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A new approach for color matching of fluorescent dyes in binary mixture

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A simple and feasible method for color matching of fluorescent dyes has been developed. Two sets of equations to relate the total radiance factors from an acrylic textile dyed with a fluorescent dye and its concentration are considered for single and mixture shades of fluorescent dyes respectively. Constants for the single and mixture shades are calculated by calibration dyeings. The amounts of dyes are determined by a correction matrix, which can minimize color chromaticity difference values (∂x and ∂y) of target sample for color recipe prediction of fluorescent dyes. The performance of the proposed method is evaluated by the color difference values, the root mean square differences of reflectance curves and the relative error of concentration prediction. This method is found simple, accurate, and suitable for quantitative analysis of samples dyed with two fluorescent dyes.

Keywords: Acrylic fabric, Cationic dye, Color matching, Correction matrix, Fluorescent dye, Total radiance factor

1 Introduction

The most important problem to reproduce a target shade is to find the exact proportions of color components[1]. In a coloration process, a color model is defined in order to correlate a scalar quantity such as dye concentration to a spectral quantity such as reflectance[2]. The color matching strategies fall into two categories, namely visual and computer colorant formulation. Visual color matching is a time-consuming and tedious job that needs an expert operator. But computer color matching can reduce the cost of the production by saving time[3-6]. The basis of most computer color matching algorithms is based on the theory postulated by Kubelka and Munk[7].

Generally, fluorescent materials absorb the shorter wavelengths of electromagnetic radiations and emit it at the longer wavelengths[8]. There are fluorescent dyes in different shades that are used in women's clothing, police and street cleaners clothing, paints and surface coatings, clothing and signs warning of safety issues related to traffic[1,9,10].

The color appearance of a non-fluorescent sample could be accurately determined from spectrophotometric measurements. But, the spectral properties of fluorescent dyes can be greatly affected by some factors such as the intensity of light source, concentration and the presence of fluorescence quenchers[11]. Therefore, finding a reliable relation between the spectral radiance factors with the dye concentration is not easy. In the other words, the Kubelka-Munk theory cannot simply explain the properties of fluorescent dyes[9]. Total radiance factor (β_T) of a fluorescent material consists of two components namely true reflection (β_S) and fluorescent reflection (β_L). Unlike fluorescent reflection, true reflection component obeys Kubelka-Munk theory like a non-fluorescent dye. Consequently, it makes color matching of fluorescent samples difficult by usual techniques[10].

Several methods for color matching of fluorescent dyes have been presented. Related to application of the Kubelka-Munk theory for fluorescent dyes, Ganz[12] has considered negative value of Kubelka-Munk coefficients for the amount of reflectance higher than 100%. In the case of a mixture of two dyes, the proportion of available energy to excite fluorescent dyes is decreased due to the absorption of light energy by other dyes. Two-monochromatic spectro-reflectometer and a set of twelve cut-off filters are used to separate the true reflection from fluorescent reflection[13]. Moreover, the Man Method[8] introduces a complicated equation that relates fluorescent reflectance to dye concentration.

According to the previous researches, the relation between the amount of real reflection (apart from

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fluorescence reflection) and the amount of used dye can be conveniently studied by Kubelka-Munk theory. However, in the case of fluorescence dyes the amount of fluorescence is also important. In the present study, by separating real reflectance from fluorescent part with Man method, it has been attempted to make a significant correlation between total radiance factor and dye concentration values in single fluorescent dye and a mixture of two fluorescent dyes.

2 Materials and Methods

2.1 Materials

The bleached acrylic fabrics were dyed with four commercial basic (cationic) dyes, namely C.I. Basic Yellow 40, C.I. Basic Red 13, C.I. Basic Red 14 and C.I. Basic Violet 16, all from Dystar, without any further purification. The used auxiliaries for dyeing were from Merck. The dyeing process including single and mixture of two fluorescent dyes was set at different dye concentrations (0, 0.05, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 2, 4 owf %). The dyeing parameters are given in Table 1. The graph of the dyeing process is illustrated in Fig. 1. Finally, the dyed samples were thoroughly washed and dried at the environment of laboratory.

