New Method for Reproducing Fluorescent Colors

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Abstract

Measurement and reproduction of fluorescent colors accurately and rapidly has been known to be a quite difficult task. This method is based on a new approach to reproduce fluorescent colors. The method can be applied to spectrophotometric or multispectral measurements. The key idea in the new method is based on utilizing a small number of sharp cut filters with optimally chosen filter wavelengths along with a stable illumination light source, using an average database of light source independent bispectral luminescence matrices of common fluorescent samples, and the fact that fluorescence in samples is often concentrated on "Gaussian tail" peaks that follow the spectral properties of spectral radiance factor of fluorescent sample.

Introduction

The most accurate way to measure fluorescent colors is to use a two-monochromator method to determine a specific bispectral luminescent radiance factor of the sample [1]. The second most accurate method is to use a series (10-12) of sharp cut filters to determine the reflected radiance factor of the fluorescent sample [2]. However, both of these methods are quite time consuming and thus, not suitable for a rapid fluorescent color reproduction. In addition, several theoretical methods have been introduced to estimate the fluorescent color appearance [3,4]. However, these methods do not necessarily work for all randomly chosen color samples.

Our method is based on a new approach to accurately reproduce fluorescent colors. The method can be applied to single spectrophotometer measurements or multispectral measurements. The new method is based on the key idea of using a very small amount of low cost sharp cut high-pass filters (1-8 filters) with optimally chosen filter wavelengths along with a stable illumination light source (Fig. 1), using an average database of light source independent bispectral luminescence matrices of common fluorescent samples, and the fact that fluorescence in samples is often concentrated on "Gaussian tail" peaks that follow the spectral properties of spectral radiance factor of a fluorescent sample.

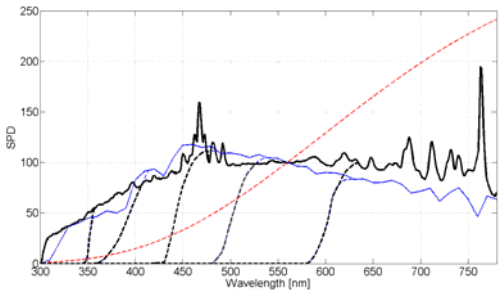

Figure 1. *Light sources: Xenon (black line), standard illuminant D65 (blue line), standard illuminant A (red dashed line), with filters at 350 nm, 400 nm, 440 nm, 500 nm and 600 nm used in fluorescent color estimations*

It is true, that some luminescence emission peaks are very sharp and not Gaussian, but for color reproduction, estimation by using Gaussian shaped peaks is sufficient.

Materials and Methods

Fluorescent samples are often evaluated by assuming that the bispectral excitation matrix of a fluorescent sample is constant and continuous from 300 nm to fluorescent sample emission wavelengths. However, this is not true, as can be seen from excitation spectra figures in this article. There are many different kinds of fluorescent sample excitation spectra depending on chemical properties of a fluorescent sample.

The fundamental procedure for evaluating the color of a fluorescent specimen is to obtain illuminant independent bispectral photometric data for specified irradiating and viewing geometries. From this data illuminant-specific spectral radiance factor and tristimulus values can be calculated.

The current fluorescent sample bispectral database (2 nm spectral resolution) was measured by using a bispectrometer built and designed by corresponding author in InFotonics Center, University of Joensuu, Finland. The wavelength accuracy of spectral data used with the method can be basically anything, e.g. between 2-20 nm. The samples in database are divided into groups according to their reflected radiance factor wavelengths to make the estimation process more accurate (e.g. "Blue fluorescents", "Green fluorescents", "Red fluorescents", "Whites" and so on). In real life fluorescent materials, the fluorescent radiance factor part of the sample spectra often "follows" the reflected radiance factor part of the sample in Gaussian tail-shaped peaks. It should be noted that not all peaks in fluorescent sample spectra are fluorescent. However, by using this method the "fluorescents" can be distinguished from the "non-fluorescents" along with reflected radiance factor of an unknown fluorescent sample.

