A "one channel" Spectral Colour Prediction Model for Transparent Fluorescent Inks on a Transparent Support*

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1. Introduction

Classical colour prediction models do not take fluorescence into account, and their predictions fail if fluorescent substances are contained in the inks. This is due to the fact that the overall spectrum of fluorescent substances depends on the spectrum of the light source. Furthermore, fluorescence is a non linear phenomenon. This study aims at predicting the spectra and the colours of uniform samples produced with one fluorescent ink at different concentrations. The method is based on a "one channel" modelization of the phenomenon where only one direction of propagation is taken into account. This model is used to compute the transmittance 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. In contrast to existing fluorescence prediction methods,[3,9,13] 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 Beer's absorption law. We hereby obtain accurate spectral predictions of colour patches. In order to limit the number of physical parameters required, the study is carried out with transparent inks on a transparent substrate, thus avoiding all problems related to light diffusion.

2. Bouguer-Lambert-Beer law

Let us consider a light-absorbing medium of infinitesimal thickness dx (see Fig. 1). According to Bouguer,[5] the intensity attenuation $d\phi$ of a monochromatic light passing through the medium is proportional to the light intensity ϕ and to the thickness dx, hence:

$$d\phi(\lambda, x) = -m(\lambda)\,\phi(\lambda, x)dx \qquad (1)$$

The factor $m(\lambda)$ is the *natural absorbance index* of the medium in question. Lambert showed that for liquids and gas this factor $m(\lambda)$ is proportional to the concentration c of the absorbing substance:[5]

$$m(\lambda) = \ln 10 \cdot c \cdot \varepsilon(\lambda) \qquad (2)$$

The function $\varepsilon(\lambda)$ is called *decadic extinction coefficient*. We therefore have:

$$d\phi(\lambda, x) = -\ln 10 \cdot c \cdot \varepsilon(\lambda) \cdot \phi(\lambda, x)dx \qquad (3)$$

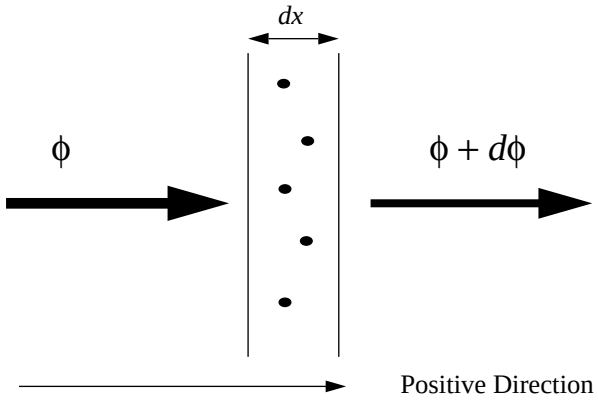

Fig. 1 Absorption in an infinitely thin layer.

By integrating equation (3) between $x = 0$ and $x = d$ we obtain the following result:

$$\phi(\lambda, d) = \phi(\lambda, 0)\, e^{-\ln 10 \cdot cd \cdot \varepsilon(\lambda)} = \phi(\lambda, 0) \cdot 10^{-cd \cdot \varepsilon(\lambda)} \qquad (4)$$

The light intensity $\phi(\lambda, 0)$ corresponds to the spectrum of the light source. Since the *absorption* $A(\lambda)$ (or optical density) equals the decimal logarithm of the inverse of the transmittance (where transmittance is defined by

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$\phi(\lambda, d) / \phi(\lambda, 0)$), we have:

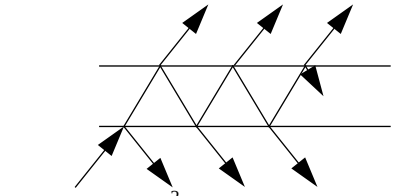
$$A(\lambda) = cd \cdot \varepsilon(\lambda) \tag{5}$$

Beer pointed out[5] that what really counts for the absorption is not the individual values of the concentration c and of the path length d, but rather the product $q = cd$ which represents a number of molecules per unit of area (or surface density). Hence the transmittance can be expressed:

$$T(\lambda, q) = \frac{\phi(\lambda, q)}{\phi(\lambda, 0)} = 10^{-q \cdot \varepsilon(\lambda)} \tag{6}$$

This equation holds as long as the medium is transparent, purely absorbing, non diffusing and non fluorescent. Furthermore, there must be no interaction between the absorbing molecules.

