

# CHAPTER 11

## Refractometry

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### 11.1 INTRODUCTION

The refractive index is a dimensionless constant determined by the character and state of the medium under specified conditions of temperature and wavelength of light. Refractive indices may be employed as criteria for the identification of materials, as an aid in the structural elucidation of molecules, to deduce molecular parameters and energies, and to determine concentration or changes in composition of a system.

When light from an optically isotropic medium (a medium in which the optical properties are the same in all directions) enters another optically isotropic medium, a change in the velocity of light occurs. This velocity

change is accompanied by a change in direction unless the light has entered perpendicularly to the boundary of the two media. The relationship between the angle of incidence of a light ray  $i$  and the angle of refraction  $r$  is given by Snell's law of refraction:

$$\frac{\sin i}{\sin r} = \frac{\eta_r}{\eta_i} \quad (11.1)$$

where  $\eta_i$  is the refractive index of the first medium and  $\eta_r$  is the refractive index of the second medium. The refraction of a light ray for isotropic media is shown diagrammatically in Fig. 11.1.

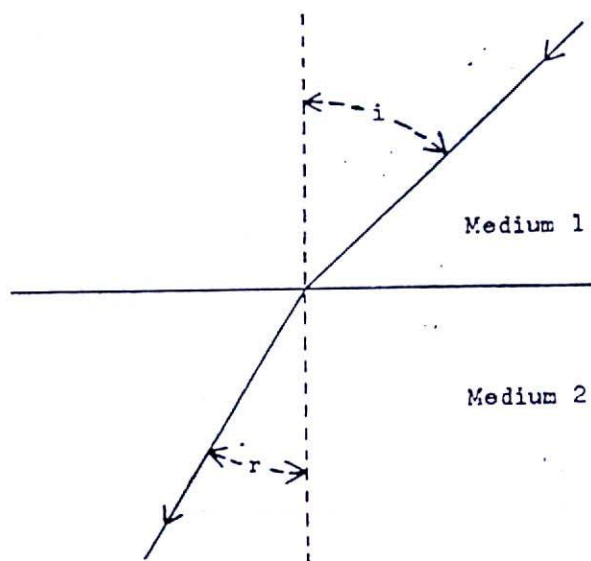


FIGURE 11.1: The fundamental geometric relationship of an isotropic light ray from medium 1 entering an optically denser medium 2. Both media are optically isotropic.

The refractive index of a single medium  $\eta$  is the ratio of the velocity of light in this medium to the velocity of light in a reference medium. Absolute refractive indices are those which are measured with reference to the velocity of light in a vacuum, which is approximately  $3 \times 10^{10}$  cm sec<sup>-1</sup> for all electromagnetic radiation. Therefore,

$$\eta_{abs} = \frac{v_{vac}}{v_{med}} = \frac{\sin i_{vac}}{\sin r_{med}} \quad (11.2)$$

where  $\eta_{abs}$  is the absolute refractive index,  $v_{vac}$  is the velocity of light in a vacuum ( $\approx 3 \times 10^{10}$  cm sec<sup>-1</sup>),  $v_{med}$  is the velocity of light in a given medium,

$\sin i_{\text{air}}$  is the sine of the angle of incidence with the normal on the plane interface between the two media, and  $\sin r_{\text{med}}$  is the sine of the angle of refraction with the normal.

It is common practice to refer the index of refraction of liquids and solids to a reference medium of air so that Eq. (11.2) becomes

$$\eta_{\text{med}} = \frac{r_{\text{air}}}{r_{\text{med}}} = \frac{\sin i_{\text{air}}}{\sin i_{\text{med}}} \quad (11.3)$$

where  $\eta_{\text{med}}$  is the refractive index of the medium. The refractive index of dry air at 0°C, 1 atm, and a wavelength of 5893 Å is 1.000277. Thus the absolute refractive index may be estimated by multiplying a relative refractive index such as  $\eta_{\text{med}}$  by 1.000277.

