



Application of the Ratio Derivative Method in Quantitative Analysis of Samples Dyed with Ternary Dye Mixtures

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ABSTRACT

In this study, a derivative method is applied for the determination of dye concentration in fabrics dyed with tricomponent dye mixtures. The reflectance of spectra of the samples were recorded between 400 and 700 nm. Initially, the obtained (K/S) spectra were divided by the spectrum of a standard sample dyed with two of the components in the ternary mixture and the derivative spectra were calculated. Then, the amounts of the dyes were determined by implementing or carrying measurements in suitably selective wavelengths in the required spectra derivative ratio. Results indicated that the developed spectra derivative ratio (K/S) method is more accurate than the normal Kubelka-Munk method. Prog. Color Colorants Coat. 1(2008) 1-9. © Institute for Colorants, Paint and Coatings.

1. Introduction

In general, the most important problem in recipes prediction processes, is to find the exact proportions of colorants used, in order to produce a match for a target or required shade [1, 2]. The colorant mixture formulation is a method for calculating the colorant ratios to produce or match a given objective (or target) color in. It is necessary for the colorant formulation method to have a function directly related to the concentration of the colorants. The Kubelka-Munk function which is derived from the reflectance spectra by Eq. (1) is directly related to the concentration of colorant.

$$\frac{K}{S} = \frac{(1-R)^2}{2 \times R} \quad (1)$$

Where K and S are the absorption and scattering coefficients respectively, and R is the reflectance factor

at a specific wavelength.

The Kubelka-Munk theory assumes that, the ratio of absorption and scattering coefficients of the related or added colorant, is directly proportional to its concentration and is additive in the mixture. It also assumes that, each colorant acts independently from others and the substrate is responsible for the majority of the scattering, then by definition of Kubelka-Munk single-constant theory; it can be shown that the K/S for a combination of n colorants with concentrations of C_i at a particular wavelength is the sum of several single elements as given by Eq. (2):

$$\left(\frac{K}{S}\right)_{mix} = \left(\frac{K}{S}\right)_{sub} + \sum_{i=1}^n C_i \times \left(\frac{K}{S}\right)_i \quad (2)$$

where 'sub' refers to substrate.

At the present, most of the color measuring

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instruments use the Kubelka-Munk theory for calculating the colorant formulation.

The usual method for recipe prediction, is first, to prepare a selection of dyes, likely to produce the target color, then apply each dye on the given substrate with different concentrations covering the range of working concentrations normally used. The reflectance values of various dyed samples for different concentrations are measured by employing a reflecting or reflection spectrophotometer. The reflectance value for each dye at the corresponding concentration and wavelength are usually converted to a Kubelka-Munk function of the reflectance, and then the relationship between the (K-M) functions of the reflectance values and the dye concentrations, is obtained. Hence, an estimation of the reflectance value for a selected mixture comprising a single dye, can be made from the (K-M) functions of the reflectance relationships of the single dye samples.

The derivatization of a curve or its mathematical function is simply an estimation of the slope over the whole region. In the same way, it is possible to differentiate a spectrum, such as Kubelka-Munk, in which the rate of (K/S) change is presented as a function of wavelength [3-7].

The intent of the present study is to show the applicability of a derivative spectrophotometric technique [8] based on the derivative ratio spectra of the (K-M) function for the quantitative analysis of samples dyed with ternary dye mixtures.

2. Experimental

2.1. Materials

In this work, bleached commercial cotton weaved fabrics were dyed with three reactive dyes namely Cibacron Yellow 2G-E, Cibacron Golden Yellow R-E and Cibacron Red G-E prepared from CIBA Chemical Corporation. Dyeing auxiliaries used, such as: salt (NaCl), alkali (Na₂CO₃), were supplied by Merck Co. A suitable soap solution was obtained commercially.

The reflectances of spectra of the dyed samples were measured by using a Color eye 7000 spectrophotometer of Gretage Macbeth Corporation. The reflectances of spectra were measured within the visible limit between 380 and 720 nm at 10 nm intervals.

2.2. Methods

Dyeing procedure

The samples were dyed with a red dye, a yellow dye and a golden yellow dye at concentrations: 1%, 0.5%, 0.1% and 0.05% on the weight of material and with different ternary mixtures of these dyes. The dyeing process was done according to the following dyeing diagram.

