

Evaluation of Vat Dye Solubility Using Derivative Spectrophotometry

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Abstract: Spectrophotometric evaluation and control of vat dye solutions usually encounters with serious difficulties due to the presence of light scattering insoluble dyes. In the preset study, virtual absorptions of light scattering dyestuff particles were eliminated through differentiation of spectra data and in this way the prerequisite of Beer-Lambert law validity was prepared. The calibration graphs were constructed by measuring the visible absorbance spectra of different concentrations of completely reduced vat dyes. Subsequently vat dye solubility was evaluated by determination of the extent of solute (leuco) dye concentration. This research is aimed to illustrate the applicability of derivative spectrophotometry in order to determine and control of vat dye solutions.

Key words: Vat die • Concentration • Derivative spectrophotometry • Beer Lambert

INTRODUCTION

Vat dyes are well known for the excellent properties they impart to textiles. These include not only resistance to light and washing, but also excellent fastness to chlorine bleach, dry cleaning, rubbing, perspiration and other color-destroying agencies encountered in textile use. The term “vat” dye is derived from the method of application of these colors rather than from any chemical family [1-5].

Generally vat dyes are water insoluble aromatic compounds and in this respect they are like pigments. There are two important types of vat dyes: anthraquinone derivatives and Indigoid derivatives [1]. However, technically these compounds are still classified as dyes because they are converted into soluble (leuco) forms during application to fibers. Vat dyes can be converted to the soluble leuco form by means of alkaline reduction with NaOH and Na₂S₂O₄ [6-8].

The vat pigment and the leuco compound often have quite different colors – blue and pale yellow in the case of Indigo – so the progress of the reduction is often easy to observe. After dyeing with the leuco compound, the pigment is regenerated in the dyed cotton by oxidation [7-10]. The overall process therefore involves three key steps [4, 5]:

- Reduction of the pigment to the soluble leuco compound, a process called vatting;
- Absorption of the leuco compound by the cotton during dyeing;
- Oxidation of the absorbed leuco compound in the cotton, reforming the insoluble pigment inside the fibers.

The use of strongly alkaline solutions (pH 12–14) for vatting and dyeing limits the use of most vat dyes to cellulosic fibers.

Recently, process optimization and waste management have become major topics for research groups involved in industrial chemistry. Thus, a significant part research groups is focused on environmental problems, particularly those originating from the textile industry. Textile dyeing and finishing can lead to effluents which have been subject to criticism for many decades.

For example dyestuffs such as sulfur and vat dyes, especially indigo, play an important role in today's dyeing industry (market about 120000 t/a) [8]. The present use of this dye category is based on the application of sodium dithionite to attain a water-soluble form of the dye by reduction (= leuco dye). Therefore the disposal of dyeing baths and rinsing water causes various problems,

because the necessary reducing agents will be ultimately oxidized into species that can hardly be regenerated. In addition, as a result of the considerable excess of reducing agent required to stabilize the oxidation-sensitive dyeing baths, the waste water may contain excess dithionite which affects aerobic processes in wastewater treatment. Therefore, the process of vat dyeing must be highly controlled.

Color controlling or shade controlling of dye solutions is a popular term for the industries dealing with colorants, namely textile, paint, printing ink industries, etc. A variety of analytical methods may be used for quantitative analysis of dye solutions; however among all the ultra violet (UV)-visible absorption, spectrophotometry is the most common procedure in determination of colorant contents in their solutions.

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 [11-13]:

$$A = \log\left(\frac{I_0}{I}\right) = alc \quad (1)$$

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.

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 reasons. A recurring problem in quantitative analyses is scattering caused by particles suspended in solution [13].

Derivative spectrophotometry 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 [14-19].

It is widely accepted that a Gaussian profile provides the best fit for peaks in UV-Visible spectra. A standard Gaussian curve function can be expressed as bellow [15, 16]:



Fig. 1: C.I.Vat Green 1 chemical structure

$$y = y_0 \exp\left\{-\ln 2 \left[2(x - x_0)/w\right]^2\right\} \quad (2)$$

Where: y_0 is the maximum band height at wavelength x_0 w is the bandwidth at half maximum band height (FWHM)

When the interference is due to a physical process (most often scattering), the interference at the analytical wavelength can be described by a polynomial [15, 16]:

$$A = a_0 + a_1\lambda^1 + \dots + a_n\lambda^n \quad (3)$$

Thus, for example, the contribution of an interfering background absorption, which can be described by a n th order polynomial interfering absorption band will be eliminated (deconvoluted) by the $(n + 1)$ th order derivative.

Spectrophotometer evaluation and control of vat dye solutions usually encounters with serious difficulties due to the presence of light scattering insoluble dyes. In This work it was tried to use the derivative spectrophotometry technique in order to eliminate the spectral scattering effect of insoluble vat dyes in the solutions and consequently exact determination of the soluble vat dye concentration.

