Refractometry

Introduction

A Bausch & Lomb Abbe-3L Refractometer.

A **refractometer** measures the extent to which light is bent (i.e. refracted) when it moves from air into a sample and is typically used to determine the **index of refraction** (aka **refractive index** or ***n***) of a liquid sample.

The refractive index is a unitless number, between 1.3000 and 1.7000 for most compounds, and is normally determined to five digit precision. Since the index of refraction depends on both the temperature of the sample and the wavelength of light used these are both indicated when reporting the refractive index:

$$n_{\mathrm{D}}^{20} \ 1.3742$$

The italicized *n* denotes refractive index, the superscript indicates the temperature in degrees Celsius, and the subscript denotes the wavelength of light (in this case the D indicates the sodium D line at 589 nm).

The refractive index is commonly determined as part of the characterization of liquid samples, in much the same way that melting points are routinely obtained to characterize solid compounds. It is also commonly used to:

- Help identify or confirm the identity of a sample by comparing its refractive index to known values.
- Assess the purity of a sample by comparing its refractive index to the value for the pure substance.
- Determine the concentration of a solute in a solution by comparing the solution's refractive index to a standard curve.

Theory

The speed of light in a vacuum is always the same, but when light moves through any other medium it travels more slowly since it is constantly being absorbed and reemitted by the atoms in the material. The ratio of the speed of light in a vacuum to the speed of light in another substance is defined as the **index of refraction** (aka **refractive index** or ***n***) for the substance.

$$\text{refractive index } (n) \text{ of substance} = \frac{\text{speed of light in a vacuum}}{\text{speed of light in substance}} \quad \text{(Eqn 1)}$$

Whenever light changes speed as it crosses a boundary from one medium into another its direction of travel also changes, i.e., it is refracted (Figure 1). (In the special case of the light traveling perpendicular to the boundary there is no change in direction upon entering the new medium.) The relationship between light's speed in the two mediums (v_A and v_B), the angles of incidence (θ_A) and refraction (θ_B) and the refractive indexes of the two mediums (n_A and n_B) is shown below:

$$\frac{v_A}{v_B} = \frac{\sin\theta_A}{\sin\theta_B} = \frac{n_B}{n_A} \quad \text{(Eqn 2)}$$

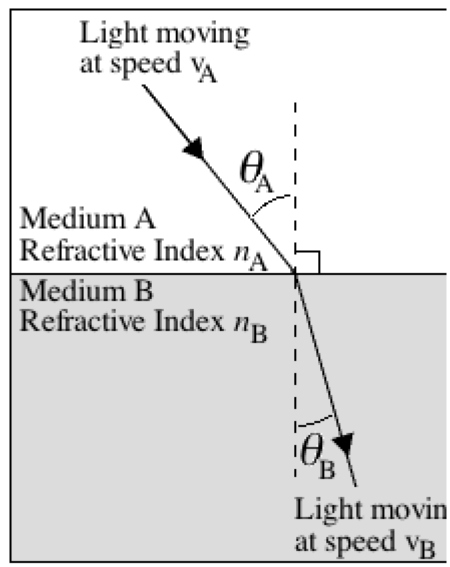


Figure 1. Light crossing from any transparent medium into another in which it has a different speed, is refracted, i.e., bent from its original path (except when the direction of travel is perpendicular to the boundary). In the case shown, the speed of light in medium A is greater than the speed of light in medium B.

Thus, it is not necessary to measure the speed of light in a sample in order to determine its index of refraction. Instead, by measuring the angle of refraction, and knowing the index of refraction of the layer that is in contact with the sample, it is possible to determine the refractive index of the sample quite accurately. Nearly all refractometers utilize this principle, but may differ in their optical design.