The parameters used for dyeing in the production of various samples, are given in Table 1. Washing of dyed samples were carried out using alternative cold wash and followed in hot soap solution at 70°C for 15 mins. Finally the samples were thoroughly washed with running tap water.

Determination of concentration by the Normal Kubelka-Munk method

In the application of the normal Kubelka-Munk method for measuring dye concentrations, the wavelength of maximum (K/S) values of samples dyed with each of the dyes, were selected and the (K/S) values at the λ_{max} wavelengths were measured. Similarly, the (K/S) values of samples dyed with ternary mixtures of the dyes, were measured and concentration of the each dye calculated from the following simultaneous equations. [2, 9].

$$\left(\frac{K}{S}\right)_{mix, \lambda_{maxi}} = \left(\frac{K}{S}\right)_{sub, \lambda_{maxi}} + C_1 \times \left(\frac{K}{S}\right)_{1, \lambda_{maxi}} + C_2 \times \left(\frac{K}{S}\right)_{2, \lambda_{maxi}} + C_3 \times \left(\frac{K}{S}\right)_{3, \lambda_{maxi}}, i=1,2,3 \quad (3)$$

In these equations everything except three concentrations C_1 , C_2 and C_3 are known

Developed derivated ratio (K/S) spectra technique:

If a sample dyed with three colorants (1, 2 and 3) is considered, and the Kubelka-Munk's law is obeyed over the whole wavelength range, the single-constant function at a specific wavelength can be written in form of the equation:

$$\left(\frac{K}{S}\right)_{mix} = \left(\frac{K}{S}\right)_{sub} + C_1 \left(\frac{K}{S}\right)_1 + C_2 \left(\frac{K}{S}\right)_2 + C_3 \left(\frac{K}{S}\right)_3 \quad (4)$$

or

$$\left(\frac{K}{S}\right)_{mix} - \left(\frac{K}{S}\right)_{sub} = C_1 \left(\frac{K}{S}\right)_1 + C_2 \left(\frac{K}{S}\right)_2 + C_3 \left(\frac{K}{S}\right)_3 \quad (5)$$

Table 1. Dyeing parameters.

X %	Dye /Dyes (o.w.f)
20	Na ₂ CO ₃ (g/l)
10	NaCl (g/l)
2	Sample weight (g)
40:1	(L:R)

A similar equation for the two compounds in the same ternary mixture as in a standard binary mixture can be written by Eq. (6):

$$\left(\frac{K}{S}\right)_{std} - \left(\frac{K}{S}\right)_{sub} = C_1^0 \left(\frac{K}{S}\right)_1 + C_2^0 \left(\frac{K}{S}\right)_2 \quad (6)$$

If Eq. (5) is divided by Eq. (6) corresponding to the spectrum of a standard sample dyed with two of the components in the ternary mixture, the ratio spectrum will be obtained in the form of Eq. (7):

$$\frac{\left(\frac{K}{S}\right)_{mix} - \left(\frac{K}{S}\right)_{sub}}{\left(\frac{K}{S}\right)_{std} - \left(\frac{K}{S}\right)_{sub}} = \frac{C_1 \left(\frac{K}{S}\right)_1 + C_2 \left(\frac{K}{S}\right)_2 + C_3 \left(\frac{K}{S}\right)_3}{C_1^0 \left(\frac{K}{S}\right)_1 + C_2^0 \left(\frac{K}{S}\right)_2} \quad (7)$$

The ratio of the sum of C₁ (K/S)₁ + C₂ (K/S)₂ to the sum of C₁⁰ (K/S)₁ + C₂⁰ (K/S)₂ is equal to a constant with respect to the wavelength in a certain point or region of the wavelength (Figures 2 and 3) and if the above constant is replaced in Eq. (7), we will have:

$$\frac{\left(\frac{K}{S}\right)_{mix} - \left(\frac{K}{S}\right)_{sub}}{\left(\frac{K}{S}\right)_{std} - \left(\frac{K}{S}\right)_{sub}} = K + \frac{C_3 \left(\frac{K}{S}\right)_3}{C_1^0 \left(\frac{K}{S}\right)_1 + C_2^0 \left(\frac{K}{S}\right)_2} \quad (8)$$

