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# Real-time Optical Measuring System for Dye Colour and Concentration—II. Dispersive Dye

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## ABSTRACT

*A real-time measuring method of a dispersive dye, i.e. oil dye, has been developed which enables us to measure the concentration and its fluctuation of the three base colours. The method is based on the light scattering theory and its principle requires three different lasers having the three base colours. The system consisted of a semiconductor laser and argon ion laser for light sources, a photodiode for a light detector and a personal computer for data processing. Detection sensitivity for the dye concentration was about 1 mg/l and was applicable for practical use.*

## 1 INTRODUCTION

We have previously reported on the real-time optical measuring method<sup>1</sup> and the monitoring system<sup>2</sup> for dye colour and concentration for ionic dye, i.e. water-soluble dye. In this case, a light attenuation method can be effectively applied since the light intensity passing through the dye decreases exponentially as dye concentration increases up to a range of practical concentration.

On the contrary, the light intensity decreases within an extremely small concentration range for a dispersive dye, i.e. an oil dye which is mainly used for a synthetic fibre. It is, therefore, necessary to dilute dye of practical concentration to a reasonable concentration. This gives up a real-time detection which is indispensable in a dyeing process. Our new method enables real-time detection.

The oil dye has roughly a spherical shape and is suspended in water with hydrophobia agent. It is then considered that the light intensity

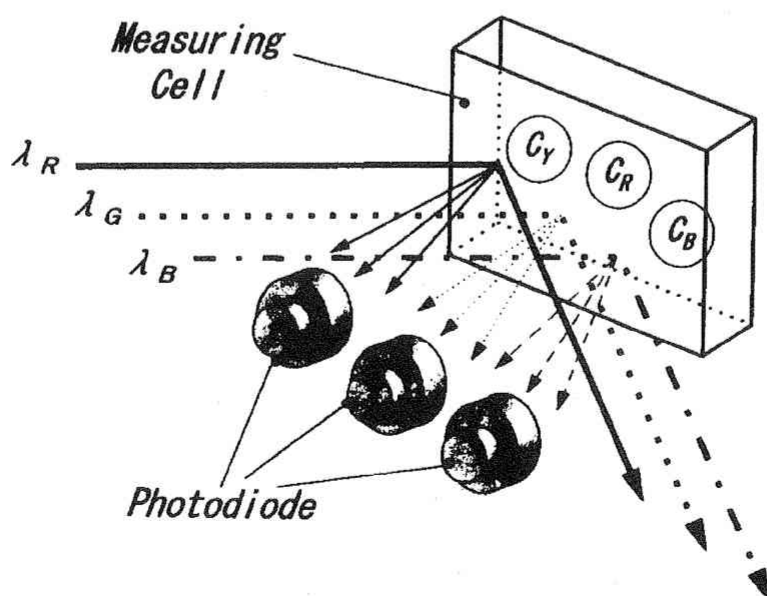
scattered on the dye sphere increases as the dye concentration increases. That is, the scattered light intensity may be applied for the measurement of the oil dye concentration. We call this 'the light scattered method'.

In this paper, the principle and the experimental result of the light scattered method are described, and the flexibility of the sensor is discussed from the viewpoint of practical use.

## 2 PRINCIPLE AND METHOD

The mathematical principle of the method is the same as used previously.<sup>2</sup> That is, three unknown parameters, i.e. each concentration of three base colour dyes, can be determined by solving a simultaneous cubic equations with three unknowns—but the method is physically quite different from the previous one, i.e. the scattered light intensity is used for three known parameters in this case. A transmitted light intensity was used for the known parameters in the previous method and an exponential function can be applied between incident and transmitted light intensities for ionic dye. Taylor expansions, however, must be used for oil dye since part of the relation is complicated, the reason of which will be discussed in Section 3. Thus, the method is, mathematically, applicable for popular use.

