

New spectroscopic method for the determination of optical rotatory dispersion

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A new spectroscopic methodology is proposed to measure optical rotatory dispersion (ORD) of optically active media. ORD is obtained from a three-step phase shifting algorithm using transmission spectra taken at three independent probing angles. Optical rotation angles of four sugar solutions are investigated. The results obtained by using the new method show excellent agreement with the reference data, indicating the new method can be used as a reliable way for studying ORD of optically active media.

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Optical rotatory dispersion (ORD)^[1], which is the change of optical rotation with wavelength, is an attractive tool for characterizing optically active samples^[2–4]. The main experimental methods devised in the past for the determination of ORD are based on two substantially different approaches^[5,6]: the null-point methods and the ratio methods. Under the null-point methods, the null-point-seeking procedure is carried out at each wavelength, making spectropolarimeters based on the methods very expensive. The ratio methods, on the other hand, are considered to be much simpler since the experimental determination of ORD can be accomplished using a simple polarizer-sample-analyzer assembly (Fig. 1) placed in the sample compartment of a spectrometer^[5–16].

The ratio methods can be classified into two groups: (1) those based on polarization angle modulation^[5–7,9–13], and (2) those based on sample-analyzer position alternation^[8,15,16]. Interferences from sample absorption and scattering are cancelled in all ratio methods.

Under the polarization angle modulation, two detector outputs are recorded with the polarization axis of the analyzer (A) aligned at $+\theta$ and $-\theta$ with respect to that of the polarizer (P). The direct ratio^[7,9–12], ratio minus its reciprocal^[11], and the difference to the sum ratio^[9,11,13,14] of the two outputs are used to extract the optical rotation (α). The advantage of this methodology is its straightforward experimental procedure since only simple rotation of the analyzer is involved, while the disadvantage is the complicated relationship that links each ratio to trigonometric functions of α and θ ^[5,6,9–13]. Exact solution is available only to the direct ratio method^[9], and typically first-order approximation of the corresponding Taylor series is proposed for extracting α ^[5,6,9,11–13]. The theoretical error, due to the first-order approximation, depends on the value of α , choice of θ , and the specific ratio method used. For example, when $\alpha=0.1$ rad and $\theta=\pi/4$ rad, the theoretical error ranges from 20% to 0.7% for the three ratio methods^[11].

Under the sample-analyzer position alternation, in contrast, the first detector output is recorded using the as-

sembly layout shown in Fig. 1 with the polarization axis of polarizer aligned at the angle θ with respect to that of the analyzer, and the second detector output is recorded with relative position of the sample and that of the analyzer switched while the angle θ remains the same^[8,15,16]. The advantage of this method is its straightforward relationship between the optical rotation (α) and the ratio of the first detector output against the second one, $R=\cos 2(\theta+\alpha)/\cos 2(\theta)$ ^[8,15,16], while the disadvantage is the relatively complicated experimental procedures for switching optical components, which could introduce alignment error especially when the size of the sample compartment is small and optical alignment is difficult^[11].

For all ratio methods, the effects of stray light and the residual transmission when the polarizer and analyzer are aligned normal to each other are treated as noise components for the determination of optical rotation α ^[6,12–14]. How to eliminate the noise components has not been investigated in the previous ratio methods. Furthermore, the calibration of angle θ , the angle between the polarization axis of the polarizer and that of the analyzer, is vital for the accurate determination of optical rotation α , especially when α is small. However, the effect of the systematic error in θ , $\Delta\theta$, the difference between the value determined from the markings of the polarizer and analyzer holders and the actual value of θ , has not been addressed before.

In this study, a new spectroscopic method is demonstrated for the accurate determination of ORD without potential drawbacks discussed above. This unique method provides straightforward relationship between the optical rotation α and transmission spectra taken at three different angles of θ , does not require re-alignment of any optical components, is capable of the determination of optical rotation α without any approximation and inherent theoretical error, is immune to the effects of stray light and the residual transmission of the polarizer and the analyzer, and especially, it eliminates the effect of the systematic error $\Delta\theta$.