However if the standard concentrations of C₁⁰ and C₂⁰ in Eq. (2), are equal or very close to each other (C₁⁰ = C₂⁰) we can write:

$$\frac{\left(\frac{K}{S}\right)_{mix} - \left(\frac{K}{S}\right)_{sub}}{\left(\frac{K}{S}\right)_{std} - \left(\frac{K}{S}\right)_{sub}} = K + \frac{C_3 \left(\frac{K}{S}\right)_3}{C_1^0 \left[\left(\frac{K}{S}\right)_1 + \left(\frac{K}{S}\right)_2 \right]} \quad (9)$$

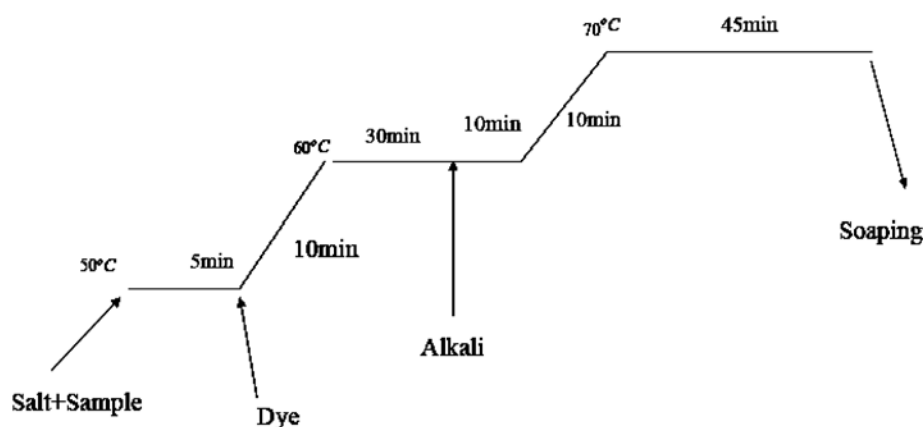


Figure 1: Dyeing Diagram used for dyeing of samples with the reactive dyes.

If the first derivative of the, Eq. (10) is taken, since the derivative of a constant is zero, Eq. (10) will be obtained.

$$\frac{d}{d\lambda} \left(\frac{\left(\frac{K}{S}\right)_{mix} - \left(\frac{K}{S}\right)_{sub}}{\left(\frac{K}{S}\right)_{std} - \left(\frac{K}{S}\right)_{sub}} \right) = C_3 / C_1^0 \times \frac{d}{d\lambda} \left(\frac{\left(\frac{K}{S}\right)_3}{\left(\frac{K}{S}\right)_1 + \left(\frac{K}{S}\right)_2} \right) \quad (10)$$

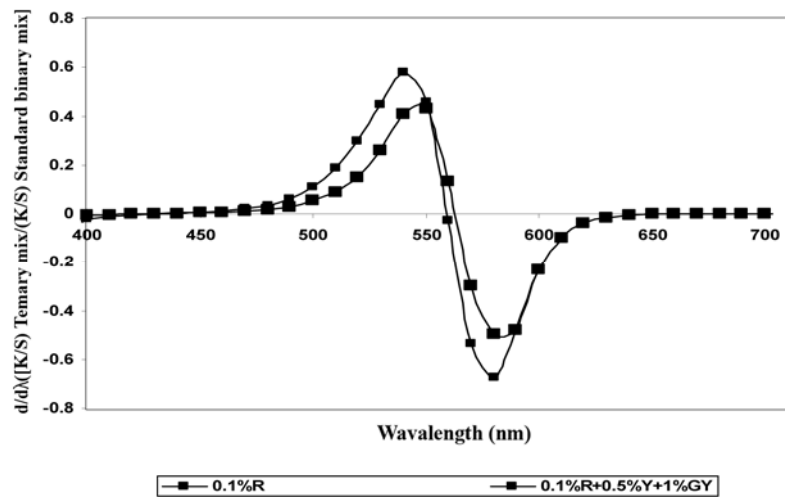


Figure 2: The coincident spectra of the first derivative of the spectra ratio of samples dyed with 0.5% Red and also a ternary mixture containing 1% GY, 0.1% R and 0.5%Y (standard sample dyed with a binary mixture of 0.5% GY and 0.5%Y as divisor).