2.2 Methods

The reflectance spectra of dyed samples were measured with a Tex Flash spectrophotometer from Datacolor from 400 nm to 700 nm at 20 nm intervals. The geometry of measurement was 0/d and an aperture of 12 mm was applied. The color parameters were calculated according to CIELAB system under illuminant D65 and the 10 degree standard observer. To analyze the data, the root mean square error (RMSE), the CIELAB color difference formula (ΔE^*_{ab}) under illuminants A and D_{65} for 1964 standard observer and the relative error of concentration prediction (RECP) were calculated, as shown in following equations:

Table 1—Dyeing parameters

Materials	Value, % (owf)
Dye	*X*
Sodium acetate	0.5
Acetic acid	2
L. ratio	40:1 (L:G)

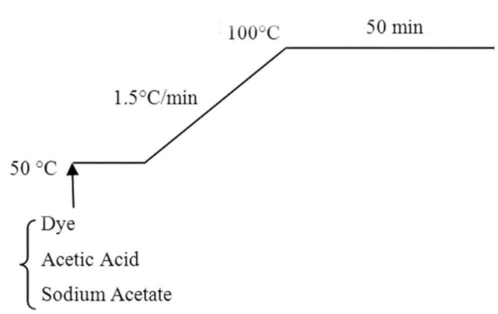

Fig. 1—Applied dyeing graph.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=400}^{700}(\mathrm{TRF_{pi}}-\mathrm{R_{ti}})^2}{16}} \quad \ldots (1)$$

where TRF_{pi} and R_{ti} are the predicted and actual spectral values respectively.

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \ldots (2)$$

where L^*, a^* and b^* are the CIELAB color parameters.

$$\mathrm{RECP} = \sqrt{\frac{\sum_{i=1}^{2}(C_{pi}-C_{ti})^2}{\sum_{i=1}^{2}(C_{ti})^2}} \quad \ldots (3)$$

where C_{pi} and C_{ti} are the predicted and actual concentrations respectively[14].

2.2.1 Theoretical Background

As mentioned before, the objective of this study is to find a reliable relation between the spectral behavior of fluorescent dyes and the amount of the used dye. This relation enables us to investigate the spectral behavior of fluorescent dyes and estimate their concentrations easily. Firstly, similar to the Man method, the real reflection should be separated from the fluorescence reflection. Then, by investigation of the fluorescence reflection curve versus dye concentration at different wavelengths, a polynomial correlation can be obtained which is much easier compared to previous methods.

2.2.2 Relationship between Dye Concentration and Fluorescent Reflection

True reflection and fluorescent reflection were separated by Man method[8] and then, an empirical polynomial equation, as shown below, was proposed to show the relationship between fluorescence reflection (β_L) and dye concentration (C) in the dyed sample with a single fluorescence dye:

$$\beta_L = (a_\lambda C^{b\lambda})-(c_\lambda C) \quad \ldots (4)$$

where a_λ, b_λ and c_λ are the wavelength-dependent constants and can be obtained by a series of calibration dyeing at the given concentration values. According to Eq. (4), the amount of fluorescent reflection increases by increasing the concentration till the extinguish point. After that, no increase will be observed in fluorescence. The second term in Eq. (4) is used to simulate the self-quenching effect of the fluorescent dye.

For mixture of two fluorescent dyes, two separate cases have been considered. The first case deals with the wavelengths at which two fluorescent dyes do not show any fluorescent emission. The second one is wavelengths at which dyes emit fluorescent emissions. To estimate the fluorescent reflection in a mixture of two dyes, following equation is defined:

$$\beta'_L = (\beta_{1L}+\beta_{2L})/(1+g_\lambda C_1{}^{h}{}_{\lambda} C_2{}^{k}{}_{\lambda}) \quad \ldots (5)$$

where g_λ, h_λ and k_λ are the constants and can be obtained by a series of calibration dyeing; β_{1L} and $\beta_{2L,}$ the estimated amount of fluorescent reflection for each fluorescent dye independently by Eq. (4); and β'_L, the estimated amount of fluorescent reflection in a mixture of two dyes. It seems that the presented equations can be used to analyze the spectral behavior of fluorescent dyes on textiles with an acceptable precision. The total predicted radiance factor is given by following equation:

$$\mathrm{TRF_p} = \beta_L(\text{or } \beta'_L) + \beta_S \quad \ldots (6)$$

where β_L(or β'_L) is calculated from Eqs (4) or (5). β_S is the real reflectance and is calculated from following equations:

