

Specific Rotation Equation vs. Optical Rotation – What's the Difference?

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Polarimetry using Polarimeters measure the degree of rotation of polarized light as it passes through an optically active material.

If you're learning about Polarimetry you might come across the terms specific rotation and optical rotation. What is the specific rotation equation and optical rotation? What are the differences between the two? We will cover this below.

Polarimetry was discovered by Étienne-Louis Malus, a French engineer who was studying reflective glass. Several years later another Frenchman, Jean-Baptiste Biot, found that molecules such as sugar could rotate polarized light as well. It was not until 1874 that Dutch chemist Jacobus Henricus van't Hoff proposed that carbon's tetrahedral structure was responsible for the optical activity – the ability to rotate plane-polarized light – of many organic compounds.

Optical activity is a property unique to chiral substances. For example 2-butanol, which possess a chiral center (one carbon bound to four different ligands). Figure 1 illustrates that 2-butanol exists as two mirror-image isomers, or enantiomers. The atomic connectivity in the S-isomer is identical to that of its mirror-image R-isomer, except that two of the groups attached to carbon were interchanged. The R and S designations are based on the Cahn-Ingold-Prelog rules for assigning priority to substituent groups. Visualize the smallest substituent pointing downward below the plane of the paper or computer screen. The three remaining groups are ranked by molecular weight. If the direction of the heaviest, next heaviest, and lightest group is clockwise the molecule is designated as R; if counter-clockwise the designation is S.

When the d and l isomers are present in exactly equal concentrations they are still chiral, but their rotations cancel out and the sample is referred to as a racemate or racemic mixture.

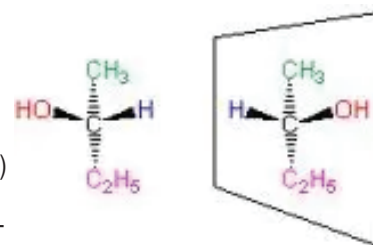
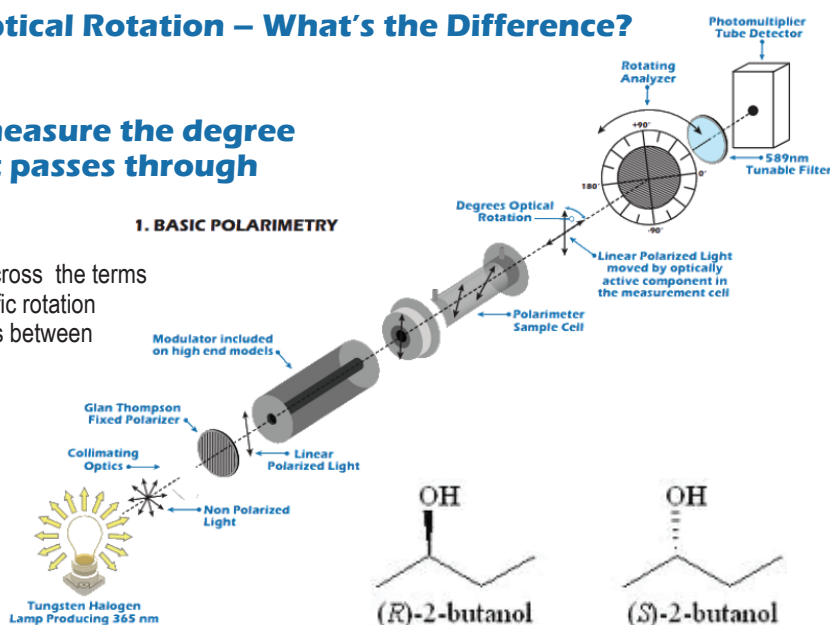
How Polarimetry Works

Normal monochromatic light emerging from a light bulb consists of an infinite number of oscillating waves in all possible planes perpendicular to the line of propagation. A polarizer is a special type of slit or opening that allows light propagating on one plane to pass through. When this light interacts with a chiral substance it speeds up or slows down, the net effect being an apparent rotation in the plane of polarized light.

Unfortunately no correlation exists between the absolute configuration of the molecule (e.g. R- or S-) and the direction in which it rotates polarized light. Molecules that shift the angle clockwise are known as dextrorotatory ("right-turning"), d or (+). Those molecules that shift the angle counter-clockwise are called levorotatory ("left-rotating"), l, or (-). Predicting the precise rotation of a molecule with more than one chiral center is difficult since both chiral centers contribute to optical rotation.

