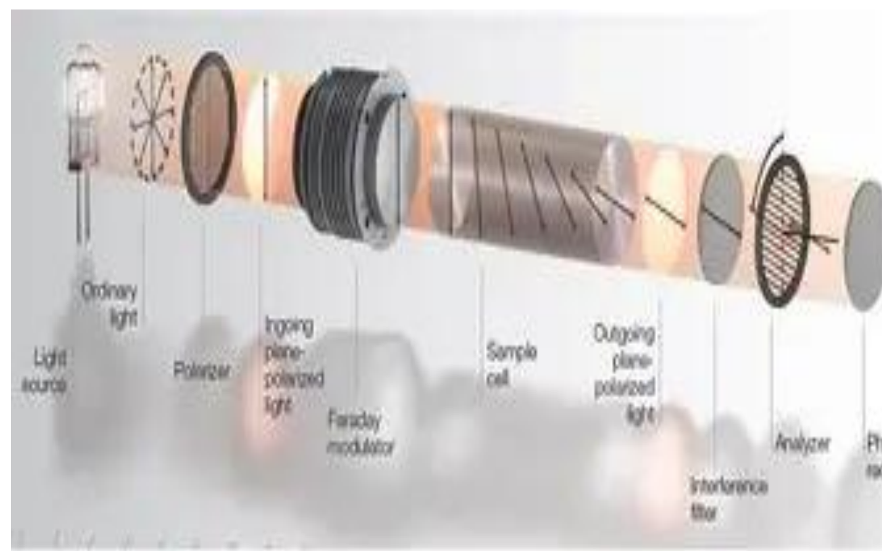
Chemistry 4631

Instrumental Analysis

Polarimetry



UV-Vis Instruments

Polarimetry Instrumentation

- Based on UV-vis Theory
- Used to analyze chiral substances in solutions.
- Used in the pharmaceutical, cosmetics, chemical, food, and medical industries

UV-Vis Instruments

Advantages

- sensitive
- nondestructive
- can measure inorganic and organic compounds

UV-Vis Instruments

What is chirality?

Chiral molecules rotate the plane of polarized light and are thus optically active.

The effect caused by this property is called optical rotation.

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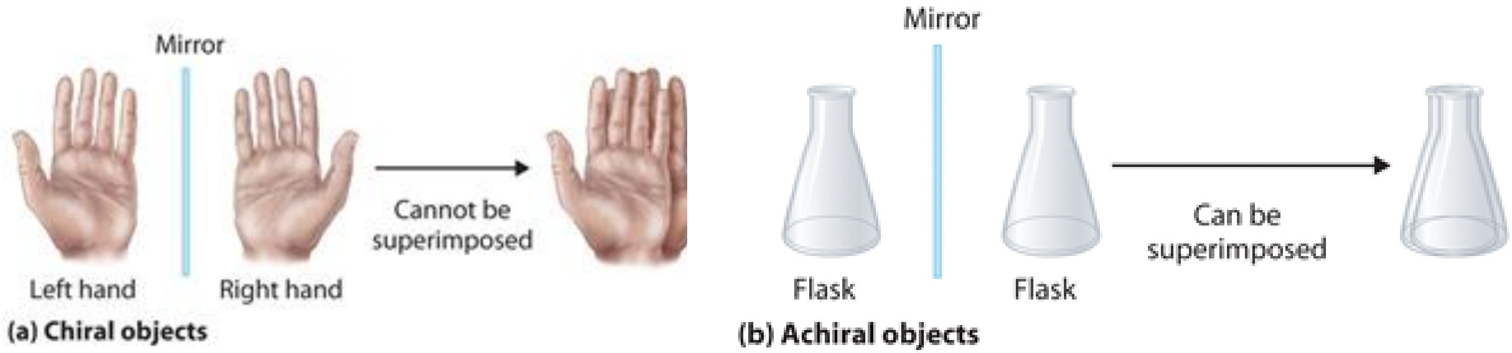
How do you know a compound is chiral?

The mirror image of chiral compounds cannot be superimposed with the original.

Achiral object can be superimposed with the original.