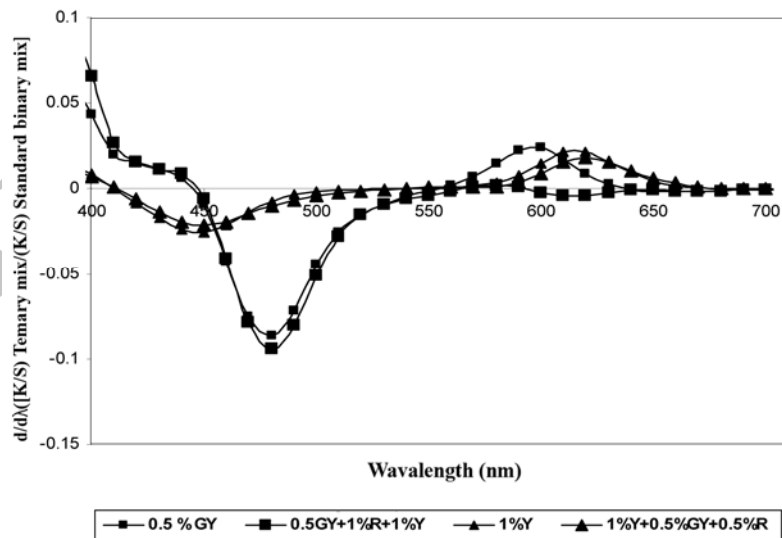


Figure 3: The coincident spectra of the first derivative of the spectra ratio of samples dyed with 0.5% GY and also a ternary mixture containing 0.5% GY, 0.5%R and 1%Y (standard spectrum of a sample dyed with a binary mixture of 0.5% R and 0.5% Y as divisor) and coincident spectra of the first derivative of the ratio spectra of samples dyed with 1% Y and a ternary mixture containing 1% Y, 0.5% GY and 0.5% R (using standard spectrum of a sample dyed with a binary mixture of 0.5% Red and 0.5%GY as divisor)

In Eq. (10), the spectrum derivative ratio of the (K-M) function of a ternary mixture depends only on the value of C_3 and C_1^0 and independent of the value of C_1 and C_2 in the ternary mixture. Eq. (10) is the mathematical foundation of tricomponent analysis which permits the determination of the magnitude of each dye concentration in samples dyed with ternary dye mixtures.

In practice, Eq. (10) corresponding to the first derivative ratio spectrum of (3) is obtained by dividing the spectrum (K/S) ratio corresponding to the ternary mixture of (1, 2 and 3) by the two standard spectra of the compounds in the ternary mixture. In the developed method, the concentration of (3) in the ternary mixture is proportional to the first derivative signals corresponding to a suitably selected point. A calibration graph is obtained by recording and storing the spectra of samples dyed with different concentrations of the pure dye 3, and the spectrum of a sample dyed with a binary mixture of pure dyes 1 and 2 of concentrations C_1^0 and C_2^0 . The stored spectra of the samples dyed with the pure dye 3 are divided by the standard spectrum of the mixture of dyes 1 and 2 (of concentrations C_1^0 and C_2^0). The ratios of the spectra, already obtained, are differentiated with respect to wavelength and the first derivative values at a given wavelength, are plotted against C_3 , so that a calibration graph, is obtained for C_3 . By using the

calibration graph, the concentration of C_3 can be determined in a sample containing unknown amounts of dye samples 1, 2 and 3. The concentration of 1 and 2 are determined by analogous procedures.

3. Results and discussion

The spectra (K/S)'s of single and ternary mixed shades of the Yellow, Golden Yellow, and Red dyes are shown in Figure 4. The proposed method was applied to a number of samples dyed with different ternary mixtures of the three dyes.