Figure 1 illustrates the optical setup for the new spec-

troscopic methodology. As shown by the figure, the light emitted from the lamp (QTH), after dispersed by the monochromator (M), is split into the reference beam (W_R) and the sample beam (W_S) by the beam splitter (BS). The reference beam (W_R), after passing through the sample compartment, is collected by the reference detector (D_R). The sample beam (W_S), after being reflected by the mirror (RM), passes through the polarizer (P), the sample (S), and the analyzer (A), reaches the sample detector (D_S). The reference detector (D_R) and the sample detector (D_S) are assumed to be insensitive to the polarization status of the incoming beam. When the sample is an optical cell containing solution of optically active molecules, the optical transmission can be expressed by the following equation^[6,8,11]

$$T(\lambda) = T_0(\lambda)10^{-k(\lambda)lc} \cos^2[\theta - \alpha(\lambda)] + \phi(\lambda), \quad (1)$$

where $k(\lambda)$ is the coefficient accounting for the absorption and scattering of the solution at each wavelength λ , l is the optical path length of the cell, c is the concentration of the optically active molecule in the solution, $\alpha(\lambda)$ is the optical rotation, $T_0(\lambda)$ accounts for the optical transmission of all optical components except the solution, and θ is the angle between the polarization axis of the polarizer and that of the analyzer. The angle θ is defined as the detection angle in rest of this article. The detection angle θ is positive if the polarization axis of the analyzer is rotated clockwise from $\theta=0^\circ$ when facing the light traveling through the sample. Similarly, the sign of $\alpha(\lambda)$ is positive if the polarization direction of the sample beam is rotated clockwise when facing the light as it leaves the sample. The term $\phi(\lambda)$ in the above equation accounts for the effects of stray light and residual transmission when the polarizer and analyzer are aligned normal to each other. Equation (1) can be modified as

$$T(\lambda) = A(\lambda) + B(\lambda) \cos[2\theta - 2\alpha(\lambda)], \quad (2)$$

$$A(\lambda) = 0.5T_0(\lambda)10^{-k(\lambda)lc} + \phi(\lambda), \quad (3b)$$

$$B(\lambda) = 0.5T_0(\lambda)10^{-k(\lambda)lc}. \quad (3b)$$

Equation (2) is similar to that used in the area of phase shifting interferometry^[17]. Therefore, the optical rotation $\alpha(\lambda)$ can be extracted using a three-step phase shifting algorithm according to the following equation, with three transmission spectra $T_i(\lambda)$ ($i=1, 2, 3$) taken at three independent detection angles, $\theta=0^\circ$, 45° , and 90° , respectively:

$$\alpha(\lambda) = \frac{1}{2} \left\{ \arctan \left[\frac{2T_2(\lambda) - T_1(\lambda) - T_3(\lambda)}{T_1(\lambda) - T_3(\lambda)} \right] \right\}. \quad (4)$$

In Eq. (4), both $A(\lambda)$ and $B(\lambda)$ are cancelled, making the new method immune to the effects of absorption and scattering of the solution, and in particular, immune to the effects of stray light and residual transmission of the polarizer and analyzer.

The systematic error $\Delta\theta$ is defined by

$$\Delta\theta = \theta_a - \theta, \quad (5)$$

where θ_a is the apparent probing angle determined from the markings of the holders for the polarizer and analyzer. Substituting Eq. (5) into Eq. (2), one obtains

$$T^a(\lambda) = A(\lambda) + B(\lambda) \cos \{2\theta_a - 2[\alpha(\lambda) + \Delta\theta]\}. \quad (6)$$

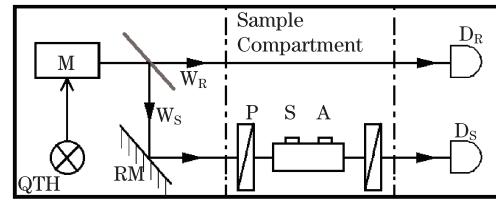


Fig. 1. Experimental layout for the new spectroscopic methodology.

Further, by taking three transmission spectra, $T_i^a(\lambda)$ ($i=1,2,3$), at the apparent probing angles, $\theta_a = 0^\circ$, 45° , and 90° , and comparing Eq. (6) with Eqs. (2) and (4), one obtains the apparent optical rotation $\alpha'(\lambda)$:

$$\alpha'(\lambda) = \alpha(\lambda) + \Delta\theta = \frac{1}{2} \left\{ \arctan \left[\frac{2T_2^a(\lambda) - T_1^a(\lambda) - T_3^a(\lambda)}{T_1^a(\lambda) - T_3^a(\lambda)} \right] \right\}. \quad (7)$$

The apparent optical rotation $\alpha'(\lambda)$ equals the systematic error $\Delta\theta$ when $\alpha(\lambda)=0$. Therefore, $\Delta\theta$ can be determined through Eq. (7) by taking another three transmission spectra $T_i^a R(\lambda)$ ($i=1,2,3$) at the same apparent probing angles, $\theta_a=0^\circ$, 45° , and 90° , with the sample cell removed from the sample compartment. The optical rotation $\alpha(\lambda)$ can then be determined by subtracting $\Delta\theta$ from $\alpha'(\lambda)$.