Equation (6) expresses only the transmission factor in the absorbing medium. The difference between the refractive indices of the medium and the air causes multiple internal reflections (see Fig. 2) which modify the global transmittance $T_g(\lambda)$ of the medium. From literature[2] we know that the intensity of each reflected ray follows a geometric sequence. The global transmittance is obtained by summing up the contribution of each reflected ray and the result is given in equation (7) in terms of $T(\lambda)$ and the internal reflection factor r.



$$\begin{aligned} T_g(\lambda) &= (1-r)^2 \cdot T(\lambda) \\ &+ (1-r)^2 \cdot T(\lambda) \cdot (r \cdot T(\lambda))^2 \\ &+ (1-r)^2 \cdot T(\lambda) \cdot (r \cdot T(\lambda))^4 + \ldots \\ &= \frac{T(\lambda) \cdot (1-r)^2}{1 - (r \cdot T(\lambda))^2} \end{aligned}$$

Fig. 2 Derivation of the transmittance of a transparent substrate (equation (7)).

$$T_g(\lambda) = \frac{T(\lambda) \cdot (1-r)^2}{1 - (r \cdot T(\lambda))^2} \tag{7}$$

According to Wyszecki,[12] r is small so $T_g(\lambda)$ can be approximated by:

$$T_g(\lambda) = T(\lambda) \cdot (1-r)^2 \tag{8}$$

3. The fluorescence phenomenon

In order to present in a few words the basic principles of molecular fluorescence,[10] let us 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 Fig. 3). Incident polychromatic light (photons) excites the molecules which are in state E_0 and makes them populate temporarily the excited vibrational states of E_1 (Fig. 3 (a)).

A vibrational excited state has an average lifetime of only 10^{-15} second. 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 solvent molecules to which the vibrational energy is transferred. This induces a slight increase of the temperature of the medium. The excited state E_1 has a lifetime varying between 10^{-6} and 10^{-9} second. 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 (Fig. 3 (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 (Fig. 3 (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.

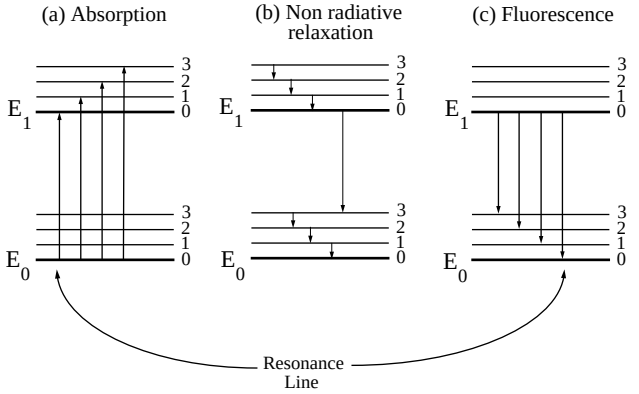


Fig. 3 Energy level diagram of (a) absorption, (b) non radiative relaxation and (c) fluorescent emission. Note that for the resonance line, absorbed and emitted photons have the same energy.

The 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 (according to the energy difference ΔE produced by the absorption of a photon of wavelength λ: $\Delta E = (hc)/\lambda$, where h is Planck's constant and c is the speed of light). The *fluorescence emission spectrum* (or fluorescence spectrum) on its part, consists of lines which correspond to the energy differences between the electronic level 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*.

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;[7] this is due to the fact that the differences between vibrational states are about the same in ground and excited states.

