A4

A4-Manual Polarimeter

Operating the Polarimeter

Figure A4.1: Laurent half-shade polarimeter with a vernier scale.

Location

Organic Chemistry Laboratory: 2232 DP.

Sample Preparation

Polarimeter Tube Pathlength
The pathlength of the polarimeter tube is 200 cm (2.00 dm). Optical rotation is directly proportional to the concentration of your sample as well as the pathlength. Use Equation A3-4 to find the specific optical rotation.

1. Orient the polarimeter tube vertically with the end labeled ***200*** at the top; then, unscrew the cap at the top end being careful not to spill any liquid inside.
2. Remove the cap, washer and glass plate.
3. Pour out any liquid. Rinse the tube, cap, washer and plate thoroughly with distilled water, acetone and then your sample's solvent.
4. Rinse the polarimeter tube with a small portion of your sample; then, fill the tube completely with your sample. (This prevents dilution.)
5. Place the glass plate on the polarimeter tube followed by the rubber washer. Then, screw the cap on hand-tight. Do not over tighten.
6. If small air-bubbles are visible, tilt the tube so that they float to the top of the bulge in the tube at the top end (labeled ***200***). If large air bubbles are visible that exceed the bulge, add more solution to the tube.
7. Place the tube into the polarimeter chamber with the end labeled ***200*** at the top.
8. Close the chamber cover by rotating.

Measurement

1. Carefully plug the polarimeter into an outlet. (There is no switch.) Observe the light source at the bottom.
2. Look into the middle eyepiece. You should see a lighted orange disc with varying shades of darkness on either half of the vertical diameter as you rotate the analyzer clockwise and counterclockwise near zero.
3. You may focus the orange image by turning the middle eyepiece while holding the analyzer lever steady.
4. Place the analyzer at approximately zero degrees.
5. Insert the polarimeter tube with your sample and close the chamber cover.
6. While looking into the middle eyepiece, rotate the analyzer clockwise or counterclockwise until you reach a range where either half of the disc becomes completely shaded upon movement of the analyzer ±10º (Figure A4.2, B and C).
7. Slowly move the analyzer within this range until both halves of the orange disc are equally shaded (Figure A4.2, A).
8. Read the optical rotation through the top eyepiece. See below for instructions on how to read a vernier scale.

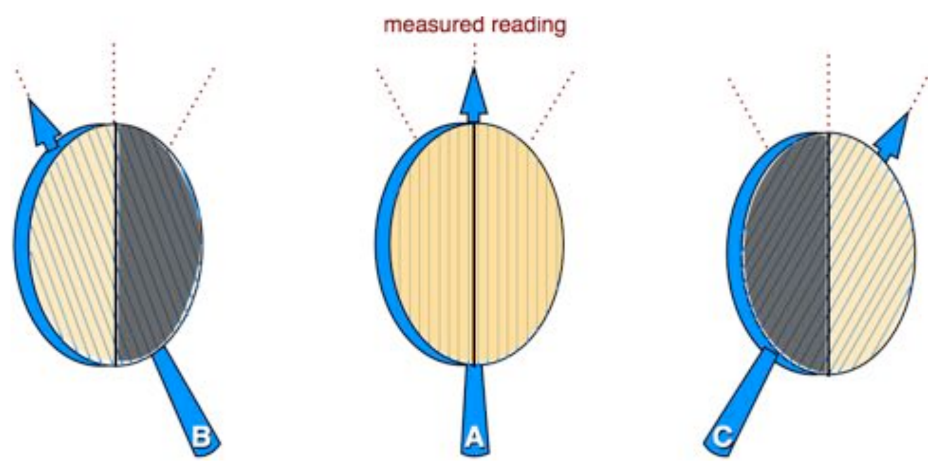


Figure A4.2: Measurement of optical rotation with a Laurent half-shade polarimeter.

Reading a Vernier Scale

The optical rotation of the polarimeter can be read within ±0.1º using the vernier scale on the analyzer (Figure A4.3). First, find the value on the fixed scale at which the vernier scale zero mark points. If the zero mark is in between two values on the fixed scale, take the smaller value as the integer. Second, find the mark on the vernier scale that exactly matches a mark on the fixed scale. Take the vernier value as the tenths place in your measurement.