A two-dimensional array of bispectral photometric values is known as the Donaldson matrix and the value of each element (μ,λ) of this array is described as the Donaldson radiance factor:

$$D(\mu,\lambda) \quad , \tag{1}$$

where (μ) is irradiation wavelengths (300-780 nm) and (λ) is emission wavelengths (380-780 nm). Diagonal values indicate reflectance and off-diagonal non-zero values fluorescence. Note that off-diagonal regions outside fluorescence are set to zero. The sum obtained at each viewing wavelengths λ is the value of the specimen's stimulus function (relative spectral radiance) $F(\lambda)$, under the specific conditions of irradiation:

$$F(\lambda) = \sum_{\mu=300}^{780} \Phi(\mu) D(\mu,\lambda) \quad , \tag{2}$$

where $\Phi(\mu)$ is the tabulated value of the relative spectral power of the illuminant at the element's irradiation wavelength. From these values either tristimulus values or spectral radiance factor values may be delivered.

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Reflected radiance factor $\beta_R(\lambda)$ can be obtained fairly easily as it is the diagonal of Donaldson matrix. For a fluorescent specimen, the spectral radiance factor $\beta_I(\lambda)$ is illuminant-specific:

$$\beta_I(\lambda) = \frac{F_I(\lambda)}{\Phi_I(\lambda)} = \sum_{\mu=300}^{780} \frac{\Phi_I(\mu)}{\Phi_I(\lambda)} D(\mu,\lambda). \quad (3)$$

Reproduction of Donaldson Matrix of a Fluorescent Sample

In our method the fluorescent sample estimation is based on dividing the physical "measurement" light source and simulated known illuminant spectra into smaller regions by using filters at (325 nm-optional), 350 nm, 400 nm, 440 nm, 500 nm, (520 nm-optional) and 600 nm, (620 nm-optional) (Fig. 1). Optional sharp cut filters are not illustrated in Fig. 1. By using the filters, estimating the light source independent/dependent characteristics of any sample becomes significantly easier. The amount of filters used (from 1-8) can be adjusted depending on sample, accuracy of estimation and the device in which the method is used. As a reference light source we used a stabilized 200W xenon lamp. As the spectral reproduction example illuminants we chose to use illuminants D65 and A. Figure 2 shows the key components of the method.

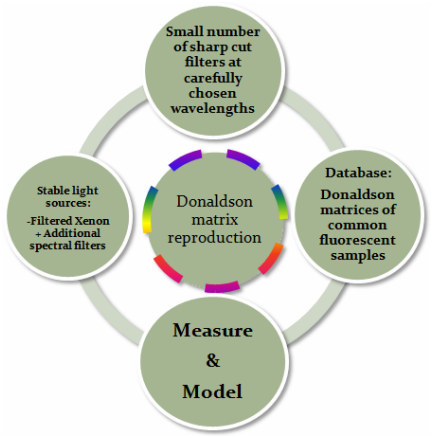

Figure 2. *Reproduction of Donaldson matrix of fluorescent samples*

Advantages of the Method

Some major advantages of this method are:

1. Modular method: Each part of the method can be adjusted depending on measurement or imaging device used or the type of the fluorescent sample.
2. Not only total radiance factor, luminescent radiance factor, and reflected radiance factor can be reproduced, but also the whole Donaldson matrix of a fluorescent sample can be estimated per each excitation and emission wavelengths.
3. Multiple wavelength sampling resolutions can be used, not only CIE recommended 5 nm; or 10 nm and 20 nm.
4. Any unknown sample can be estimated-no need to know in advance whether the sample is fluorescent or not.

Sample Definition (Fluorescent or Non-fluorescent Sample?)