Experience shows that fluorescence is favoured in rigid molecules which contain aromatic rings.[11] This can easily be understood since a rigid molecule has less possibilities of relaxing by a non radiative process. In fact, the lower the probability of non radiative relaxation is, the higher the quantum yield. Hence, a rise in the medium's viscosity induces a higher fluorescence. In the particular case of inks, the liquid substance fluoresces less than the printed one whose molecules have less degrees of freedom. On the other hand, a rise of the ambient temperature implies a higher probability of non radiative relaxation due to collisions with other molecules and a drop in fluorescence is observed.

The fluorescence spectrum is measured with a fluorescence spectrometer.[6] A sample of the unknown fluorescent substance is excited with a monochromatic light beam whose wavelength is within the excitation band of the molecule. The emitted light is analysed and the resulting spectrum is the fluorescence spectrum. Its amplitude is maximal when the wavelength of the incident light corresponds to the maximum of absorption of the fluorescent molecule. We denote by $f(\lambda)$ the normalized fluorescence spectrum whose integral equals 1.

The method we used to determine the quantum yield is described in the literature.[8] It is based on a measurement made relatively to a standard fluorescent substance of known quantum yield. To be reliable, the spectral emitting properties of the chosen standard fluorescent substance must closely match those of the unknown fluorescent substance.

The quantum yield of the unknown substance is given by:[8]

$$Q_u = \frac{A_s F_u n^2}{A_u F_s n_0^2} \cdot Q_s \qquad (9)$$

In this equation the subscript *u* stands for *unknown* and the subscript *s* for *standard*. A is the absorption at the excitation wavelength and Q is the quantum yield. The refractive indices of the solvent of the standard fluorescent substance (n_0) and of the medium of the unknown fluorescent substance (n) are also taken into account. The variable F is the total amount of energy emitted by fluorescence. This value is computed by integrating the spectrum emitted by fluorescence during the experiment.

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. Hence, to make a reliable quantum yield measurement the absorption has to be smaller than 0.1 over the whole spectrum $(A(\lambda) \le 0.1)$. 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.

4. Infinitely thin layer

In order to establish a mathematical formula to predict the behaviour of a transparent medium which contains fluorescent molecules, we consider a slice of thickness dx. We denote by $m(\lambda)$ the natural absorbance index of the fluorescent molecules and by Q their quantum yield in this medium. In this model, only the positive direction of propagation is taken into account, hence the name "one channel" model.

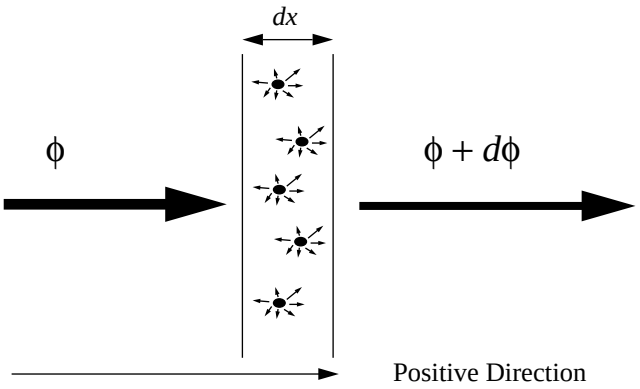


Fig. 4 Absorption and emission in an infinitely thin fluorescent layer

The intensity variation $d\phi$ of the light emerging in the positive direction has two components. The first, $d\phi_1(\lambda)$, is

due to the light which has been absorbed according to Beer's law: $d\phi_1(\lambda, x) = -m(\lambda)\,\phi(\lambda, x)\,dx$ (see equation (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:

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

The integral between square brackets multiplied by dx equals the amount of absorbed energy. Equation (10) leads to the following differential form which is an extension of Beer's law (equation (1)):

$$d\phi(\lambda, x) = -m(\lambda)\,\phi(\lambda, x)\,dx + \frac{Q}{2} \cdot f(\lambda) \left[\int_\Delta m(\mu)\,\phi(\mu, x)\,d\mu \right] dx \qquad (11)$$