All spectroscopic measurements were carried out using a commercial computer-controlled dual-beam UV-VIS spectrometer (Lambda-14, Perkin-Elmer). Detectors of the spectrometer were insensitive to the polarization status of the incoming beams. The employment of the dual-beam spectrometer ensured that the measurement results were not affected by the power drifting of the light source. All spectra were collected in the range from 400 to 750 nm with 0.5-nm data interval and 60-nm/min scanning speed. For each spectrum, the baseline was taken with the polarizer-sample-analyzer assembly removed from the sample compartment. Dichroic sheet polarizers (CVI Melles Griot, 03FPG003, 380–780 nm) were used as both the polarizer (P) and the analyzer (A). Extinction ratios of the polarizer and the analyzer were from $10^4:1$ to $10^6:1$. The polarizer and the analyzer were both mounted on the polarizer holders (CVI Melles Griot, 07HPR221) with 360° rotation capability and 1.0° interval. The rotation accuracy of the polarizer holder was within $\pm 0.15^\circ$ under the experimental condition. Sucrose (Fisher Scientific, S5-500), D(+)-glucose (ACROS, 170080010), and D(-)-fructose (Fisher Scientific, L96-500) solutions were prepared by dissolving corresponding chemicals into HPLC grade water (Fisher Scientific, W5-4). The optical cell with 5-cm light path length was purchased from Starna Cells, Inc. (34-SOG-50). All data were collected at room temperature ($24 \pm 1^\circ\text{C}$). The absolute optical rotation of each solution was determined at 589 nm using a polarimeter (Jasco P1010). The measurement error of the polarimeter at 589 nm is about $\pm 0.2\%$, as calibrated by a quartz standard.

The solid curves $T_i^a(\lambda)$ ($i=1,2,3$) in Fig. 2 shows the three transmission spectra of 45.2% w/w sucrose solution taken at three apparent probing angles $\theta_a = 0^\circ$, 45° , and 90° , respectively, where % w/w is given as grams of sucrose per 100 mL of water. The dashed curves $T_i^a R(\lambda)$ ($i=1,2,3$) in Fig. 2 are the three transmission spectra

taken at the same apparent probing angles $\theta_a = 0^\circ, 45^\circ,$ and 90° , with the sucrose solution removed from the sample compartment. All spectra are dominated by the wavelength dependent optical transmission of the polarizer (P) and that of the analyzer (A). The negative band at about 560 nm is a grating Woods anomaly.

$\Delta\theta$ is then determined by the three transmission spectra when the sucrose solution is removed from the sample compartment. Figure 3 shows the average systematic error $\Delta\theta$ and its standard deviation based on eight sets of independent measurements. The higher noise in the spectra region near 400 nm is due to weaker signal mainly caused by low source light power and low detector response of the spectrometer. The average systematic error is about 3.39° , and the standard deviation of the systematic error is about 0.07° in the entire wavelength region, reflecting the precision of the experiments. The precision is lower than conventional ORD spectropolarimeter, which may be caused by the rotation accuracy of the polarizer holder and the polarization response of the detectors of the spectrophotometer.

Figure 4 shows the results of optical rotation. The solid curve in Fig. 4 corresponds to the apparent optical rotation $\alpha'(\lambda)$ obtained from Eq. (7), while the dashed curve represents optical rotation $\alpha(\lambda)$ obtained by subtracting the systematic error, $\Delta\theta=3.39^\circ$, from $\alpha'(\lambda)$. The solid triangles in Fig. 4 represent the reference optical rotation $\alpha_R(\lambda)$ at wavelengths 447, 479, 508, 535, 589, and 656 nm, as calculated by

$$\alpha_R(\lambda) = \frac{\alpha_{R589}}{[\alpha_{589}]}[\alpha(\lambda)], \quad (8)$$

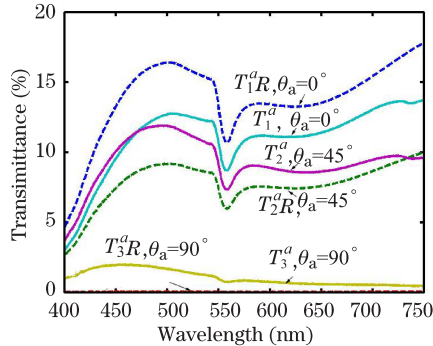


Fig. 2. Transmission spectra of 45.2% w/w sucrose solution taken at three apparent probing angles and the spectra taken at the same probing angles when the solution is removed from the sample compartment.