1. At first the measurements are performed with filtered xenon for both white reference and the sample: This defines the total radiance factor of the sample under the xenon light source. At this point it is still unclear whether the sample is fluorescent or not.
2. Next, the spectra are measured with 400 nm sharp cut filter in front of the filtered xenon, again for both the white reference and the sample. This defines the total radiance factor of a sample in xenon light without the excitation wavelengths below 400 nm. By comparing the radiance factors between the first and the second measurements it can be detected whether the sample is fluorescent or not. During this phase all the fluorescent peaks of a sample can be detected.
3. For a fluorescent sample and the white reference, total radiance factor measurements are repeated with each filter, e.g. with a typical filter set with filters at 350 nm, 400 nm, 440 nm, 500 nm, 520 nm, 600 nm, and at 620 nm.

Separation of Fluorescent Radiance Component and Reflected Radiance Component in Overlapping Wavelength Regions

Combination of Three Factors:

1. Reflected radiance components are stored to database as principal components:

$$\beta_R(\lambda) = \sum_{j=1}^{M} y_j v_j \ , \quad (4)$$

where y_j is the eigenvectors and v_j is the expansion coefficient.

2. From the sharp cut filter data at each separation points it is possible to calculate the reflected radiance factor points at filter wavelengths (for example at [400 nm, 440 nm-"Blue fluorescents"], [500 nm, 520 nm-"Green fluorescents"], [600 nm, and 620 nm-"Red fluorescents").

Calculation of reflected radiance points at selected filter wavelengths are performed by using Eq. (5):

$$\beta_{R\lambda} = \frac{\Gamma_{sample} \times \beta_{white}}{\Gamma_{white}} \ , \quad (5)$$

where $\beta_{R\lambda}$ is the reflected radiance point of the sample at wavelength λ, Γ_{sample} the measured value for the sample with the sharp cut filter at wavelength λ, β_{white} is the absolute reflectance of the white reference and Γ_{white} the measured value for the reference white with the filter.

3. From the above data the evaluation of the reflectance spectra of a fluorescent sample is easy (by interpolating the missing points and using the spectral database).

Figure 3 shows the interpolation results for white sample with blue fluorescent whitening agent, with filters at 400 nm and 440 nm. Calculated reflected radiance points at selected filter wavelengths are shown with black circles. Note that in Figs. 3,4, and 5 (luminescent) radiance factors with filters are plotted for the wavelengths below each filters' wavelengths even in practise the wavelengths below the filter average "central" wavelengths cannot be directly defined, but only after some estimations and calculations.

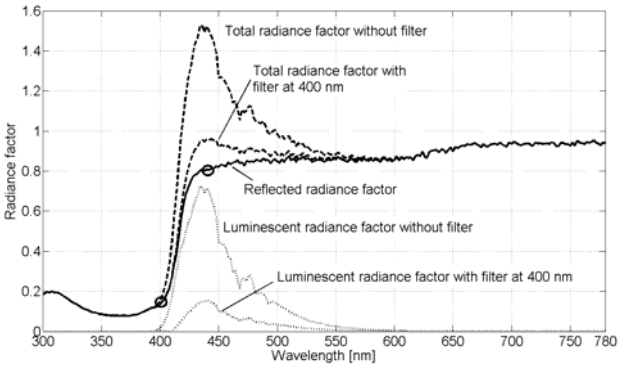

Figure 3. *Interpolation results for fluorescent textile sample ("Scott Dic CN100") with whitening agent*

Figure 4 shows the interpolation results for fluorescent green sample with filters at 500 nm and 520 nm. Calculated reflected radiance points at selected filter wavelengths are shown with black circles.

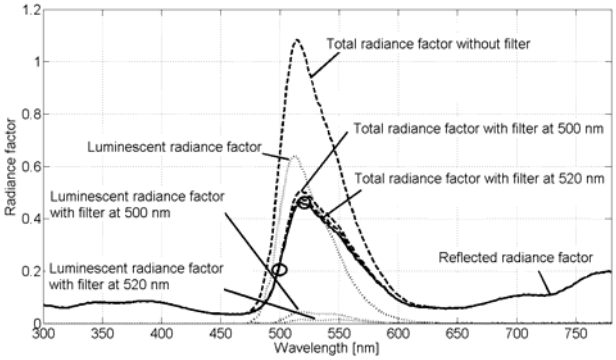

Figure 4. *Interpolation results for fluorescent green paint sample*

Figure 5 shows the interpolation results for fluorescent pink sample with filters at 600 nm and 620 nm. Calculated reflected radiance points at selected filter wavelengths are shown with black circles.

