Chapter 1: Optical Activity and Polarimetry

Chiral, non-racemic compounds have the ability to rotate polarized light. This phenomenon is known as circular birefringence, and is where the phrase "optically active" comes from. The specific rotation of a material is an intrinsic, constant value at a given temperature and wavelength of light; specific rotation can be found by using polarimetry.

1.1 Optical Activity

Normal light contains a mixture of all vibrational directions that are perpendicular to the direction of travel. We can use polarized filters to block most of the components of normal light and only allow through one direction of polarization (Figure 1-1).
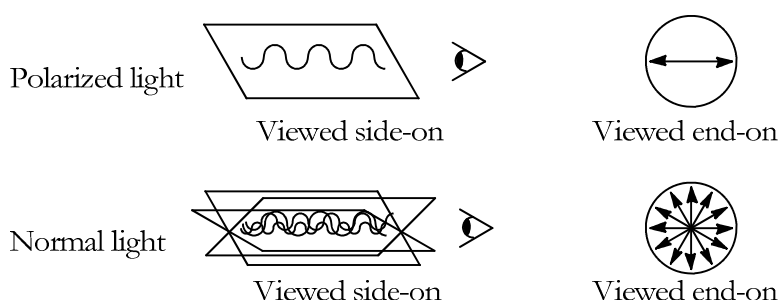

Figure 1-1: Polarized light vibrates only in one plane, while normal light vibrates in all planes.

When we use two filters in series, the first one is called the polarizer (because it converts the light to polarized light) and the second is called the analyzer (because it allows you to analyze the light you just polarized). If the polarizer and analyzer are parallel to each other, the polarized light gets through fine. But if they're at right angles, no light can pass through the analyzer, as shown in Figure 1-2.
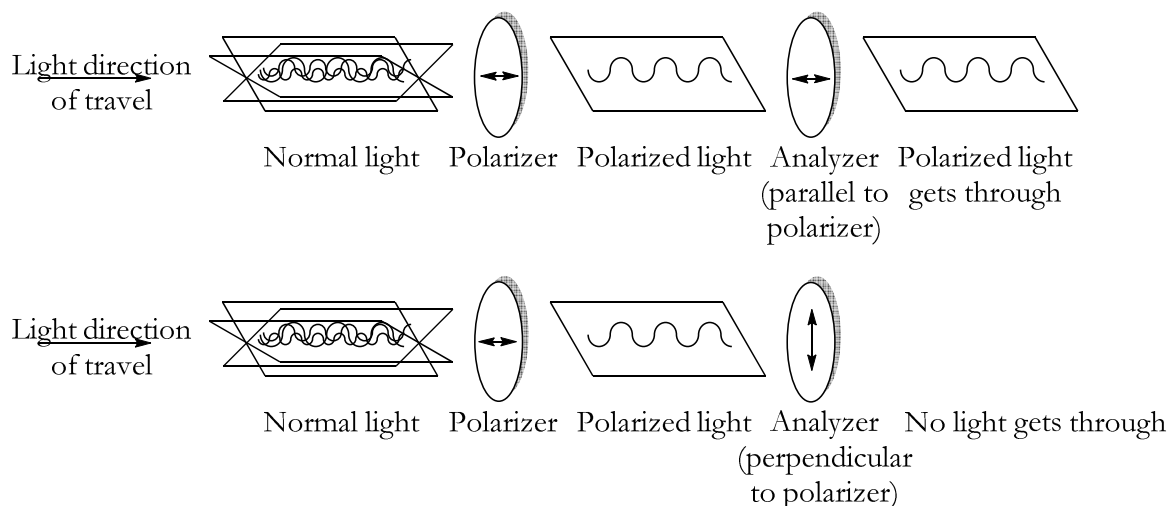

Figure 1-2: Whether polarized light can pass through the analyzer depends on its orientation to the polarizer.

Since optical activity gives a compound the ability to rotate plane-polarized light, we can put a sample of the compound in between the polarizer and analyzer. This will rotate the light, allowing some of it to get through the analyzer even when the filters are at right angles (Figure 1-3).