Experimental: In this work, the spectrophotometric determinations were made by a UV-visible CINTRA 10 spectrophotometer. Absorbance Spectra of the working solutions were measured between 400 and 700nm. Soda and sodium hydrosulphite were supplied by Merk and the C.I. Vat Green 1 dye which its chemical structure is shown in Figure 1 was used in all the experiments.

In order to evaluate the solubility of the vat dye in different reduction sates, solutions containing 0.05 g/l of the vat dye and different concentrations of soda and sodium hydrosulphite (0.0, 3, 6, 9, 12 and 15 g/l) and (0.0, 0.01, 0.02, 0.03, 0.04 and 0.05 g/l) respectively were used.

RESULTS AND DISCUSSION

The first to second order derivative absorbance spectra of a 0.05 g/l solution of the vat dye in both insoluble and completely soluble conditions are shown

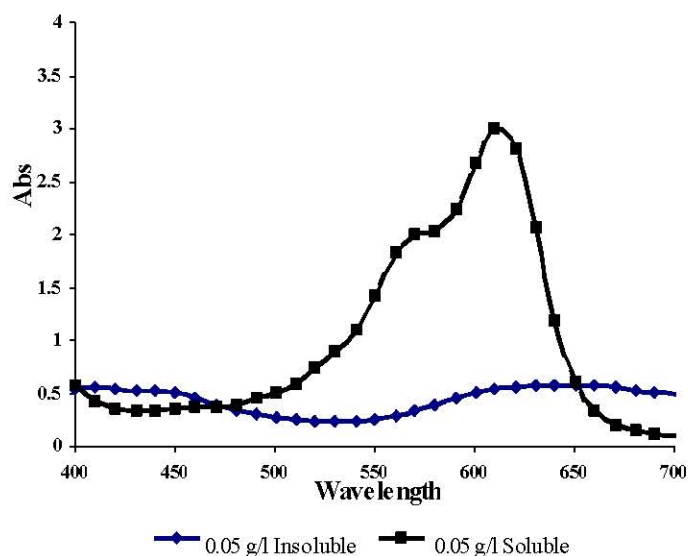


Fig. 2: Absorbance spectra of 0.05 g/l of the soluble and insoluble vat dye solutions

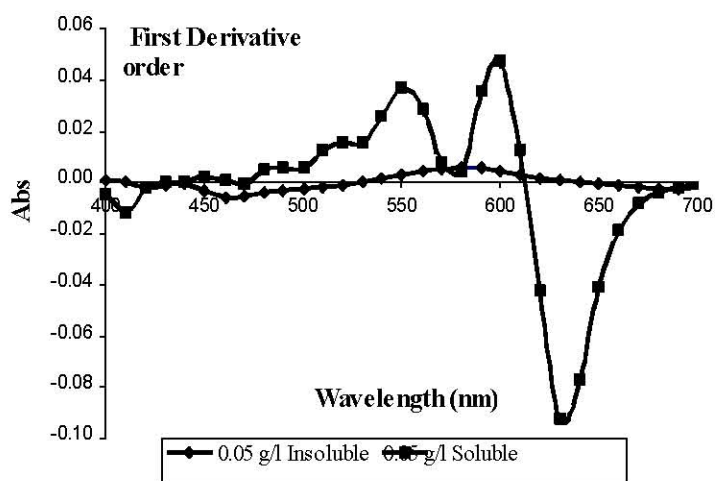


Fig. 3: Second order derivative spectra of 0.05 g/l of the soluble and insoluble vat dye solutions

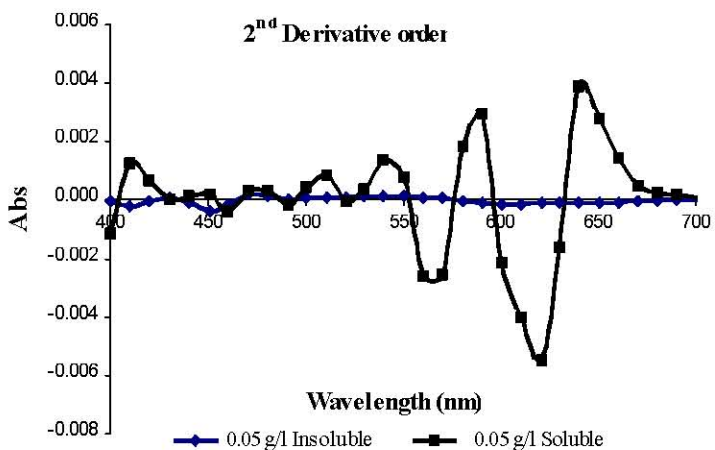


Fig. 4: Second order derivative spectra of 0.05 g/l of the soluble and insoluble vat dye solutions

