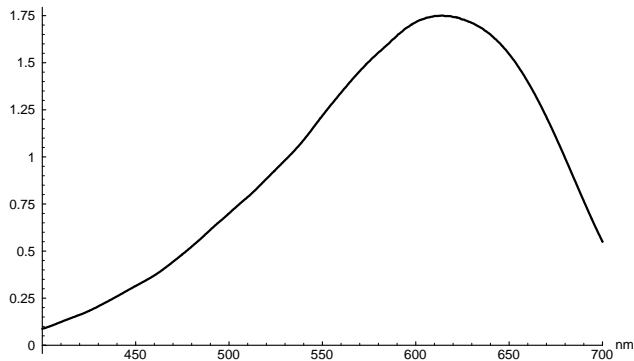


Figure 7. Relative radiance spectrum of the tungsten light source.

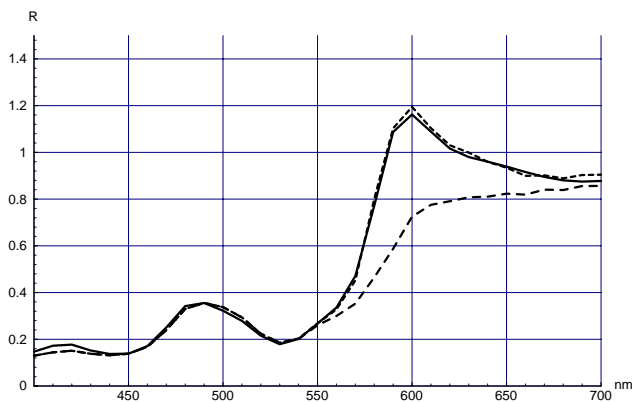


Figure 8. Predicted spectrum of a fluorescent orange sample using our model (dotted line), predicted spectrum when only absorption is taken into account (dashed line) and measured spectrum of the fluorescent orange ink printed on MPA paper (continuous line).

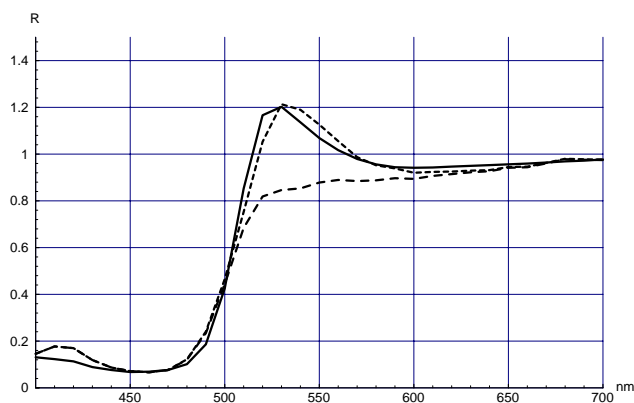


Figure 9. Predicted spectrum of a fluorescent yellow sample using our model (dotted line), predicted spectrum when only absorption is taken into account (dashed line) and measured spectrum of the fluorescent yellow ink printed on cardboard (continuous line).

For each ink-paper combination, three samples of different ink concentration were produced and measured. The prediction results were compared with the measured spectra and their colour deviations were computed in CIELAB. The average prediction errors are summarized in Table 1. Figure 8 shows the measured spectrum of a fluorescent orange sample

(continuous line), the predicted spectrum by using our method (dotted lines) and the predicted spectrum when only the absorption is taken into account (dashed line).

Figure 9 shows similar results for a fluorescent yellow sample. In this case, light is absorbed by the yellow ink and the substrate between 400 and 500 nm. The hump observed between 500 and 600 nm corresponds to the light emitted by fluorescence. Beyond 600 nm, the ink does not absorb, and the measured spectrum is the reflectance of the substrate.

Table 1. Colour deviations ΔE in CIE-Lab between predicted and measured spectra for inks at different densities.

Type of sample	Average ΔE using the new model with fluorescence	Average ΔE using the model without fluorescence	Quantum yield
Orange on cardboard	2.00	24.17	0.8
Orange on MPA paper	1.60	23.64	0.8
Yellow on cardboard	2.37	13.18	0.7
Yellow on MPA paper	2.25	11.47	0.7
Magenta on cardboard	2.84	19.86	0.6
Magenta on MPA paper	2.49	22.99	0.6

Conclusions

The new spectral prediction method we propose is based on a mathematical formalism which generalizes the Kubelka-Munk theory. The fluorescent ink printed on high quality paper is modeled by means of three matrices: the interface correction matrix, the matrix exponential and the reflection matrix of the substrate. This model requires measuring the transmittance spectra, the normalized fluorescence spectra and the quantum yield of the fluorescent inks. In contrast to previous methods, with our approach, once the fluorescence density matrix is computed, prediction can be made for different illuminants and different ink concentrations.

Using this method we predicted the reflection spectra of 18 uniform samples. The average prediction error is about $\Delta E = 2.25$ with a maximum of $\Delta E_{Max} = 4.37$. Since ink fluorescence is also taken into account, the prediction accuracy is improved by about $\Delta E = 17$ in comparison with Beer's law for diffuse light.

The method can be extended for two and more inks but several cases must be investigated because of the non-commutativity of fluorescent inks. For two inks A and B , three cases must be considered: (a) ink A is above ink B ; (b) ink B is above ink A ; and (c) the inks A and B are mixed. For each case the resulting reflection spectrum is different. This subject requires a deeper investigation and should be ad-

dressed in a future work.

This model does not take the whole complexity of the fluorescence emission phenomenon into consideration. For instance, it does not include the quenching effects due to high concentrations. However, it enables the spectra of fluorescent inks to be predicted qualitatively and quantitatively under different illumination and concentration conditions.

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