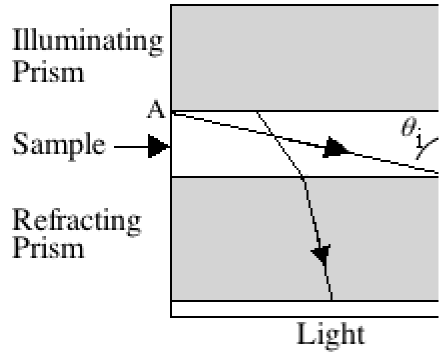


Figure 2. Cross section of part of the optical path of an Abbe refractometer. The sample thickness has been exaggerated for clarity.

In the Abbe' refractometer the liquid sample is sandwiched into a thin layer between an illuminating prism and a refracting prism (Figure 2). The refracting prism is made of a glass with a high refractive index (e.g., 1.75) and the refractometer is designed to be used with samples having a refractive index smaller than that of the refracting prism. A light source is projected through the illuminating prism, the bottom surface of which is ground (i.e., roughened like a ground-glass joint), so each point on this surface can be thought of as generating light rays traveling in all directions. Inspection of Figure 2 shows that light traveling from point A to point B will have the largest angle of incidence (θ_i) and hence the largest possible angle of refraction (θ_r) for that sample. All other rays of light entering the refracting prism will have smaller θ_r and hence lie to the left of point C. Thus, a detector placed on the back side of the refracting prism would show a light region to the left and a dark region to the right.

Samples with different refractive indexes will produce different angles of refraction (see Equation 2 above and recall that the angle of incidence and the refractive index of the prism are fixed) and this will be reflected in a change in the position of the borderline between the light and dark regions. By appropriately calibrating the scale, the position of the borderline can be used to determine the refractive index of any sample. In an actual Abbe' refractometer there is not a detector on the back of the refracting prism, and there are additional optics, but this is the essential principle.

(It is also possible to design a refractometer based on the reflection of light from the boundary between the prism and the sample. These types of refractometers are often used for continuous monitoring of industrial processes.)

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.

If white light were used in the simple Abbe' refractometer optics shown in Figure 2, dispersion would result in the light and dark borderline being in different places for different wavelengths of light. The resulting "fuzziness" of the borderline would make precise work impossible. However, many Abbe' refractometers are able to operate satisfactorily with white light by introducing a set of "compensating prisms" into the optical path after the refracting prism. These compensating prisms are designed so that they can be adjusted to correct (i.e., compensate for) the dispersion of the sample in such a way that they reproduce the refractive index that would be obtained with monochromatic light of 589 nm, the sodium D line.

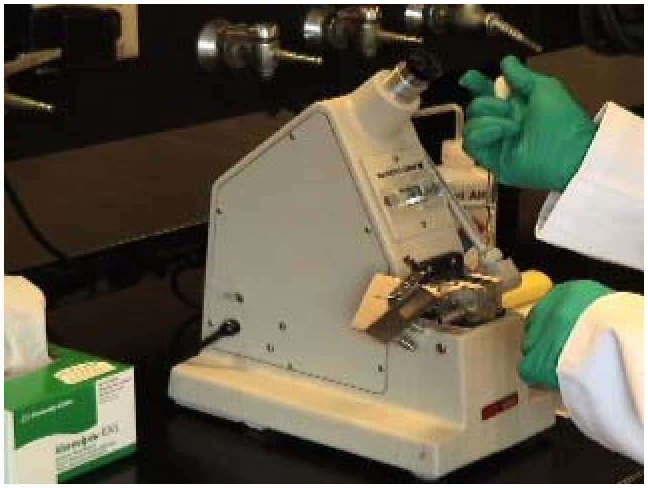
As mentioned earlier, the speed of light in a substance is slower than in a vacuum since the light is being absorbed and reemitted by the atoms in the sample. Since the density of a liquid usually decreases with temperature, it is not surprising that the speed of light in a liquid will normally increase as the temperature increases. Thus, **the index of refraction normally decreases as the temperature increases** for a liquid (Table 1). 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.

Operating the Abbe Refractometer

Some labs store the refractometer with a piece of tissue in the prism assembly to keep the prism glass from being scratched.

Open the prism assembly and remove the tissue.



Use a pipet to apply your liquid sample to the prism.

