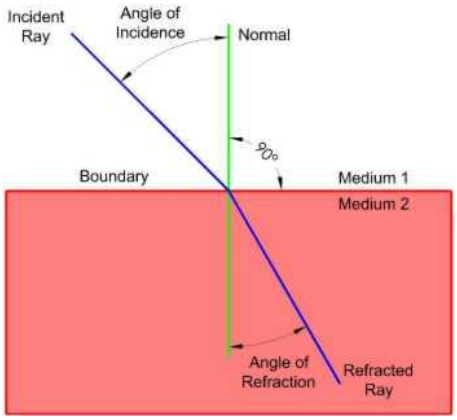
REFRACTOMETRY

1. Refraction

When a light ray passes from a less dense medium to a more dense medium (e.g., from air to glass), it bends towards the normal and when it passes from a denser medium to a less dense medium (e.g., from glass to air) it bends away from the normal. This phenomenon of deviation of light rays from their original path, when they pass from one medium to another, is called refraction of light.



When the light travels from one medium to another medium the speed of light changes. A ray of light from a rarer medium to a denser medium slows down and bends towards the normal. On the other hand the ray of light going from a denser medium to a rarer medium is speeded up and bends away from the normal due to the interactions between the bound electrons of the medium and the electric field of the radiation. It shows that the speed of light in different substances varies. Therefore, different substances have different abilities to bend or refract light. We call this bending ability of a material as the ***index of refraction*** or ***refractive index*** of that material.The refractive index (η_i) of a material is defined as the ratio of the speed of light in vacuum to that in the material medium. Therefore refractive index of a medium;

(η_i) = speed of light in vacuum / speed of light in medium= c / v_i

where v_i is the velocity of the propagation of the radiation in the medium and c is the velocity in a vacuum; c is a constant under all conditions.

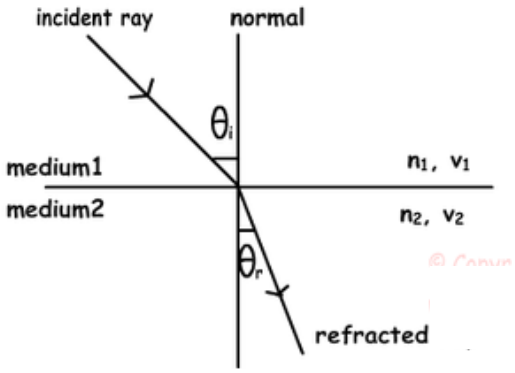
2. Laws of Refraction

The extent to which a ray bends, depends not only on the refractive index of medium, but also on the angle of incidence. The laws of refraction are:

(i) First law of refraction: The incident ray, the refracted ray and the normal at the point of incidence all lie in the same plane.

(ii) Second law of refraction: This law is called as the ***Snell's law of refraction***.

Snell's Law:



$$n_1 . \sin\theta_1 = n_2 . \sin\theta_2$$

$$\frac{n_1}{n_2} = \frac{v_2}{v_1}$$

When **medium 1** is a vacuum, n_1 is unity because v_1 becomes equal to **c**. then n_2 becomes n_{vac} which is called ***absolute refractive index*** of **medium 2.**

It is much more convenient to measure the refractive index with respect to some medium other than vacuum and air is commonly employed as a standard for this purpose. Most compilations of n for liquids and solids in the literature are with reference to air at laboratory temperatures and pressures. Fortunately, the change in refractive index of air with respect to temperature and pressure is small enough so that a correction from ambient laboratory conditions to standard conditions is needed only for the most precise work.

3. Variables That Affect Refractive Index Measurments

(1) Temperature, (2) wavelength and (3) pressure are the most common experimentally controllable variables that affect refractive index measurements.

Temperature: Temperature influences the refractive index of a medium primarly because of the accompanying change in density. Since the density of a liquid usually decreases with temperature, it is not surprising that the speed of light in a liquid will normally increase as the temperature increases. Thus, **the index of refraction normally decreases as the temperature increases** for a liquid. For many organic liquids the index of refraction decreases by approximately 0.0005 for every 1 °C increase in temperature. However for water the variation is only about 0.0001/°C.

Many refractometers are equipped with a thermometer and a means of circulating water through the refractometer to maintain a given temperature. Most of the refractive index measurements reported in the literature are determined at 20 or 25 °C.