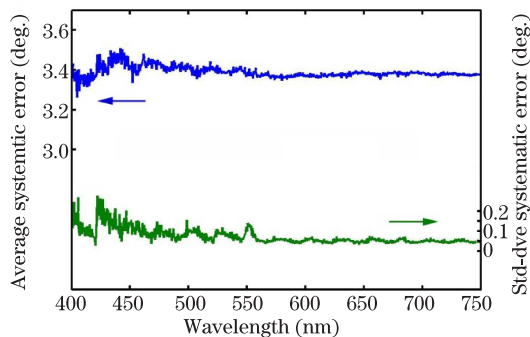


Fig. 3. Average and standard deviation of systematic error $\Delta\theta$.

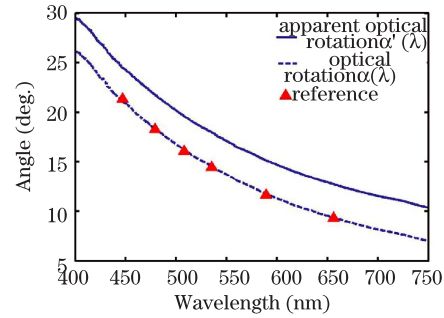


Fig. 4. Apparent optical rotation $\alpha'(\lambda)$, optical rotation $\alpha(\lambda)$ and the reference optical rotation of 45.2% w/w sucrose solution.

Table 1. Comparison of the Optical Rotation of 45.2% w/w Water Solution of Sucrose (Unit: deg.)

λ	$\alpha_R(\lambda)$	$\alpha(\lambda)$	$\varepsilon(\%)$
447 nm	21.35	21.08	-1.2
479 nm	18.3	18.39	+0.5
508 nm	16.07	16.23	+1
535 nm	14.44	14.44	0
589 nm	11.672	11.77	+0.9
656 nm	9.34	9.38	+0.4

ε : at each wavelength is calculated by $[\alpha(\lambda) - \alpha_R(\lambda)]/\alpha_R(\lambda)$.

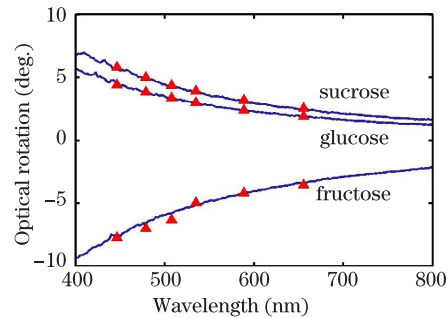


Fig. 5. Optical rotation of 10% w/w sucrose, glucose and fructose solutions. The solid curves are measured by the new spectroscopic method and the solid triangles represent the reference data.

where $[\alpha(\lambda)]$ represents the specific optical rotation measured by Grossmann and Bloch^[18], $[\alpha_{589}]$ is the specific optical rotation at 589 nm, α_{R589} is the optical rotation of the solution measured at 589 nm on Jasco P1010 in our experiment. As shown, the measured results by the new spectroscopic method agree well with the reference data. The comparisons between optical rotations measured by the new method and the reference data are list in Table 1.

The solid curves in Fig. 5 show the optical rotation of sucrose, glucose and fructose solutions with 10% w/w concentration, as determined by the new spectroscopic method with the systematic error corrected. The three curves are compared to the reference data represented by solid triangles. Similar to the data shown in Fig. 3, the reference data of optical rotation of the three solutions at 589 nm are measured on Jasco P1010. Reference data at the remaining wavelengths are obtained from the specific

optical rotations^[18] of the three solutions according to Eq. (8). The agreements of measured results with the reference data shown demonstrate great accuracy of the new spectroscopic method.

In conclusion, a simple yet powerful spectroscopic method is demonstrated to measure ORD of four sugar solutions. The new method is immune to the effects of stray light and the residual transmission when the polarizer and the analyzer are aligned normal to each other, and especially, it eliminates the systematic error in θ , leading to accurate determination of ORD of optically active solutions. The optical rotation of sucrose, glucose and fructose solutions obtained with the new method are in excellent agreement with the reference data, suggesting that the new method can be used as a reliable way to study ORD of optically active media.

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