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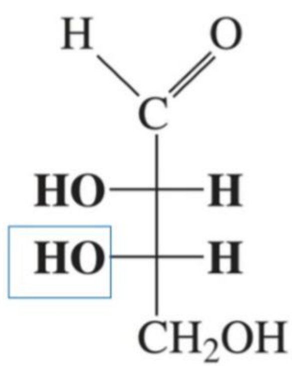
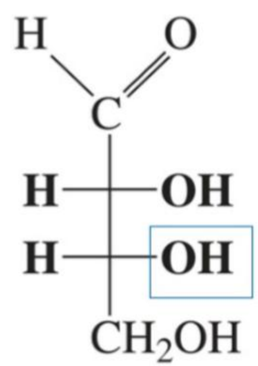
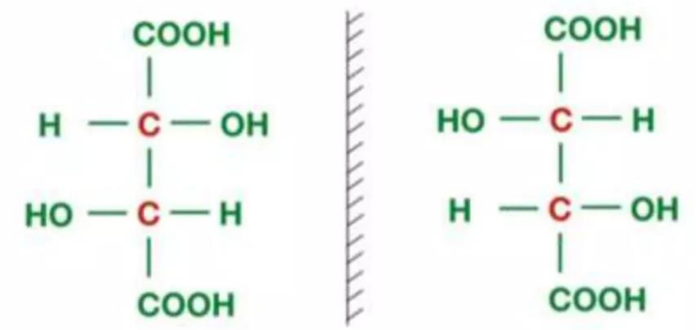
Chiral molecules are typically organic and can be sugars, starch, flavors, essential oils, pharmaceuticals, amino acids, and various other biomolecules.



L-Erythrose



D-Erythrose



Tartaric acid
Optically Active)

Mirror Image
(Optically Active)

Examples: Quartz and cinnabar are examples of optically active crystals (solids), while aqueous mixtures of sugar, tartaric acid, erythrose, are optically active solutions.

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How can chiral molecules rotate the plane of polarized light?

Left- and right-handed enantiomers (mirror images) interact with light and turn the polarization plane in opposite directions.

The angle by which the polarization plane is rotated is called optical rotation.

It is measured in degrees [°OR].

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Types of Polarized Light

- Liner or plane polarized light

Travels in a **single plane** perpendicular to the direction of propagation

- Circular polarized light

Path of light is along a **circle lying in a plane** perpendicular to the direction of propagation

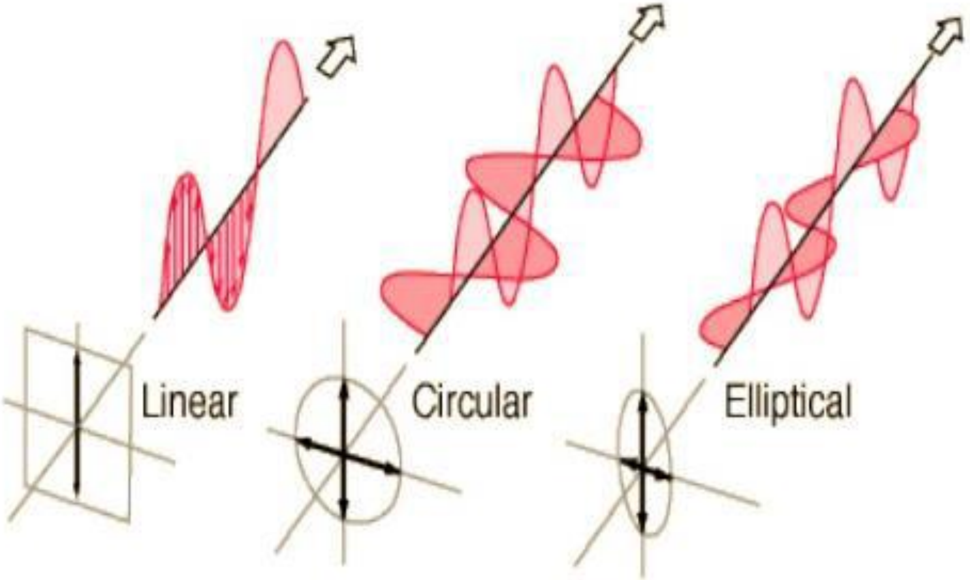
- Elliptical polarized light

When light travels along an **ellipse lying in a plane** perpendicular to the direction of propagation

UV-Vis Instruments

Types of Polarized Light

- Linear or plane polarized light
- Circular polarized light
- Elliptical polarized light