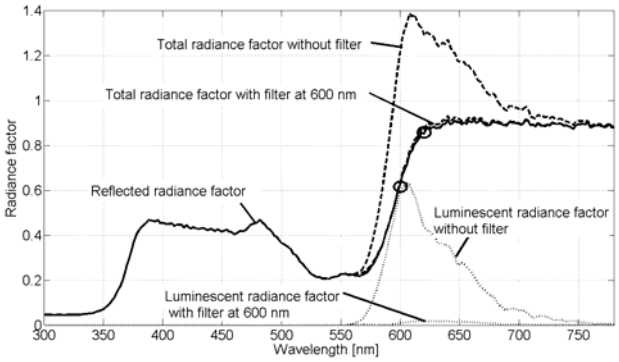

Figure 5. *Interpolation results for fluorescent pink sample*

In addition, the samples that have white, grey, or "similar, constant" reflectances, are also often associated to blue, green, red, near-IR luminescent radiance factors and usually separation of luminescent component for these is fairly easy. In these types of samples, the excitation often occurs at UV-wavelengths.

Simulation of Maximum Excitation Function of Donaldson Matrix Luminescence Component

After separating the luminescent radiance factor and reflected radiance factor under used illumination (e.g. xenon with and without filters), light source independent Donaldson matrix off-diagonal non-zero values for fluorescence, i.e. the value of each element (μ, λ) Donaldson matrix luminescent part:

$$D(\mu,\lambda)_{lum} \quad , \tag{6}$$

can be estimated.

The Donaldson luminescent matrix can be estimated from stimulus function (relative spectral radiance) $F(\lambda)_{est}$, under each specific conditions of irradiation:

$$F(\lambda)_{est} = \sum_{\mu=300}^{n} \Phi(\mu)_m \, D\left(\mu_{peak\,\max}, \lambda_{lum.peak.norm}\right)_{est.lum.peak} \quad , \tag{7}$$

where $F(\mu)$ is light source (e.g. xenon) used with and without m filters that alter its spectral (for example ND-filter) value of the relative spectral power of the illuminant at the element's irradiation wavelength, n is the last excitation wavelength value of each luminescent peak maximum excitation (divided into pieces), $\mu_{peakmax}$ the maximum excitation value of each fluorescent peak, $\lambda_{lum.peaknorm}$ is the average Gaussian shaped luminescent peak value with its maximum value normalized to 1.

Finding the Maximum Excitation Spectra of Each Luminescent Peak:

By using:

1. The previous equation m-illuminants piecewise, e.g. "pieces" from 300-325 nm, 325 nm-350 nm, 350-400 nm, 400-440 nm, 440-500 nm and so on until each fluorescent samples excitation wavelength n,
2. luminescent sample peak maximum excitation categorized per each color ;["Blue fluorescents", "Green fluorescents", "Red fluorescents", "Whites" etc.]as principal components,
3. some partial correlation between the absorption and excitation spectra of a fluorescent sample, mainly at VIS-wavelengths, [peaks vs. valleys], and
4. using the least square method for m-illuminants,

the maximum excitation spectra of each luminescent peak of a sample can be estimated.

Some Maximum Excitation Spectra Modelling Possiblities:

General form of the illuminant independent (piecewise) central excitation function of each luminescent peaks of Donaldson matrix can be simulated by:

$$f(\mu) = ae^{-\frac{(\mu-\mu_c)^2}{2c^2}} + b \quad , \tag{8}$$

where a is the the height of Gaussian function, μ the excitation wavelengths of the Donaldson matrix luminescence part, μ_c the position of the center wavelength of the peak used for fitting, c is the width of the fitting peak, and b the baseline of the peak. Each parameter is adjusted accordingly depending on wavelength region. It also possible to use other estimation methods such as sin/cos-based estimations.

