<u>Optical activity and the use of the polarimeter</u>

General comments on notation:
Over the years, several schemes have been used to represent the differences between optical isomers. These schemes have been based either on the orientation of the structure of the molecule (absolute configuration) or the direction in which the plane polarised light is rotated by that isomer.

In the former case, the terms D and L have been used in the past. These have largely been superseded by the terms *R* and *S* for organic molecules, and 7 and) for octahedral inorganic species. (+) and (-) are commonly used for designating the isomers with respect to the result of the rotation of the polarised light. Unfortunately, the configuration cannot be directly linked to the (+)/(-) assignment. Not only do some D isomers have (-) rotation, but also the rotation for the same optical isomer can even vary with the wavelength of light used in the polarimeter (giving rise to Optical Rotatory Dispersion).

In the earlier literature, *d* and *l* were used for designating both the direction of rotation and the absolute configuration and as a result of the confusion, are not used at all now!

Generally, one measures the angle of rotation, ", and then corrects this value to a specific rotation, ["], to standardize the units used.

$$[\alpha]_{\lambda} = \frac{\alpha}{l c}$$

where 8 is the wavelength of light used in the polarimeter. This is usually the 589.3 nm line of the emission spectrum from a sodium lamp. This line is identified as the D line, and hence the specific rotation is often written as $["]_D$.
" is the angle of rotation measured by the polarimeter, measured in degrees.
l is the path length of the sample cell measured in <u>decimeters</u>.
c is the concentration in g mL^{-1} (or the density of a neat liquid).

Note also it is customary to state the temperature, solvent and the concentration used when quoting an $["]_D$. Sometimes these parameters can cause even the specific rotation to vary. $["]_D$ must carry a sign.

Sample preparation and cell use:
The sample should be accurately prepared in solution at quite a weak concentration. Unless advised otherwise, an appropriate concentration is between 0.5% and 1.0%. The cells are made of glass, and are usually of path length 1 decimeter (10 cm). Those with outer water jackets are approximately 5-10 mL volume, whereas those without the water jacket are about 25 mL. The latter have plastic cradles to support them in the polarimeter.

It is obviously important that the cells should be clean, and free from air bubbles when filled. Filling is best achieved with a Pasteur pipette, but be careful to avoid breaking the tip inside the cell. If this happens, consult your instructor. You should be able to see through the long axis of your solution.

If you cannot, then likely the polarimeter will not be able to.

Commercially produced cells are unbelievably expensive (about $800 at the last look) and that is why many have been produced with great difficulty by our skilful glassblower. Please treat them with respect.

Operating the Rudolph Research Autopol III Polarimeter:
This instrument has few controls and is very easy to operate. It takes only a few seconds to warm up after the power has been switched on. It is ready to use when the LED display records a number. Because the warm up time is so short, it is better to switch off the power if the instrument is not going to be used for one hour or longer. This will conserve the life of the light source.

Switching on:
It is best if the sample compartment is empty and closed when the power is switched on. Dial the wavelength to the desired value (normally 589 nm). As soon as a numerical reading is displayed on the LED, press *RESET*. This should give 0.000 on the LED display. This is a sufficient blank for most cases, but to be rigorous one should record a blank with the sample cell present, containing only solvent.

The sample compartment has a trough running along the axis of the light beam. The cell should rest in this trough with an additional support if necessary. There is a target bull's-eye available for checking if the light is passing correctly through the cell. Close the sample compartment and allow the LED reading to settle to the value of ". There should be no significant fluctuation in the third decimal place. Note that the sign is also recorded.

If successive samples are to be run, leave the sample door open between each sample. This will speed the response time.

If a reading should go over 90° please advise a Senior Lab Instructor. Although subsequent operation will appear normal, an internal reset must be made by a technician.

When the polarimeter is not to be used for one hour or longer, remove the sample and switch off the power. If the wavelength was not 589 nm, please return the dial to 589.

The value of " is recorded in degrees. This value should be converted to ["]$_D$ (["]$_{589}$) before comparing to literature values. To determine the optical purity, compare the observed ["]$_D$ with that of the literature and express as a percentage.