Wavelength of Radiation: In most liquids and solids the speed of light, and hence the index of refraction, varies significantly with wavelength. This variation is referred to as **dispersion**, and it is what causes white light moving through a prism to be refracted into a rainbow. Shorter wavelengths are normally refracted more than longer ones. Thus, for the most accurate measurements it is necessary to use monochromatic light. The most widely used wavelength of light for refractometry is the sodium D line at 589 nm and the corresponding refractive index is designated as $\mathbf{n_D}$. Often temperature in °C is also indicated by a superscript; for example $\mathbf{n_D^{20}}$.

Pressure: the refractive index of a substance increases with pressure because of the accompanying rise in density. The effect is most pronounced in gas rather than solids and liquids.

4.Specific and Molar Refraction

Refractive index is temperature dependent. However, combining refractive index and substance density it is possible to define a quantity that is temperature independent known as Lorentz and Lorenz relationship. It is called specific refraction:

$$r = \frac{n^2 - 1}{d(n^2 + 2)}$$

The **molar refraction R** is equal to **rM** where M is the molecular weight of the substance.

4. Instruments for Measuring Refractive Index

Critical Angle Rrefractometers

The most widely used for the measurement of the refractive index are of the critical angle type.

Critical Angle

Critical angle is the incident angle at which light - instead of getting to the other side of phase boundary - gets refracted in such a way that it becomes parallel to the phase boundary surface. For smaller incident angle rays get through the boundary, for larger they get reflected back. Critical angle can be easily calculated if we know refractive indices of both media.

We start with the Snell's law:

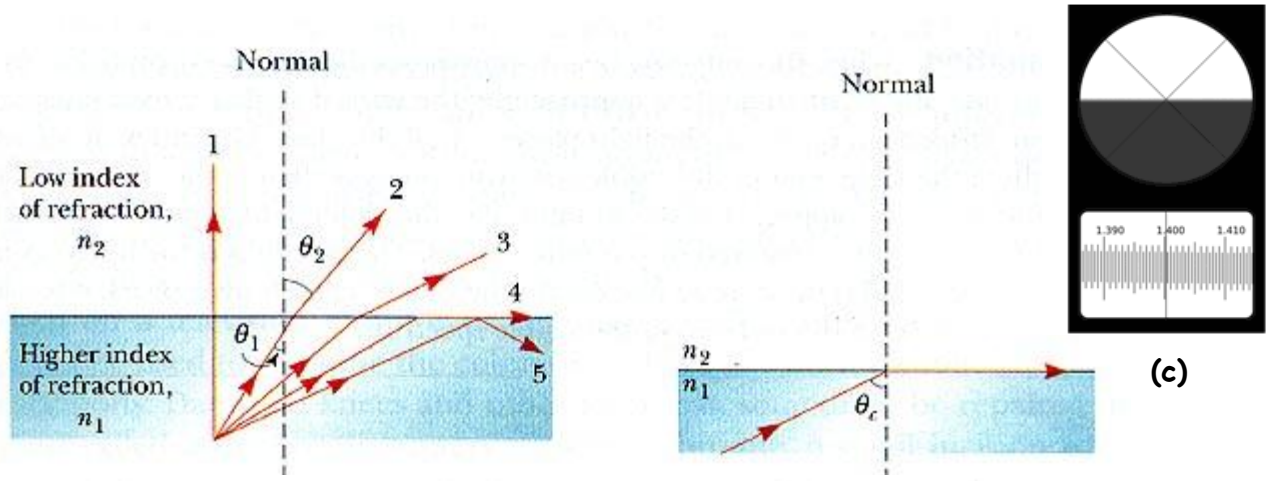
$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{v_1}{v_2} = \frac{n_2}{n_1}$$

θ_1 is the incident angle, θ_2 is the refracted angle. When refracted light gets paralell to the surface, refraction angle is 90°. That means $\sin(\theta_2)$ is 1 and critical angle can be

$$n_1 \sin\theta_c = n_2 \sin 90^0$$

$$\sin\theta_c = n_2 / n_1$$

Construction of most refractometers is based on the fact that critical angle is very easy to detect - instead of measuring the angle at which light gets refracted, we just measure angle at which boundary between light and dark appears.