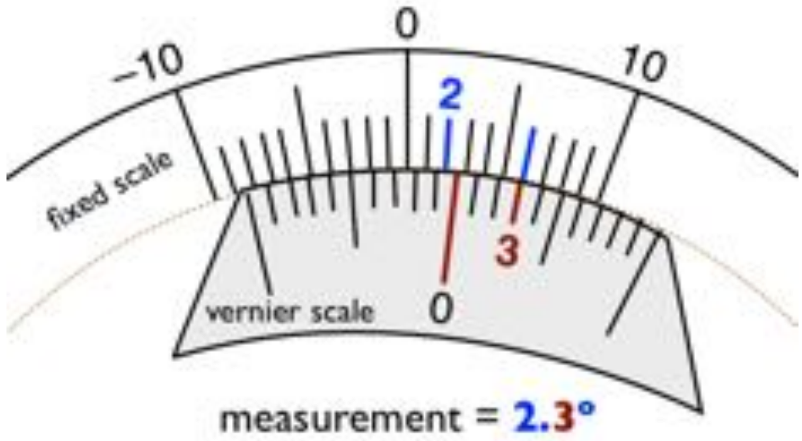


Figure A4.3: Reading the vernier scale on the Laurent half-shade polarimeter.

How Does It Work?

Malus's Law and Sensitivity

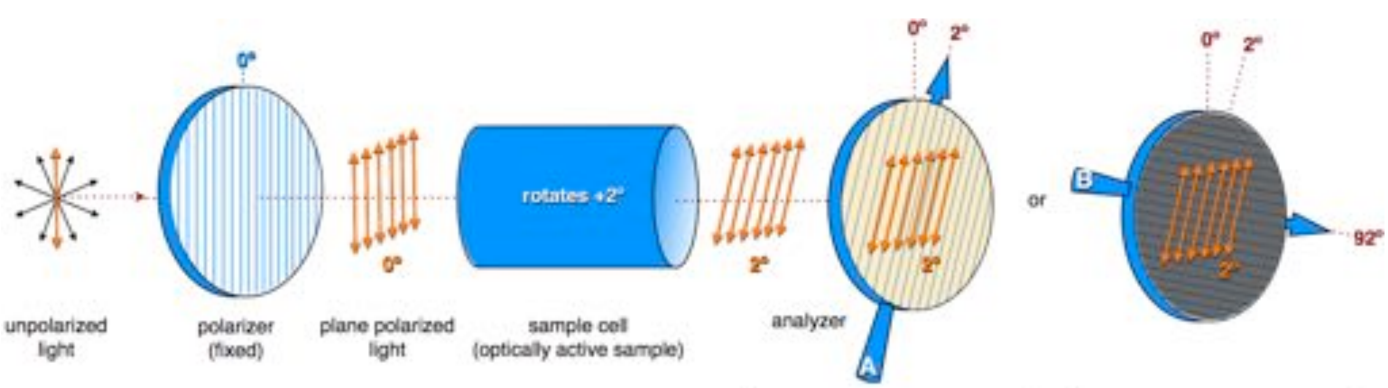
The Laurent half-shade polarimeter is a remarkably simple device that significantly increases the sensitivity of measuring optical rotation. The key piece of equipment in this instrument is a lens called a half-shade device. To understand how a half-shade device works, let's first imagine a simple polarimeter with only two polarizers, one fixed and one movable (the analyzer) (Figure A4.4).

Malus's Law
The resultant intensity (I) of plane-polarized light passing through two polarizers is proportional to the product between $\cos^2$ of the angle between their transmission axes (θ) and the original intensity of light (I_0).

$$I = I_0 \cos^2 \theta$$

Equation A4-1: Malus's Law.

When unpolarized light is incident on the fixed polarizer, only those light waves parallel to the transmission axis pass through. We say the emerging light is plane polarized or linearly polarized. The plane-polarized light then passes through an optically active sample and, through the phenomenon of optical rotation, is rotated clockwise or counterclockwise. In the figure shown, the polarized light has been rotated 2° clockwise by the sample. To measure the optical rotation, another movable polarizer called the analyzer is rotated and the intensity of light passing through it is observed. The intensity of light seen by the chemist (I) varies according to Malus's Law (Equation A4-1); it is at a maximum when the analyzer's transmission axis is parallel (0°) to the polarized light passing through it (cos 0 = 1) and at a minimum when perpendicular (90°) to each other (cos 90 = 0).



$$I = I_0 \cos^2(2-2) = I_0$$

$$I = I_0 \cos^2(92-2) = 0$$

Figure A4.4: Simple polarimeter with a fixed polarizer and a movable polarizer.

