Determination of Madder Dye Concentration via Derivative Spectrophotometry and Peak to Peak Technique

E. Ekrami, H. Goodarzian and M. Okazi

Islamic Azad University, Behshahr Branch, Behshahr, Iran

Abstract: In the present work, first and second derivative orders of the absorbance spectra were used in order to determine the madder concentration in different dye solutions. The difference between neighboring extremmum values at the second derivative spectra of the madder dye solutions was also used for determining the dye contents. The efficiency of methods in determination of dye concentration was evaluated via recovery factor and relative error (%). The obtained results show the higher accuracy of determination by caring out the measurements in first and second orders of absorbance derivative spectra. In addition the peak to peak technique in second order of derivative spectra was found to be the most precise method in determination of madder dye concentration.

Key words: Natural Dye · Madder · Concentration · Determination · Derivative · Peak to Peak

INTRODUCTION

The main principle in quantitative UV-visible spectrophotometry techniques is the linear relation between absorbance and concentration of either a dissolved sample, a transparent liquid or a solid which is given by Beer-Lambert law [1, 2].

$$A = \log(\frac{I_0}{I}) = alc \qquad (1)$$

Where A is the absorption at a specific wavelength (normally λ_{max}), a is specific absorbance or extinction coefficient, l is the path length and C is the concentration of dye.

An absorption spectrum (a plot A vs. λ_{max}) is used to show what wavelengths of light are absorbed by sample. The peaks in the spectrum correspond to the wavelengths that are strongly absorbed. These peaks are often referred to an absorption maxima and the wavelength at which these peaks occurred are called λ_{max}. These values can be used to predict what color sample may look like. When white light (containing all the visible wavelengths) is shined on a sample, those colors corresponding to λ_{max} will be usually 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 the λ_{max} values can be used to help identify the 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, 2].

Under many circumstances, the absorption of a solution at a particular wavelength of light is directly proportional to the concentration of the substance in solution.

Beer's Law shows that at a given wavelength, the absorbance is proportional to the concentration of absorbing compound in solution. This fact can be used to make a calibration curve. A calibration curve is prepared by plotting the absorbance of a series of standards (solutions of known concentrations) at a particular wavelength (λ_{max}) as a function of their concentration. In general it is possible to determine the concentration of colored species in a given solution by measuring the absorbance of the solution at a certain specific wavelength and comparing g the value with a calibration curve obtained at the same wavelength [1, 2].

Ideally, the absorbance that occurs during UV-visible measurements should be due only to the target analyte. In practice, however, absorbances that interfere with the measurements often occur for chemical or physical
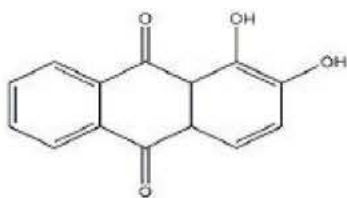
Corresponding Author: E. Ekrami, Islamic Azad University, Behshahr Branch, Behshahr, Iran.
E-mail: ekrami.ehsan@gmail.com.

Fig. 1: Alizarin (1, 2-dyhydroxyanthraquinone)

reasons. A recurring problem in quantitative analyses is scattering caused by particles suspended in solution. This problem is very common in determination of natural dye solutions because of presence scattering particles namely dust, parts of the plant etc.

Derivative spectrophotometry [3-9] is a spectral technique in which the rate of absorbance change is measured as a function of wavelength. Derivative spectra can be used to enhance differences among spectra, to resolve overlapping bands in qualitative analysis and, most importantly, to reduce the effects of interference from scattering, matrix, or other absorbing compounds in quantitative analysis. Principles of derivative spectrophotometry have been described by Talskey [8].

Madder plant, (rubia tinctorium L.), is on of the most important plant sources for the manufacture of red pigments. Its root contains principally alizarin (1, 2-dyhydroxyanthraquinone) (Fig 1) and several other anthraqinones in minor proportions such as purpurine, pseudo-purpurin, alizarin 2-methyl ester, Rubiadin, munjistin. [10-13].