Figure 1 shows the principle of the method. Laser light containing the three base colours (red,  $\lambda_R$ ; green,  $\lambda_G$ ; blue,  $\lambda_B$ ) is guided into a measuring cell, in which three base colours of oil dye (red,  $C_R$ ; yellow,  $C_Y$ ; blue,  $C_B$ )



**Fig. 1.** Optical principle of the method. Part of the incident light of three base colours is scattered from an oil dye consisting of the three base dye colours.

are suspended. The oil dye scatters light on the surface. The scattered light intensity,  $I_d$ , is expressed by a Taylor expansion as follows:

$$I_d/I_i = K_0 + K_1n + K_2n^2 + K_3n^3 + \dots \quad (1)$$

where  $I_i$  shows the incident intensity of the laser light,  $n$  the concentration of the oil dye and  $K_i$  ( $i = 0, 1, 2, 3, \dots$ ) the scattering coefficient in a broad sense. In particular,  $K_0$  shows the scattered light intensity from a glass plate and pure water without dye. It is obvious from a physical point of view that  $I_d$  increases linearly with increasing dye concentration,  $n$ , if it is reasonably diluted. However, the relation between scattered light intensity and the dye concentration is not so simple in practice, as shown later (Fig. 4(b)). It depends not only on the dye concentration but also on a combination of dye colour and wavelength of the laser light.

The basic relation between scattered light intensity  $I_d$  and dye concentration  $\mathbf{n}(n_R, n_Y, n_B)$  is concretely expressed as follows:

$$\begin{aligned} I_{dR}(n_R)/I_{iR} &\equiv [\mathbf{a}_R][\mathbf{n}_R^j] \\ I_{dR}(n_Y)/I_{iR} &\equiv [\mathbf{a}_Y][\mathbf{n}_Y^j] \\ I_{dR}(n_B)/I_{iR} &\equiv [\mathbf{a}_B][\mathbf{n}_B^j] \end{aligned} \quad (2)$$

where  $I_{iR}$  and  $I_{dR}$  show an incident and scattered laser light intensities of wavelength  $\lambda_R$ ,  $j = 0, 1, 2$  and  $3$ , and the matrices  $[\mathbf{a}]$  and  $[\mathbf{n}^j]$  are expressed as follows:

$$\begin{aligned} [\mathbf{a}] &\equiv \begin{bmatrix} \mathbf{a}_R \\ \mathbf{a}_Y \\ \mathbf{a}_B \end{bmatrix} = \begin{bmatrix} \mathbf{a}_{0R}, \mathbf{a}_{1R}, \mathbf{a}_{2R}, \mathbf{a}_{3R} \\ \mathbf{a}_{0Y}, \mathbf{a}_{1Y}, \mathbf{a}_{2Y}, \mathbf{a}_{3Y} \\ \mathbf{a}_{0B}, \mathbf{a}_{1B}, \mathbf{a}_{2B}, \mathbf{a}_{3B} \end{bmatrix} \\ [\mathbf{n}_R^j] &\equiv \begin{bmatrix} 1 \\ n_R^1 \\ n_R^2 \\ n_R^3 \end{bmatrix}, \quad [\mathbf{n}_Y^j] \equiv \begin{bmatrix} 1 \\ n_Y^1 \\ n_Y^2 \\ n_Y^3 \end{bmatrix}, \quad [\mathbf{n}_B^j] \equiv \begin{bmatrix} 1 \\ n_B^1 \\ n_B^2 \\ n_B^3 \end{bmatrix} \end{aligned}$$

where  $[\mathbf{a}]$  shows a scattered coefficient in a broad sense, as shown in eqn (1). The same relations are given for the laser light of wavelength  $\lambda_G$  by replacing  $[\mathbf{a}]$  with  $[\mathbf{b}]$ , and  $I_{dR}$  and  $I_{iR}$  with  $I_{dG}$  and  $I_{iG}$ , and also, for the laser light of wavelength  $\lambda_B$  by replacing  $[\mathbf{a}]$  with  $[\mathbf{c}]$ , and  $I_{dR}$  and  $I_{iR}$  with  $I_{dB}$  and  $I_{iB}$ . These 36 scattering coefficients were determined by the method of least squares from nine relations between scattered light intensity and dye concentration obtained experimentally.

