Polarimetry: Optical Rotation

HINDS INSTRUMENTS

APPLICATION NOTE

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When linear polarized light passes through an "optically active" or "chiral" material, a rotation of the plane of polarization of the light may occur. This phenomenon is called Optical Rotation. The measurement of optical rotation of a sample is called "Polarimetry" by chemists.[1] Optically active materials include chiral organic molecules such as dextrose and crystals with asymmetric structures such as quartz.

Optical rotation can be interpreted by physicists as the result of circular birefringence. Circular birefringence is the difference in refractive indices for right and left circularly polarized light. Linearly polarized light can be represented by the linear combination of right and left circularly polarized light. When a linearly polarized light beam enters an optically active sample, the circular birefringence of the sample produces a relative phase shift between the right and left circularly polarized components. The net phase shift integrated along the pathlength inside the sample is called circular retardation or circular retardance. When the light beam exits the sample, the circular retardation produces a rotation of the plane of linear polarization (optical rotation). Circular birefringence, circular retardation, circular retardance and optical rotation are sometimes loosely used interchangeably. However, optical rotation (α) is different in value from circular retardation (δ_C = 2α) by a factor of 2.

The simplest optical rotation polarimeter is constructed by using a polarizer and a crossed analyzer. The optical rotation is the angular difference in the null positions on the analyzer with and without a chiral sample. Simple optical rotation polarimeters have been used in the sugar industry for nearly two centuries. In a modern polarimeter, a polarization modulator, such as the photoelastic moduator (PEM) produced by Hinds Instruments, is employed to provide high measurement sensitivity.

One simple setup using a PEM for measuring optical rotation is shown in Figure 1.

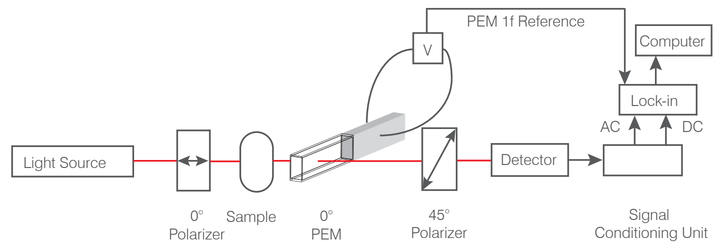

Figure 1. Optical Bench Set-up for Measurement of Optical Rotation

If the light source is a laser, the optical setup is particularly simple since no collimating and focusing lenses are required. The first polarizer after the light source should be mounted in a precision rotator to allow precise alignment with the PEM retardation axis. For this configuration (with no sample in place) there is no AC signal at the detector but there is a DC signal. When a sample is inserted and a rotation occurs, a signal at twice the PEM frequency (2f) will appear at the detector. This signal is used to measure optical rotation of the sample.

Theoretically, the signal reaching the detector may be derived using Mueller calculus. The Mueller matrix for a sample with an optical rotation of α (radians or degrees) is:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\alpha) & \sin(2\alpha) & 0 \\ 0 & -\sin(2\alpha) & \cos(2\alpha) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Using Mueller calculus, we derive the signal at the detector to be:

$$I(t) = \frac{1}{2}\,[1 - \sin(2\alpha)\cos\Delta_t] \qquad (1)$$

[1] Other measurement processes called "Polarimetry", such as Stokes polarimetry and Mueller polarimetry, are addressed in separate notes.

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When we express the time varying retardation of the PEM, $\Delta t = A\cos(2\pi ft)$, in terms of Bessel functions, we rewrite the detector signal as:

$$I(t) = \frac{1}{2}[1 - J_0(A)\sin(2\alpha) + 2J_2(A)\cos(2\pi ft)\sin(2\alpha) + higher\_terms] \quad (2)$$

where A = PEM peak retardation in radians,
f = PEM frequency, and
J_0 and J_2 are Bessel functions of the PEM peak retardation A

The first two terms in the square brackets are the "DC" term and the third term is the "AC" term which is at 2f, twice the PEM frequency. V_{DC} or the DC term is given by Equation 3.

$$V_{DC} = \frac{K}{2}[1 - J_0(A)\sin(2\alpha)] \quad (3)$$

where K is an experimental constant of proportionality.

V_{2f}, the amplitude (Not rms value) of the AC signal at 2f is given by Equation 4

$$V_{2f} = KJ_2(A)\sin(2\alpha) \quad (4)$$

where K is the same experimental constant that is in Equation 3.

For an optimum setup, the PEM retardation is chosen to be A = 0.383 waves = 2.405 radians. For this retardation, $J_0(A) = 0$ and the DC term is independent of the optical rotation.

Experimentally, the signal conditioner splits both an AC signal and a DC signal from the detector output. The lock-in amplifier measures the rms value of V_{2f} and many lock-ins can also measure V_{DC}. The computer reads both values through the RS232 interface with the lock-in.

The ratio of measured AC and DC signals is related to optical rotation in Equation 5.

$$R_{2f} = \frac{V_{2f}^{rms}}{V_{DC}} = \frac{V_{2f}/\sqrt{2}}{V_{DC}} = \sqrt{2}J_2(A = 2.405)\sin(2\alpha) \quad (5)$$

The factor √2 converts between the lock-in rms voltage and peak voltage. R_{2f} is insensitive to fluctuations in the light source, changes in optical transmission, etc.

The optical rotation α is given by Equation 6.

$$\alpha(radians) = \frac{1}{2}\sin^{-1}\left[\frac{R_{2f}}{\sqrt{2}J_2(A = 2.405)}\right] \quad (6)$$

For A = 2.405 radians, $J_2 = 0.4318$, and $\alpha \leq 15°$, putting numerical values in and converting the expression to degrees, a practical formula for α is given in Equation 7.

$$\alpha(degrees) = 46.91R_{2f} \quad (7)$$

The small angle approximation used in calculating optical rotation in Equation 7 is accurate to within about 1% in the range of 0° to 15°. Equation 6 can be used for more accurate calculation.

Finally, there is a well established sign convention for optical rotation of chiral materials. When building a polarimeter, one should use a known sample to calibrate both the sign and accuracy of the polarimeter. The sign of the measured optical rotation depends on lock-in phase setting, PEM phase property, polarizer orientations (0° vs. 90°, 45° vs. 135°) and other parameters. All of these factors are addressed and incorporated into systems designed and configured by Hinds Instruments. However, when building a polarimeter from components, a researcher must pay special attention to these factors as a part of instrument calibration.

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