In order to determine the dye contents in samples dyed with ternary mixed dyes, a mathematical procedure was followed that consist of carrying out the derivatives of the spectra ratios of the Kubelka-Munk function with respect to wavelength. The spectra (K/S) of samples dyed with different concentrations of Red were recorded in the range 400 to 700 nm and divided by the spectrum of the standard sample dyed with a binary mixture of 0.5% Yellow and 0.5% Golden Yellow. The first derivative of the obtained spectra ratios were plotted with $\Delta\lambda=10$ nm in Figure 5. The previously obtained superimposed spectral ratios (Figure 2) assist us to find the proper wavelengths of calibration. Therefore, the concentration of Red was determined by measuring the amplitudes at 590 nm.

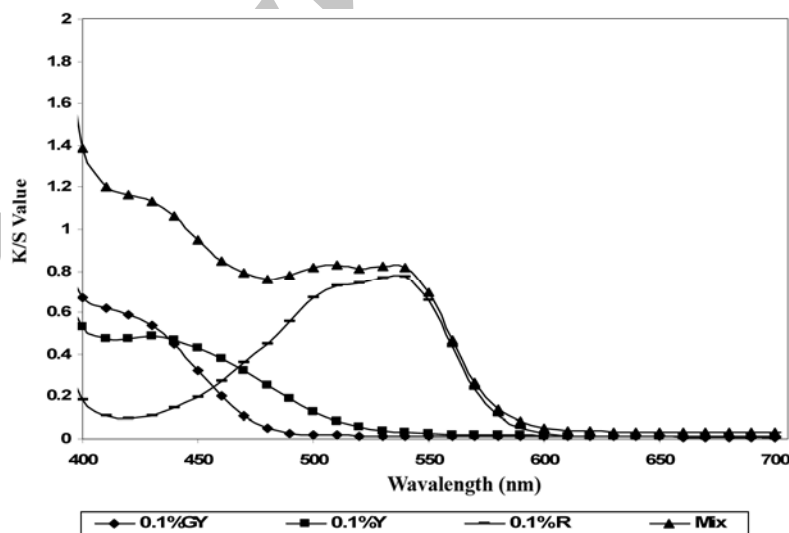


Figure 4: (K/S) values for dyed samples – 0.1% Golden Yellow dye, 0.1 % Red dye, 0.1 % Yellow dye and a mixture containing 0.1% of the three dyes.

The spectra (K/S) of the samples dyed with different concentrations of Yellow were recorded between 400-700 nm and divided by the spectrum of the standard sample dyed with a binary mixture of 0.5% GY and 0.5% R dyes. The first derivatives of the resulting spectra ratios were plotted in Figure 6 and the concentration of Yellow was determined by measuring the amplitudes at 470 nm corresponding to the selected point in the previously obtained coincident spectra (see Figure 3).

In the same way, the spectra (K/S) of samples dyed with different concentrations of Golden Yellow in the

range 400-700 nm were stored and divided by the spectrum of the standard sample dyed with a binary mixture containing 0.5% Yellow and 0.5% Red. The derivative spectra were prepared and the concentration of Yellow was determined by measuring the amplitudes at 470 nm, as seen in Figure 7.

The performance of the developed derivative ratio spectra (K/S) and the normal Kubelka-Munk methods in determination of the magnitude of each dye concentration in samples dyed with different tricomponent mixtures of dyes is presented in Tables 2 and 3.

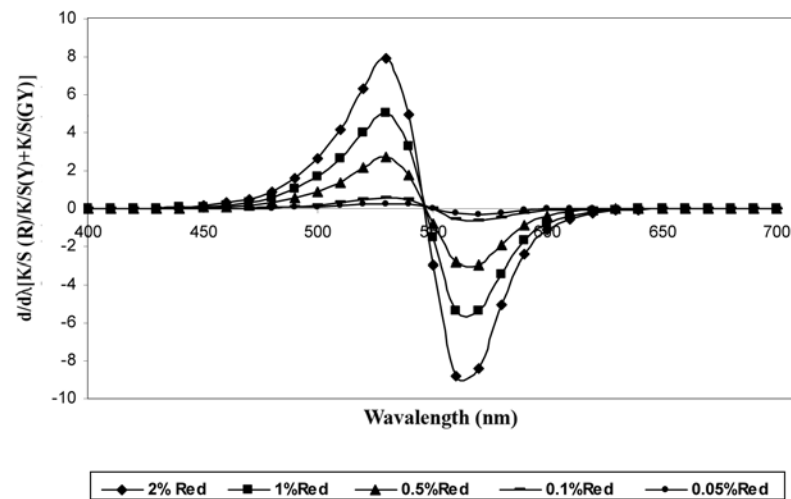


Figure 5: First derivative of the ratio spectra of samples dyed with different concentrations of Red dye (using a standard spectrum of a sample dyed with a binary mixture of 0.5% GY and 0.5%Y as divisor).