Normal light   Polarizer   Polarized light   Sample   Rotated light   Analyzer   Rotated light
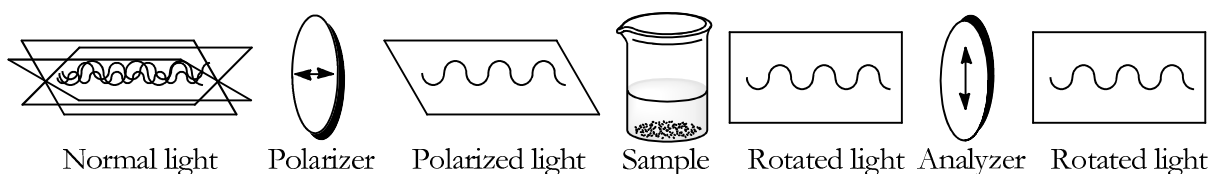
Figure 1-3: Placing an optically active sample between the filters allows some light to pass through, even when the polarizer and analyzer are perpendicular.

This device is called a polarimeter. The polarimeter used by the organic teaching labs contains a vertical glass tube to hold the sample in solution. A beam of light is polarized, directed up through the bottom of the sample, and then analyzed at the top. The analyzer is attached to a detector which can be rotated, causing more or less light to pass through.

Each optically active material will rotate polarized light by a characteristic amount, called its "specific rotation". The specific rotation is a constant number for a given compound, under specified conditions (which wavelength of light is being used, what the temperature is, which solvent is being used, and so forth). However, this is not the same as the observed rotation – the number of degrees that light is actually rotated, as measured by the polarimeter. Specific rotation, [α], is given by the following formula:

$$[\alpha] = \frac{\alpha}{l \cdot c}$$

where α is the observed rotation in degrees, l is the path length of the polarimeter tube in decimeters (dm), and c is the concentration in g/mL or g/cm^3. For example, the literature value of a particular compound might be given as 47°. (Technically, the units for specific rotation are degrees•dm^{-1}•cm^3•g^{-1}, but most of the time it is reported simply in degrees.) This means that if this compound is dissolved to make a solution of 1 g/cm^3 with a path length of 1 dm, this solution will give an observed rotation of 47°.
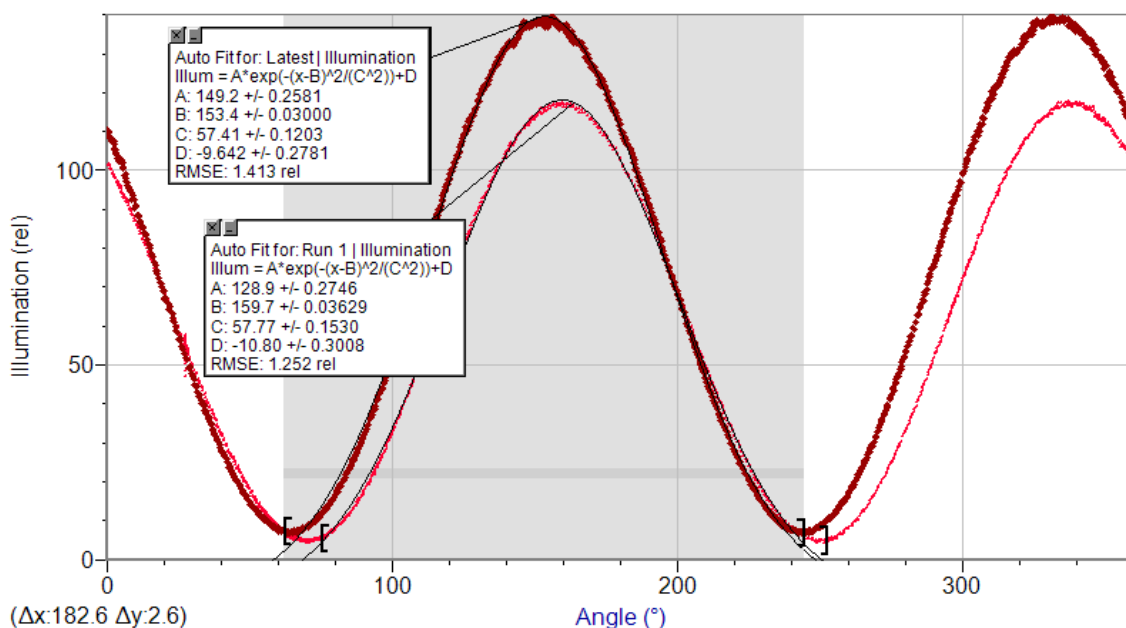
1.2 Using the Polarimeter