$$\left(\frac{K}{S}\right)_b = \left(\frac{K}{S}\right)_s + A_1C_1 + A_2C_2 \quad \ldots (7)$$

$$\beta_S = 1 + \left(\frac{K}{S}\right)_b - \left[\left(\frac{K}{S}\right)_b^{\,2} + 2\left(\frac{K}{S}\right)_b\right]^{0.5} \quad \ldots (8)$$

where $\left(\frac{K}{S}\right)_b$ and $\left(\frac{K}{S}\right)_s$ are the Kubelka-Munk functions for a no-fluorescent dye and substrate respectively; A_i, the unit *K*/*S* value of fluorescent dyes; and $C_{i,}$ the dye concentrations.

2.2.3 Binary Color Matching of Fluorescent Dyes

First, the total radiance factors curve of the target standard is matched as closely as possible with two selected dyes by a least squares method via following equations:

$$\textstyle\sum_\lambda A_1\left[\left(\frac{K}{S}\right)_m - \left(\frac{K}{S}\right)_s - A_1C_1 - A_2C_2\right] = \sum_\lambda A_1\left[\left(\frac{K}{S}\right)_m - \right.$$
KSs−λA12C1−λA1A2C2=0 … (9)

$$\textstyle\sum_\lambda A_2\left[\left(\frac{K}{S}\right)_m - \left(\frac{K}{S}\right)_s - A_1C_1 - A_2C_2\right] = \sum_\lambda A_2\left[\left(\frac{K}{S}\right)_m - \right.$$
KSs−λA22C2−λA1A2C1=0 … (10)

where subscripts s, m and p indicate substrate, measured and predicted respectively.

During this computation, the Kubelka-Munk constants (A_1, A_2) at the fluorescent region of the fluorescent dye are taken to be zero. In the other words, no absorption or fluorescence is assumed in this region. By solving Eqs (9) and (10) for C_1 and C_2 the initial match recipe is obtained.

The next stage is to use the "Iteration Technique" to match the total radiance curve again by varying C_1 and C_2 obtained previously until a minimum in chromaticity difference in standard illuminant D_{65} with the supplementary standard 10° observer is achieved.

According to following equation, a correction matrix is used, which can minimize ∂x and ∂y amounts of target sample for color recipe prediction of fluorescent dyes:

$$\frac{\partial x}{\partial C_i} = \sum k.\left(\frac{\partial \beta_T}{\partial C_i}\right).E_\lambda \bar{x}_\lambda = \sum k.\left(\frac{\partial \beta_S}{\partial C_i} + \frac{\partial \beta'_L}{\partial C_i}\right).E_\lambda \bar{x}_\lambda =$$
k.Eλxλ∂[f(βS)]∂Ci×∂βS∂[f(βS)]+∂β′L∂Ci … (11)

Similarly, such a relationship is established for the Y and Z and other dyes. Non-fluorescent component is calculated by following equation:

$$\frac{\partial[f(\beta_S)]}{\partial C_i} = A_i, \frac{\partial \beta_S}{\partial[f(\beta_S)]} = \frac{2R^2}{R^2-1} \quad \ldots (12)$$

To calculate $\frac{\partial \beta'_L}{\partial c_i}$ from Eq. (5), derivative with respect to the concentration of each dye that is given by following equation:

$$\frac{\partial \beta'_L}{\partial C_1} = \frac{[ab\left(C_1^{b-1}-c\right)\left(1+gC_1^hC_2^k\right)-\left(ghC_1^{h-1}C_2^k\right)\left(aC_1^b-cC_1+dC_2^e-fC_2\right)]}{\left(1+gC_1^hC_2^k\right)^2} \quad \ldots (13)$$

$$\frac{\partial \beta'_L}{\partial C_2} = \frac{[de\left(C_2^{e-1}-f\right)\left(1+gC_1^hC_2^k\right)-\left(gkC_1^hC_2^{k-1}\right)\left(aC_1^b-cC_1+dC_2^e-fC_2\right)]}{\left(1+gC_1^hC_2^k\right)^2} \quad \ldots (14)$$

All of a,b,c,g,h,k have λ index.