Spectrophotometer determination of natural dye solutions usually encounters with serious difficulties due to the presence of light scattering particles in the solution. In this work it was tried to use the derivative spectrophotometry technique in order to eliminate the effect of light scattering particles in the dye solution and increase the accuracy of madder dye concentration determination.

Experimental: Madder plant, (rubia tinctorium L.) was purchased from Iranian traditional natural dyers. Absorption spectra of the dye solutions were measured using a (Cintra 10 uv-visible) spectrometer. Madder dye solutions containing different concentrations of the natural dye 0.6 '0.5 '0.4 '0.3 '0.2 '0.1 '0.075. '0.05 '0.0375)g/l) were used for spectrphotometric determinations. The accuracy of the methods in determination of dye concentration was evaluated by calculation of recovery factor (Eq 3) and relative error (Eq4).

$$R_f\left(\%\right) = \frac{C_p}{C_a} \times 100 \qquad (3)$$

$$E_r\left(\%\right) = \frac{\left|C_p - C_a\right|}{C_a} \times 100 \qquad (4)$$

Where C_p and C_a are the predicted and actual concentrations respectively.

RESULTS AND DISCUSSION

In spite of fine filtrations, solutions of natural dyes usually contain amounts of light scattering particles. On the other hand the amount of this particles differ from one sample to another and consequently the obtained absorbance spectra of the dye solution would be affected by this light scattering elements. The absorbance spectra of different concentrations of madder dye solution are shown in Fig 2.

Usually the best degree of linearity between concentration and absorbance can be obtained in the peaks. In case of madder dye solution, the best degree of linearity with correlation coefficient of (R_2=0.974) was obtained in 410_{nm}.

The first and second order derivative spectra of the madder dye solution are shown in Fig 3 and 4 respectively. As illustrated in Fig 6, the correlation coefficient increases with increase in the order of differentiation.

Application of derivative absorbance spectra enables us to use techniques such as peak to peak in which the difference between neighboring extremmum values at the derivative spectra of solutions can be used for determining the dye contents.

As seen in Fig.4 in second order absorbance spectra of the madder dye solution we can apply the P-P technique by using the difference between the absorbance magnitudes of wavelengths of 430 and 455nm.

In order to evaluate the efficiency of the techniques in determination of madder dye concentration, dye solutions of known concentration were prepared and subsequently the magnitude of dye in the sample was calculated by each of the methods. A shown in Fig. 1 and 2 the accuracy of dye concentration determination was improved by using the derivative spectra and peak to peak techniques. The results are average of six separate determinations.
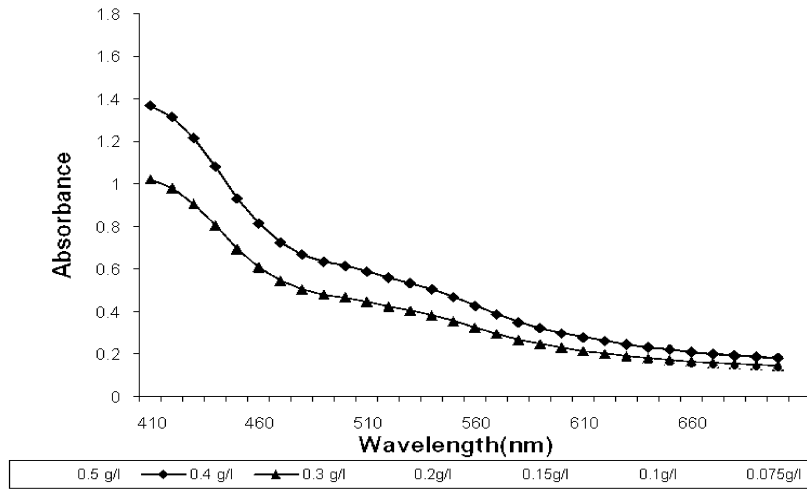
Fig 2: The absorbance spectra of different concentrations of madder dye solution
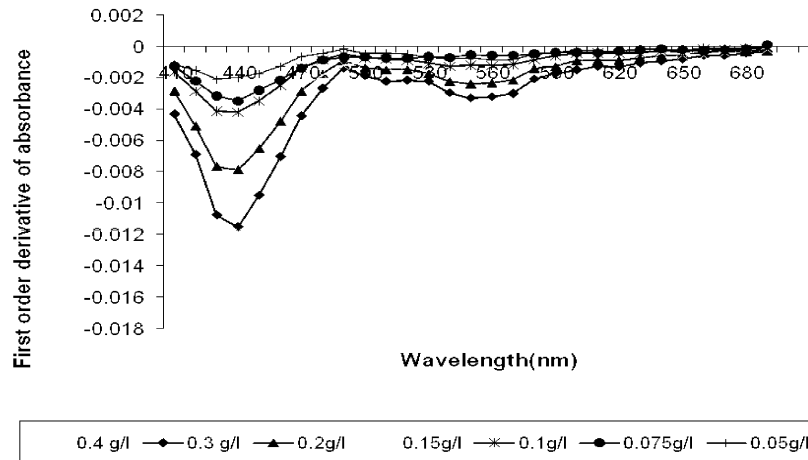