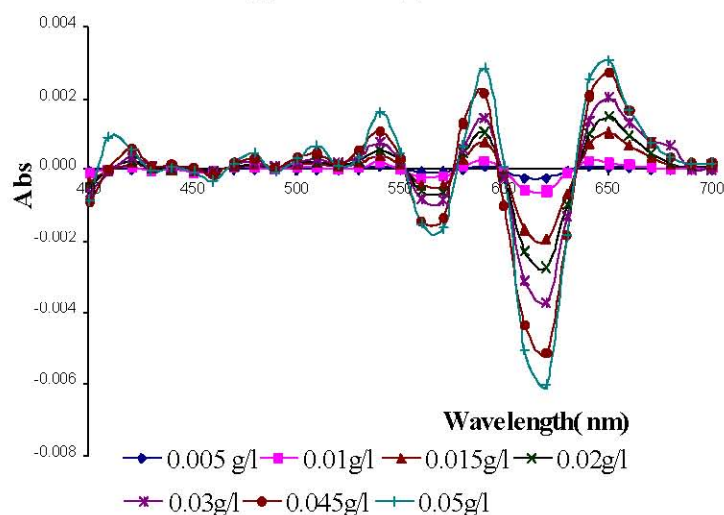


Fig. 5: Second order derivative spectra of different concentrations of the reduced vat dye

Table 1: Results of the reduced dye concentration estimation in different reduction conditions for a solution of 0.05 g/l of vat dye

No	Soda concentration (g/l)	Hydro sophite concentration (g/l)	Reduced dye Concentration (g/l)	Reduced dye (%)
1	3	0.01	0.0011	6.78
		0.02	0.0024	6.81
		0.03	0.0034	6.98
		0.04	0.0036	7.11
		0.05	0.0037	7.23
2	6	0.01	0.0049	9.77
		0.02	0.0160	32.91
		0.03	0.0240	49.21
		0.04	0.0250	51.86
		0.05	0.0290	58.34
3	9	0.01	0.0051	10.32
		0.02	0.0226	11.47
		0.03	0.0286	57.14
		0.04	0.0327	65.45
		0.05	0.0359	71.77
4	12	0.01	0.0060	12.23
		0.02	0.0280	57.64
		0.03	0.0370	75.62
		0.04	0.0410	82.66
		0.05	0.0450	91.23
5	15	0.01	0.0060	12.42
		0.02	0.0290	58.38
		0.03	0.0380	76.16
		0.04	0.0470	95.51
		0.05	0.0490	98.81

in Figures 2 to 4. As can be seen the absorbance spectra of the insoluble dye solution only show a broad band and no distinct absorption maxima can be observed. This can be attributed to the presence of light scattering insoluble vat dye in the solution. However in completely reduced condition, the absorbance peak at 610 nm appears. As illustrated in Figures 2 and 3 the differentiation process could lead to reduce the effects of scattering and ultimately their complete elimination.

In order to accurately adjust the condition for achieving the complete reduction of the vat dye, the amounts of alkali as well as reducing agent should be exactly being controlled.

Due to the presence of amounts of insoluble vat dyes in the dye solution, some degrees of errors in calculation of dye concentration by using normal spectrophotometric uv-visible methods are inevitable. In this way Spectrophotometric evaluation and control of vat dye solutions usually encounters with serious

difficulties when the degree of vat dye reduction is low. Application of derivative spectra of the vat dye solutions (in each degree of reduction) enables us to apply the Beer-Lambert's law in a correct manner and consequently exact determination of dye concentration through elimination of virtual absorptions of insoluble vat dyes. Therefore in order to determine the magnitude of reduced vat dye in different reduction conditions, second order derivative spectra of the vat dye were used. The calibration absorbance spectra of the vat dye are shown in Fig. 5 which are selected from different concentrations of completely reduced vat dye.

The results of leuco (reduced vat dye) magnitude determination under different reduction conditions in a solution of 0.05 g/l of the vat dye are given in the Table 1.

It can be seen that in different concentrations of soda, increasing the amount of the reducing agent (sodium hydrosulphite) leads to the increase in the amount of the leuco vat dye. The obtained results indicate that in lower levels of soda, the effect of hydrosulphite increase on degree of vat dye reduction is negligible. For example in concentration of 3 g/l of soda, increasing the amount of hydrosulphite does not affect the degree of vat dye reduction. This shows the importance of alkali condition on efficiency of vatting process.

CONCLUSION

In the preset study, virtual absorptions of light scattering dyestuff particles were eliminated through differentiation of spectral data and in this way the prerequisite of Beer-Lambert law validity was prepared. The developed approach can be used in order to exact determination of the vat dye concentration in dyeing solutions and consequently achieving the optimized reduction condition in vatting process.

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