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Figure 6 shows some fluorescent sample maximum excitation spectra examples in the blue region (the "Blue fluorescents").

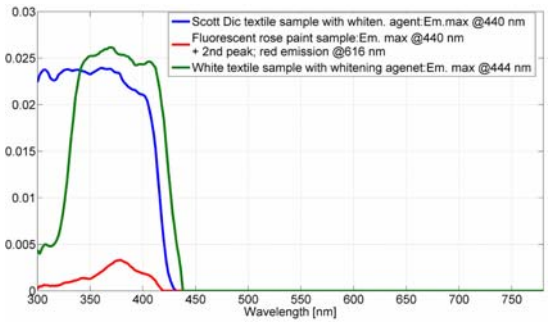

Figure 6. *Some fluorescent sample maximum excitation spectra examples in the blue region*

Figure 7 shows some fluorescent sample maximum excitation spectra examples in the green region (the "Green fluorescents").

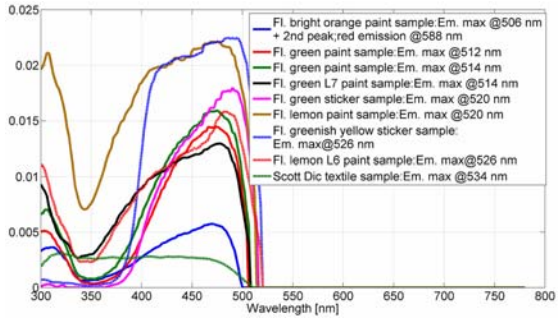

Figure 7. *Some fluorescent sample maximum excitation spectra examples in the green region*

Figure 8 shows some fluorescent sample maximum excitation spectra examples in the red region (the "Red fluorescents").

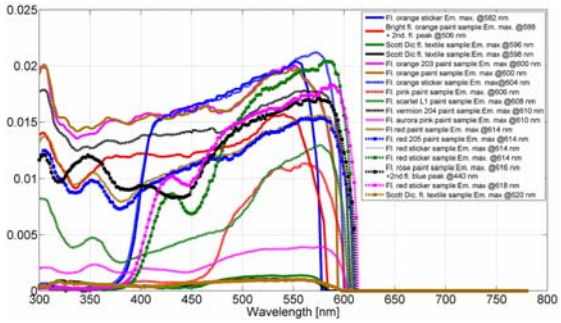

Figure 8. *Some fluorescent sample maximum excitation spectra examples in the red region*

Results

Simulation of Maximum Excitation Function of Donaldson Matrix Luminescence Component: Some Examples

There is always some partial correlation between normalized absorption and excitation spectra of a fluorescent sample, often at VIS-wavelengths, and especially on peaks and valleys of the spectra. This can be seen from each fluorescent color examples below. Figure 9 shows this partial "excitation vs. absorption" match for a fluorescent textile sample with whitening agent (an example of the "Blue fluorescents"). Information about exicitation vs. absorbption properties of a fluorescent sample can be utilized in spectral reproduction.

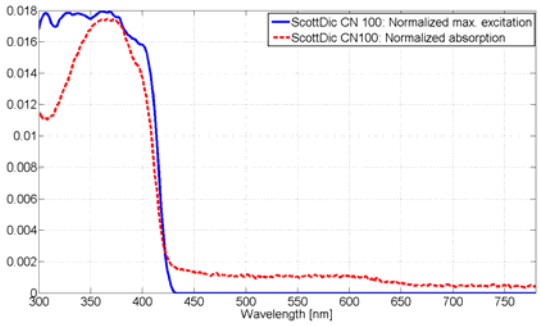

Figure 9. *Fluorescent textile sample ("Scott Dic CN100") with whitening agent: Normalized maximum excitation spectrum vs. normalized absorption spectrum*

Figure 10 shows that the method reproduces the maximum excitation spectra very well, and in addition Fig. 11 confirms this for Donaldson matrix luminescent part.