$$\eta_{\text{abs}} = 1.000277 \eta_{\text{rel}} \quad (11.4)$$

In reporting refractive indices the wavelength is commonly designated by a subscript and the temperature by a superscript. For example,  $\eta_{\text{D}}^{25}$ , 25 refers to the temperature of the measurement, 25°C, D refers to the wavelength of the light used for the measurement, the D line of sodium, 5893 Å (actually a doublet  $D_1 = 5890$  Å and  $D_2 = 5896$  Å). Other commonly used wavelengths of measurement are the hydrogen lines,  $H_{\alpha}(C) = 6563$  Å,  $H_{\beta}(F) = 4861$  Å, and  $H_{\gamma}(G) = 4340$  Å, and the mercury lines at 5790, 5461, 4358, and 4047 Å.

## 11.2 ORIGIN OF REFRACTIVE INDEX

The index of refraction of a substance has its origin in its tendency to undergo distortion in an electric field. This tendency, termed "optical polarizability," is related to the number, charge, and mass of the vibrating particles in the material, which in turn is determined by the atoms in the structure and by the type of electronic bonding. The refractive index is principally related to the motion of electrons in molecules and therefore both refraction and absorption of light may be considered to be two different aspects of the same phenomenon—the interaction of electromagnetic radiation with valence electrons.

The relationship between refractive index and absorption is illustrated in Fig. 11.2. If we select a hypothetical compound which has only one important absorption band as the wavelength of light changes in the visible and ultraviolet region of the spectrum, then the refractive index decreases as the wavelength of the radiation increases in a region of "normal" dispersion, and the refractive index increases as the wavelength increases in a region of "anomalous" dispersion. The curve obtained by plotting  $\eta$  vs. wavelength is called a "dispersion curve" since natural or "white" light of many wavelengths is dispersed or refracted to different angles by a given medium.

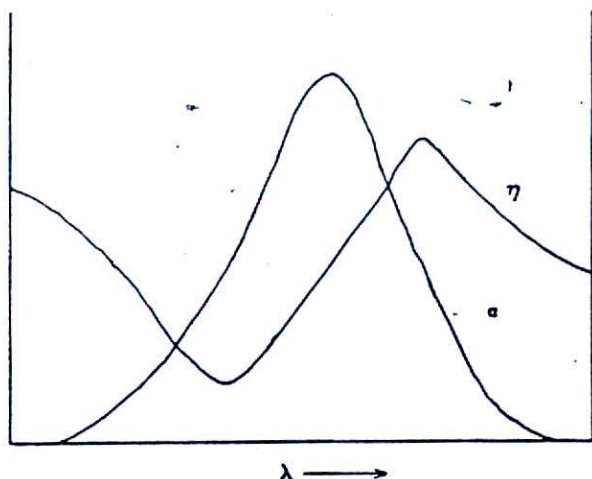


FIGURE 11.2: Theoretical absorption and dispersion curves;  $\eta$  = refractive index,  $\alpha$  = absorptancy index,  $\lambda$  = wavelength increasing from left to right from the ultraviolet to the visible region of the spectrum.

One of the first attempts to empirically correlate wavelength and refractive index is the Cauchy formula

$$\eta = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (11.5)$$

or

$$\eta = A + \frac{B}{\lambda^2} \quad (11.6)$$

where  $A$  and  $B$  are constants evaluated from data  $\eta_1$  and  $\eta_2$  at  $\lambda_1$  and  $\lambda_2$ . Thus

$$A = \frac{\eta_1 \lambda_1^2 - \eta_2 \lambda_2^2}{\lambda_1^2 - \lambda_2^2} \quad (11.7)$$

and

$$B = (\eta_1 - A) \lambda_1^2 \quad (11.8)$$

In a region of normal dispersion the Cauchy formula may be used for a rough interpolation of refractive index, however serious errors will occur as the absorption band is reached. The Cauchy formula is without theoretical basis.