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 (12) where the index i runs through the wavelength bands.

$$d\phi(\lambda_i, q) = -m(\lambda_i)\,\phi(\lambda_i, x)\,dx + \frac{Q}{2} \cdot f(\lambda_i) \left[\sum_{j \in \Delta} m(\lambda_j)\,\phi(\lambda_j, x)\,\Delta\lambda \right] dx \qquad (12)$$

Writing equation (12) 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 $K_{i,j} = m(\lambda_j)\frac{Q}{2} f(\lambda_i)\,\Delta\lambda$ we obtain equation (13).

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

The solution of equations such as (13) has already been investigated by mathematicians.[1] Systems of differential equations whose general expression is $\frac{d\Phi}{dx} = \boldsymbol{M} \cdot \Phi$ (where $\boldsymbol{M}$ is the constant square matrix of equation (13) and Φ is the column vector containing $\phi(\lambda_1, x)$, ..., $\phi(\lambda_n, x)$) admit as solution, when x is integrated between 0 and d:

$$\Phi(d) = \exp(\boldsymbol{M}d) \cdot \Phi(0) \qquad (14)$$

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 $\boldsymbol{M}d$ is defined as follows:

$$\exp(\boldsymbol{M}d) = \sum_{i=0}^{\infty} \frac{(\boldsymbol{M}d)^i}{i!} \qquad (15)$$

Note that the natural absorption index $m(\lambda)$ is proportional to the concentration c of the fluorescent substance (see equation (2)). In section 2 the surface density q (product of concentration and path length) was introduced. By factorising out $-c$ in equation (13), we can make the change of variable $-q = -cd$ and obtain:

$$\frac{\boldsymbol{M}'}{\ln 10} = \begin{pmatrix} \varepsilon(\lambda_1) & 0 & \cdots & 0 \\ K'_{2,1} & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ K'_{i,1} & \cdots & K'_{i,j} & \varepsilon(\lambda_i) & \cdots & \vdots \\ \vdots & & \vdots & & \ddots & \vdots \\ K'_{n,1} & \cdots & K'_{n,j} & \cdots & K'_{n,n-1} & \varepsilon(\lambda_n) \end{pmatrix} \qquad (16)$$

$$\begin{pmatrix} \frac{d\phi(\lambda_1, x)}{dx} \\ \vdots \\ \frac{d\phi(\lambda_i, x)}{dx} \\ \vdots \\ \frac{d\phi(\lambda_n, x)}{dx} \end{pmatrix} = \begin{pmatrix} -m(\lambda_1) & 0 & \cdots & 0 \\ K_{2,1} & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ K_{i,1} & \cdots & K_{i,j} & -m(\lambda_i) & \cdots & \vdots \\ \vdots & & \vdots & & \ddots & \vdots \\ K_{n,1} & \cdots & K_{n,j} & \cdots & K_{n,n-1} & -m(\lambda_n) \end{pmatrix} \begin{pmatrix} \phi(\lambda_1, x) \\ \vdots \\ \phi(\lambda_j, x) \\ \vdots \\ \phi(\lambda_n, x) \end{pmatrix} \qquad (13)$$

where:

$$K'_{i,j} = -\varepsilon(\lambda_j)\frac{Q}{2} f(\lambda_i)\,\Delta\lambda \qquad (17)$$

The solution (14) then becomes:

$$\Phi(q) = \exp(-q\boldsymbol{M}')\cdot\Phi(0) \qquad (18)$$

where:

$$\boldsymbol{M}' = -\frac{\boldsymbol{M}}{c} \quad \text{and} \quad \exp(-q\boldsymbol{M}') = \sum_{i=0}^{\infty}\frac{(-q\boldsymbol{M}')^i}{i!}. \qquad (19)$$

We will call $\boldsymbol{M}'$ 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 $\phi(\lambda, q)/\phi(\lambda, 0)$ where $\phi(\lambda, q)$ and $\phi(\lambda, 0)$ are respectively components of $\Phi(q)$ and $\Phi(0)$.