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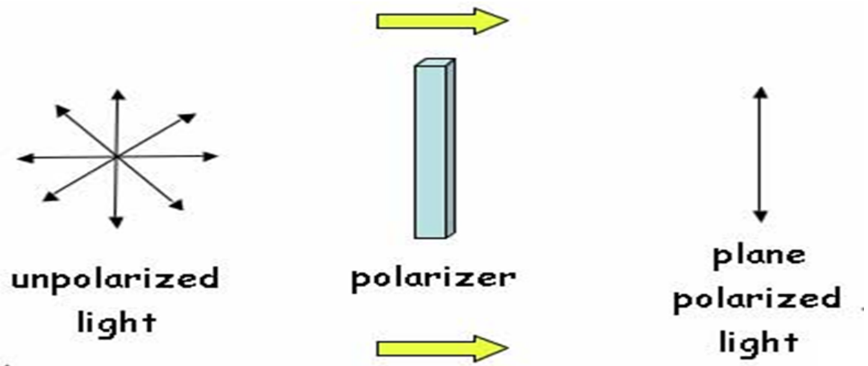
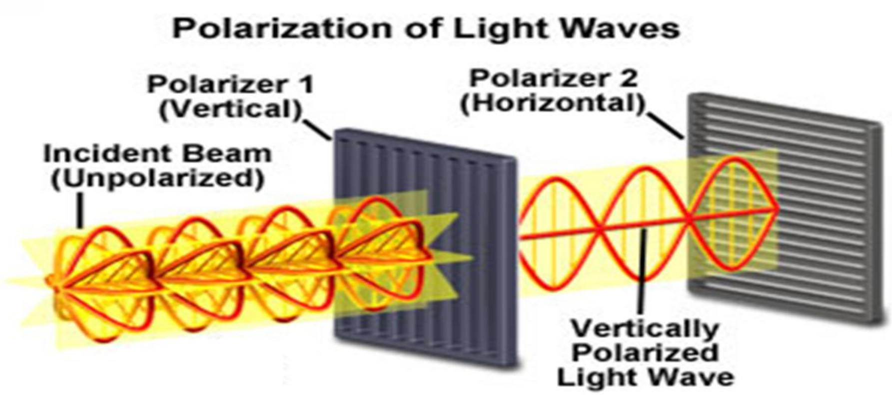
Light is vibrating in all directions – if the light is passed through a special prism it will continue traveling along one plane only.





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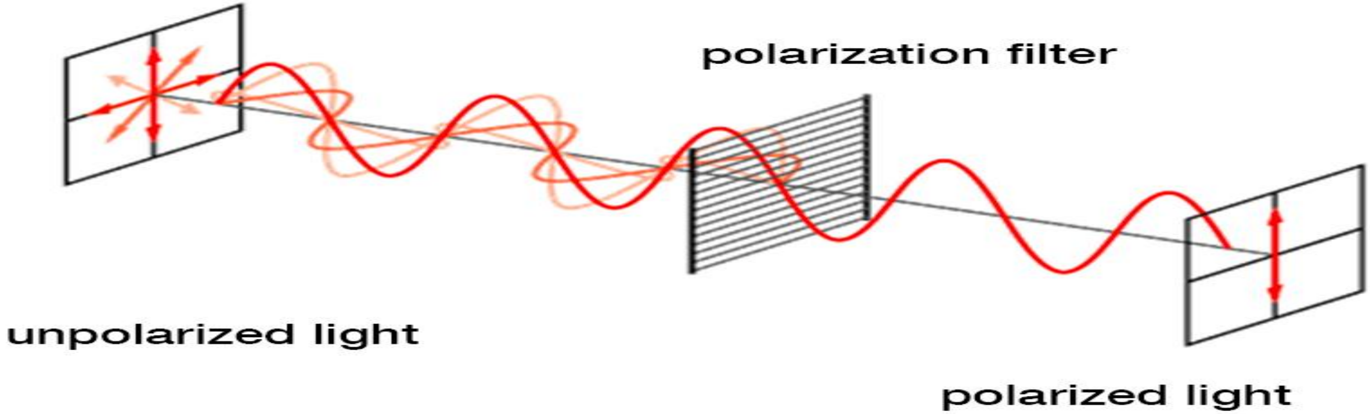
Concentration and physical properties of chiral molecules in a solution influence the plane of polarized light.



This is detected as the angle of optical rotation.

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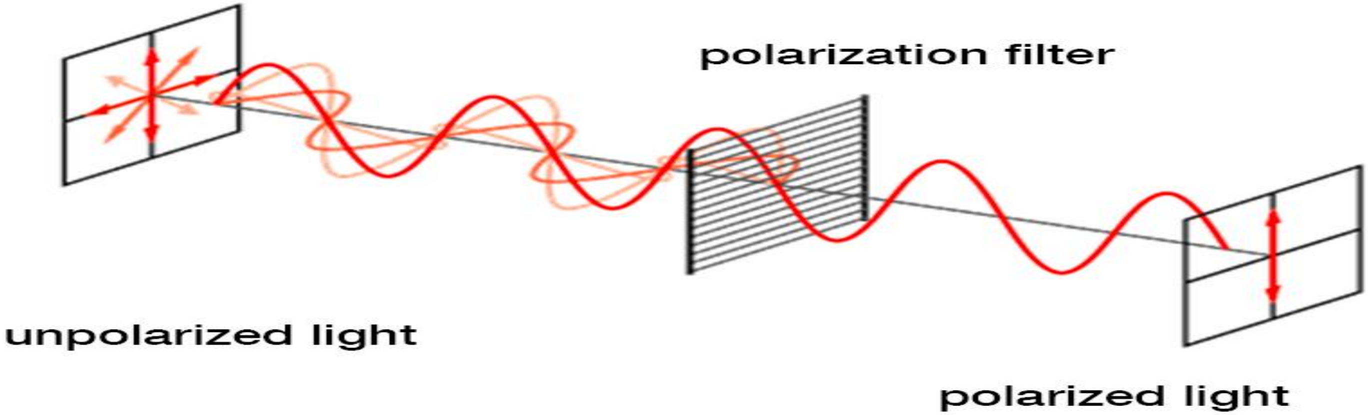
From this measurement, different parameters can be defined, such as specific rotation, concentration, sugar content, and purity.



