Ratio Derivative Spectrophotometric Study of Binary Mixture of Dye Solution

A. Shams-Nateri[a], S.H. Amirshahi[b]

[a] *Textile Engineering Dep., Guilan University, Rasht, Iran*
[b]*Textile Engineering Dep., Amirkabir University of Technology, Tehran, Iran*

Abstract

In this work, new method was used for prediction the concentration of binary mixture of textile dyes by using spectrophotometric data. New method is based on ratio derivative spectra of dyes mixtures solution. The obtained results by this method have been compared with usual spectroscopy methods. In special mixture with overlap spectra such as red and yellow mixtures, the derivative method was better than normal spectroscopy method.

Keywords: Color matching, Dye Solution, Ratio derivative, Spectroscopy.

1. Introduction

An absorption spectrum (a plot of A vs. λ) is used to show what wavelengths of light are absorbed by a sample. The peaks in the spectrum correspond to wavelengths that are strongly absorbed. These peaks are often referred to as "absorption maxima" and the wavelength at which these peaks occur are called λmax's. We can use λ max values to predict what color the sample may look like. When white light (containing all the visible wavelengths) is shined on a sample. Those colors corresponding to λ max's will be absorbed while the others pass through. The complementary color to the λ max will usually be the color that dominates and will therefore determine what color the sample appears. The absorption spectrum and λ max values can be used to help identify a substance, but are usually used to determine the amount of a known substance in a sample. This is done using Beer's Law and a calibration curve[1-5].

Under many circumstances, the absorbance of a solution at a particular wavelength of light is directly proportional to the concentration of the substance in solution. This is the Beer-Lambert Law (often just called Beer's Law) and is written as:

$$A = Log(\frac{I_0}{I}) = \varepsilon \times L \times C \qquad (1)$$

Where A= absorbance

ε = absorptivity (a constant for a substance at a given wavelength)
L = path length (the distance the light travels through the sample)
C = concentration

Typically, molarity is used for concentration, cm for path length and liter mole-1 cm-1 for absorptivity. Absorbance has no units, and the proportionality constants inherent in both the Beer and Lambert observations are combined into one factor known as the extinction coefficient, ε. An extinction coefficient is constant at a given wavelength for a given solute that absorbs light. Since absorbance values are unitless, the extinction coefficient is most often expressed in units of inverse concentration times inverse path length (i.e., $M^{-1}cm^{-1}$, $mM^{-1}cm^{-1}$, $(mg/ml)^{-1}cm^{-1}$).

Beer's law showed us that, at a given wavelength, the absorbance is proportional to the concentration of the absorbing compound in solution. This fact can be used to create a calibration curve. A calibration curve is prepared by plotting the absorbance of a series of standards (solutions of known concentration) at a particular wavelength (usually at a λ max) as a function of their concentration (use any units you choose as long as they are consistent). The result will be a straight line. If the unknown sample's absorbance is also measured, its concentration can be determined from the calibration curve.

In general, it is possible to determine the concentration of a colored species in a given solution by measuring the absorbance of the solution at a certain specific wavelength and comparing the value obtained with a calibration curve obtained at the same wavelength. The calibration curve consists of a plot of absorbance (vertical axis) against concentration (horizontal axis) for a number of solutions of known concentration. Such a plot is often called a Beer's law plot. This experiment will involve:

i.   preparing a series of solutions containing known concentrations of dye,
ii. selecting a suitable wavelength at which to make the absorbance measurements,
iii. measuring the absorbance of each of the solutions at the selected wavelength and constructing a calibration curve, and
iv. Determine the concentration of the "unknown" solution [1-5].

Since the practical introduction of the concept of drivatization of spectral data over last decades, the derivative Technique had received, until fairly recently, only sporadic attention from analysts working with UV-visible spectrophotometers. The uv-visible Technique in many instances is not enough to characterize adequately individual compounds in solution, particularly in presence of other absorbing molecular species and scattering particles. In these cases the broad bands and shoulders arise from the overlap of adjacent peaks, which can not be fully resolved even with the highest performance spectrophotometers.