Fig. 3: First order absorbance spectra of different concentrations of madder dye solution
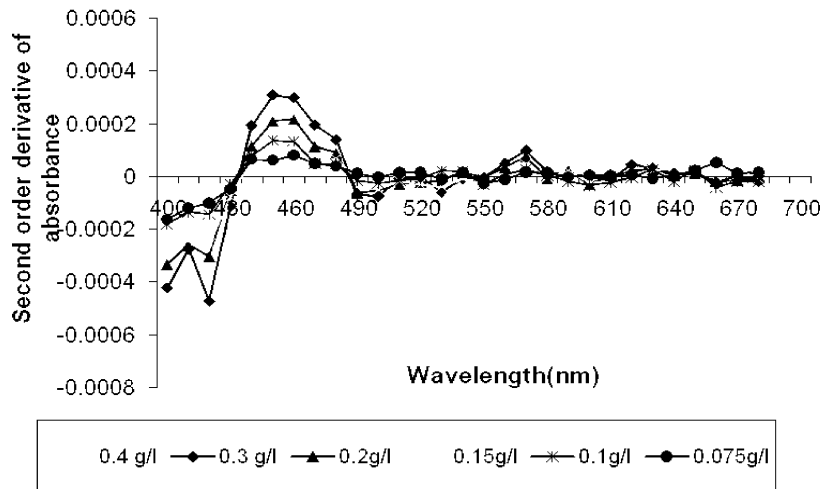