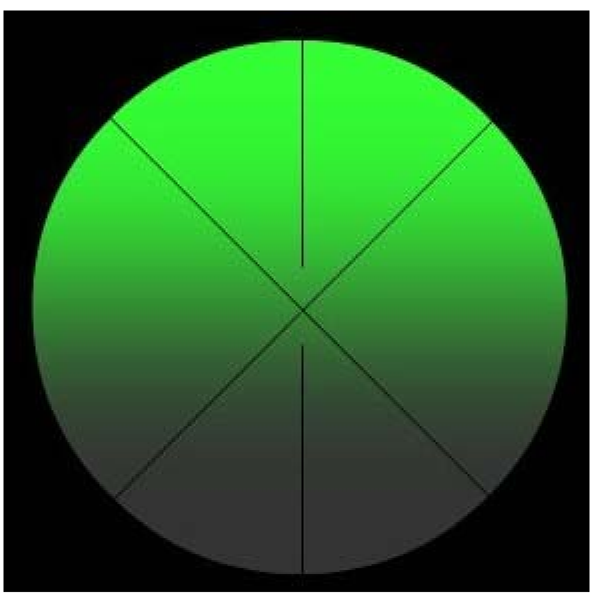
Be careful not to let the glass pipet tip touch the prism since this may scratch the soft prism glass.

Close the prism assembly.

Turn on the lamp using the switch on the left side. (On some models the switch may be in the power cord.)

Adjust the lamp so the light shines on the prism.

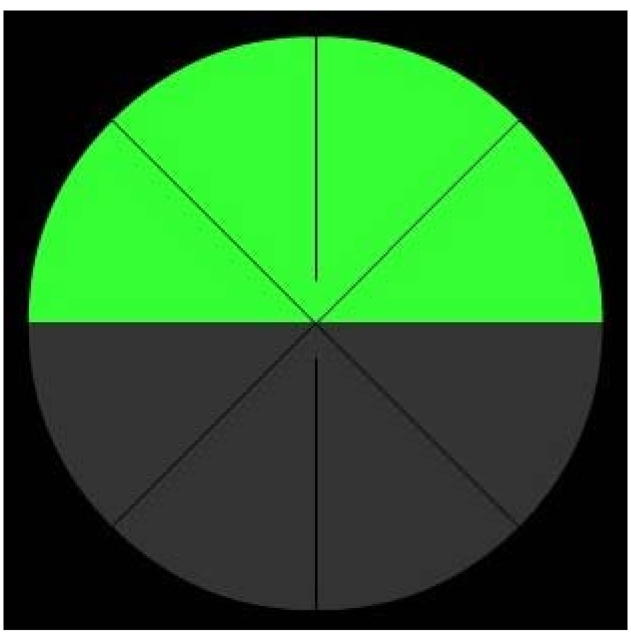
Look through the eyepiece.



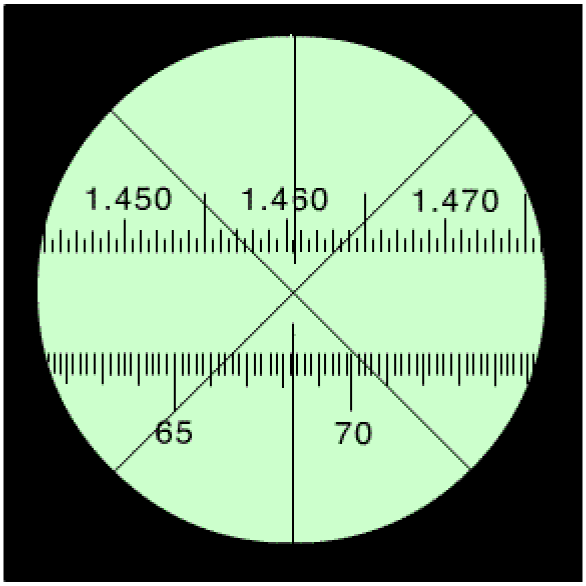
If you are close to the index of refraction of your sample you should see that the view in the eyepiece shows a dark region on the bottom and a lighter region on the top.