(a) **(b)** **(c)**

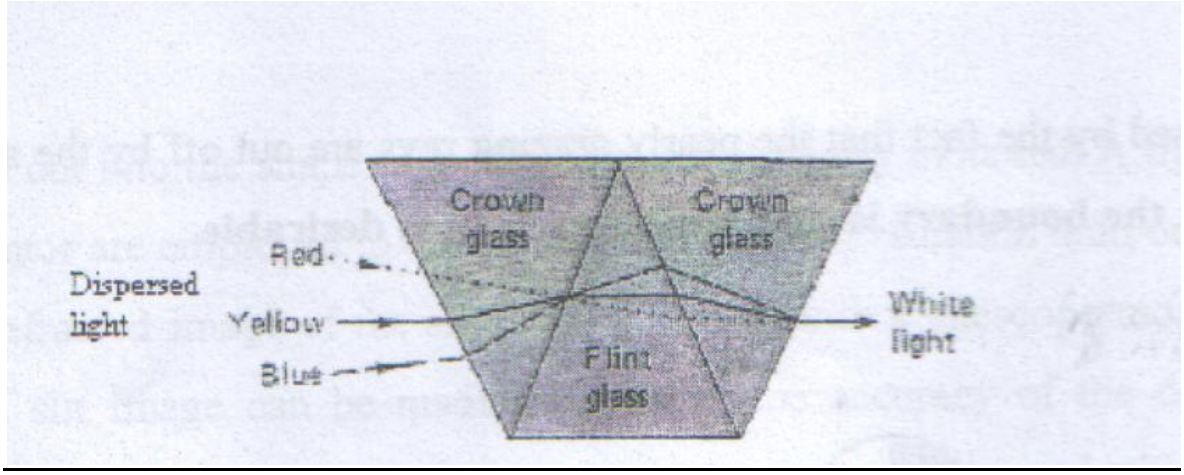
If the medium could be viewed end-on, the critical ray would appear as the boundary between a dark and a light field. It should be noted, however, that the illustration **(b)** is unrealistic in that the ray is shown as entering the medium at but one point; in fact, it would be expected to enter at all points along the surface and thus create an entire family of critical rays with the same angle θc. A condensing or focusing lens is needed to produce a single dark-light boundary such as shown in **(c)**.

It is important to realize that the critical angle depends upon the wavelength, thus if polychromatic radiation is employed, no single sharp boundary such as that in **(c)** is observed. Instead, a diffused chromatic region between the light and dark areas develops; the precise establishment of the critical angle is does impossible. This difficulty is often overcome in refractometers by the use of monochromatic radiation.

As a convenient alternative, many critical angle refractometers are equipped with a **compensator** that permits the use of radiation from a tungsten source but compensates for the resulting radiation in such a way as to give a refractive index in terms of sodium D line. The compensator consists of one or two **Amici prisms**. The properties of this complex prism are such that the dispersed radiation is converged to give a beam of white light that travels in the path of the yellow sodium D line.

Amici Prism

Amici prism is a triprism constructed from different varieties of glass and is so designed that it does not deviate a ray of light corresponding to the sodium D line. Rays of other wavelengths are deviated, however, and by rotating the amici prism about the axis of the instrument it is possible to counteract the dispersion of light caused by refraction at the liquid interface. The important feature enables white light to be used for illumination.