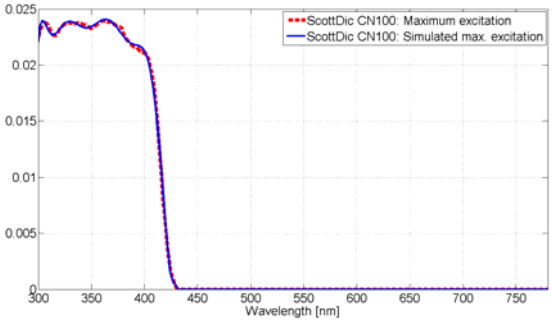

Figure 10. *Fluorescent textile sample ("Scott Dic CN100") with whitening agent: Maximum excitation spectrum vs. simulated maximum excitation spectrum*

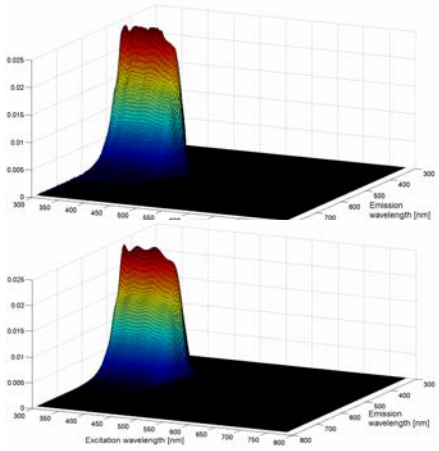

Figure 11. *Fluorescent textile sample ("Scott Dic CN100") with whitening agent: Original Donaldson matrix-luminescent part (upper Fig.) vs. Simulated Donaldson matrix-luminescent part (lower Fig.)*

From Fig. 12 we can see fluorescent textile sample's original radiance factors under standard illuminants D65 and A

(red lines) vs. reproduced radiance factors under standard illuminants D65 and A (blue lines). It is quite difficult to separate the red and blue lines in spectra which indicates that the current method gives accurate results for D65 and A simulations. Figures 13-16 show similar examples and results for fluorescent green sample (an example of the "Green fluorescents") and Figs 17-20 for fluorescent pink sample (an example of the "Red fluorescents"). In addition, all fluorescent peaks of the samples could be found and distinguished from non-fluorescent peaks of the sample.

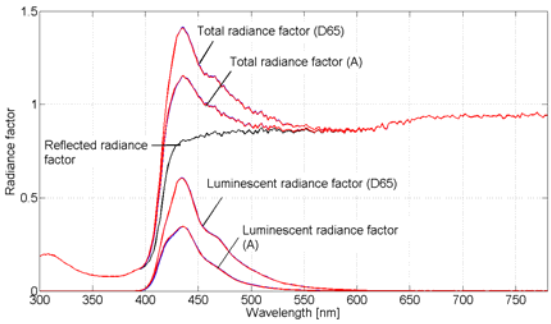

Figure 12. *Fluorescent textile sample ("Scott Dic CN100") with whitening agent: Original radiance factors under standard illuminants D65 and A (red lines) vs. reproduced radiance factors under standard illuminants D65 and A (blue lines)*

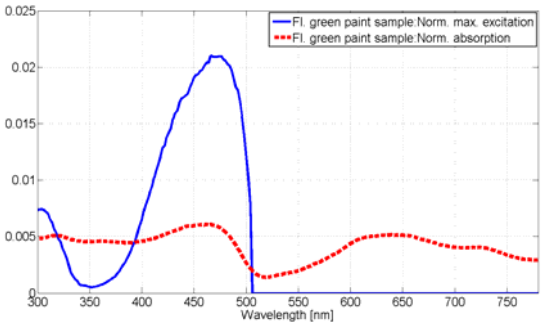

Figure 13. *Fluorescent green paint sample: Normalized maximum excitation spectrum vs. normalized absorption spectrum*