The scattered light intensity from mixed dye may be superposed of each light intensity from three colour dyes. This is indispensable to our method and is realized within a reasonable range of dye concentration, as shown

in Fig. 3. That is, the expressions for this superposition principle can be shown as follows;

$$\begin{aligned}
 \{I_{dR}(n_R + n_Y + n_B)/I_{iR} - 1\} &= \{I_{dR}(n_R)/I_{iR} - 1\} + \{I_{dR}(n_Y)/I_{iR} - 1\} \\
 &\quad + \{I_{dR}(n_B)/I_{iR} - 1\}, \\
 \{I_{dG}(n_R + n_Y + n_B)/I_{iG} - 1\} &= \{I_{dG}(n_R)/I_{iG} - 1\} + \{I_{dG}(n_Y)/I_{iG} - 1\} \\
 &\quad + \{I_{dG}(n_B)/I_{iG} - 1\}, \\
 \{I_{dB}(n_R + n_Y + n_B)/I_{iB} - 1\} &= \{I_{dB}(n_R)/I_{iB} - 1\} + \{I_{dB}(n_Y)/I_{iB} - 1\} \\
 &\quad + \{I_{dB}(n_B)/I_{iB} - 1\}
 \end{aligned} \tag{3}$$

The left-hand terms in these equations are the total light intensities from the oil dye mixed with three base colours and then the known quantities. On the right-hand side, the unknown quantities, i.e. the dye concentrations  $n(n_R, n_Y, n_B)$ , are contained in the form of eqn (2). The equation can be solved by the Levenberg–Marquardt–Morrison method.<sup>3</sup>

Figure 2 shows the system for the measurement. A semiconductor laser was used for red light of wavelength  $\lambda_R = 670$  nm and a multiline Ar ion laser was used for green and blue light of wavelengths  $\lambda_G = 515$  nm and  $\lambda_B = 458$  nm, respectively. The output intensity of the laser light scattered from the oil dye filled in the cell was measured on a photodiode and converted to an electric signal. The signal was amplified, sampled and digitized in 12 bits. The maximum sampling frequency of the data acquisition was limited to about 1 kHz by the A/D converter. The digitized signal was used to obtain the relations between the scattered laser light intensity and the dye concentration. The 36 scattering

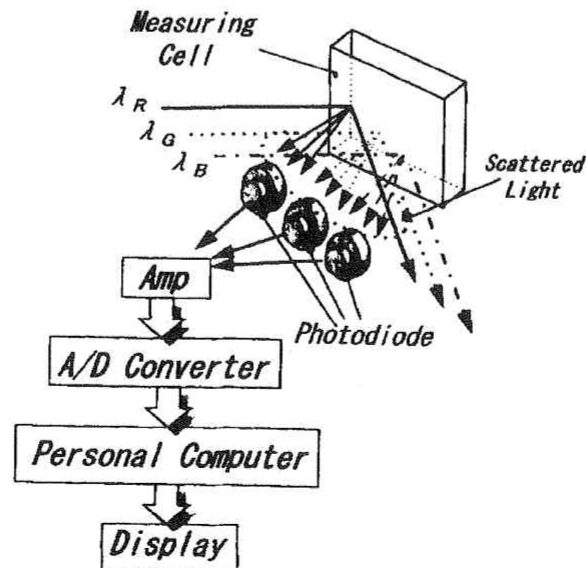
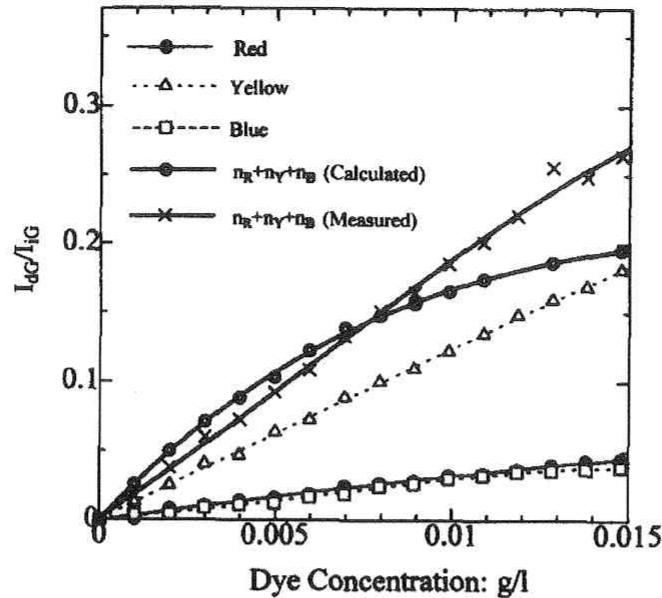