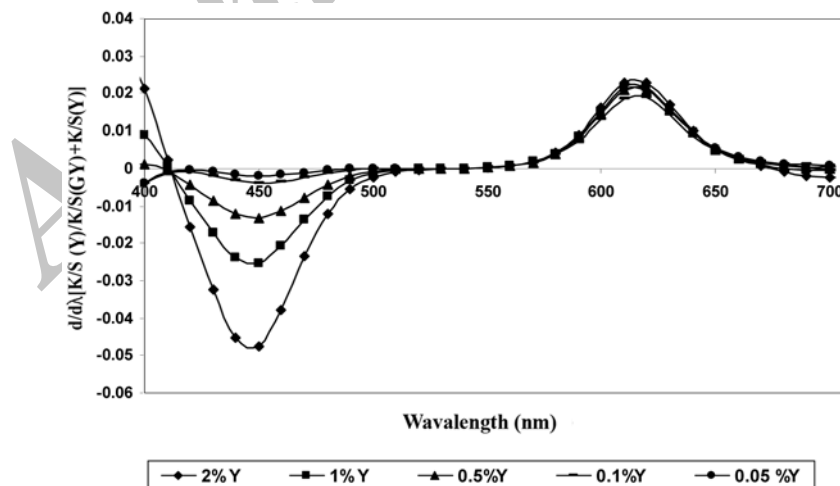


Figure 6: First derivative of the ratio spectra of samples dyed with different concentrations of yellow dye (using standard spectrum of a sample dyed with a binary mixture of 0.5% R and 0.5%Y as divisor).

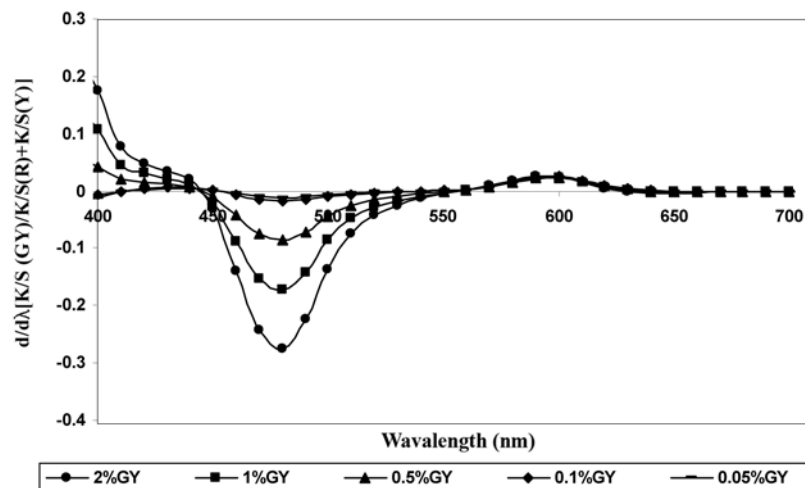


Figure 7: First derivative of the spectra ratio of samples dyed with different concentrations of Golden Yellow dye (using a standard spectrum of a sample dyed with a binary mixture of 0.5% Red and 0.5%Y as divisor).

Table 2: Relative errors (%) in determining the concentration of samples, using the proposed ratio derivative and normal Kubelka-Munk methods.