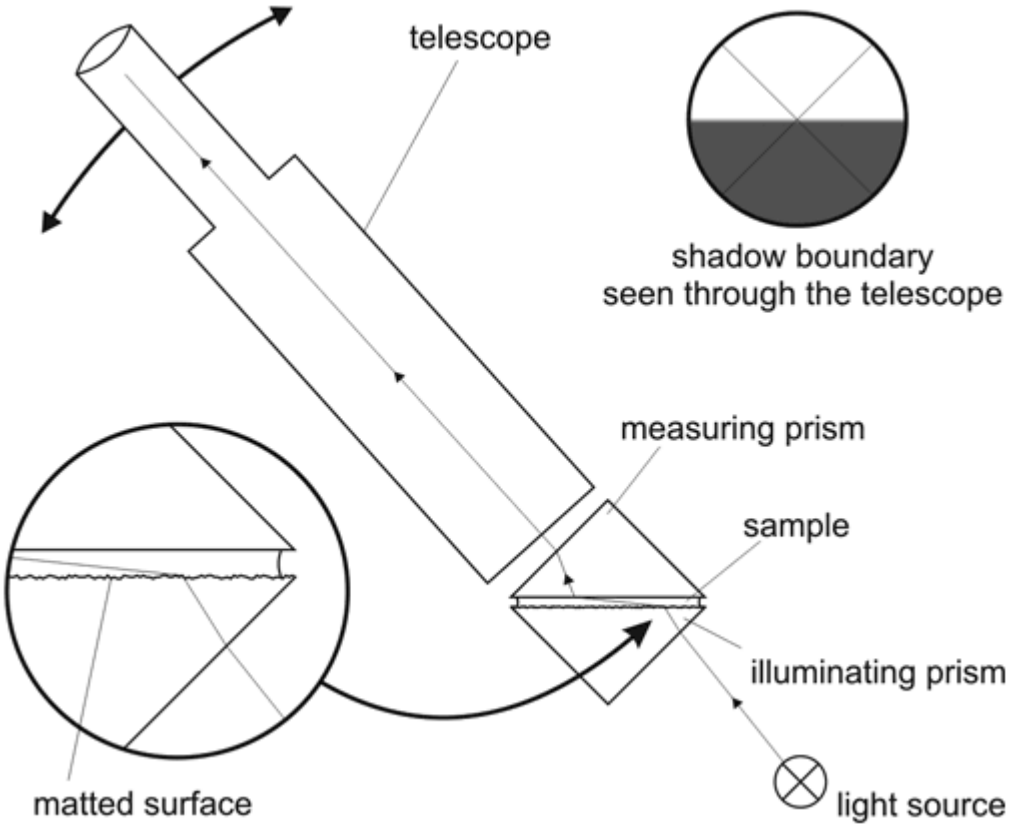


Abbe Refractometer

Abbé refractometer was the first refractometer to be offered commercially. Its original design was so successful that even through today it is over 141 years old, it is still used and copied in new devices.

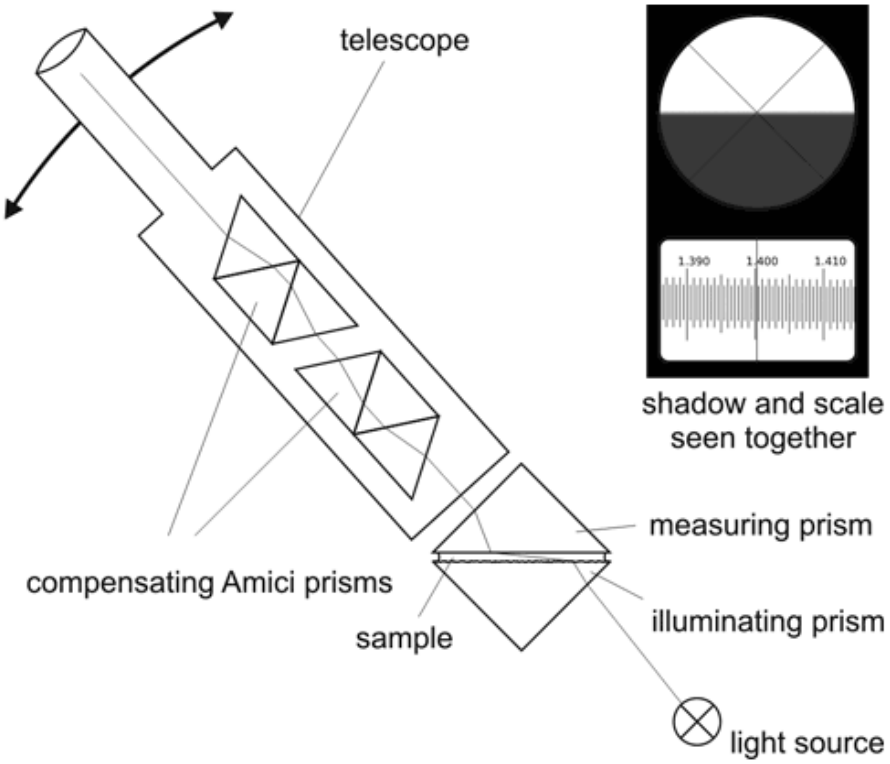
Abbé refractometer working principle is based on critical angle. Sample is put between two prisms - measuring and illuminating. Light enters sample from the illuminating prism, gets refracted at critical angle at the bottom surface of measuring prism, and then the telescope is used to measure position of the border between bright and light areas. Telescope reverts the image, so the dark area is at the bottom, even if we expect it to be in the upper part of the field of view. Knowing the angle and refractive index of the measuring prism it is not difficult to calculate refractive index of the sample. Surface of