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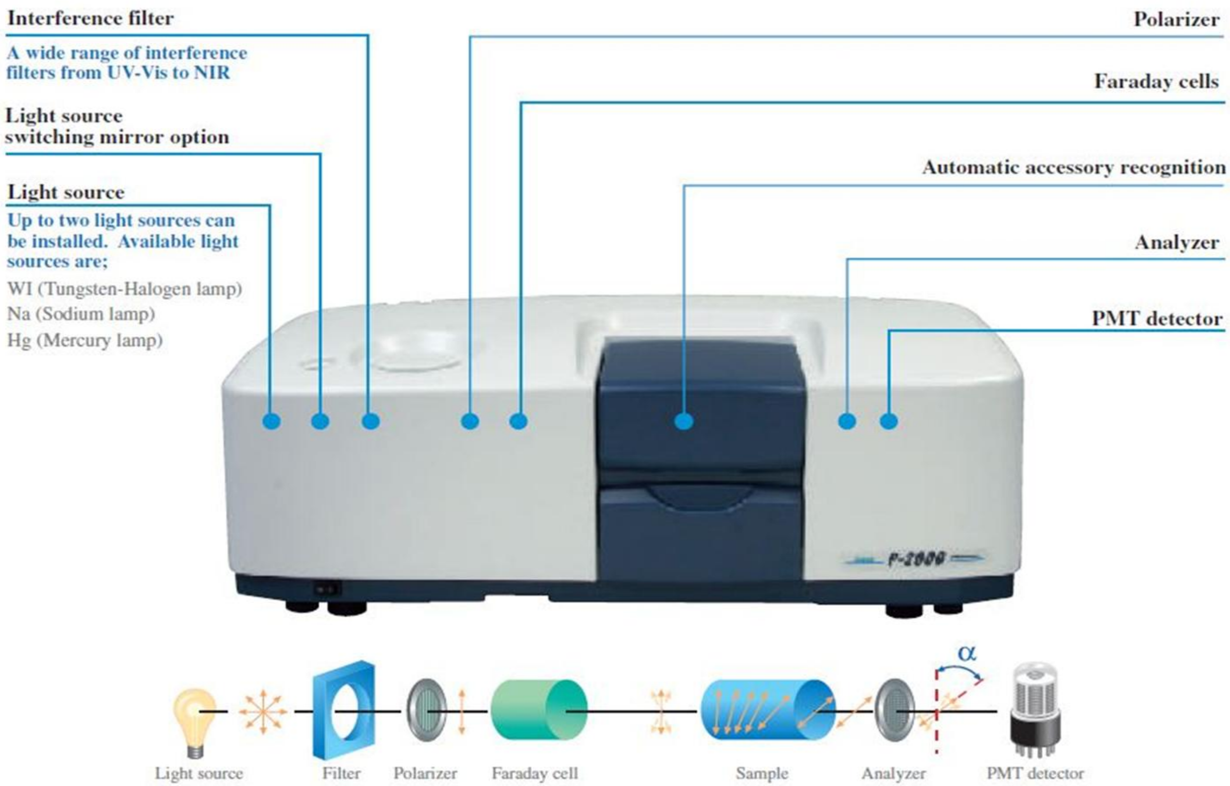
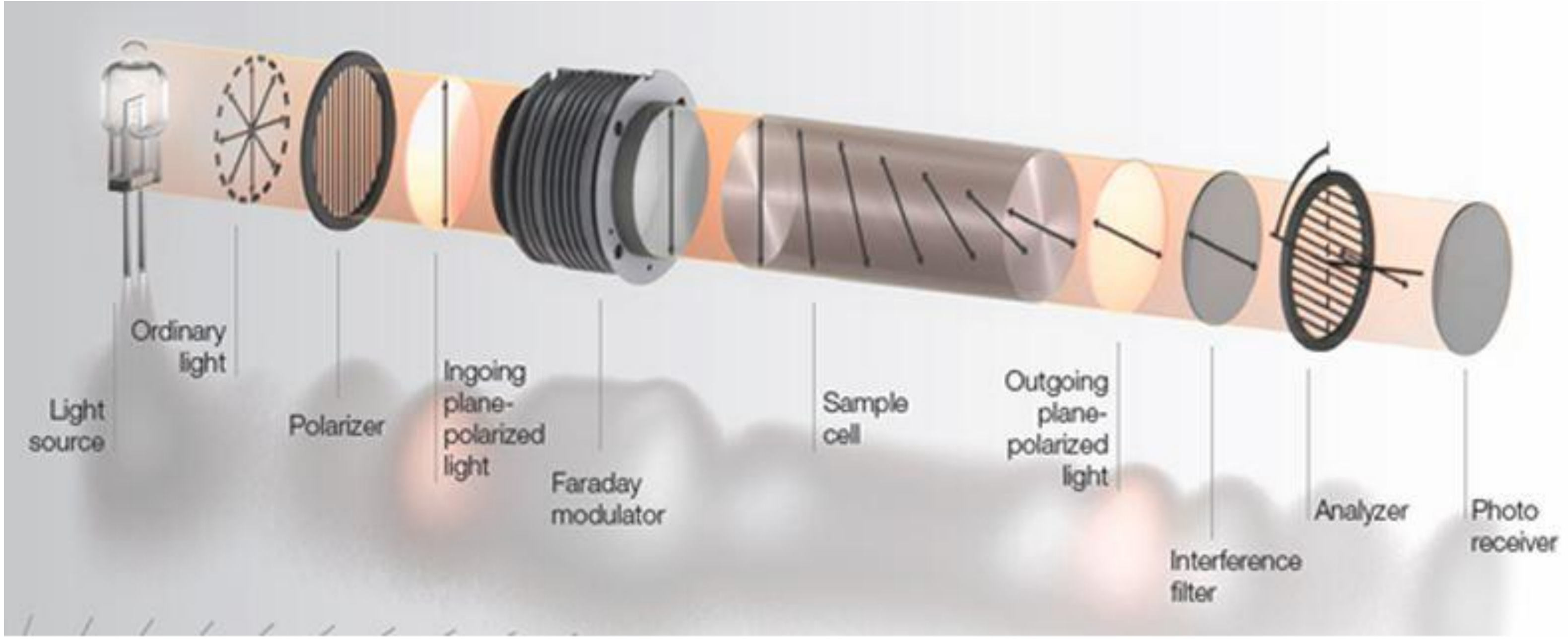
Polarimeter Instrumentation