A more satisfactory relationship for normal dispersion curves, which is based on classical electromagnetic theory, is the Sellmeier equation

$$n^2 - 1 = \sum_i \frac{K_i \lambda^2}{\lambda^2 - \lambda_i^2} \quad (11.9)$$

where  $\eta$  is the refractive index,  $\lambda$ , represents the wavelength of the absorption band of the substance,  $\lambda'$  is the wavelength of measurement of  $\eta$ , and  $K$ , is a constant arising from electromagnetic theory, which contains factors involved with transition probabilities of the absorption band. Another form of this expression, the Lorenz form, is:

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \sum_i \frac{K_i \lambda_i^2}{\lambda^2 - \lambda_i^2} \quad (11.10)$$

Because of the complexity of Eq. (11.9) and (11.10) graphical methods are usually used to show the quantitative variation of refractive index with wavelength in regions of normal dispersion.

Regions of anomalous dispersion in the dispersion curve are explained by interaction of the scattered light (oscillating electrons) of the absorption phenomenon with the original incident light. It is possible to develop theoretical relationships between absorption curves and dispersion curves and to discuss them both qualitatively and quantitatively using classical electromagnetic theory and modern quantum theory. Such a discussion is beyond the scope of this present chapter.

### 11.3 REFRACTIVE INDEX AND TEMPERATURE

From the foregoing section it may be understood that the spectral characteristics of a molecule may be related to the refractive index measurement. This is a factor in the explanation of the temperature dependence of refractive index. An increase in temperature tends to shift ultraviolet absorption bands to longer wavelengths, which will lead to an increased refractive index. Conversely infrared absorption is shifted to shorter wavelengths by an increase in temperature, which tends to decrease the refractive index.

Other factors which cause the refractive index to be temperature dependent are changes in density of the sample medium and reference medium as the temperature changes. If the temperature increases, the light beam will encounter fewer molecules per unit volume in passing through a given medium. Thus a decrease in density of the sample will decrease the absolute refractive index, whereas a decrease in density of air will increase the relative refractive index.

In general the refractive index of organic liquids will decrease by a factor of  $4.5 \times 10^{-4}$  for every centigrade degree of increase in temperature. Therefore it is necessary to specify the temperature of a refractive index measurement and to control the temperature at which the measurement is taken to within  $\pm 0.2^\circ\text{C}$  for a precision of  $\eta$  of  $1 \times 10^{-4}$ . For even rough qualitative measurement the temperature should be controlled to within  $3^\circ\text{C}$  for an accuracy of  $\eta$  of  $\pm 0.002$ .

## 11.4 REFRACTIVE INDEX AND DIELECTRIC CONSTANT

At low frequencies the refractive index may be related to the dielectric constant by electromagnetic theory. If the measurement of refractive index is made with infrared radiation in a region where the radiation is not absorbed, then it may be demonstrated that the refractive index  $\eta$  is related to the dielectric constant  $\epsilon$  by the equation:

$$\eta^2 = \epsilon \quad (11.11)$$

This relationship is derived with the assumption that the substance contains no dipoles or that contribution to  $\eta$  of the permanent dipoles of the substance is negligible since permanent dipoles of nuclei cannot keep up with a very rapidly alternating electric field such as that associated with light waves and only electrons in molecules can adjust themselves.

At low frequencies, long wavelengths, the dielectric constant is a measure of the total moment of the substance in an electric field. The equation relating the dielectric constant and the polarization of a substance is:

$$P_m = \frac{\epsilon - 1}{\epsilon + 2} \frac{m}{d} \quad (11.12)$$

where  $P_m$  is the polarization per mole,  $m$  is the molecular weight, and  $d$  is the density. The total molar polarization may also be expressed by the following equation:

$$P_m = 4/3\pi N \left( \alpha + \frac{\mu^2}{3kT} \right) \quad (11.13)$$

where  $N$  is Avogadro's number,  $\alpha$  is the electrical polarizability of the molecules,  $\mu$  is the moment of the permanent dipoles,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

The term  $4/3\pi N$  gives the contribution of the induced dipoles to molar polarization, which is proportional to  $\alpha$ , and the term  $\mu^2/3kT$  gives the contribution corresponding to permanent dipoles.