The solution given by equation (18) is a generalization of Beer's law: for a purely absorbing substance when no fluorescence is present, the matrix $\boldsymbol{M}'$ consists of the terms $\ln 10\cdot\varepsilon(\lambda_i)$ on the diagonal and of zeros anywhere else. This allows us to simplify equation (18) and leads to equation (4).

Like in the case of Beer's law, let us now have a look at the influence of internal reflection. In this short analysis we denote $\boldsymbol{E} = \exp(-q\boldsymbol{M}')$ and r is the internal reflection factor. According to Fig. 2 we can write the following relation between the spectrum of the emerging light $\Phi_g(q)$ and the spectrum of the source $\Phi(0)$:

$$\Phi_g(q) = (1-r)^2\cdot\boldsymbol{E}\cdot (\boldsymbol{I} + (r\boldsymbol{E})^2 + \ldots + (r\boldsymbol{E})^{2n} + \ldots)\cdot\Phi(0) \qquad (20)$$

In media made of classical plastic compounds the internal reflection factor r is about 0.04, hence $r^2 = 0.0016$. This value is small enough to be neglected, so equation (20) can be approximated by:

$$\Phi_g(q) = (1-r)^2\cdot\boldsymbol{E}\cdot\Phi(0) \qquad (21)$$

This approximation is similar to the one used for the case of Beer's law (see equation (8)). Furthermore, by measuring directly $\Phi'(0) = (1-r)^2\Phi(0)$ (the spectrum of the light emerging from the unprinted transparency) a simpler relation can be used:

$$\Phi_g(q) = \boldsymbol{E}\cdot\Phi'(0) = \exp(-q\boldsymbol{M}')\cdot\Phi'(0) \qquad (22)$$

5. Measuring the elements of the fluorescence density matrix

To compute the fluorescence density matrix $\boldsymbol{M}'$ four elements have to be determined: the excitation spectrum, the decadic extinction coefficient $\varepsilon(\lambda)$, the normalized fluorescence function $f(\lambda)$ and the quantum yield Q. (Note that $\boldsymbol{M}'$ contains discrete values of the functions $\varepsilon(\lambda)$ and $f(\lambda)$).

Since the dye concentration in an ink is unknown, it is impossible to determine the decadic extinction coefficient $\varepsilon(\lambda)$. However according to equation (5), the absorption spectrum $A(\lambda)$ and the decadic extinction coefficient $\varepsilon(\lambda)$ are proportional and the proportionality factor is the dye surface density q. Note that each non-zero element of the fluorescence density matrix $\boldsymbol{M}'$ contains the factor $\varepsilon(\lambda_i)$ (see equations (16) and (17)). Since in equation (18) $\boldsymbol{M}'$ is multiplied by q, each occurrence of $\varepsilon(\lambda_i)$ is multiplied by q, and this product equals the absorption $A(\lambda_i)$. Hence, for a given sample of absorption $A(\lambda_i)$ we do not need the actual values of q and of $\varepsilon(\lambda_i)$, and we can work relatively to the absorbance $A'(\lambda_i)$ of a reference sample so that:

$$A(\lambda_i) = q\varepsilon(\lambda) = q'A'(\lambda_i) \qquad (23)$$

where q' is the proportionality factor between $A'(\lambda_i)$ and $A(\lambda_i)$.