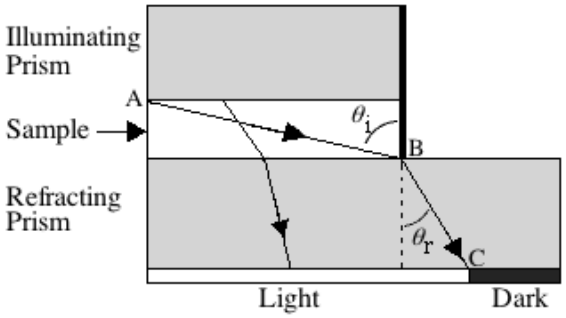
the illuminating prism is matted, so that the light enters the sample at all possible angles, including those almost parallel to the surface.



While the image above already explains the basic principle, it is not yet a complete desing of the Abbé refractometer. Refractive index of a substance is a function of a wavelength. If the light source is not monochromatic (and in simple devices it rarely is) light gets dispersed and shadow boundary is not well defined, instead of seeing sharp edge between white and black, you will see a blurred blue or red border. In most cases that means measurements are either very inaccurate or even impossible.

To prevent dispersion Abbé added two compensating Amici prisms into his design. Not only telescope position can be changed to measure the angle, also position of Amici prisms can be adjusted, to correct the dispersion. In effect edge of the shadow is well defined and easy to locate.





Abbé refractometers come in many variants, that differ in details of their construction. In original design whole telescope was rotated around stationary sample and scale. In modern designs telescope position is fixed, what moves is an additional mirror between sample and telescope. Abbé refractometer can be used to measure both refractive index of liquids and solids. In both cases refractive index of the substance must be lower than the refractive index of the glass used to made measuring prism.

To use the refractometer we simply put the sample between illuminating and measuring prisms, use rotating knob to place the shadow boundary on the telescope cross hairs, and read the refractive index from the scale. Liquid samples must be non corrosive, to not damage surface of the prisms.

As refractive index changes with temperature - for a correct result of refractive index measurement we have to either use thermostated sample, or - after measuring the refractive index - measure temperature and read correction from tables. Most laboratory models of Abbé refractometers are ready to be attached to the source of constant temperature water.

Applications of Abbe Refractometer

The Abbe refractometer is employed for determining the concentration of solutions, for purity tests and quality checks of liquid, plastic, and solid substances, and as an auxiliary instrument for investigating macromolecular substances. Bright, transparent, and opaque samples can be analyzed. Amongst the substances preferably tested with Abbe refractometers are aqueous, alcoholic, and ethereal solutions, oils and waxes of any kind, foodstuffs such as fruit juices, syrups, sugar solutions, fats, and salad oils, tinctures, spirit preparations, brandies, resins and synthetic materials, optical glass. Abbe refractometers are predominantly used in research and industrial laboratories, inspection departments of enterprises, test institutions, colleges and teaching institutions.

5. Applications of Refractometry

Finding Refractive Indices

One of the most common uses of the refractive index is to compare the value you obtain with values listed in the literature. This comparison is used to help confirm the identity of the compound and/or assess its purity.

There are also many computer-based chemical databases that contain refractive indexes. These can be particularly useful if your sample is an unknown and you want to search for compounds with similar indexes of refraction.

Comparing Refractive Indices

Since the refractive index of a substance depends on the wavelength it is important that the refractive index you are comparing to was obtained at the same wavelength as the one you determined. This is usually not an issue since the vast majority of refractive indexes are obtained using the sodium D line at 589.3 nm. Even refractometers that use white light are normally constructed so that the refractive index obtained corresponds to that for light at 589.3 nm.

The refractive index also depends on the temperature. Thus, it is best to obtain the refractive index of your sample at the same temperature as the value you plan to compare with; in most cases this will be 20 °C. However, if your refractometer is not equipped with a temperature regulating system, you may simply be stuck with room temperature, whatever that happens to be.

For most organic liquids the index of refraction decreases by approximately 0.00045 ± 0.0001 for every 1 °C increase in temperature. Note that the index of refraction for water is much less dependent on temperature than most organic liquids, decreasing by about 0.0001 for every 1 °C increase in temperature.

If you determined your index of refraction at a different temperature than that reported in the literature you will need to correct your value for the temperature variation before comparing it to the literature value.

A typical laboratory refractometer can determine the refractive index of a sample to a precision of ± 0.0002. However, **small amounts of impurities can cause significant changes in the refractive index of a substance.** Thus, unless you have rigorously purified your compound, a good rule of thumb is that anything within ± 0.002 of the literature value is a satisfactory match.