The contribution of the induced dipoles to the dielectric constant may be evaluated by a calculation of the molar refraction  $R_m$ :

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \frac{m}{d} = 4/3\pi N_0 \alpha \quad (11.14)$$

A discussion of the significance and application of the calculation of molar refraction follows in the next section.

## 11.5 MOLAR REFRACTION

It may be shown that the refractive index is related to the polarizability of a substance through the molar refraction  $R_m$ . Thus

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \frac{m}{d} = 4/3\pi N_0 \alpha = \frac{Ne^2}{3\pi m_e} \sum_i \frac{f_i}{\nu_i^2 - \nu^2} \quad (11.15)$$

where  $N_0$  is the number of atoms per cubic centimeter,  $e$  is the electronic charge,  $m_e$  is the electron mass,  $f_i$  is the oscillator strength of an individual absorption band, a unitless measure of absorption intensity  $\nu_i$  is the frequency of the absorption band, and  $\nu$  is the frequency of the radiation used for measurement. The equations used in expression (11.15) apply for the steady state condition in which the electron moves in phase with the electromagnetic radiation and contributions to molar refraction from any permanent dipoles are ignored (see previous section).

As a consequence of the final expression in Eq. (11.15), it may be seen that weak absorption bands which have small oscillator strengths will make small contributions to the refractive index at all frequencies not close to the frequency of the weak band. Nearly all the molar refraction, calculated from measurement at the sodium D line, of organic compounds that do not have significant molar extinction coefficients above 200  $m\mu$  arises from absorption bands in the far ultraviolet. For example, the molar extinction coefficient of the carbonyl band of simple aliphatic ketones,  $\epsilon_{\max}$  15–20 near 290  $m\mu$ , has an  $f_i$  value of  $3 \times 10^{-4}$  and contributes very little to refractive index even at measurements made near the absorption maximum. Oscillator strengths close to unity are found for these substances with molar extinction coefficients of the order of  $10^4$  and  $10^5$  at wavelengths below 200  $m\mu$ .

As discussed previously, molar refraction is a calculation of the contribution of the induced dipoles in an electric field to the dielectric constant and is therefore a calculation of the "polarizability" of the substance. The molar refraction may be found from the measurement of refractive index using the Lorenz-Lorentz equation

$$R_m = \frac{\eta^2 - 1}{\eta^2 + 2} \frac{m}{d} \quad (11.16)$$

or it may be estimated by adding up the contributions of individual atoms or groups of atoms in the molecule. The latter method, the summing of individual atomic refractivities to give an estimation of molar refractivity, does not always yield results which agree with the Lorenz-Lorentz calculation. If the electronic structure of the substance under consideration is altered by bringing two or more atoms together the mean value of the frequency of absorption of all effective bands is changed. An example of

this is the introduction of a carbon-carbon double bond to a system of conjugated double bonds or to a system which creates conjugation and thus delocalization of electrons. In such instances, the calculated molar refractivity becomes the sum of atomic refractivities plus "exaltations" due to unsaturation, ring formation, or special groups which may be considered chromophores in the ultraviolet region of the spectrum.

TABLE 11.1: Atomic Refractivities of Some Elements and Structural Units at 20°C (D line)



C	2.418	C=C (double bond)	1.733
H	1.100	C≡C (triple bond)	2.398
O (hydroxyl)	1.525	N in amines	2.322
O (carbonyl)	2.211	primary	2.499
O (ester)	1.64	secondary	2.840
O (ether)	1.643	tertiary	7.69
—CH <sub>3</sub> —	4.618	S (mercaptan)	5.459
Cl	5.967	C≡N	0.71
Br	8.865		
			0.48

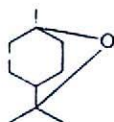
Table 11.1 presents values for the atomic refractivities of some elements and structural units.