If you do not see a light and a dark region, turn the handwheel on the right side of the instrument until you do.

Before making the final adjustment, it will usually be necessary to adjust the lamp position and to sharpen the borderline between the light and the dark regions using the compensator dial on the front of the refractometer.



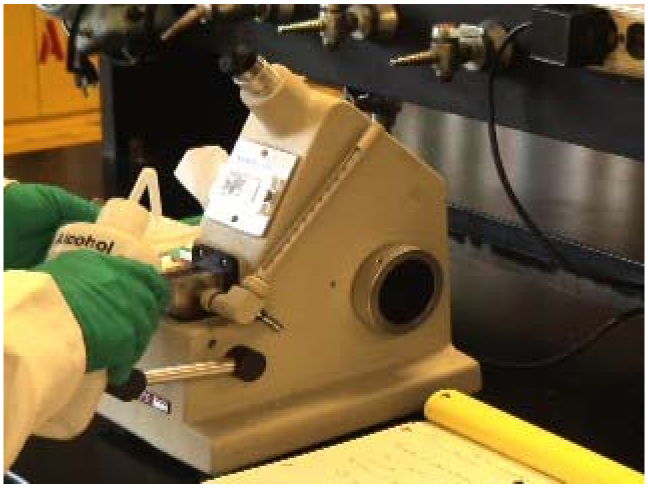
Once you have a crisp demarcation between the light and dark regions, turn the handwheel on the right hand side to place the borderline exactly on the center of the crosshairs as shown.



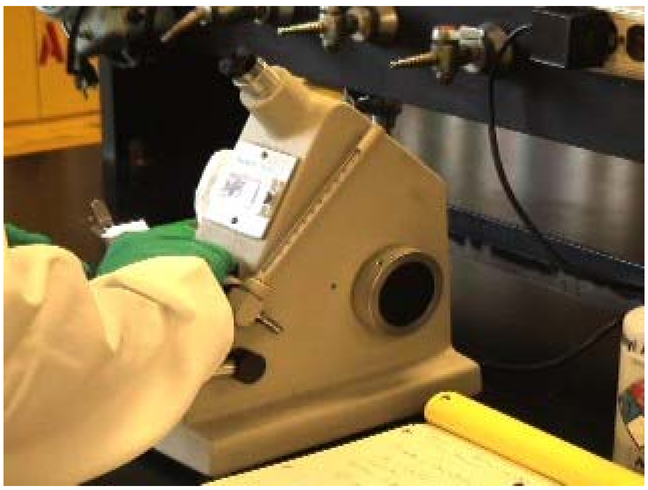
To read the index of refraction, depress the switch on the left hand side of the refractometer until you see the scale through the eyepiece. The upper scale indicates the index of refraction. By carefully interpolating you can read the value to 4 decimal place accuracy. The example shown here has a refractive index of 1.4606.

Record the refractive index in your lab notebook. Then read the thermometer and record the temperature.

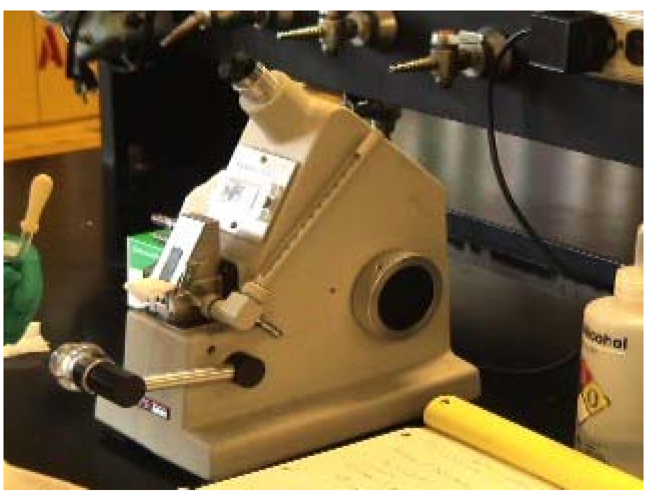
After you are finished, clean the refractometer. First use a tissue to dab away most of your sample.