NO.	Actual concentration %(OWM)			Relative error (%) in determination of concentration					
	Red	Golden yellow	Yellow	Derivative method			Normal method		
1	0.1	0.1	0.1	59.56	9.89	26.37	63.43	12.61	26.96
2	0.1	0.1	0.5	25.42	26.44	22.59	37.14	31.13	35.03
3	0.1	0.1	1	11.43	52.65	2.42	20.39	64.18	9.76
4	0.1	0.5	0.1	23.68	25.48	36.21	32.16	21.92	67.19
5	0.1	0.5	0.5	20.02	15.33	14.62	21.54	17.36	53.83
6	0.1	0.5	1	9.89	6.29	5.49	7.52	6.83	10.52
7	0.1	1	0.1	28.93	4.58	34.59	3.29	4.36	43.87
8	0.1	1	0.5	11.77	1.06	12.48	1.35	1.75	37.81
9	0.1	1	1	0.34	2.35	8.71	1.43	2.89	16.19
10	0.5	0.1	0.1	12.64	10.44	17.11	17.76	10.25	53.41
11	0.5	0.1	0.5	2.47	15.65	2.12	2.10	18.80	2.32
12	0.5	0.1	1	15.60	51.85	8.71	17.75	65.58	19.68
13	0.5	0.5	0.1	0.25	14.53	3.63	2.59	12.03	11.66

Table 2: Continue

NO.	Actual concentration %(OWM)			Relative error (%) in determination of concentration					
	Red	Golden yellow	Yellow	Derivative method			Normal method		
				Red	Golden yellow	Yellow	Red	Golden yellow	Yellow
14	0.5	0.5	0.5	13.09	4.28	3.56	16.51	6.30	21.51
15	0.5	0.5	1	15.77	13.47	1.43	29.71	17.65	1.96
16	0.5	1	0.1	2.42	1.51	68.39	5.51	7.71	27.28
17	0.5	1	0.5	2.25	23.05	4.80	20.86	34.23	11.47
18	0.5	1	1	36.25	16.11	10.64	40.72	18.22	25.03
19	1	0.1	0.1	3.22	14.43	29.36	2.24	16.62	46.01
20	1	0.1	0.5	10.00	21.06	3.52	15.02	31.94	10.15
21	1	0.1	1	14.54	8.34	7.81	21.06	5.24	13.95
22	1	0.5	0.1	18.00	25.62	2.39	23.21	21.77	10.20
23	1	0.5	0.5	5.13	3.24	2.48	4.74	6.10	6.19
24	1	0.5	1	25.55	9.36	8.74	30.02	14.51	13.41
25	1	1	0.1	33.57	10.65	28.57	48.85	15.19	57.87
26	1	1	0.5	11.24	4.39	3.27	1.43	9.32	0.55
27	1	1	1	21.00	13.70	3.22	26.31	54.23	7.70

Note: Relative error (%) = $E_r(\%) = \frac{|C_p - C_a|}{C_a} \times 100$

Where C_p and C_a are the predicted and actual concentrations respectively

Table 3: Analysis of relative error (%) in determination of dye concentration.

Parameter	Method	Red	Golden Yellow	Yellow
Mean	Normal	24.66	24.67	37.98
	Derivative	16.23	17.19	24.5
Max	Normal	63.43	64.18	67.19
	Derivative	52.56	52.65	51.21
Min	Normal	1.43	1.75	0.55
	Derivative	0.25	1.06	1.27
SD	Normal	18.99	23.91	31.83
	Derivative	14.06	17.07	27.32

Note, SD: Standard deviation, Mean: Average relative error (%)

4. Conclusions

In This work, a derivative spectroscopic technique was applied for the quantitative analysis of samples dyed with ternary dye mixtures. The most important advantage of the proposed technique in comparison with the normal Kubelka-Munk method is that it does not need a system of equations with a number of unknowns to calculate the dye concentrations. As a result, the developed method is less sensitive to the spectrally similar dye mixtures. The analysis of the predicted magnitudes of concentrations via the proposed derivative and normal (K-M) methods,

shows the higher accuracy of the applied derivative method in determination of dye contents. The mean relative errors (%) in the estimation of Red, Golden Yellow and Yellow dyes concentrations via the derivative method, were 12.26, 9.25 and 13.82 and those of the normal Kubelka-Munk method were 24.66, 24.67 and 37.98 respectively.

In general, this method is very useful because it permits one to achieve an enhanced accuracy in determination of dyes concentration in samples dyed with tricomponent mixtures of dyes.

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