A correction matrix is used, which can minimize ∂x and ∂y amounts of target sample for color recipe prediction of fluorescent dyes. If the concentration of the two dyes is slightly altered, the slight variations in the chromaticity can be written by following equations:

$$\Delta x = \left(\frac{\partial x}{\partial c_1}\right)\Delta C_1 + \left(\frac{\partial x}{\partial c_2}\right)\Delta C_2 \quad \dots (15)$$

$$\Delta y = \left(\frac{\partial y}{\partial c_1}\right)\Delta C_1 + \left(\frac{\partial y}{\partial c_2}\right)\Delta C_2 \quad \dots (16)$$

$$\frac{\partial x}{\partial C_i} = \left[\frac{\partial X}{\partial c_i}(X+Y+Z) - X\left(\frac{\partial X}{\partial c_i}+\frac{\partial Y}{\partial c_i}+\frac{\partial Z}{\partial c_i}\right)\right] / [(X+Y+Z)^2] \quad \dots (17)$$

$$\frac{\partial y}{\partial C_i} = \left[\frac{\partial Y}{\partial c_i}(X+Y+Z) - Y\left(\frac{\partial X}{\partial c_i}+\frac{\partial Y}{\partial c_i}+\frac{\partial Z}{\partial c_i}\right)\right] / [(X+Y+Z)^2] \quad \dots (18)$$

At this point, we can examine the chromaticity values, given as examples of how much of the target sample is far from established. Then use the iteration till a minimum in chromaticity difference is achieved. By substituting the chromaticity values in Eqs (15) and (16), ΔC_i is obtained. New concentration is given by following equation:

$$C_{i,new} = C_{i,old} + \Delta C_i \quad \dots (19)$$

3 Results and Discussion

The total radiance factor curves for the dyed samples with C.I. Basic Yellow 40, C.I. Basic Red 13, C.I. Basic Red 14 and C.I. Basic Violet 16 in different concentration ranges are plotted in Fig. 2. A dual behavior for the total radiance factor (TRF) is obtained. The first change occurs in fluorescence emission region. It can be seen that the TRF values increase by increasing the dye concentration. At the second part, in extinction point, the fluorescence reflection and as a result the total radiance factors reduce as the concentration increases.

As mentioned before, total radiance factor curve consists of two components, viz real reflection and fluorescent reflection. According to Man's method, the fluorescent component for the obtained curves in Fig. 2, is separated from the real reflection and the results are plotted against the concentration at different wavelength (Fig. 3). It is observed that in the fluorescent reflection area, the reflectance values at first increase with the concentration and then decrease at extinction point of dye.

Color matching of fluorescent mixtures is complex. It seems that the properties of a fluorescent component in a mixture may be affected by other