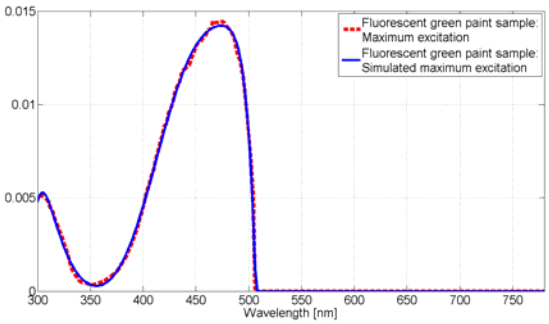

Figure 14. *Fluorescent green paint sample: Maximum excitation spectrum vs. simulated maximum excitation spectrum*

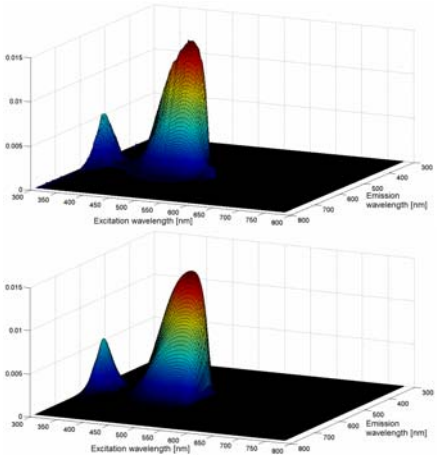

Figure 15. *Fluorescent green paint sample: Original Donaldson matrix-luminescent part (upper Fig.) vs. Simulated Donaldson matrix-luminescent part (lower Fig.)*

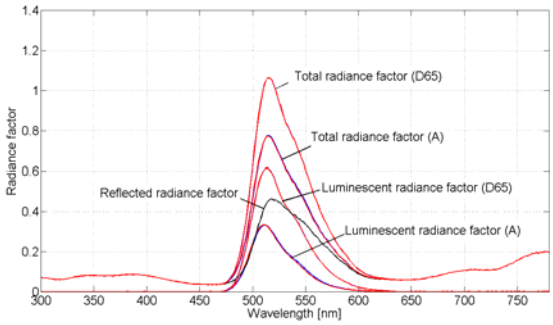

Figure 16. *Fluorescent green paint sample: Original radiance factors under standard illuminants D65 and A (red lines) vs. reproduced radiance factors under standard illuminants D65 and A (blue lines)*

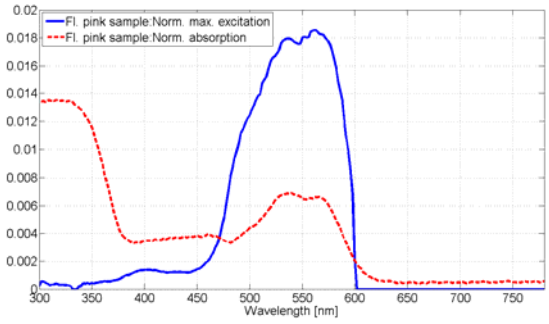

Figure 17. *Fluorescent pink sample: Normalized maximum excitation spectrum vs. normalized absorption spectrum*

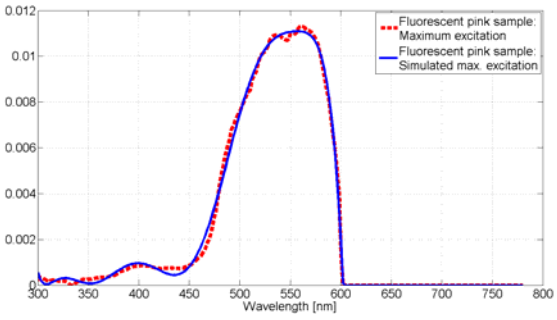

Figure 18. *Fluorescent pink sample: Maximum excitation spectrum vs. simulated maximum excitation spectrum*