The drivatization process of zero-order spectrum can lead to enhancement of the resolution of overlapping peaks and

elimination or reduction of back ground or matrix absorption. The derivative spectroscopy technique consists of calculating and plotting one of the mathematical derivates of a spectral curve. To give the first order derivative plot, The determined individual gradient values are plotted against the wavelength values. The derivative spectra are always more complex than the zero-order spectrum. This technique is either applied directly to the signals, or after the curve is fitted with numeric algorithms. The obtained spectra yield a more characteristic profile in comparison to the parent one. The Principles of derivative spectrophotometry have been described by talskey et al. Based on scientific literature, the various trends in application of derivative spectrophotometer can be distinguished. However the multi component analyses are the most numerous among others. Analysis of food, cosmetics colorant and dyes, and also Determination of organic compounds, can be classified in this group. In color industries, Color matching is defined a procedure of adjusting a color mixture until all visually apparent differences from a target color are eliminated. Different synthetic mixtures of colorants are usually used to produce certain types of shades. Probably one of the most important color problems of industries dealing with colorants and color matching is to find the proportions of the colorants required to produce a color match for a specimen showing the color of the customer's, choice. Hence determination of dye contents in Dyeing solution is necessary for an accurate color matching. UV-visible absorption spectroscopy is one of the use full techniques that have been used for quantitative determination of the dye components in their mixtures. In many instances because of spectral overlap of zero-order spectra, The simultaneous determination of colorants is not possible by direct absorption measurement. Derivative spectrophotometry is an analytical technique of great utility for resolving mixtures with overlapping spectra. The advantage of derivative UV-visible spectroscopy in quantitative analysis and interpretation of overlapping bands are well known[6-17].

In this work, derivative spectra was used to color matching textile dyes mixture. The intent of the present work was to apply the ratio derivative technique to predicting the dyes concentration in binary mixture.

2. Material and Methods:

In this work, two commercial direct dyes with overlapping spectra were used for synthesis binary mixture. Single and binary mixture of dyes was create with concentration of 0.0025, 0.005, 0.01, 0.015, 0.025, 0.05 gram per liter for red dye and 0.01, 0.025, 0.05, 0.075, 0.1, 0.125 gram per liter for yellow dye. The full visible spectra (380 nm to 700 nm) of dyes solution was measured by Cintra10 UV-Visible Spectrophotometer. Then, dye concentration of binary mixture solutions was predicted by normal and derivative spectroscopy methods.

In ordinary spectroscopy methods for binary combination, the concentration of components was predicted by using absorbance values in their λ_{max} as follow:

$$\begin{bmatrix} A_{\lambda 1} \\ A_{\lambda 2} \end{bmatrix} = \begin{bmatrix} l \times \varepsilon_{\lambda 1}^1 & l \times \varepsilon_{\lambda 1}^2 \\ l \times \varepsilon_{\lambda 2}^1 & l \times \varepsilon_{\lambda 2}^2 \end{bmatrix} \times \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} \qquad (2)$$

Where $\lambda 1$ and $\lambda 1$ are λ_{max} of components of binary mixture. A is the absorbance values, ε is absorptivity (a constant for a substance at a given wavelength), C is dye concentration.

In derivative methods, original function obtained from

Beer-Lambert's linear theory about absorbance of dyes mixture solution. in normal or zero-order spectra of binary mixture, there is following linear relationship between absorbance(A), absorptivity (ε) and concentration (C):

$$A_{\lambda 1} = l \times \varepsilon_{\lambda 1}^1 \times C_1 + l \times \varepsilon_{\lambda 1}^2 \times C_2 \qquad (3)$$

In first order ratio derivative spectroscopy, relative spectra was obtained by dividing absorbance spectra of mixture over absorbance of one component as standard. The firs order ratio derivative spectra was obtained by drivatization of relative spectra. The first order ratio derivative spectra depend on dyes concentration as follow:

$$\left(RA_{\lambda 1} \right)' = \frac{(RA_{\lambda i+1}) - (RA_{\lambda i})}{\lambda_{i+1} - \lambda_i} = \frac{d(RA_{\lambda i})}{d(\lambda_i)} = C_2 \times \left(\frac{\varepsilon_{\lambda 1}^1}{C_1^0 \varepsilon_{\lambda 1}^1} \right)' \qquad (4)$$

Similarly, the relationship between second order ratio derivative spectra and concentration of dyes are as follow:

$$\left(RA_{\lambda i} \right)'' = \frac{(RA_{\lambda i+1})' - (RA_{\lambda i})'}{\lambda_{i+1} - \lambda_i} = \frac{d^2(RA_{\lambda i})}{d(\lambda_i)^2} = C_2 \times \left(\frac{\varepsilon_{\lambda 1}^1}{C_1^0 \varepsilon_{\lambda 1}^1} \right)'' \qquad (5)$$

In ratio derivative spectroscopy method the effect of one component has been cancelled and the derivative spectra value depends on the concentration of other component.
In this work, the first and second order ratio derivative spectra of single and binary mixture of dyes was compared with zero order derivative spectra. In next step, ratio derivative spectra data was used to predicting dye concentration.