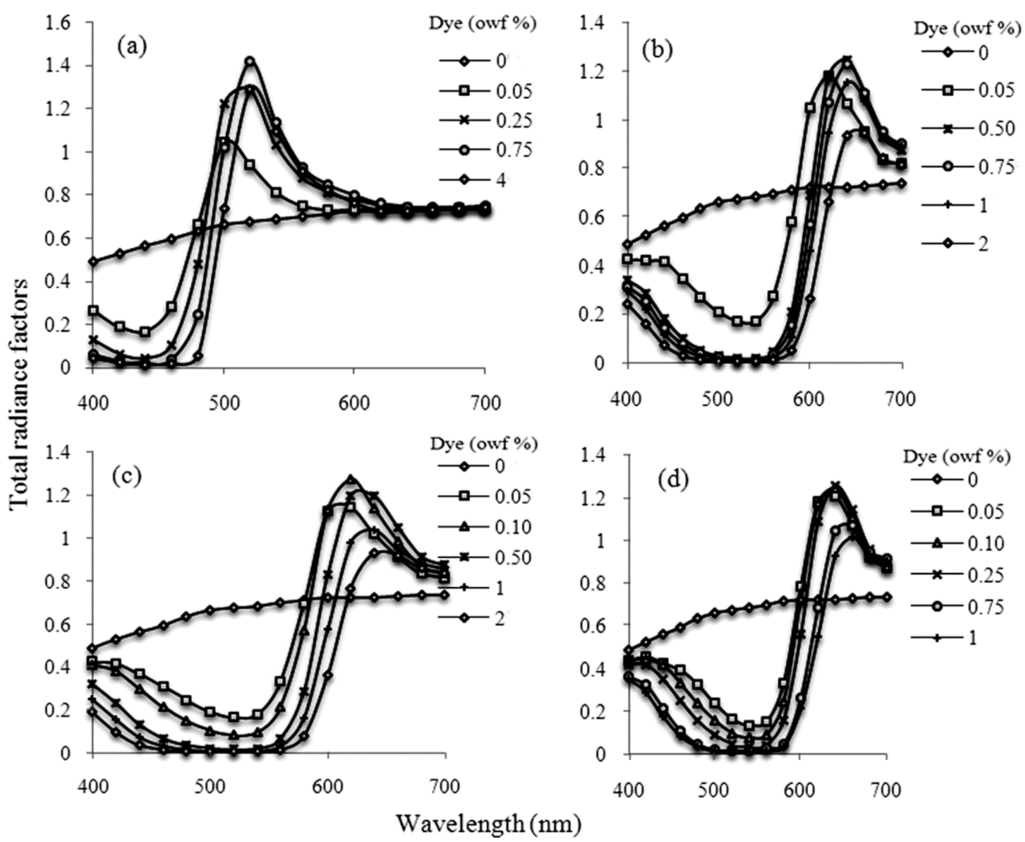

Fig. 2—Total radiance factors (TRF) for the dyed sample with fluorescent dyes at different concentration (%) [(a) C.I. Basic yellow 40, (b) C.I. Basic Red 13, (c) C.I. Basic Red 14, and (d) C.I. Basic Violet 16]

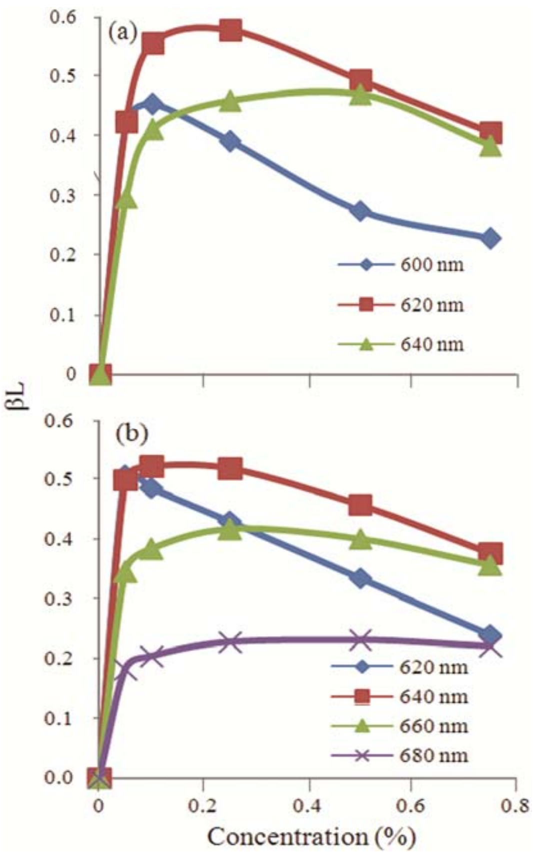

Fig. 3—Fluorescent reflection for the dyed sample with (a) C.I. Basic Red 14 and (b) C.I. Basic Violet 16 at different wavelengths