Then wash the prism with a little solvent, we usually use a simple alcohol such as ethanol for cleaning organic samples.



A dabbing motion rather than a rubbing motion is preferred to minimize the chances of scratching the prism.



After you have finished cleaning the prism, place a clean tissue in the assembly. Before you leave make sure that the light has been turned off.

Troubleshooting FAQ's

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1. There is no obvious distinction between light and dark regions.

a) Check to make sure that you have enough sample on the measuring prism. Volatile samples may evaporate before you can take a reading.

b) Check that the illuminating light is on and adjusted properly.

c) If you know the approximate refractive index for your sample, depress the scale display switch on the side of the refractometer and turn the adjustment handwheel until you are near the expected refractive index. Then release the scale display switch. If you don't see the light and dark regions try adjusting the compensator dial.

d) If you don't know the approximate refractive index for your sample, clean the refractometer and then add a standard sample with a known refractive index. Follow the instructions for part c above. (If possible choose a standard that is similar in structure to the sample.) Then clean off the standard and add your sample.

e) If even the scale is hard to read, adjust the focus by moving the eyepiece in and out.

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2. The borderline between light and dark regions never becomes sharp, even after adjusting the compensator dial.

a) Check to make sure that you have enough sample on the measuring prism. Volatile samples may evaporate before you can take a reading.

b) Try readjusting the illuminating light.

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3. Everything is blurry, even the scale and crosshairs.

a) Adjust the focus by moving the eyepiece in and out.

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4. The refractive index measured isn't correct (or at least not consistent with what is expected).

a) Repeat the measurement, making sure that you are reading the scale correctly.

b) Make sure you are at the same temperature as the value you are comparing to.

c) Check the calibration of the instrument by using a sample of known refractive index. If this value also isn't correct, have the instructor or appropriate person adjust the calibration.

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5. The scale doesn't show up when the switch is pressed.

a) Make sure you are pressing the switch correctly.

a) The light may be burned out. Consult your instructor or service technician to have it replaced.

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6. The illuminating light doesn't come on.

a) Make sure the instrument is plugged in, and that it is a live circuit.

b) The light may be burned out. Consult your instructor or service technician to have it replaced.

Prudent Practice

Avoid Scratching the Prism

The measuring prism in many refractometers is constructed out of soft glass that is easily scratched. Be careful not to touch the glass with any hard and/or sharp object, such as a pipet tip or metal spatula. Never rub the measuring prism.

Clean the Prism Immediately After Use

Use a wetted tissue or cotton ball for cleaning the prism glass and use a dabbing motion rather than a rubbing motion to minimize the chance of scratching the prism. Good choices as cleaning solvents are ethanol or isopropanol since they are inexpensive, relatively nontoxic, and won't degrade the prism seal. If aqueous solutions are being measured, the refractometer may be cleaned with distilled water, possibly containing a small amount of nonionic detergent if necessary.

Avoid Solvents That Degrade the Prism Sealant

The sealer around the prism may be degraded by certain solvents. For example, the Bausch & Lomb Abbe' Refractometer should not be used with the following solvents:

Dimethylformamide

Dimethylacetamide

Phenols

Acetic Acid Solutions

Other solvents may degrade the sealer at slower rates and should not be used as the normal cleaning solvent:

Tetrahydrofuran

Simple Esters

Acetone

Avoid Strong Acids or Bases

Strong acids and bases will etch the prism glass.

Reporting Results

The standard format for reporting the index of refraction is shown below:

$$n_{\mathrm{D}}^{20} \ 1.3742$$

The italicized *n* denotes refractive index, the superscript indicates the temperature in degrees Celsius (most values are determined at 20 °C), and the subscript denotes the wavelength of light (in this case the D indicates the sodium D line at 589.3 nm). Routine refractive indexes are nearly always measured using the sodium D line, but if a different wavelength of light is used the wavelength (in nm) is inserted in place of the subscript D.