3. Results and Discussion:

The zero , first and second order derivative spectra of single solution of red and yellow dye respectively are shown in figures 1 to 6. As shown in this figure, in derivative spectra, number of peak is more than the zero order spectra. The new peaks are sharper than zero order spectra. Similar results have been achieved in comparison second order derivative spectra with zero and first order derivative spectra. Second order derivative spectra have more and sharper picks than zero and first order derivative spectra.
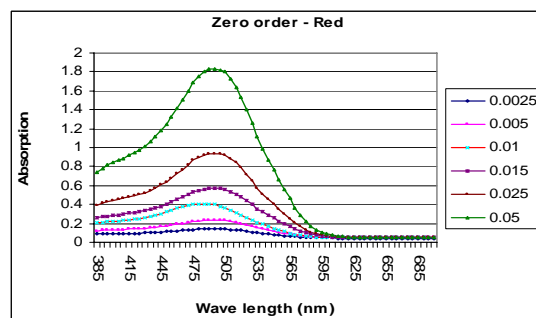

Figure 1. Zero-order derivative spectra of red dye
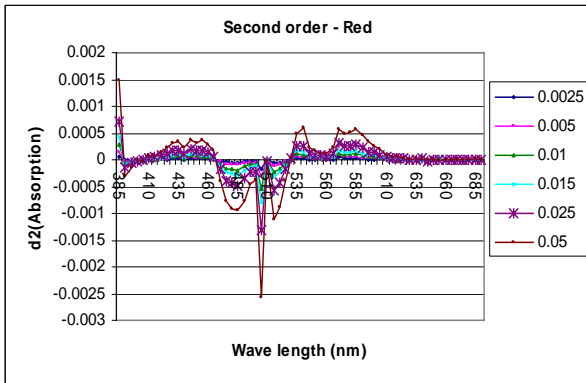
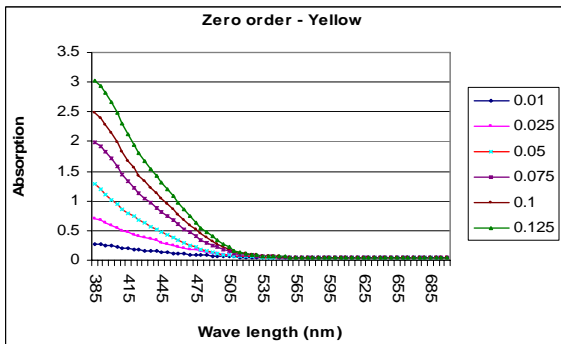Figure 2. First-order derivative spectra of red dye

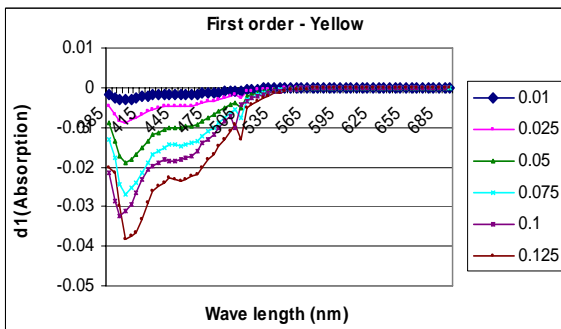Figure 3. Second-order derivative spectra of red dye

Figure 4. Zero-order derivative spectra of yellow dye
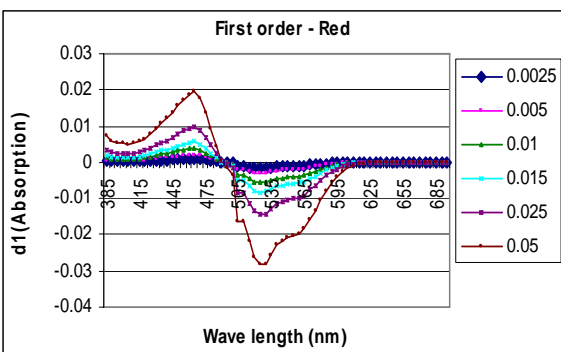

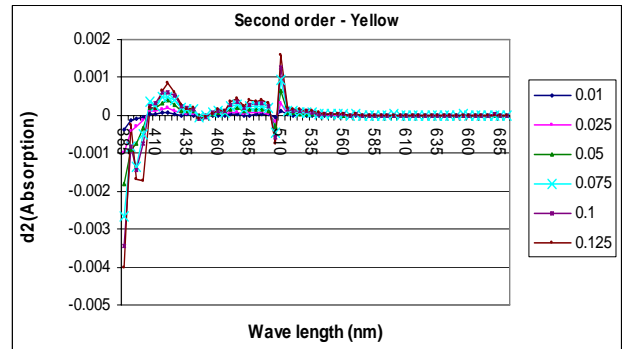Figure 5. First-order derivative spectra of yellow dye

Figure 6. Second-order derivative spectra of yellow dye

The first and second order derivative spectra of binary mixture of dyes was calculated. In derivative spectra, number of peak is more than the zero order spectra. The peaks of spectra become sharper in high order derivative spectra than zero order. In next stage, the zero, first and second order derivative spectra data have been used to predict dye concentration of binary mixture solution. The result of dyes concentration prediction of red and yellow dyes mixture are shown in table 1 as means of absolute difference between actual and predicted concentration. From this table, the results of high order derivative spectrophotometry are comparable with zero order.