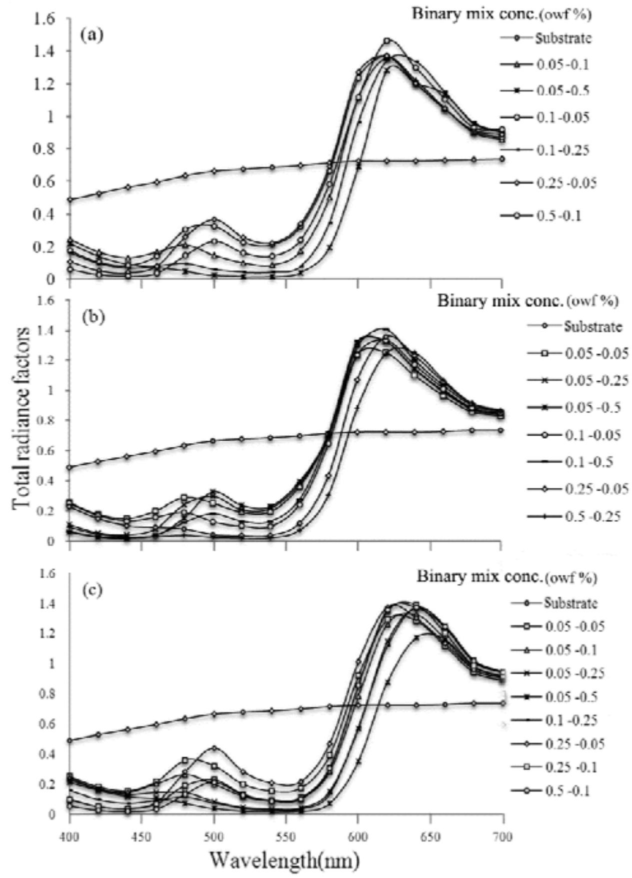

Fig. 4—Total radiance factors for the dyed sample with a binary mixture of (a) C.I. Basic Yellow 40 and C.I. Basic Red 13, (b) C.I. Basic Red 14 and C.I. Basic Yellow 40, and (c) C.I. Basic Yellow 40 and C.I. Basic Violet 16 at their different concentrations

components. It is resulted in a specific variation in its absorption, emission and quenching. The total radiance factor curves for the binary mixtures are presented in Fig. 4.

Table 2 illustrates the results of an actual prediction for the total radiance factors. The second column shows the total radiance factors of the target. The third column is the total radiance factors calculated as the first trial. The last column is resulted in an iteration process to minimize the color difference so that we have a color chromaticity matching. Figure 5 shows the total radiance factors curves for data given in Table 2.

As can be seen from Fig. 5, the difference between total radiance factor of the target and predicted samples is negligible and therefore match prediction is acceptable. In Table 3, the predicted and target samples are compared together in terms of RMSE, ΔE^*_{ab} and RECP. The color difference between target and predicted sample in the first trial is very high, that is reduced by using the correction matrix in the final

Table 2— Target and predicted total radiance factor values of the sample dyed with 0.1% C.I. Basic Yellow 40 and 0.25% C.I. Basic Red 13.

Wavelength nm	Total radiance factors		
	Final trial	First trial	Target
400	0.163	0.1723	0.1721
420	0.0959	0.0967	0.0967
440	0.0691	0.0662	0.0660
460	0.0821	0.0902	0.0882
480	0.0971	0.0952	0.0898
500	0.0616	0.0738	0.0684
520	0.0463	0.0519	0.0482
540	0.0454	0.0498	0.0463
560	0.0811	0.1005	0.0943
580	0.3496	0.3466	0.3279
600	0.9688	0.9616	0.9450
620	1.3443	1.4034	1.3998
640	1.3368	1.3164	1.3223
660	1.1491	1.1559	1.1618
680	0.9614	0.9681	0.9725
700	0.9013	0.9018	0.904379

trial. It is obvious that the performance of the color matching algorithm is appropriate.

Match predictions together with formulations of dye binary mixtures are listed in Table 4. RMSE, ΔE^*_{ab} and RECP values are those calculated in the prediction program between final trial and target [Eqs (1) – (3)]. The values differ from zero because it is not possible, in general, to match a color using two dye combinations.

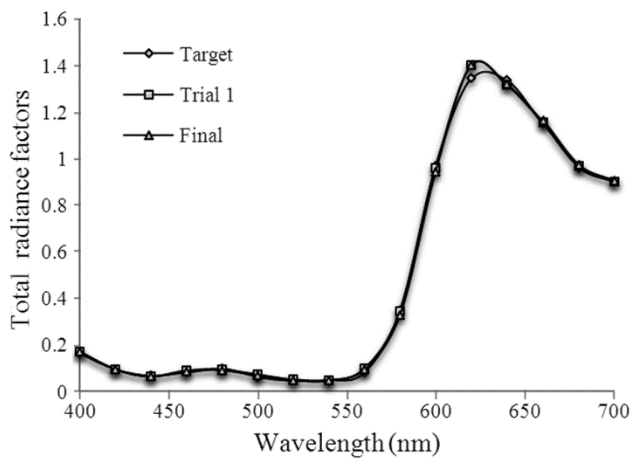

Fig. 5—Total radiance factor of target and predicted sample for a binary mixture containing 0.1% Flavin 10GFF and 0.25% Pink FG

Table 3— Spectral and colorimetric analysis of results of Fig. 5.