The excitation spectrum is determined in a two-step procedure. In order to avoid deviations due to self absorption, the fluorescence measurement must be performed on a sample whose maximal absorption is smaller than 0.1 over the whole spectrum ($A(\lambda)\le 0.1$). This means that light emitted by fluorescence is not reabsorbed by another molecule of the sample. At first, the whole absorption spectrum $A(\lambda)$ of our sample is measured with a spectrophotometer. This instrument uses a monochromatic collimated light beam which goes through the transparent sample before reaching a light detector. Since only a small fraction of the fluoresced light passes through the entrance slit of the detector, the deviation induced by the fluorescent emission can be neglected.

In the second step the location of the excitation spectrum within the absorption spectrum is determined. This can be done, once we have an *a priori* knowledge of the approximate position of the fluorescence spectrum (for example, by a preliminary measurement), using a fluorescence spectrometer. This device has two monochromators: the first one is used to generate a monochromatic light beam which excites the sample, and the second monochromator is used to analyse the light emitted by the sample. In our present measurement, the second monochromator is set to a fixed wavelength which is supposed to be within the fluorescence

spectrum (the *a priori* knowledge). The first monochromator sweeps the whole spectrum and the intensity of the emitted light is recorded. This provides the excitation spectrum and its location.

To determine the normalized fluorescence function a fluorescence spectrometer is needed. The sample is excited with a monochromatic light beam whose wavelength corresponds to the maximum absorption in the excitation spectrum. Since the shape of the fluorescence emission spectrum does not depend on the excitation wavelength (see section 3), the normalized fluorescence function is easy to compute by dividing the measured fluorescence spectrum by its integral value which corresponds to the fluoresced energy.

Once the excitation spectrum and the fluorescence function have been measured, a standard fluorescent substance can be chosen in order to calculate the quantum yield using a relative measurement method[8] (see section 3). In order to perform a comparison, the location of the excitation spectrum and the location of the fluorescence spectrum of the standard substance must correspond to those of our sample. Based on these criteria, the standard substance is chosen from tables given in literature.[4]

Within the excitation spectrum we must select a single wavelength which gives the highest possible fluorescence in both the standard substance and our sample. These two substances are excited using the same fluorescence spectrometer at the selected wavelength and the spectrum of the fluoresced light is measured. By integrating the fluorescence spectra of the standard substance and of our unknown sample, we get the respective energy amounts F_s and F_u emitted by fluorescence. Since the excitation spectra of both substances are known, we have the respective absorption factors A_s and A_u at the selected excitation wavelength. Finally, the quantum yield Q_u of our sample is calculated using equation (9). Note that three values must be found in the literature: the quantum yield Q_s of the standard substance,[8] the refraction index n_0 of the medium containing it and the refraction index n of our sample's medium.

This experimental determination of the quantum yield is rather difficult to perform. We preferred therefore in some cases to estimate the quantum yield by using a best-fit method applied on a test sample. Note that this choice reduces the number of experiments to be performed but does no longer guanrantee that the real physical quantum yield is used.

6. Results of the spectral and colorimetric predictions

Three different inks were used at various concentrations and on three different supports. The spectra of all samples were measured and compared to the results given by the prediction model. The three fluorescent inks are the magenta ink used in HP 500 C desktop printers, and the orange and yellow inks used in fluorescent markers. Transparencies from three different manufacturers (3M, Epson and Sihl) were used as support. We measured all the elements necessary to establish the fluorescence density matrix for these inks: the absorption spectrum, the fluorescence spectrum, the absorption band and the emission band. The quantum yield was either measured or estimated by applying a best-fit procedure. Note that the quantum yield of a given ink depends on the support.

The reference absorption spectra $A'(\lambda)$ of the inks were measured on samples obtained by applying the ink uniformly on the transparent substrate. These measurements were performed on a Variant spectrophotometer.

We illustrate our method with the results obtained for the magenta ink. The absorption spectrum of the magenta ink is given in Fig. 5.