Jasco makes a Polarimeter similar to this configuration.

UV-Vis Instruments

Polarimeter Instrumentation



Anton-Parr makes a Polarimeter similar to this configuration.

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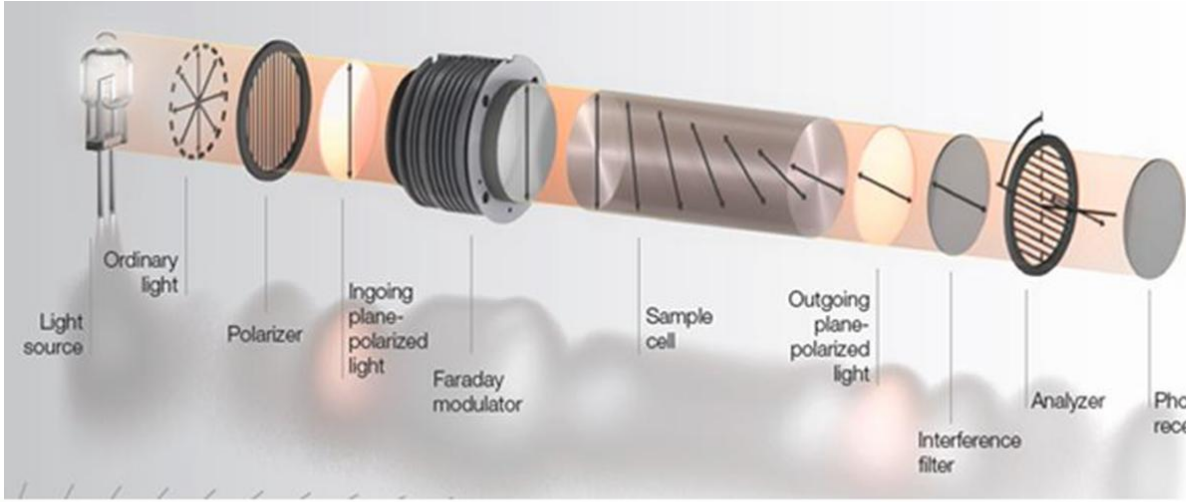
To measure optical rotation, a Light Emitting Diode (LED) or Lamp (Na vapor lamp) produces a beam of ordinary light.