Parameter	Target	First trial	Final trial
$C_{\text{C.I. Basic Yellow 40}}$	0.10%	0.1549	0.1538
$C_{\text{C.I. Basic Red 13}}$	0.25%	0.2585	0.2784
RMSE	-	0.0173	0.0177
ΔE^*_{ab} under D65	-	1.1053	0.1058
ΔE^*_{ab} under A	-	0.7147	0.2471
RECP	-	0.0939	0.1028

Furthermore, the results of predictions with two fluorescent dyes are illustrated in Fig. 6. In each case the reflectance curves of target, trial 1 and final are illustrated; where final curve refers to the calculated reflectance curve for the recipe calculated to give the minimum color difference from the target.

Although the amounts of the primary prediction are on the threshold of acceptance, the fluorescent effects have not been regarded. However, by using the correction matrix, concentration difference between the real and predicted amounts will be decreased.

The results of the match prediction according to Table 4 show that average values of spectral difference (RMSE), color difference under D65 and A (ΔE) and concentration difference (RECP) are 0.00189, 1.097271, 1.271271, 0.124729 units respectively. The final total error might be due to the errors in the dyeing, the measurement, as well as the small change in energy distribution of the illuminating source during measurement.

The maximum color difference under D65 light source (ΔE) for the mixture of two dyes is 1.2542, the difference amount of the reflective spectrum is (RMSE) 0.0260 and the error amount of concentration prediction (RECP) is 0.2572, which can be acceptable, according to problems of fluorescent dyes.

Table 4— Dye concentration and spectral-colorimetric accuracies of match prediction

Parameter	Mixture 1	Mixture 2	Mixture 3	Mixture 4	Mixture 5	Average
Dye (1)	C.I. Basic Yellow 40	C.I. Basic Yellow 40	C.I. Basic Red 14	C.I. Basic Red 14	C.I. Basic Yellow 40	-
Dye (2)	C.I. Basic Red 13	C.I. Basic Red 13	C.I. Basic Yellow 40	C.I. Basic Yellow 40	C.I. Basic Violet 16	-
Target dye concentration, %	0.05 0.05	0.25 0.1	0.25 0.5	0.05 0.5	0.05 0.1	- -
First trial dye concentration, %	0.0616 0.0324	0.3537 0.0668	0.2165 0.6637	0.0263 0.7336	0.0650 0.1052	- -
Final trial dye concentration, %	0.0618 0.0493	0.3331 0.0979	0.2480 0.6650	0.0508 0.6907	0.0601 0.1086	- -
RMSE	0.0260	0.0183	0.0164	0.0191	0.0177	0.0189
ΔE^*_{ab} under D65	1.0369	0.8109	1.2542	0.4881	0.2204	0.7621
ΔE^*_{ab} under A	1.2976	1.1087	1.5445	0.9105	0.4739	1.06704
RECP	0.0374	0.1405	0.1906	0.2572	0.0343	0.132