Another possible source of error is miscalibration of the refractometer. This is readily checked by using a sample of known refractive index. Distilled water is a particularly

convenient standard since it is nontoxic, readily available in pure form, and its refractive index varies only slightly with temperature.

Probably the most common source of error in analog refractometers is misreading of the scale. If the index of refraction you determined seems inconsistent with other data, try repeating the measurement.

Determining Concentrations of solutions

Determining the concentration of a solute in a solution is probably the most popular use of refractometry. For example, refractometer-based methods have been developed for determining the percentage of sugar in fruits, juices, and syrups, the percentage of alcohol in beer or wine, the salinity of water, and the concentration of antifreeze in radiator fluid. Many industries use refractometer-based methods in quality control applications.

In most cases the refractive index is linearly (or nearly linearly) related to the percentage of dissolved solids in a solution. By comparing the value of the refractive index of a solution to that of a standard curve the concentration of solute can be determined with good accuracy. Many refractometers contain a "Brix" scale that is calibrated to give the percentage (w/w) of sucrose dissolved in water.

Structural Information

The refractive index does not provide detailed information about a molecule's structure, and it is not usually used for this purpose since spectroscopic techniques are much more powerful at revealing details of molecular structure. One structural factor that influences the refractive index of a sample is its polarizability. Substances containing more polarizable ("soft") groups (e.g., iodine atoms or aromatic rings) will normally have higher refractive indexes than substances containing less polarizable ("hard") groups (e.g., oxygen atoms or alkyl groups).

POLARIMETRY

Polarimetry is an instrumental analytical method using rotation of ***polarized light*** by some substances as a measure of their concentration in a solution.

Anisotropic crystalline solids, and samples containing an excess of one enantiomer of a chiral molecule, can rotate the orientation of plane-polarized light. Such substances are said to have optical activity. Measurement of this change in polarization orientation is called ***polarimetry,*** and the measuring instrument is called a ***polarimeter***.

1. Polarization

A light wave that is vibrating in more than one plane is referred to as ***unpolarized light***. Light emitted by the sun, by a lamp in the classroom, or by a candle flame is unpolarized light. Such light waves are created by electric charges that vibrate in a variety of directions, thus creating an electromagnetic wave that vibrates in a variety of directions. It is possible to transform unpolarized light into ***polarized light***. Polarized light waves are light waves in which the vibrations occur in a single plane. The process of transforming unpolarized light into polarized light is known as ***polarization***. A special optical filter called a polarizer can be used to obtain polarized light.

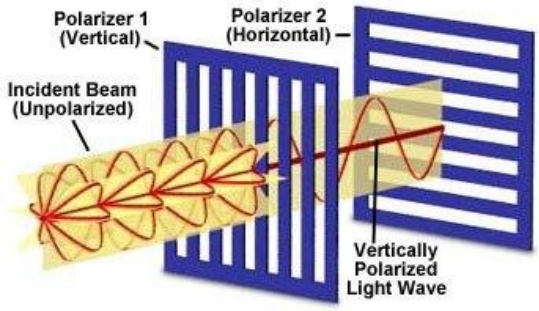


Figure 1. Illustration of the basic concept of polarization.

2. Polarization by Refraction

Polarization can also occur by the refraction of light. Refraction occurs when a beam of light passes from one material into another material. At the surface of the two

materials, the path of the beam changes its direction. Anisotropic crystals, exp: mineral calcite, refract incident light into two different paths. The light is split into two beams upon entering the crystal. Subsequently, if an object is viewed by looking through the crystal, two images will be seen. The two images are the result of the double refraction of light. Both refracted light beams are polarized - one in a direction parallel to the surface and the other in a direction perpendicular to the surface.

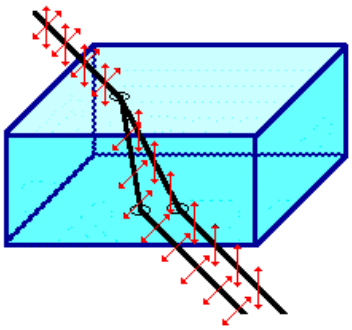


Figure 2. The illustration of the two refracted rays passing through the crystal that are polarized with perpendicular orientations.