This light first passes through a polarizer (polarization filter) to obtain a defined orientation of the plane of polarization.

The polarized light then passes through the sample cell.



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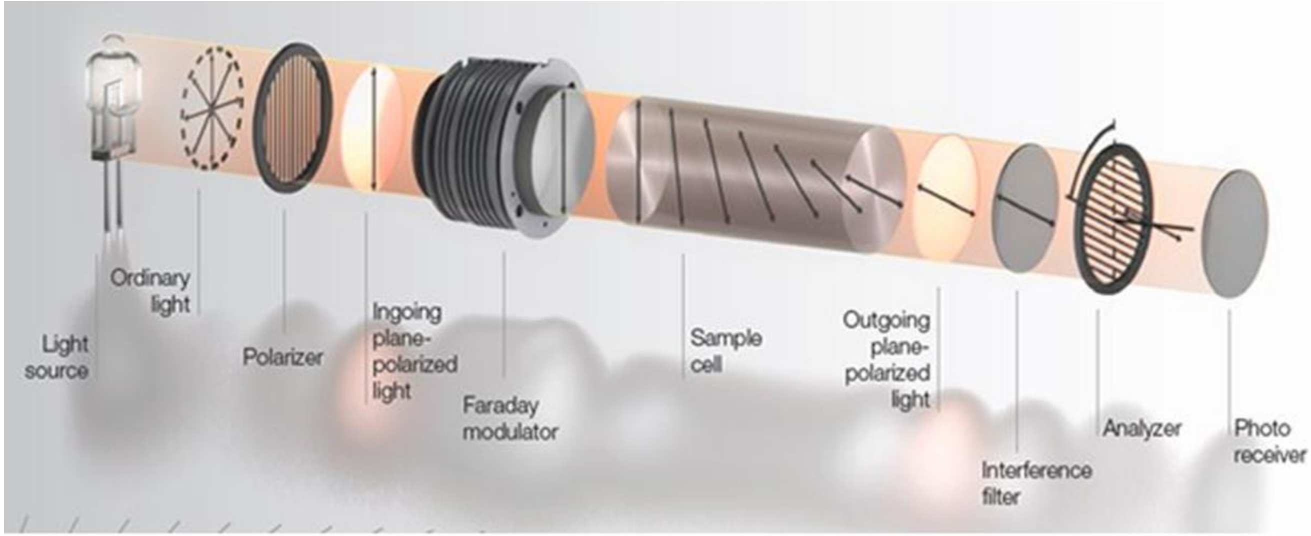
If the sample is optically active, the plane of polarization becomes rotated.

The light with the rotated plane of polarization passes through an analyzer, which is a second polarization filter.



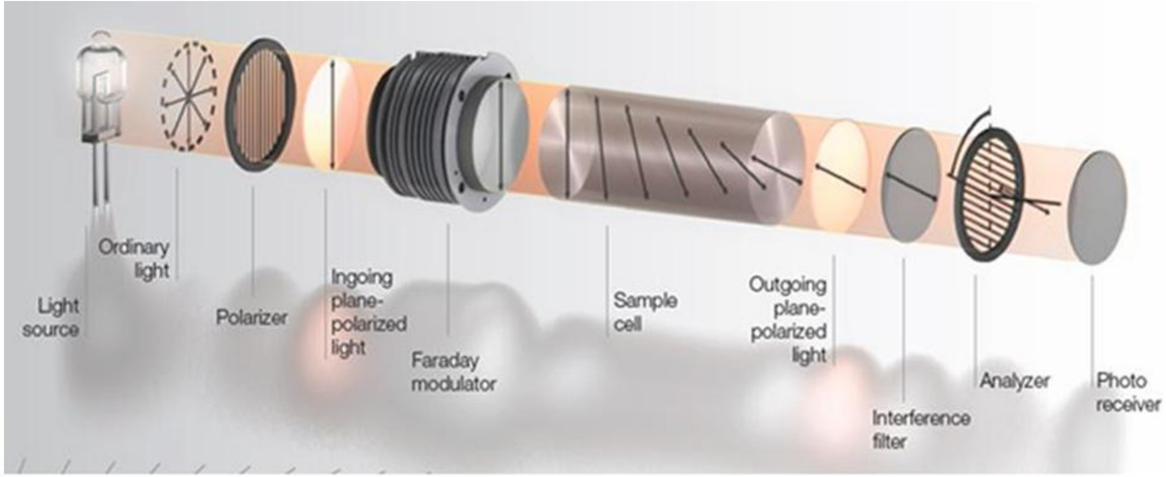
The polarimeter rotates the first polarizer until the photo receiver (detector – PMT) measures a transmission minimum.