Fig. 2. Optics and sensor system.



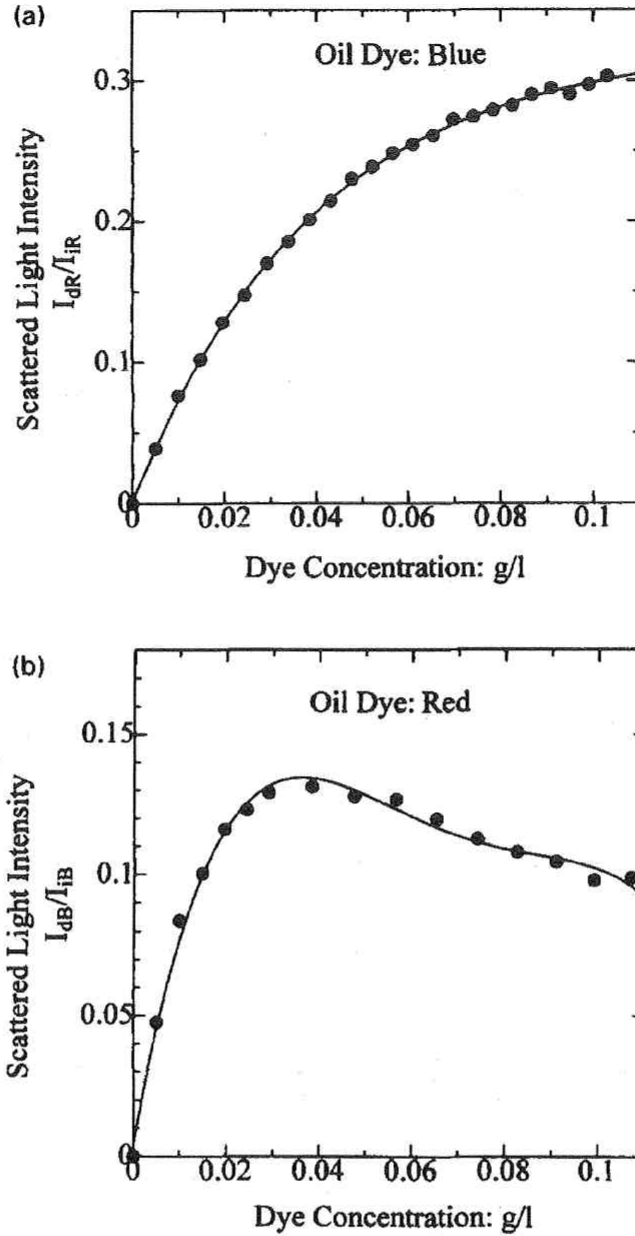
**Fig. 3.** Scattered light (wavelength of 670 nm) intensity from each colour of dye concentration and the one for mixed dye concentration with a theoretical intensity.

coefficients were obtained by the method of least squares from these relations and were used in eqn (3) to calculate the concentration. The results were displayed on the monitor. All the data in this calculation were obtained by averaging 80 samples.

