Optical Polarimetry

In a typical polarimetry experiment, monochromatic light is passed through the sample. A sodium lamp is usually used as the light source and the wavelength of its D line is 589.3 nm. The light provided by the source is not polarized so its electromagnetic waves oscillate in all planes perpendicular to the transverse axis. After passing through a polarizing lens (prism), the only light remaining is oscillating in one plane (plane polarized), whose angle is determined by the angle of the lens itself. This light is then passed through a solution of an optically active compound, which results in a rotation of the plane of oscillation. A second polarizing lens (prism) is used in conjunction with a detector to find the angle of rotation.

The magnitude of the rotation is not only determined by the intrinsic properties of the molecule, but also on the concentration, path length, and wavelength of light. These parameters should be familiar from use of a UV/Vis spectrometer. In order to standardize the optical rotations reported in the literature, a parameter has been defined as the specific rotation \( [\alpha]_\lambda \):

\[
[\alpha]_\lambda = \frac{\alpha_{\text{meas}}}{l c}
\]

The parameters are:
- \( \alpha_{\text{meas}} \) the rotation measured by the polarimeter in degrees
- \( \lambda \) the wavelength used to measure the rotation in nanometers
- \( l \) the path length in decimeters (usually this is 2 dm, note that 1 dm = 0.1 m or 10 cm)
- \( c \) the concentration measured in g/mL

Normally \([\alpha]_\lambda\) values are quoted in the literature at 20 °C. There is a slight temperature dependence on optical rotation, which can be corrected using:

\[
[\alpha]_\lambda(20 ^\circ C) = [\alpha]_\lambda(T) [1 + 0.0001(T - 20)]
\]

The percent optical purity (x) of a material is the ratio of the measured specific rotation, \([\alpha]_{\lambda(\text{meas})}\), to the standard pure specific rotation, \([\alpha]_{\lambda(\text{std})}\), where \( x = [\alpha]_{\lambda(\text{meas})}/[\alpha]_{\lambda(\text{std})} \times 100 \). The percentage of the major enantiomer in a mixture of enantiomers can be calculated as:

\% (major enantiomer) = \( x + (100 - x)/2 \)

Thus, if a sample is an equal mixture of (+) and (-) enantiomers, the measured rotation is zero and \( x = 0 \), so the \% (major enantiomer) = 50 %.