If the sample is optically inactive, polarizer and analyzer are now oriented perpendicular to one another.

If the sample is optically active, the polarimeter rotates the polarizer until the plane of polarization behind the sample cell is again perpendicular to the polarization plane of the analyzer.

The resulting degree of rotation is a measure of the optical rotation of the sample.

The correct wavelength for the measurement is precisely selected by an interference filter positioned in the beam in front of the photo receiver.

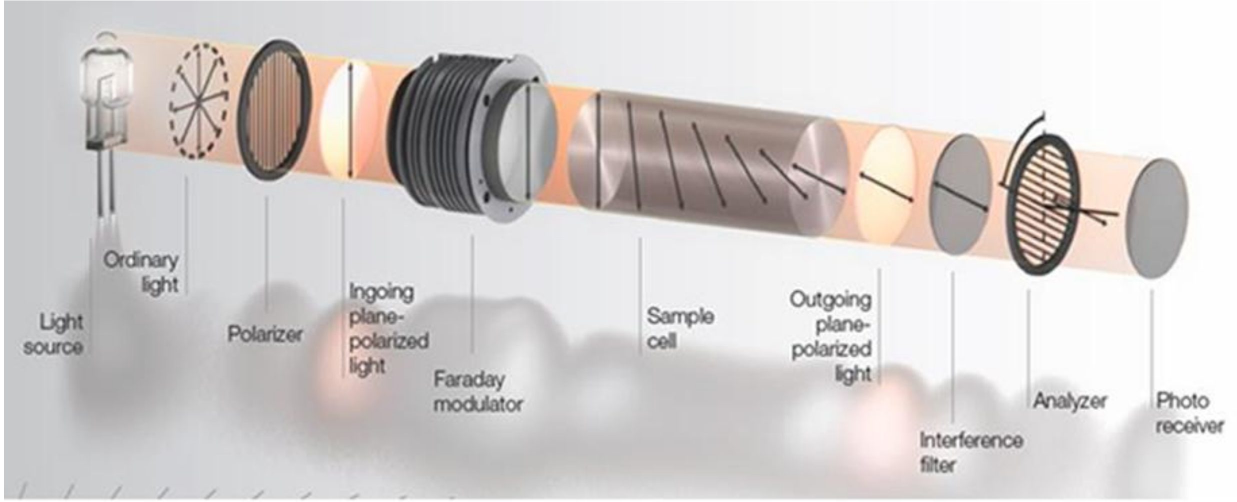


The measuring range of the polarimeter extends from -89.9 °OR to +89.9 °OR.

To obtain a result within +/-89.9 °OR, the sample has to be diluted or the cell length reduced.

Both options have a linear effect on the optical rotation value.

Standards follow recipes to ensure optical rotation values between -89.9 °OR and +89.9 °OR

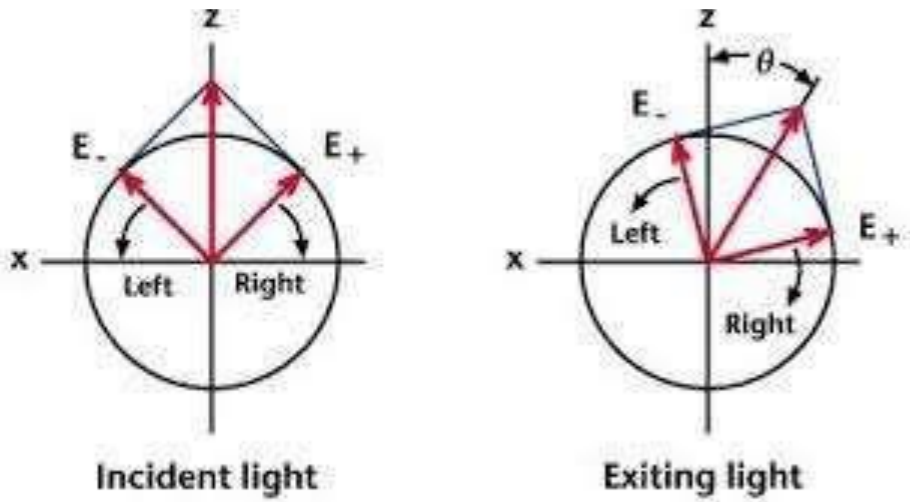


The specific rotation is:

The optical rotation for a concentration of 1 g/100 mL and a cell length of 100 mm.

Ex: Penicillin has a specific rotation of 223 °OR, it can be measured with an MCP polarimeter.