The molar refraction of an organic compound may be calculated from the observed refractive index using the Lorenz-Lorentz equation. For example in order to calculate the molar refraction of eucalyptol (cineol), C<sub>10</sub>H<sub>18</sub>O, the values of the molecular weight, 154.24, the density ( $d_4^{20}$ ), 0.9267, and the observed refractive index  $n_D^{20}$ , 1.4584, are substituted in the Lorenz-Lorentz equation:

$$R_{m(\text{obs})} = \left[ \frac{(1.4584)^2 - 1}{(1.4584)^2 + 2} \right] \frac{154.24}{0.9267}$$

$$= 45.45$$

The molar refraction may also be calculated from the values of the atomic refractivities listed in Table 11.1. Using the previous example, eucalyptol, the  $R_{m(\text{calc})} = 45.62$ .



eucalyptol

$$\begin{aligned} 10 \text{ carbon atoms} &= 10 \times 2.418 = 24.78 \\ 18 \text{ hydrogen atoms} &= 18 \times 1.100 = 19.8 \\ 1 \text{ oxygen atom (ether)} &= 1 \times 1.643 = 1.643 \\ R_{m(\text{calc})} &= 45.62 \end{aligned}$$



The values in Table 11.1 may also be used to estimate the value of refractive index for a given structure. For example in order to calculate the refractive index of  $\alpha$ -pinene at 20°C using the sodium D line, the calculated molar refraction is found using the values from Table 11.1:



$$\begin{aligned} 10 \times C &= 10 \times 2.418 = 24.18 \\ 16 \times H &= 16 \times 1.100 = 17.6 \\ 1 \times C_{\text{=C}} &= 1 \times 1.733 = 1.733 \\ 1 \times C-C &= 1 \times 0.48 = 0.48 \\ &\quad \begin{array}{c} | \quad | \\ C-C \end{array} \end{aligned}$$

$$R_{\text{m(calc)}} = 43.99$$

The value of the calculated molar refraction for  $\alpha$ -pinene, 43.99, the molecular weight, 136.23, and the density ( $d_4^{20}$ ), 0.8585, are then placed in the Lorenz-Lorentz equation and the refractive index calculated:

$$43.99 = \frac{\eta^2 - 1}{\eta^2 + 2} \cdot \frac{136.25}{0.8585}$$

$$\frac{\eta^2 - 1}{\eta^2 + 2} = 0.27721$$

$$\eta^2 - 1 = 0.2772\eta^2 + 0.5544$$

$$\eta^2 = 2.1505$$

$$\eta = 1.466$$

The observed refractive index (found experimentally) is 1.4663. The molar refraction, calculated from the observed refractive index using the Lorenz-Lorentz equation, is 43.97.

Since molar refraction is an additive property of substances, the refractive index of mixtures may be calculated using equations of the following form:

$$R_{1,2} = X_1R_1 + X_2R_2 \quad (11.17)$$

and

$$R_{1,2} = \frac{\eta^2 - 1}{\eta^2 + 2} \frac{X_1m_1 + X_2m_2}{d_{1,2}} \quad (11.18)$$

where  $X$  is the mole fraction,  $\eta$  is the refractive index of the mixture, and  $d$  is the density of the mixture.

If the volume does not change when two substances are mixed, it may be possible to calculate the approximate refractive index using the following equation:

$$\eta = \frac{\eta_1v_1 + \eta_2v_2}{v_1 + v_2} \quad (11.19)$$

where  $v$  is volume and  $\eta$  is the refractive index. The refractive index, however, will more often vary linearly with the mole fraction of the components.

The specific refraction  $r$  defined by Lorenz and Lorentz is

$$r = \frac{\eta^2 - 1}{\eta^2 + 2} \left( \frac{1}{d} \right) \quad (11.20)$$

Specific refraction like molar refraction is an additive property of substances and therefore it is possible to calculate the refractivity of a mixture from the specific refractivity of the components with an equation of the type

$$C_{r,m} = Ar_a + Br_b \quad (11.21)$$

where  $C$  is a mixture of  $A$  grams of  $a$  and  $B$  grams of  $b$  with specific refractivities  $r_a$  and  $r_b$ , respectively.