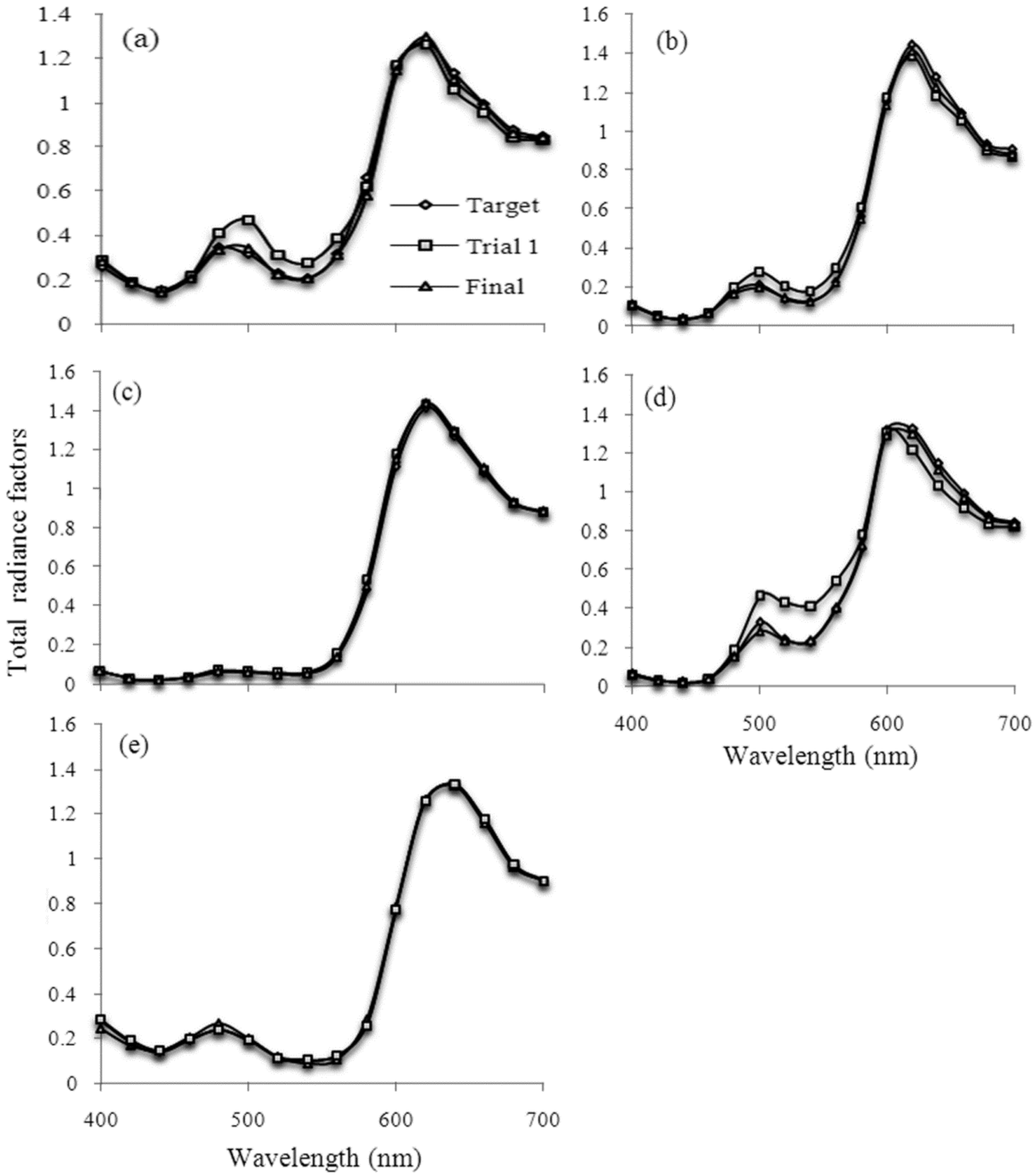

Fig. 6—Match prediction for a target sample containing (a) 0.05% Flavin 10GFF-0.05% Pink FG, (b) 0.25% Flavin 10GFF-0.1% Pink FG, (c) 0.25% Brilliant Red 4G-0.5% Flavin 10GFF, (d) 0.05% Brilliant Red 4G-0.5% Flavin 10GFF and (e) 0.05% Flavin 10GFF-0.1% Red Violet 3RN

4 Conclusion

In this study, a new technique has been applied for the quantitative analysis of acrylic samples dyed with binary mixtures of fluorescent dyes. Similar to the Man method, the real reflection is separated from the fluorescence reflection. Then, by investigation of the fluorescence reflection curve versus dye concentration at different wavelengths, an empirical polynomial equation is proposed to show the relationship between fluorescence reflection (β_L) and dye concentration (C) in the dyed sample.

For color matching of binary fluorescent dye mixtures, the first initial match recipe is obtained by using Kubelka-Munk theory and least square error method. Then, a correction matrix for minimizing the color difference between the real and the predicted dye concentrations is applied. The results show that the maximum RMSE, ΔE^*_{ab} and RECP for match prediction of the mixture of two dyes are 0.0260, 1.2542, 0.2572 respectively, which is acceptable for fluorescent dyes.

In general, this method is very useful because it is simple and accurate and also permits one to achieve an enhanced accuracy in determination of dyes concentration in colorant formulation processes.

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