In the simple polarimeter in Figure A4.4, the optical rotation can be determined by either finding the angle where transmitted light intensity is at a maximum (2º) or by finding the angle where the intensity is at a minimum and subtracting 90º from that value (92º–90º).

Here lies the problem. The sensor in this device is you–well, your eye. It is difficult for the human eye to precisely determine the maximum and minimum light intensities in this situation. If we examine a plot of Malus's law (Figure A4.5), we see why. The rate of change for light intensity with respect to angle is the least (slope = 0) at the maximum (θ = 0) and minimum (θ = 90) values of light intensity. Alternatively, we could calibrate the analyzer so that the true reading occurs when the slope is at a maximum (θ = 45) and the observed light intensity (*I*) is half of the original light intensity (I_o). The problem? The human eye cannot precisely determine at what point the intensity is half the original value without a side-by-side comparison.

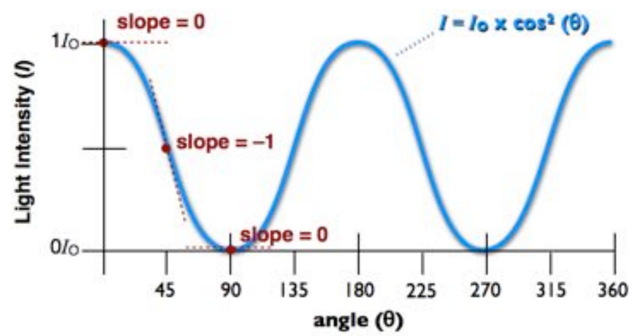


Figure A4.5:Plot of Malus's Law.

IMPROVED SENSITIVITY WITH A HALF-SHADE DEVICE

The solution to this dilema, then, is just that! The half-shade device is a lens divided into two halves that allows us to make a side-by-side comparison of light intensities. Our eyes (and brain!) are very adept at determining when those intensities are equal or unequal.

A half-shade lens (Figure A4.7) is constructed by fusing semicircles of glass and a quartz half-waveplate (Figure A4.6) together. Quartz is a naturally birefringement material (doubly refracting) and when cut to a specific width, is able to change the angle of plane polarized light passing through it. As shown in Figure A4.6, a half-waveplate rotates the incident polarized light through an angle 2θ. In other words, if the polarized light was at an angle of –30º before the waveplate, it would be oriented at +30º after the waveplate.

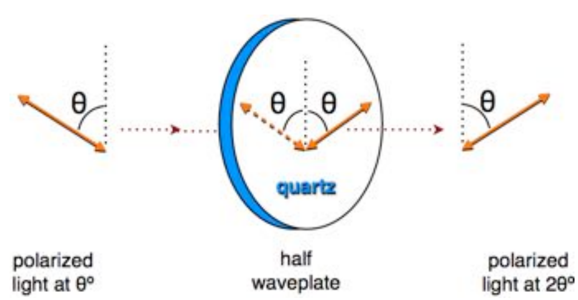


Figure A4.6: Quartz half waveplate.

In our improved polarimeter (Figure A4.7), a half-shade device has been placed in between the sample cell and the first fixed polarizer, which has been oriented at an angle of -85°. The emerging polarized light then passes through the glass-half of the half-shade lens and emerges unchanged. As it passes through the quartz-half, however, it is rotated by 2θ and emerges at an angle of 85°. We now have two semicircular columns of light passing through the sample cell–the left half at -85° and the right half at 85°. If the sample cell is blank, neither column of light is rotated and both are incident on the analyzer unchanged (i.e., the optical rotation is 0°). As we move the analyzer left and right, three cases are possible:

Case A: The analyzer is at 0° relative to the optical axis of quartz (vertical). The incident light in both cases is at an angle of 85° from the optical axis (vertical) and the intensities of polarized light on the left and right sides of the analyzer are equal, as shown by solving Malus's Law.

Case B: The analyzer is rotated 5° counterclockwise (–5°) at which point its transmission axis is perpendicular to the plane polarized light on the right side (85 - -5); no light gets through and the right half is dark. On the left-hand side of the analyzer, the incident light is at angle of 80° (-85--5) to the transmission axis, which allows some light through ($0.03I_o$) according to Malus's Law. The left half is slightly brighter than in Case A.

Case C: The situation is opposite to Case B. The analyzer is rotated 5° clockwise at which point its transmission axis is perpendicular (90°) to the plane polarized light on the left side (-85 - 5); no light gets through and left half is dark.

Why 85°?