By reducing the path length of the sample cell from 100 mm to 2.5 mm or reducing the concentration of the sample, can measure sample using the polarimeter.



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The plane of polarization light is rotated by optically active compounds: enantiomers.

Enantiomers are dextrorotatory (d or +; Latin: right; clockwise) or levorotatory (l or -; Latin: left; counterclockwise).

What if you have more than one compound in solution?

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What if you have more than one compound in solution?

The optical activity of the enantiomers is additive.

If different enantiomers coexist in one solution, their optical activity adds up.

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What if you have more than one compound in solution?

Solutions with the same concentration of both enantiomers of a chiral compound are racemic mixtures.

These solutions are optically inactive as the clockwise and counterclockwise optical rotations cancel each other out.

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What information can we get from these measurements?

From the optical rotation, the specific rotation of a substance can be derived.

The rotation depends on:

-concentration,

-sample cell length,

-temperature of the solution,

- nature of solvent, and

-wavelength of light (λ = 589 nm (corresponding to Na_d-line)**.**

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What information can we get from these measurements?

Or if you know the substance's <u>specific rotation</u>, the concentration can be determined from the optical rotation measurement.

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The measured value in a polarimeter is the optical rotation, α [°OR].

The relation of optical rotation, α, and specific rotation,[α], is summarized by Biot's law

$$\alpha = \frac{[\alpha]_{\lambda}^{T} \cdot l \cdot c}{100}$$

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To determine a substance's <u>specific rotation</u>, must:

-measure the optical rotation α,

-know the concentration c from sample preparation,

-know the cell length l from the instrument.

$$[\alpha]_{\lambda}^{T} = \frac{\alpha \cdot 100}{l \cdot c}$$

desired quantity | measured value | input values

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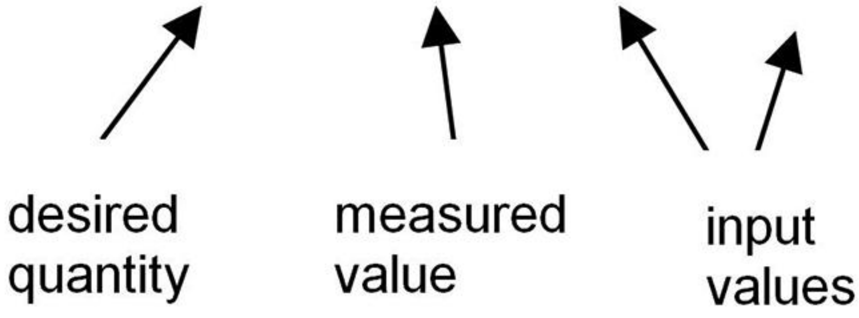
To determine a substance's <u>specific rotation:</u>

Given the input parameters, the polarimeter works out the specific rotation automatically.

$$c = \alpha \cdot \frac{1}{[\alpha]_{\lambda}^{T}} \cdot \frac{100}{l}$$



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To determine a substance's Concentration, we have to:

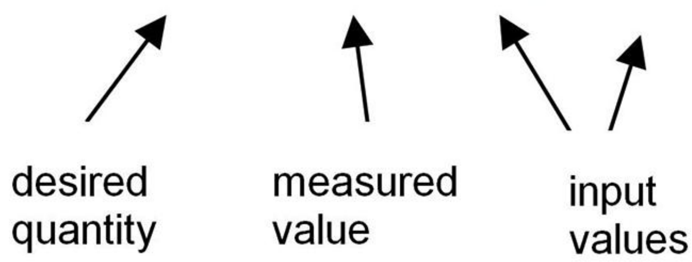
-measure the optical rotation α

-know the specific rotation [α] of the optically active constituent in the sample, and

-know the cell length from the instrument l

- with the input parameters, the polarimeter works out the concentration automatically.

$$c = \alpha \cdot \frac{1}{[\alpha]_{\lambda}^{T}} \cdot \frac{100}{l}$$



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Difference Between ORD and CD

Optical Rotatory Discpersion (ORD)	**Circular Dichroism Spectrometer (CD)**
If the refractive indices of the sample for left and right handed polarized light are different, when the components are recombined, the plane polarized radiation will be rotated through and angle α	Circular dichroism is the differential absorption of left and right handed circularly polarized light
ORD spectra are dispersive	CD spectra are absorptive
The circular polarized light used is not converted to elliptical light	The circular polarized light is used and is converted to elliptical light
ORD graphs are obtained by plotting specific rotation vs wavelength	CD graphs are obtained by plotting molar ellipticity vs wavelength

Assignment

- See book and manufacturer websites for more instrument diagrams
- See Class Notes (Extra) – at class website