# On Experimental Conditions for the Half-shadow Polarimetry.*

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Measurement of optical rotation of coloured substances is generally very difficult and consequently the accuracy of the measurement is considerably deteriorated especially in the spectral regions of their absorption bands. For the purpose of overcoming the difficulty, the author has carried out the following calculation, making use of a proposed definition of sensitivity of the measurement.

(1) **The Position of the Analyser Corresponding to the Maximal Sensitivity.** On traversing a layer of an optically active substance, a linearly polarised ray has only its plane of vibration changed in the spectral regions in which no absorption takes place. In the absorption bands, however, an elliptically polarised ray will result according to the circular dichroism of the substance. The incident plane polarised light whose amplitude is $a_0$ may be regarded as a resultant of two circularly polarised light of opposite sense and of equal amplitude $\frac{a_0}{2}$. After passing through $d$ cm. of $c$ mol/$l$. solution of an optically active substance, the two rays will have their amplitudes changed as follows,

$$\left\{\begin{aligned} a_r &= \frac{a_0}{2} e^{-\frac{1}{2}\varepsilon_r cd} \\ a_l &= \frac{a_0}{2} e^{-\frac{1}{2}\varepsilon_l cd} \end{aligned}\right. \qquad (1)$$

where $\varepsilon_l$ and $\varepsilon_r$ denote the molar extinction coefficient of the substance for left and right circularly polarised light. Then $a_L$ and $a_K$, the amplitudes corresponding to the major and the minor axis of the resultant elliptically polarised light may be expressed as

$$\left\{\begin{aligned} a_L &= \frac{a_0}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd} + e^{-\frac{1}{2}\varepsilon_r cd}\right\} \\ a_K &= \frac{a_0}{2}\left\{e^{-\frac{1}{2}\varepsilon_l cd} - e^{-\frac{1}{2}\varepsilon_r cd}\right\} \end{aligned}\right. \qquad (2).$$

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In half-shadow polarimetry two such elliptically polarised rays will be produced in front of the analyser and the angle between their major axes is equal to the aparture between the two vibration directions of the polariser i.e. $2\theta$.

Let the angle between the bisectrix and the vibration direction of the analyser be $\omega$, then the intensities of the two rays after passing through the analyser are given by

$$\left.\begin{aligned} I_1 &= a_L^2\cos^2(\omega+\theta)+a_K^2\sin^2(\omega+\theta) \\ I_2 &= a_L^2\cos^2(\omega-\theta)+a_K^2\sin^2(\omega-\theta) \end{aligned}\right\} .$$

$$\therefore \quad I_1-I_2 = (a_K^2-a_L^2)\sin 2\omega \sin 2\theta \tag{3}$$

$$\begin{aligned} I_1+I_2 &= 2a_L^2(\cos^2\omega\cos^2\theta+\sin^2\omega\sin^2\theta) \\ &\quad + 2a_K^2(\sin^2\omega\cos^2\theta+\cos^2\omega\sin^2\theta) \end{aligned} \tag{4}.$$

When $I_1 = I_2$, we obtain from (3)

$$\sin 2\omega = 0 \qquad \therefore \quad \omega = 0 \text{ or } \frac{\pi}{2} .$$

That is the two fields will be of equal brightness when $\omega$ takes the value 0 or $2\pi$.

Next it must be decided which value of $\omega$ is more suitable for the measurement. As can be easily seen, the comparison of the brightness of the two fields will be easier when the difference between $\frac{\partial I_1}{\partial\omega}$ and $\frac{\partial I_2}{\partial\omega}$ is greater and the intensity is smaller. The following function $S$, therefore, will give the measure of sensitivity.

$$S = \left\{\frac{\partial(I_1-I_2)}{\partial\omega}\cdot\frac{1}{I_1+I_2}\right\}^2 \tag{5}.$$

From (3)

$$\frac{\partial(I_1-I_2)}{\partial\omega} = 2\, a_K^2-a_L^2)\cos 2\omega\sin 2\theta \tag{6}.$$

Substituting (4), (6) and $\omega = 0$ or $\omega = \frac{\pi}{2}$, we obtain from (5)

$$(S)_{\omega=0} = \left\{\frac{(a_K^2-a_L^2)\sin 2\theta}{a_L^2\cos^2\theta+a_K^2\sin^2\theta}\right\}^2$$

and

$$(S)_{\omega=\frac{\pi}{2}} = \left\{\frac{(a_L^2-a_K^2)\sin 2\theta}{a_L^2\sin^2\theta+a_K^2\cos^2\theta}\right\}^2 \tag{7}.$$

Since $\theta < \frac{\pi}{4}$ and consequently $\sin\theta < \cos\theta$,

$$(S)_{\omega=0} < (S)_{\omega=\frac{\pi}{2}} .$$

Thus the sensitivity should be greater, when the analyser is placed at right angles to the bisectrix of the acute angle between the major axes of the elliptically polarised rays. This conclusion coincides with our experience.