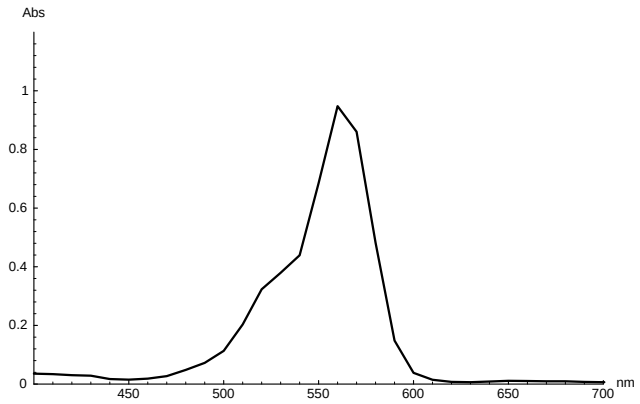


Fig. 5 Absorption spectrum $A'(\lambda)$ of the magenta ink.

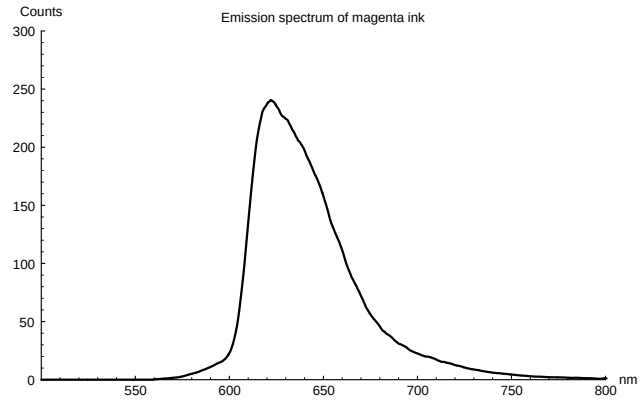


Fig. 6 Fluorescence emission spectrum of magenta ink excited at 550 nm.

The excitation band of the magenta ink is 450-600 nm, and its emission band is 570-800 nm. In order to measure the quantum yield of the magenta ink, Rhodamine 6G dissolved

in ethanol was chosen as the reference substance. The measurement was performed on a fluorescence spectrometer Perkin-Elmer LS50B as described in section 5. The quantum yield for the 3M transparency was computed with equation (9) and we obtained $Q = 0.122$. The quantum yield for the other substrates were estimated by a best-fit algorithm. These data are summerized in the first column of Table 1. The measured fluorescence spectrum of the magenta ink is shown in Fig. 6. With these elements the fluorescence density matrix $\boldsymbol{M}'$ is computed using wavelength bands of width $\Delta\lambda = 10$ nm.

	Magenta	Yellow	Orange
Absorption band (nm)	450-600	310-520	310-580
Emission band (nm)	570-800	480-700	550-750
Quantum yield on transparency:			
3M	0.12*	0.15	0.6
Epson	0.5	0.8	0.5
Sihl	0.3	0.6	0.6

Table 1: Absorption band, emission band and quantum yields of the inks. The only measured case is marked by *; the other cases were estimated by a best-fit algorithm.

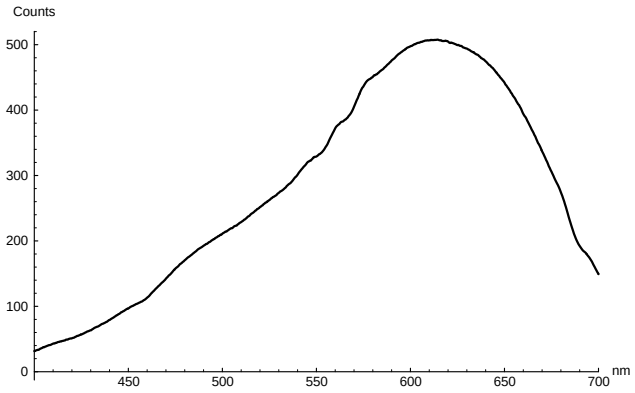


Fig. 7 Relative spectrum of the light source.