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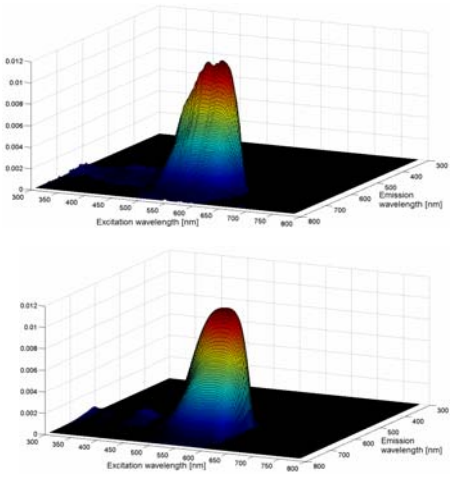

Figure 19. *Fluorescent pink sample: Original Donaldson matrix-luminescent part (upper Fig.) vs. Simulated Donaldson matrix-luminescent part (lower Fig.)*

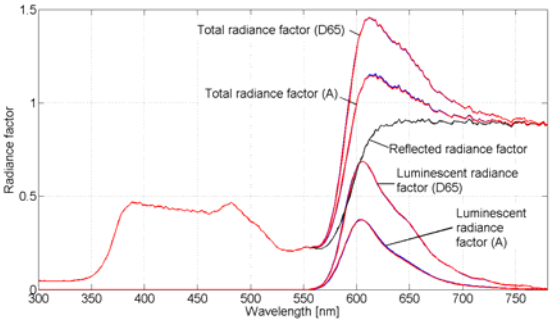

Figure 20. *Fluorescent pink sample: Original radiance factors under standard illuminants D65 and A (red lines) vs. reproduced radiance factors under standard illuminants D65 and A (blue lines)*

Table 1 shows some examples of CIE 1976 CIELAB color differences ΔE^*_{ab} between original and reproduced fluorescent spectra samples. The color differences ΔE^*_{ab} between original and reproduced fluorescent spectra are minimal under both standard illuminants D65 and A. The color differences cannot be perceived by human eye, which means that the method reproduces the fluorescent sample spectra very well.

Table 1: Color differences ΔE^*_{ab} between original and reproduced fluorescent spectra

Fluorescent color	ΔE:D65	ΔE:A
Scott Dic "CN100-Blue"	0.105	0.056
Fluorescent green paint	0.100	0.739
Fluorescent pink paint	0.170	0.215
Scott Dic fl. green	0.231	0.178
Fluorescent rose paint	0.452	0.501
Fluorescent aurora pink paint	0.342	0.635
Fluorescent orange sticker	0.444	0.490
Fluorescent green sticker	0.220	0.150
White textile sample with whitening agent	0.130	0.110

Conclusions

The method is an accurate method to be used in rapid fluorescent sample spectral color reproduction. However, there is still a lot of room for improvement. For example, the amount of filters will be reduced and the reference database will be extended with wider variety of fluorescent samples, with some special or "difficult" spectral properties. In addition, our goal is to optimize the system for multispectral imaging applications.

References

[1] R. Donaldson, "Spectrophotometry of fluorescent pigments," Brit. J. Appl. Phys. 5, 210 (1954).

[2] F.T. Simon, "Serial filter method for fluorescence evaluation," Anal. Chim. Acta 380, 417 (1999).

[3] H. Haneishi et al, "Modelling and estimation of spectral reflectance characteristics of fluorescent objects", ICIS, pg. 427 (2002).

[4] T. Nakashima, S.Tominaga, "Spectral reflectance estimation of fluorescent objects by using a spectral camera system", IEICE pg. 148 (2007) (in Japanese).

Author Biography

Jarkko Mutanen received his MSc degree in 1999 and PhD degree in 2004 in physics from the University of Joensuu, Finland. From 1998-2006, he worked on different color research projects at the University of Joensuu. Currently he is a JSPS-funded researcher at the Tokyo Institute of Technology, Japan. His current research interests include color research and fluorescent colors. He is a member of the Finnish Optical Society and Pattern Recognition Society of Finland.