3. Polarimeter

Figure 3 shows a principle of a polarimeter set up and its main components together with their function. Unpolarized light from the light source is first polarized. This polarized light passes through a sample cell. If an optical active substance is in a sample tube, the plane of the polarized light waves is rotated. The rotation is noticed by looking through the analyzer as a change in intensity of illumination. To reach the same illumination as was without an optical active sample the analyzer must be turned around for an angle. Readings are taken in degrees (angle).

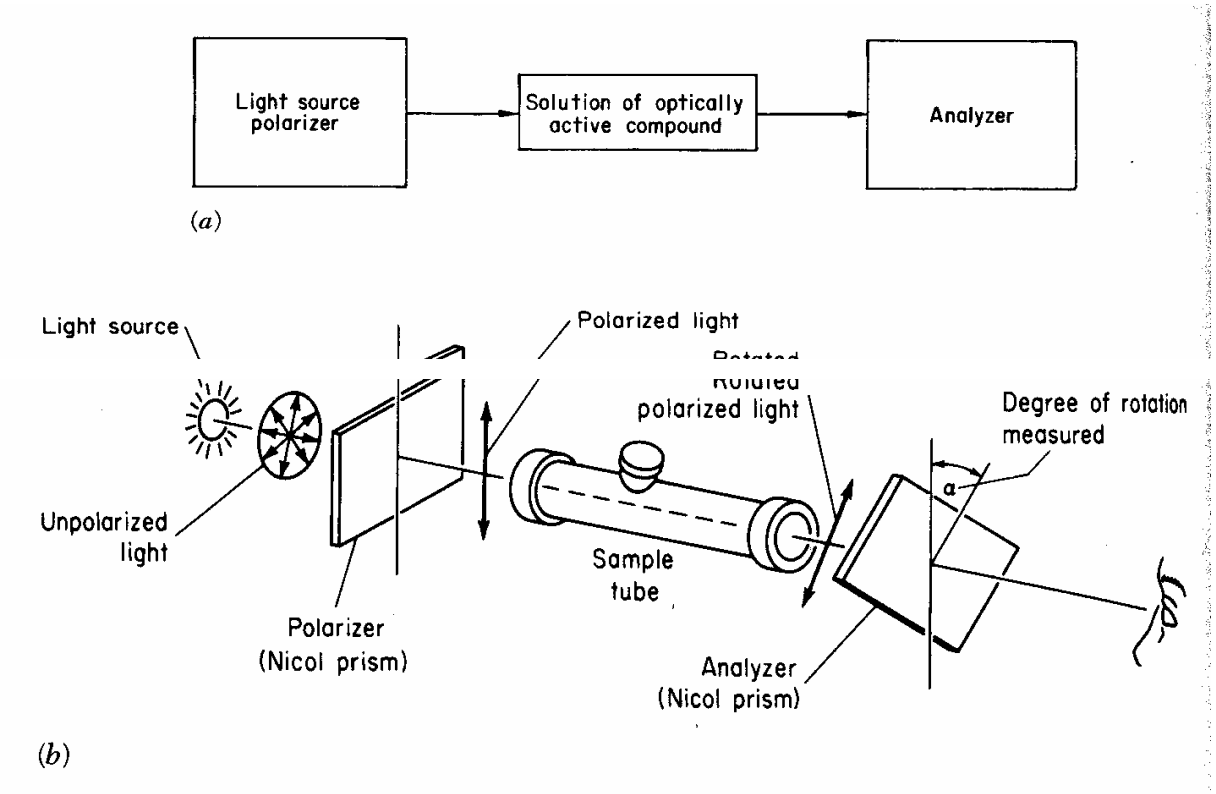


Figure 3. a) principle of a polarimeter set up

b) components of a polarimeter

Sources

Because optical rotation varies with wavelength, monochromatic radiation is employed. Historically, the sodium D line was obtained by introducing a sodium salt into a gas flame. Suitable filters then removed other lines and background radiation. Sodium vapor lamps with a filter to remove all but the D line are now employed. Mercury vapor lamps are also useful, the line at 546 nm being isolated by a suitable filter system.

Polarizer and Analyzer

Nicol prisms are most commonly employed to produce plane-polarized light and to determine the angle through which the light has been rotated by the sample.

Figure 4 depicts a Nicol prism, a device that exploits the double-refracting properties of crystalline calcite ($CaCO_3$) to produce plane-polarized radiation. A layer of Canada balsam, a transparent substance with a refractive index intermediate between the two

refractive indexes of calcite, is placed between the two crystal halves. This layer is totally reflecting for one beam, but transmits the other beam that is passed into the medium under study.