The organic teaching labs use a polarimeter produced by Vernier to analyze optical activity.

1. Prepare the polarimeter for data collection, if it has not already been prepared.
    a. Check that the polarimeter is connected to a laptop via a LabQuest Mini, and that the driver is installed (there should be a green light on the LabQuest Mini).
    b. Start the Logger Pro program. It's a white icon in the taskbar that looks like graph paper.
    c. Logger Pro should be showing a single graph with Angle on the X-axis and Illumination on the Y-axis. If this is not the case, select File → New and wait a moment.
2. Calibrate the polarimeter with a blank sample.
    a. Obtain an empty polarimeter tube and fill it with solvent, to a volume specified by your lab procedure. The tube has a cross-sectional area of 2.5 cm^2, so each cm of depth contains 2.5 mL of volume.
    b. Place the cell into the polarimeter by snapping it into the black brackets along the front.
    c. Click the "Collect" button (green arrow), then manually rotate the dial on the top of the polarimeter. For best accuracy, rotate it smoothly and slowly. The graph should fill in with a sine-wave
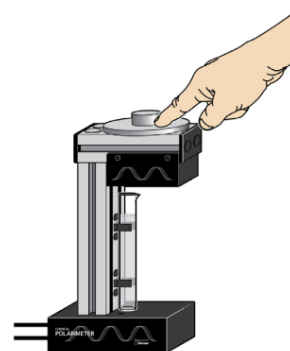
pattern, and data collection should stop automatically after 15 seconds.

d. Use a curve fit to find the point of maximum illumination. Drag a grey box around one of the two peaks of your curve as shown below, then go to Analyze -> Curve Fit. Scroll down to the last option (Gaussian) and select it, then click "Try Fit" – a black curve should appear that closely matches the data curve. If it doesn't fit closely, you may have to click "Try Fit" a few more times. If you still cannot get a good fit, make sure that you successfully drew a box around a single peak, without including either neighboring peak. When the fit looks good, click "OK" - the coefficients should appear in a window next to the peak. The value that matters is the "B" value – this should tell you the angle of maximum illumination, to an accuracy of 0.3 degrees.

Auto Fit for: Latest | Illumination
Illum = A*exp(-(x-B)^2/(C^2))+D
A: 149.2 +/- 0.2581
B: 153.4 +/- 0.03000
C: 57.41 +/- 0.1203
D: -9.642 +/- 0.2781
RMSE: 1.413 rel

Auto Fit for: Run 1 | Illumination
Illum = A*exp(-(x-B)^2/(C^2))+D
A: 128.9 +/- 0.2746
B: 159.7 +/- 0.03629
C: 57.77 +/- 0.1530
D: -10.80 +/- 0.3008
RMSE: 1.252 rel

e. Go to Experiment -> Store Latest Run.

3. Run your sample.

a. Prepare your sample by placing your optically active material into a polarimeter tube, then adding enough solvent to top it up to a total depth of 10 cm. Mix thoroughly.

b. Place the cell into the polarimeter by snapping it into the black brackets along the front.

c. Click the "Collect" button (green arrow), then manually rotate the dial on the top of the polarimeter for 15 seconds again.

d. Again apply a Gaussian curve to the latest run of data, to find where the point of maximum illumination is on the new curve.

e. Compare the "B" values of the two curves. Calculate (B value of sample) – (B value of blank) to get the observed rotation. For instance, in the graph above, the observed rotation would be (153.4 – 159.7) = -6.3 degrees.