### 3 EXPERIMENTAL RESULTS AND DISCUSSION

We performed first of all, an experiment to confirm the superposition principle. Figure 3 shows the result. As is shown, the scattered light intensity from the mixed oil dye almost equals the sum of light intensities from each colour of dye. The relation, however, can be realized only in the limited range of concentration up to about 0.01 g/l. The concentration of 0.01 g/l is slightly insufficient for a practical dye concentration used in the dye process. This is the only one weak point of our method. The actual sensitivity of the method depends on this accuracy of the superposition principle. However, the small change of dye concentration in the neighbourhood of practically used concentrations may be detected with high sensitivity by this method, which is discussed below. This seems to be most important in practical use.

Figures 4(a) and (b) show examples of the relation between scattered light intensity and dye concentration. Figure 4(a) shows an example of a simple relation and Fig. 4(b) a relatively complicated one. In Fig. 4(a), it is naturally considered, in the diluted dye, that the scattered light intensity



**Fig. 4.** Scattered light intensity for dye concentration: (a) for laser light of wavelength  $\lambda_R = 670$  nm and for blue dye; (b)  $\lambda_B = 458$  nm and red dye.

increases linearly as the number of dye particles in the unit volume increases, i.e. dye concentration,  $n$ . The light intensity, however, may become proportional to  $n^{2/3}$  since the scattered light from the inner area cannot pass through the dye cell to the photodiode due to a screening effect of the outer particles, and then the effective scattered light into the photodiode results from only an extremely thin layer of the surface. In Fig. 4(b), on the contrary, the complexity may be caused by the scattering and absorption of laser light on the dye particle. However, it can easily be fitted to the experimental results with high accuracy by using a Taylor expansion up to  $n^3$  terms. The other relations were obtained for all



TABLE 1

Scattering Coefficients Obtained from the Relation Between the Scattered Light Intensity and the Dye Concentration by the Least Squares Method for all Combinations of Light Colours and Dye Colours

| $\lambda$   | $C$      | Scattering coefficient |         |        |         |         |
|-------------|----------|------------------------|---------|--------|---------|---------|
|             |          | $j$                    | 0       | 1      | 2       | 3       |
| $\lambda_R$ | $a_{jR}$ |                        | 1.2015  | 205.49 | 171.41  | -4998.2 |
|             | $a_{jY}$ |                        | 1.0056  | 99.099 | 306.93  | -1964.3 |
|             | $a_{jB}$ |                        | 1.0665  | 106.51 | -1068.4 | 3930.5  |
| $\lambda_G$ | $b_{jR}$ |                        | 1.0270  | 29.693 | -144.21 | 2100.3  |
|             | $b_{jY}$ |                        | 0.84900 | 184.24 | -1224.6 | 2855.9  |
|             | $b_{jB}$ |                        | 1.0246  | 28.167 | -314.25 | 1162.4  |
| $\lambda_B$ | $c_{jR}$ |                        | 1.0573  | 21.224 | -330.86 | 1426.9  |
|             | $c_{jY}$ |                        | 1.0703  | 37.943 | -599.78 | 2970.7  |
|             | $c_{jB}$ |                        | 1.0180  | 21.583 | -191.84 | 544.36  |

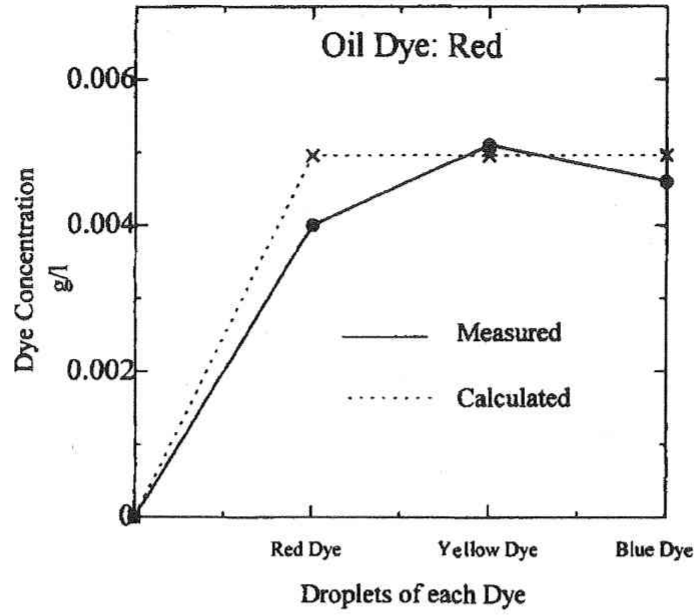
combinations of the three base colours of dye and laser light. All the scattering coefficients were obtained from these nine relations between scattered light intensity and dye concentration by the least squares method.