Table 1. Dyes concentration prediction

No.	Method	Training		Testing	
		Red	Yellow	Red	Yellow
1	Zero order	0.001	0.0116	0.0008	0.0101
2	First order	0.00097	0.01110	0.00065	0.0082

4. Conclusion

In this work, initially, first order derivative spectra of single and binary mixture of textile dyes compared with zero order derivative spectra. Then, zero and first order derivative spectra data was used to predict dye concentration. In comparison spectra of dyes mixture solution, in derivative spectra, number of peak is more than the zero order spectra. The peaks of spectra become sharper in high order of derivative spectra than zero order. When two component of mixture have closely overlapping absorption spectra for example red and yellow mixture, the derivative spectrophotometry methods is more significant than ordinary techniques.

The color matching of binary mixture solution was done by using zero, first derivative spectra data. The results of high order derivative comparable with zero order. From obtained results, it can be stated that first derivative spectrophotometry offers a relatively simple, accurate and inexpensive method for color matching binary mixture of dyes. Specially, when components of mixture have closely overlapping absorption spectra, the derivative spectroscopy method is more significant advantage over normal spectroscopy techniques.

Reference:

[1] Gary, N. M;   "Modern Concepts of Color and Appearance"; Science Publishers Inc. U.S.A; 2000.

[2] .H. Logan ; "UV and Visible Spectrophotometry in Organic Chemistry"; http://members.aol.com/logan20/uv.html; 1997.

[3] ; "Spectrophotometric Analysis" ; http://www.chem.queensu.ca/PROGRAMS/UG/Firstyearlabs/apsc100/manual.htm

[4] ; "Beer's Law"; http://www.serverlogic3.com/lm/rtl3.asp?si=1&k=t%20vs .

[5] Warren J. Jasper, Eva T. Kovacs, and Gordon A. Berkstresser IV; " Using neural networks to predict dye concentrations in multiple-dye mixtures"; Textile Researcher Journal; 63(9); 545-551;1993.

[6] Talsky, G.,   "Derivative spectrophotometry", First edition, VCH, WEINHEIM.1994.

[7] Aydogmus, Z.,   S.M. Cetin and M.U. Ozgur;" determination of ascorbic acid in vegetables by derivative spectrophotometry"; Turk J. Chem. Vol. 26; 697-704; 2002.

[8] Alpdogan, G.; K. Karabina; S. Sungur; " Derivative spectrophotometric determination of caffeine in some beverages";   Turk J. Chem. Vol. 26; 295-302; 2002.

[9] Savitzky, A. and Golay, M.J.E. (1964) Smoothing and differentiation of data by simplified least squares procedures. Anal.Chem. 36: 1627-1639.

[10]   Bosch Ojeda, C., F. Sanchez Rojas, "Recent developments in derivative ultraviolet/visible Absorption spectrophotometry", Analytica Chimica Acta , 518 (2004), 1–24.

[11]   Kaprpinska, J., " Derivative spectrophotometry-recent applications and directions of developments",   Talanta , 64 (2004),   801-822.

[12]   Abdel-aziz,Y., EL.-sayed and Najeb A. EL-Salem, " Recent developments of derivative spectrophotometry and their analytical application",   Analytical Science, (2005) VOL, 21.

[13]   SacideAltın .O., Toptan, T. ," Simultaneous determination of Indigotin and Ponceau-4R in,food samples by using ,vierordt's method, ratio spectra first order derivative and derivative UV spectrophotometry", Journal of Food Composition and Analysis, 16 (2003) 517–530.

[14]   Aydogmus, Z., S.M. Cetin and M.U. Ozgur;" Determination of ascorbic acid in vegetables by derivative spectrophotometry", Turk J. Chem. Vol. 26; 697-704; 2002.

[15]   Alpdogan, G., K. Karabina; S. Sungur; " Derivative spectrophotometric determination of caffeine in some beverages";   Turk J. Chem. Vol. 26; 295-302; 2002.

[16]   Popovice, G., M. cakar; D. Agaba; " Determination of bifonazole in creams containing methyl- and propyl p-hydroxybenzoate by derivative spectrophotometric method"; Journal of pharmaceutical and biomedical analysis; 33; 131-136; 2003.

[17]   Micalizzi, D.C.,   N.B. Pappano; N.B. Debattia; " First and second order derivative spectrophotometric determination of benzyl alcohol and diclofenac in pharmaceutical forms; " Talanta; 47; 525-530; 1998.