Our new model was applied to predict the spectra of uniform patches having different concentrations (four different patches for each ink-substrate combination). The proportionality factor q' (see equation (23)) was computed relatively to reference samples by comparing the absorption of the reference sample and the absorption of the corresponding unknown sample in a wavelength band where no emission takes place. The spectra of the unknown samples were measured by transparence using an Oriel 77400 radiospectrometer combined with an Oriel integrating sphere. The light source is the measurement spot of the Spotlight light table from Light Source. Its relative spectrum has been measured and is shown in Fig. 7. The matrices $\exp(-q\boldsymbol{M}')$ were computed numerically (see section 4). Fig. 8 illustrates the obtained results: the continuous line is the measured spectrum, the dotted line shows the prediction when fluorescence is taken into account and the dashed line corresponds to the prediction given by Beer's law. Note that the three lines almost perfectly superpose when only absorption takes place. In the emission band, only small deviations are observed between the measured spectrum and the spectrum predicted when fluorescence is taken into account. The colour deviation between predicted and measured spectrum is CIE-Lab $\Delta E = 1.92$ whereas the colour deviation between the measured spectrum and the spectrum computed with Beer's law is $\Delta E = 8.59$.

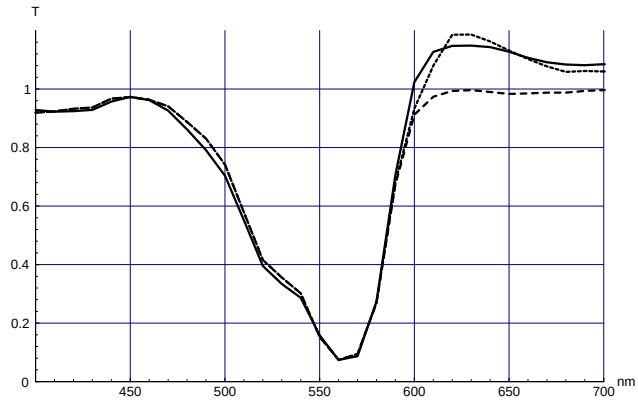


Fig. 8 Measured spectrum of the magenta ink on Epson transparency (continuous line); spectrum predicted with our method taking fluorescence into account (dotted line); and spectrum predicted by Beer's law (dashed line).

The colorimetric deviations of all samples have been computed in the CIE-Lab colour space, and the results are summarized in Table 2. In order to highlight the contribution of fluorescence, we give the average deviation of the four samples for each ink-substrate combination when using our model (second column), and when only Beer's law is taken into account (third column). As it can be seen in the table, prediction improvements are significant only when the quantum yield is relatively high. Note also that the quantum yield depends not only on the inks but also on the substrate: the quantum yields of the magenta and yellow inks are significantly reduced when these inks are applied on a 3M transparency. This is also confirmed by visual observation: 3M transparencies reduce the observed colourfulness for magenta and yellow inks, but do not influence the colourfulness of the orange ink.

7. Conclusions

Our proposed new spectral prediction method is based on a mathematical formalism which generalizes Beer's law. 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 transmittance spectra of uniform samples. The average prediction error is about $\Delta E = 1.56$ with a maximum of $\Delta E_{Max} = 3.08$. Since ink fluorescence is also taken into account, the prediction accuracy is improved by about $\Delta E = 4$ in comparison with Beer's law.

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.

Type of sample	Average ΔE using the new model with fluorescence	Average ΔE using the model without fluorescence	Quantum yield
Magenta on 3M	1.22	1.54	0.12
Magenta on Epson	1.83	7.08	0.5
Magenta on Sihl	1.56	4.68	0.3
Yellow on 3M	1.29	2.39	0.15
Yellow on Epson	1.29	6.94	0.8
Yellow on Sihl	1.52	6.24	0.6
Orange on 3M	2.13	6.81	0.6
Orange on Epson	1.44	5.16	0.5
Orange on Sihl	1.84	6.70	0.6

Table 2: Colour deviations ΔE in CIE-Lab between predicted and measured spectra for inks at different densities.

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