Table 1 shows all the coefficients. The coefficients independent of the dye concentration, i.e.  $a_0$ ,  $b_0$  and  $c_0$ , have to be one essentially, as seen in eqn (1), and almost equal to one practically as shown in this table.

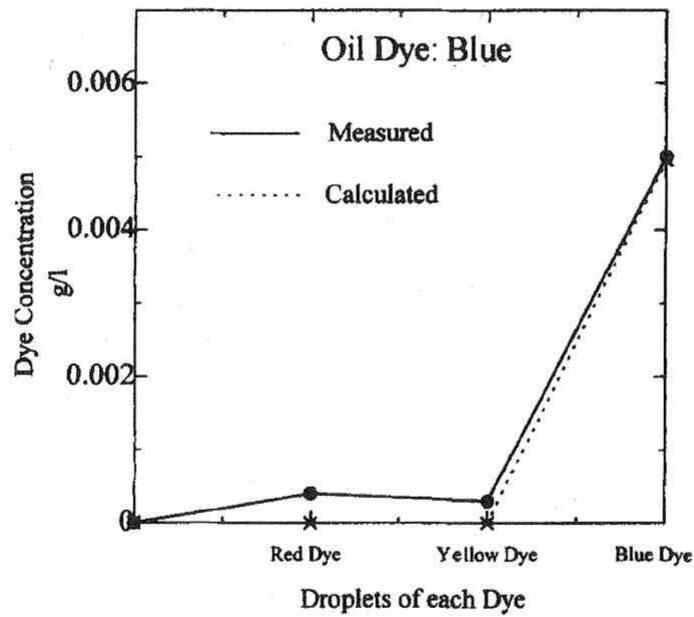
The experiment of increasing each colour dye successively was carried out to confirm the reliability of the method. The dye concentration in the cell filled with pure water was increased successively by the droplets of high concentration dye. Figures 5(a) and (b) show examples of the calculated concentration from eqn (3) and the theoretical one for blue and red dye, respectively. The experimental sensitivity is restricted to the error between calculated and theoretical concentrations. It can be seen that the experimental sensitivity is about 1 mg/l, which is sufficient for practical use.

As discussed above, the reliability of this method is based on the fact that the superposition principle is realized. The concentration range of high accuracy is between 0 and 20 mg/l, which is inadequate in practical use. However, the small change of dye concentration  $\Delta n$  around the practically used concentration  $n_0$  due to the small change of scattered light intensity  $\Delta I_d$  can be calculated by using the differential coefficient of the graphs in Fig. 3,  $(I_d)'_{n=n_0}$ . Since the relation between scattered light





(a)



(b)

**Fig. 5.** Calculated dye concentration and the real one, i.e. theoretical concentration, for the droplets of each dye into the water: (a) for red dye; (b) for blue dye.

intensity  $I_d$  and the dye concentration  $n$  can be expressed as in eqn (2),  $\Delta n$  can be expressed as follows:

$$[\Delta n] = [(I_d)'_{n=n_0}]^{-1} [\Delta I_d] \quad (4)$$

In this sense, Fig. 5 shows the results around  $n = 0$ .

#### 4 CONCLUSION

A real-time measuring method has been developed for oil dye colour and concentration detection. The system consisted of a semiconductor laser and an argon ion laser, a photodiode as a light detector and a personal computer.

The sensitivity of the method was about 1 mg/l and may be satisfactory for dyeing machines presently on the market. The system can then be effectively used for monitoring or detecting a small change of dye concentration. The method is based on the principle of light scatter and is applicable for dispersive dyes, etc.

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