## 11.6 MEASUREMENT OF REFRACTIVE INDEX

When light passes from a less-dense medium to a more-dense medium, the angle of refraction is always less than the angle of incidence. As the angle of incident light is increased, the angle of refracted light will also increase. The angle of refracted light will reach a maximum as the angle of incidence approaches  $90^\circ$ . If the angle of refraction is increased to a value at which the angle of incidence is  $90^\circ$ , light no longer enters the denser medium, no refracted light is possible, and light will be reflected through the less-dense medium. The value of the angle of refraction where the incident light approaches  $90^\circ$  incidence (also termed "grazing incidence") and which separates refracted and reflected light is called the "critical angle of refraction." In this limiting instance, since  $\sin 90^\circ = 1$ , Snell's law may be simplified to

$$\frac{\eta_r}{\eta_i} = \frac{1}{\sin r_c} \quad (11.22)$$

where  $r_c$  is the critical angle in the denser medium at the wavelength used,  $\eta_r$  is the refractive index of the denser medium, and  $\eta_i$  is the refractive index of the less-dense medium. The critical angle is characteristic of each substance and the critical-angle principle is used to measure refractive indices by means of so-called critical-angle refractometers. If either  $\eta_r$  or  $\eta_i$  are known and the critical angle  $r_c$  is observed, then the refractive index may be found. In most critical-angle refractometers  $\eta_i$  is the refractive index of the unknown sample and  $\eta_r$  is the known refractive index of a prism.

A typical design of a critical-angle refractometer (Abbe) is schematically shown in Fig. 16.3 and a commercial instrument, the Bausch & Lomb "Abbe 3L" refractometer, is pictured in Fig. 11.4. A thin layer of liquid is placed between the illuminating and refracting prisms, which may be equipped

with water jackets to provide temperature control. Light enters from below by means of a reflecting mirror. The angle of emergence of the critical ray is measured by scanning the upper edge of the refracting prism with a telescope. Since each wavelength of light has a critical angle, wavelengths other than that of the desired wavelength (usually the  $\text{D}$  line of sodium) are dispersed by Amici prisms—small direct vision spectroscopes. These compensating prisms are rotated to obtain a sharp colorless light-dark boundary and the sharp edge of the boundary is centered on the cross hairs of the telescope. The refractive index of the liquid in terms of monochromatic sodium light can be obtained directly from a calibrated glass or metal scale.

The accuracy that can be obtained with an instrument of this type is  $\pm 0.0001$  in a range of  $\eta$  from 1.30 to 1.70. Substances which have refractive indices greater than that of the refracting prism of the Abbe refractometer cannot be measured since total reflection would be the result.

The dispersion of the sample may be estimated with some instruments of the Abbe type. Dispersion  $\nu$  is calculated from the equation

$$\nu = \frac{\eta_{\text{D}} - 1}{\eta_{\text{F}} - \eta_{\text{C}}} \quad (11.23)$$

where  $\eta_{\text{D}}$  is the refractive index for the sodium  $\text{D}$  line,  $\eta_{\text{F}}$  is the refractive index for blue hydrogen line (4681 Å), and  $\eta_{\text{C}}$  is the refractive index for red hydrogen line (6563 Å). The values for partial dispersion  $\eta_{\text{F}} - \eta_{\text{C}}$  may be obtained from the reading ("Z" value) of the Amici compensator drum and reference to a table furnished with the instrument. The partial dispersion and dispersion are sometimes useful for characterization purposes. Another parameter that has characteristic values for certain classes of compounds is the specific dispersion  $\delta$ .

$$\delta = \frac{\eta_{\text{F}} - \eta_{\text{C}}}{d} \times 10^4 \quad (11.24)$$

Values found for dispersion, partial dispersion, and specific dispersion may vary depending on the actual instrument and must be used with caution.