Fig. 4: Second order absorbance spectra of different concentrations of madder dye solution
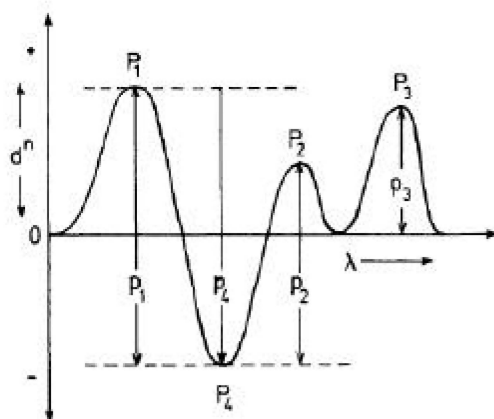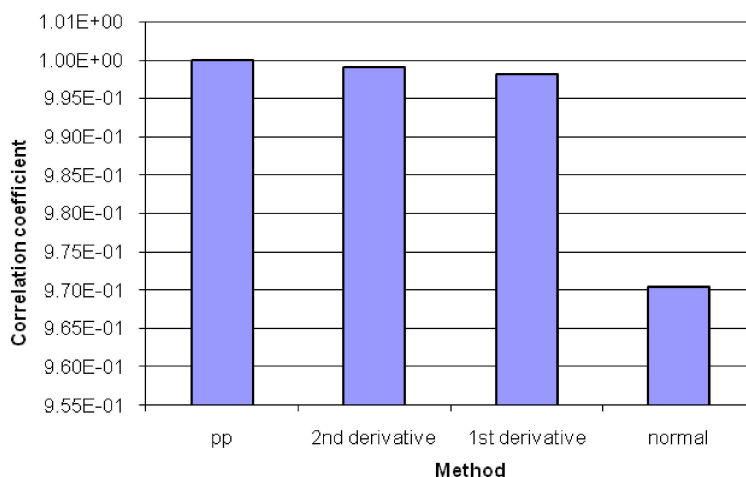
Fig. 5: Peak-Peak (PP) evaluation method

Fig. 6: Comparison of correlation coefficients obtained by different methods

Table 1: Analysis of recovery factor (%) of different methods in determination of dye concentration

Method	Average	Max	Min	SD
Normal	99.2	106.99	89.25	7.65
First order Derivative	101.42	105.91	97.22	2.92
Second order Derivative	98.99	101.33	103.91	2.42
Peak-Peak	100.49	101.22	99.24	0.75

Table 2: Analysis of relative error (%) of different methods in determination of dye concentration

Method	Average	Max	Min	SD
Normal	5.92	10.70	0.28	4.12
First order Derivative	2.04	3.91	0.90	2.14
Second order Derivative	0.97	1.28	0.13	0.54
Peak-Peak	0.71	1.21	0.36	0.30

CONCLUSION

Determination of madder dye concentration by using derivative absorbance spectra can increase the accuracy of estimations. In this approach by eliminating the effects of spectral interfering scattering particles present in the natural dye solution and through differentiation of absorbance spectra the accuracy of determinations increases. The peak to peak method resulted the best results and was found to be the most precise method in determination of madder dye concentration.

ACKNOWLEDGMENT

REFERENCES

1. Gary, N.M., 2000. Modern concepts of color and appearance", Science Publishers Inc., U.S.A. 2000.
2. Stearns, E.I., 1969. The Practice of Absorption Spectrophotometry, Wiley- Interscience.

3. Varian 'Instruments at Work', 1984. Application of derivative spectrophotometry UV-24.
4. Bosch Ojeda, C. and F. Sanchez Rojas, 2004. Recent developments in derivative ultraviolet/visible Absorption spectrophotometry Analytica Chimica Acta, 518: 1-24.
5. Varian' instruments at work, 1986. Application of derivative spectrophotometry UV, pp: 31.
6. Joanna Kaprpinska, 2004. Derivative spectrophotometry-recent applications and directions of developments. Talanta., 64: 801-822.

7. Abdel Aziz, Y. eEL. sayed, Najeb A. EL-Salem, 2005. Recent developments of derivative spectrophotometry and their analytical application. Analythical Sci., pp: 21.
8. Talsky, G., 1994. Derivative Spectrophotometry. First edition, VCH, Weinhem.
9. Savitzky, A. and M.J.E. Golay, 1964. Smoothing and differentiation of data by simplified least square procedures. Anal. Chem., 36: 1627-1639.
10. De Candolle, 1885. Origin of Cultivated Plants, New York, 237: 1885.
11. John Uri Lloyd, Punica Grantum The Western Druggist, Chicago, May, 1897.
12. Forbes, R.J., 1964. studies in ancient technology, Brill. Leiden.
13. Keheyan, Y. and L. Giulianelli, 2006. Identification of historical ink ingredients, e-ps, 3: 5-10.