This number was not chosen arbitrarily. You can confirm that the fixed polarizer and the transmission axis of the half-shade device are 85° to each other in our polarimeters by finding the angles where either side is completely shaded when no sample is present. It should be around +5° and –5°. This provides a reasonable range that is easy to find. If the range was too small (e.g., ±0.01°) it would be difficult to find; if it were too large (e.g, ±45°) sensitivity would decrease.

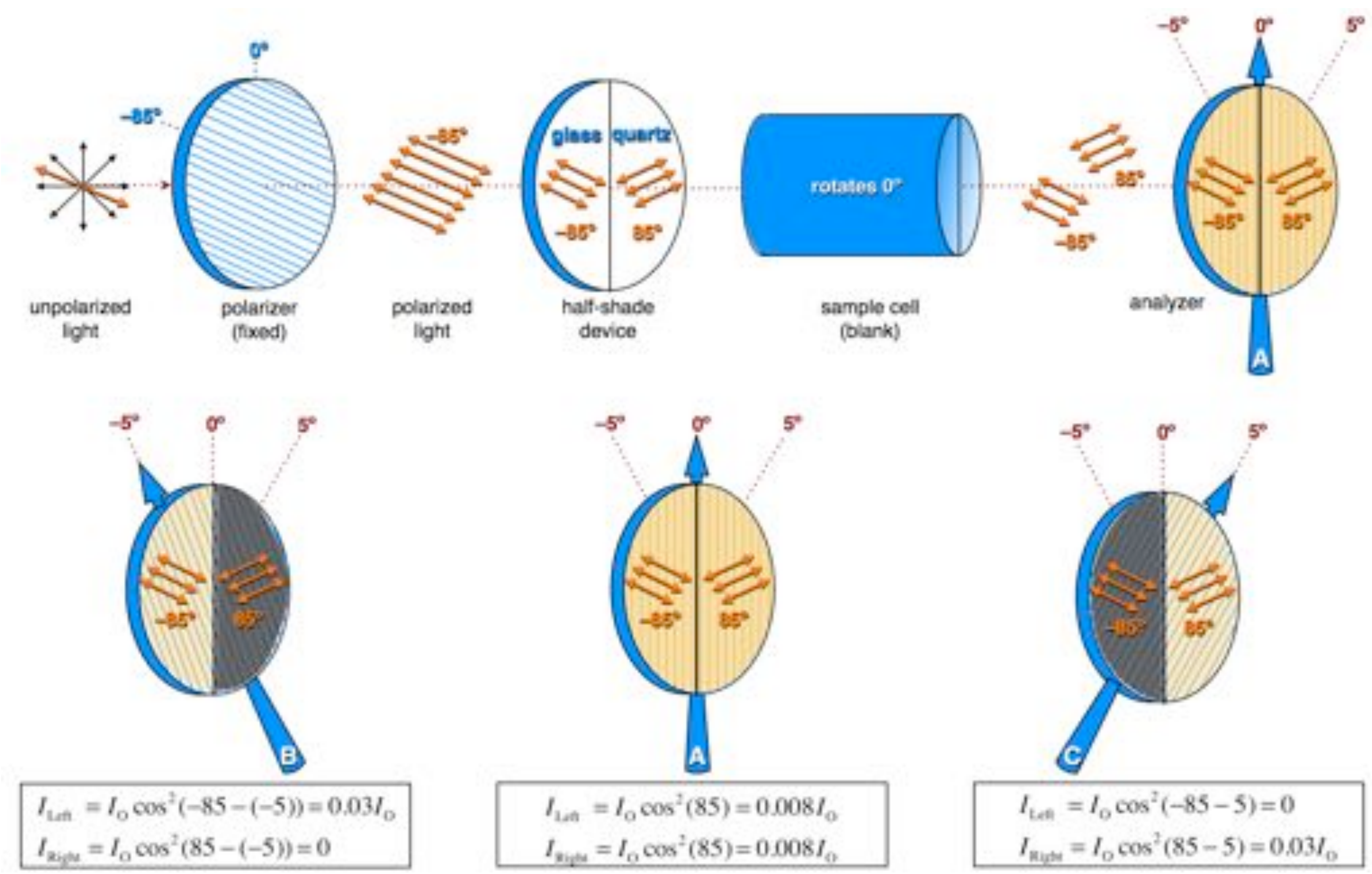


Figure A4.7: Schematic Diagram of a Laurent Half-Shade Polarimeter with a Blank Sample Cell.