Another type of critical-angle refractometer is the dipping or immersion type. See Fig. 11.5. This instrument differs from the Abbe type in that it does not have an illuminating prism and the single refracting prism which is immersed in the liquid sample is rigidly mounted in the telescope containing the compensator and the eyepiece. A scale below the eyepiece is moved by means of a micrometer screw at the top of the instrument until the nearest division falls on the light-dark boundary. Both the scale and the micrometer are read and the refractive index found by reference to a table. The immersion type of critical-angle refractometer yields a greater precision than the standard Abbe refractometer. By the use of ten interchangeable prisms the range of  $\eta$ , 1.325 to 1.647, can be read with a precision of  $\pm 3 \times 10^{-5}$ . However this type of refractometer requires a sample size of 5 to 30 ml, whereas the Abbe

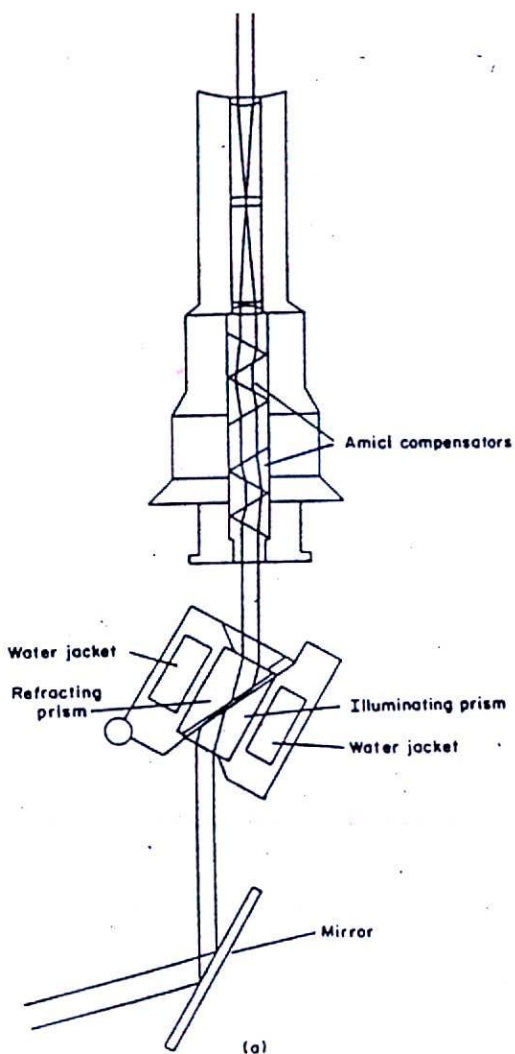


FIGURE 11.3: (a) Schematic diagram of a typical critical ray refractometer; (b) enlarged view of prisms of refractometer ( $r_c$  = critical angle,  $\alpha$  = angle of emergence of critical ray); (c) enlarged view of Amici compensator.