(2) **The Angle between the Two Vibration Directions of the Half-shadow Polariser.** Next let us determine the angle $\theta$ which gives the maximal value of $S$ when the analyser is set so as to conform with the above conclusion.

From (7)

$$\left(\frac{\partial S}{\partial \theta}\right)_{\omega=\frac{\pi}{2}} = \frac{4(a_L^2 - a_K^2)^2(a_K^2\cos^2\theta - a_L^2\sin^2\theta)\sin 2\theta}{(a_L^2\sin^2\theta + a_K^2\cos^2\theta)^3} .$$

Therefore $(S)_{\omega=\frac{\pi}{2}}$ will be maximal when

$$a_K^2\cos^2\theta - a_L^2\sin^2\theta = 0 \qquad \tan\theta = \pm\frac{a_K}{a_L} .$$

Substituting (2) in the relation, we obtain

$$\tan\theta = \frac{e^{-\frac{1}{2}\varepsilon_l cd} - e^{-\frac{1}{2}\varepsilon_r cd}}{e^{-\frac{1}{2}\varepsilon_l cd} + e^{-\frac{1}{2}\varepsilon_r cd}} = \frac{1 - e^{\frac{1}{2}(\varepsilon_l - \varepsilon_r)cd}}{1 + e^{\frac{1}{2}(\varepsilon_l - \varepsilon_r)cd}} .$$

When $(\varepsilon_l - \varepsilon_r)cd$ is small,

$$\theta \simeq \frac{1}{4}(\varepsilon_r - \varepsilon_l)cd \qquad (8).$$

Thus the angle between the two vibration directions of a half-shadow polariser which would give the maximal accuracy is theoretically $\frac{1}{2}(\varepsilon_r - \varepsilon_l)\,cd$, and depends on the concentration of the solution and the thickness of the layer as well as the circular dichroism of the substance. The circular dichroism, however, has been measured only for a limited number of optically active substances, and the above conclusion could not be applied to substances whose circular dichroism is unknown. Moreover, the intensity of available light-sources and the sensitivity of photographic plates are also limited and consequently the theoretical value of $\theta$ could not be attained in practical measurement.

For practical purpose the angle between the polarising prisms may be varied according to the following calculation. The light intensity after passing through the analyser is from (4) and (2)

$$I = \frac{I_1+I_2}{2} = a_{\mathrm{L}}^2\sin^2\theta + a_{\mathrm{K}}^2\cos^2\theta$$

$$= \frac{a_0^2}{4}\left\{e^{-\varepsilon_l cd} + e^{-\varepsilon_r cd} - 2e^{-\frac{1}{2}(\varepsilon_l+\varepsilon_r)cd}\cos 2\theta\right\} .$$

Let the extinction coefficient of the racemic substance be $\varepsilon$, then

$$\varepsilon = \frac{\varepsilon_l+\varepsilon_r}{2} .$$

Assuming the initial intensity of the plane polarised light as $I_0 = a_0{}^2$,

$$I = \frac{I_0}{4}e^{-\varepsilon cd}\left\{e^{(\varepsilon-\varepsilon_l)cd} + e^{(\varepsilon-\varepsilon_r)cd} - 2\cos 2\theta\right\}$$

$$= \frac{I_0}{2}e^{-\varepsilon cd}(1-\cos 2\theta) = I_0 e^{-\varepsilon cd}\sin^2\theta .$$

$$\therefore \quad \sin^2\theta = \frac{I}{I_0}e^{\varepsilon cd} \qquad \theta \simeq \sqrt{\frac{I}{I_0}}\,e^{\frac{1}{2}\varepsilon cd} . \qquad (9).$$

For the spectral regions in which no absorption bands exist, the ratio of $I$ to $I_0$, which depends on the intensity of light source and the sensitivity of photographic plates used, is usually of the order of $10^{-2}$ to $10^{-3}$.

Therefore $$\theta \simeq \sqrt{\frac{I}{I_0}} = 10^{-1} \sim 10^{-1.5} = 5.7^\circ \sim 1.8^\circ.$$

That is, the mean value of $2\theta$ is 7.5°. In other words, for wave lengths for which no absorption takes place the angle of the vibration directions should be 7.5°. This conclusion is coincident with the fact that in ordinary fixed half-shadow polariser, the two parts of the split prism contain an angle of about 8°.

In the spectral regions of absorption bands, the angle $2\theta$ should be adjusted so as to contain $7.5^\circ \times e^{\frac{1}{2}\varepsilon cd}$; or approximately $7.5^\circ \times (1 + \frac{1}{2}\varepsilon cd)$.

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