In this 3D projection of 2-butanol the structure on the left has the R-configuration, while its mirror image on the right is the S-isomer according to the Cahn-Ingold-Prelog rules. However, the structure on the left rotates plane-polarized light counter-clockwise. It is designated as (-) or l, while the S-isomer is (+) or d.

If this were not confusing enough, biochemistry employs a third nomenclature that employs the small capital letters D and L. This system is related to R and S but does not strictly follow Cahn-Ingold-Prelog or directly relate to optical rotation. It is therefore beyond the scope of this article. Here we are concerned only with d and l or (+) and (-), respectively.



Specific Rotation Equation vs Optical Rotation

Specific Rotation Equation

Specific rotation equation, $[\alpha]$, is a fundamental property of chiral substances that is expressed as the angle to which the material causes polarized light to rotate at a particular temperature, wavelength, and concentration.

The term for specific rotation equation is given by where T is the measurement temperature, λ is the wavelength of light employed (normally the sodium D-line, or 589 nm), α is the observed rotation. l is the path length, and c is the concentration in grams per milliliter (for pure substances the density) or grams per 100 milliliters. The solvent (often ethanol, methanol, DMSO, acetone, water, etc.) is also specified. Specific rotation may also be expressed as degrees per mole of the substance where the conditions of measurement (i.e. solvent, light source, and path length) are also specified.

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

Use of various wavelengths in Polarimetry to control sensitivity

Use of wavelengths lower than 589 nm, which are available with the mercury and deuterium lamp lines isolated through filters to provide wavelengths of 578, 546, 436, 405, and 365nm, may sometimes provide advantages in sensitivity. Generally, the observed optical rotation at 436nm is approximately double and at 365nm about three times that at 589nm.

Polarimeter Light Sources

It is now common practice to use other light sources such as xenon or tungsten halogen. With appropriate filters, these light sources offer advantages of cost, long life, and broad wavelength emission range over traditional light sources.

Polarimeters measure the observed rotation designated by the Greek lower case letter α . From this value, and knowledge of the specific rotation, one can easily calculate the concentrations of both isomers of a pure substance. For example it is possible to determine the conversion of an achiral material to a chiral substance, or the relative concentrations of optical isomers, known as enantiomeric excess.

Let's say a chemist was attempting to manufacture pure (-)-2-butanol, which has a specific rotation of -13.5° under standard measurement conditions. But when the liquid product is placed into a polarimeter cell as a neat solution the observed rotation is only -4.5° , or one-third the specific rotation. This tells us that one third of the 2-butanol in the sample consisted of the l or (-) isomer, and the remaining two-thirds consists of racemate (equal quantities of (+) and (-). Therefore two-thirds of the butanol is (-)-2-butanol, and one-third is (+)-2-butanol.

Observed Rotations

More relevant to industry are observed rotations of mixtures. For example of food ingredients, perfumes, flavorings, chemicals, pure or formulated pharmaceuticals – virtually any industry that produces or uses chiral organic molecules in pure or diluted form. In these situations, polarimetry provides a rapid, reliable, quality check. This eliminates the need of using conventional analysis like liquid chromatography. This can take an hour to do what the polarimeter accomplishes in minutes.

Polarimetry provides an additional check on a pure substance before it is added to an expensive batch. This determines the ingredient's concentration or purity. For example a 25% glucose syrup will have an observed rotation that is five-sixths that of a 30% syrup.

Similarly the optical rotation of a mixed-component ingredient, intermediate, or finished product will have a characteristic optical rotation that may arise from the presence of several chiral compounds. Once a standard is determined for the composite observed rotation, one can establish quality criteria based on optical rotation. In these situations the polarimeter measurement becomes a type of screen for further testing. This determines which ingredient is out of specification.

Polarimetry Conclusion

In conclusion, Optical rotation is an indispensable quality and identity assay for a wide range of critical industries. Research organic chemists use polarimetry to test the effectiveness of catalysts and asymmetric synthetic processes. Food, drug, as well as flavors industries utilize polarimetry as a quality attribute for raw ingredients and finished products

Polarimeters in today's Labs

Although polarimetry is a mature technique, today's instrumentation provide features and benefits that purely manual-optical systems do not. Busy labs process multiple samples per day. They now have the option of automated data capture, variable wavelength and temperature. Labs can now get readouts accurate to 0.0001° Arc (optical rotation, α). This is a high level of precision for process industries and formulators. Armed only with a polarimeter, labs can set extremely narrow quality standards based on optical rotation.