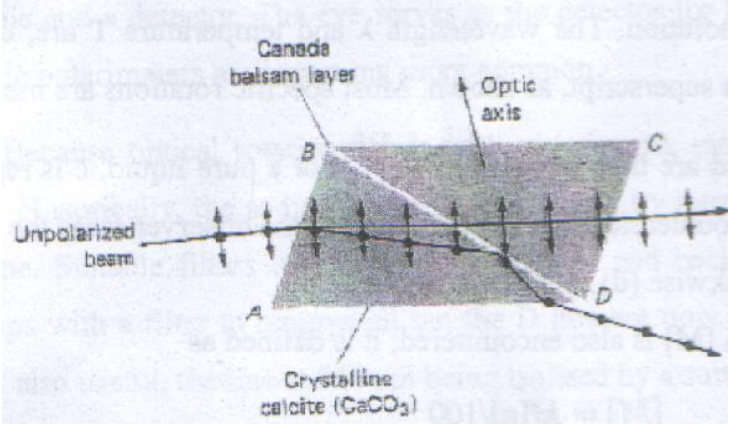


Figure 4. A nicol prism for resolving an unpolarized beam into two beams plane-polarized at 90° to one another.

Sample Tubes

The sample for polarimetry contained in a cylindrical tube, usually 5, 10 or 20 cm in length. For precise measurements, the tubes are surrounded by a jacket for temperature control. Tubes can be calibrated for length by measuring the rotation of a liquid of known rotation; nicotine/alcohol or sucrose/water mixtures are often used for this purpose.

4. Variables That Affect Optical Rotation

The rotation of plane-polarized radiation by optically active compounds can range from several hunderth to a few hunderths of degree. Experimental variables that influence the observed rotation include:

The type or nature of sample (example: sugar solution)
Concentration of the optical active components
The length of the sample tube
The wavelength of the light source
Temperature of the sample

The specific rotation $[\alpha]^T_\lambda$ is widely employed to describe the rotatory characteristics of a liquid. It is defined as

$$[\alpha]^T_\lambda = \frac{\alpha}{cl}$$

where a is the observed rotation in degrees, l is the length of the sample tube in decimeters, c is the grams of solute in 100mL of solution. The wavelength λ and temperature T are usually specified with a subscript and a superscript, as shown. Most specific rotations are measured at 20 °C with sodium D line. For a pure liquid, c is replaced by its density in g/cm^3.

5. Applications of Polarimetry

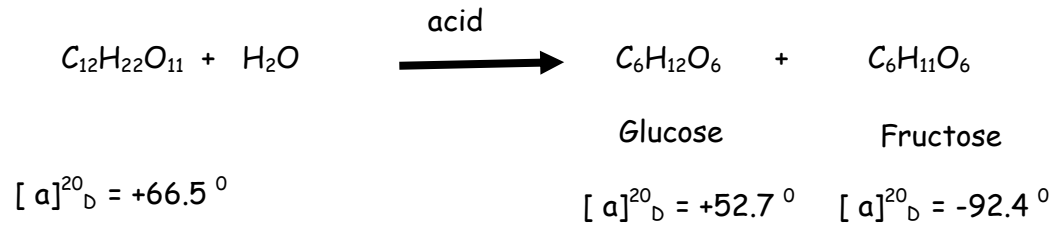
Qualitative Analysis

The optical rotation of a pure compound under a specified set of conditions provides a basic physical constant that is useful for identification purposes in the same way as its melting point, boiling point or refractive index. Optical activity is characteristic of many naturally occuring substances such as amino acids, steroid, alkaloids and carbohydrates; polarimetry represents a valuable tool for identifying such compounds.

Quantitative Analysis

The most extensive use of optical rotation for quantitative analysis is in the sugar industry. For example, if the only optically active constituent is sucrose, its concentration can be determined from a simple polarimetric measurement of an aqueous solution of the sample. The concentration is directly proportional to the measured rotation. If other optically active materials are present, a more complex procedure is required; the change in rotation resulting from the hydrolysis of the sucrose is determined.

The basis for this analysis is shown by the equation



This reaction is termed an inversion because of the change in sign of the rotation that occurs. The concentration of sucrose is directly proportional to the difference in rotation before and after inversion.

References

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