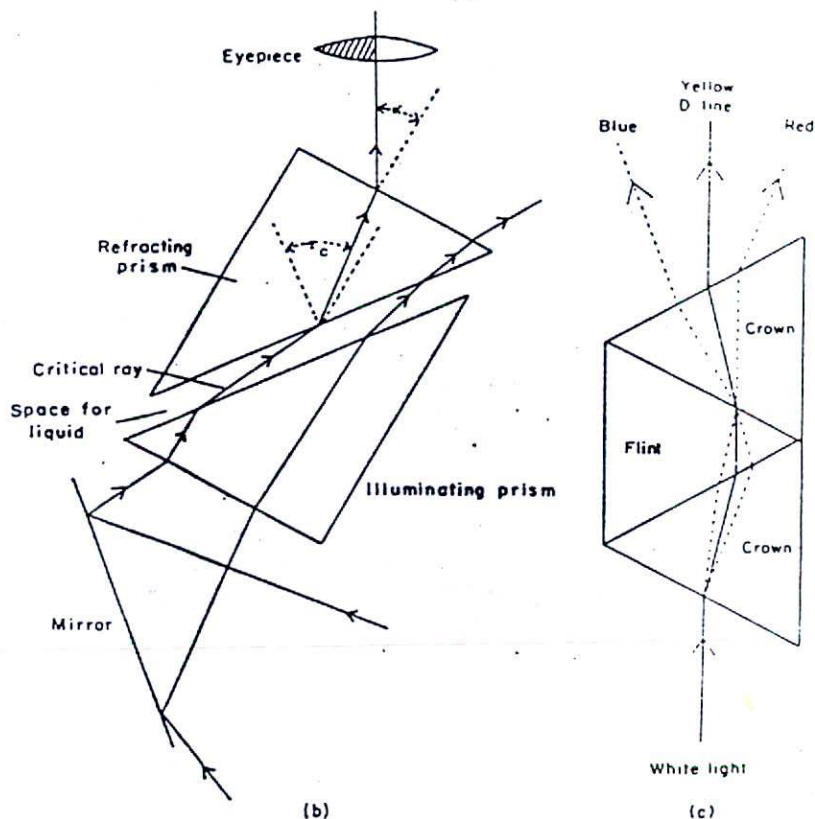


FIGURE 11.3 (continued)

instrument may require from 0.05 to 0.10 ml. The immersion refractometer is especially useful for the routine precision analysis of the concentration of aqueous and alcoholic solutions.

The most precise measurements of refractive index are made with instruments using the principle of interference of light waves. In this type of refractometer parallel rays of white or monochromatic light pass through matched cells containing the sample substance and a standard of known refractive index. The light then passes to a slit at the end of each cell. If the two light beams are of equal length, they will arrive in phase on a plane surface perpendicular to the light path and result in a series of bright bands. At places on the plane surface the two light beams are not the same length (out of phase) and dark bands are produced. Thus a pattern of interference

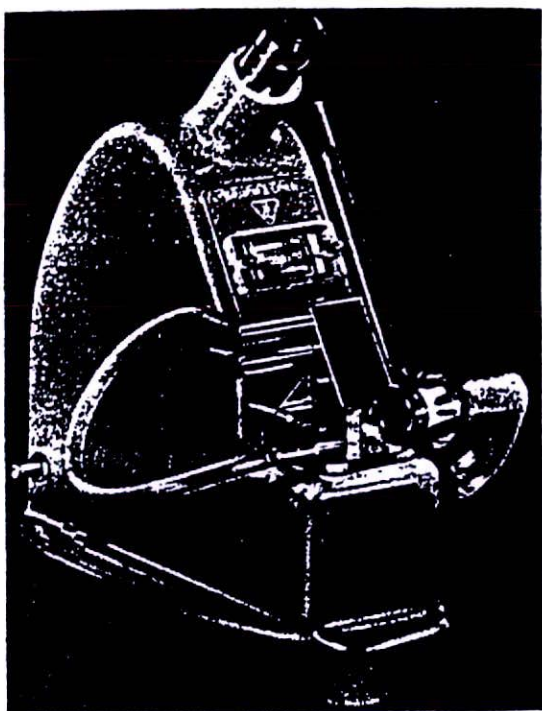


FIGURE 11.4: Bausch & Lomb Abbe 3L refractometer.

bands is produced. The relative position of the interference bands will depend on the optical length of the light paths. If the sample has a slightly greater refractive index than the standard, the optical path of light through the sample will be increased since the velocity of light through the sample is decreased. The change in the interference pattern produced by unequal optical paths is noted visually as a shift in the position of the interference pattern. The changed interference pattern may be matched with a fixed band pattern by means of a variable glass compensator in the sample path. A differential reading of refractive index  $\Delta\eta$  is obtained from the scale of the compensator micrometer screw. A schematic diagram of a typical Rayleigh (interference) refractometer is shown in Fig. 11.6.

Interference refractometers are usually used for the differential measurement of refractive indices over a narrow range. The maximum difference  $\Delta\eta$  that may be obtained with liquids is 0.05 units of  $\eta$ . These measurements may be made with an ultimate precision of  $\pm 2 \times 10^{-7}$  units of  $\eta$  for liquids and  $\pm 3 \times 10^{-8}$  units of  $\eta$  for gases. The interferometer may be used to

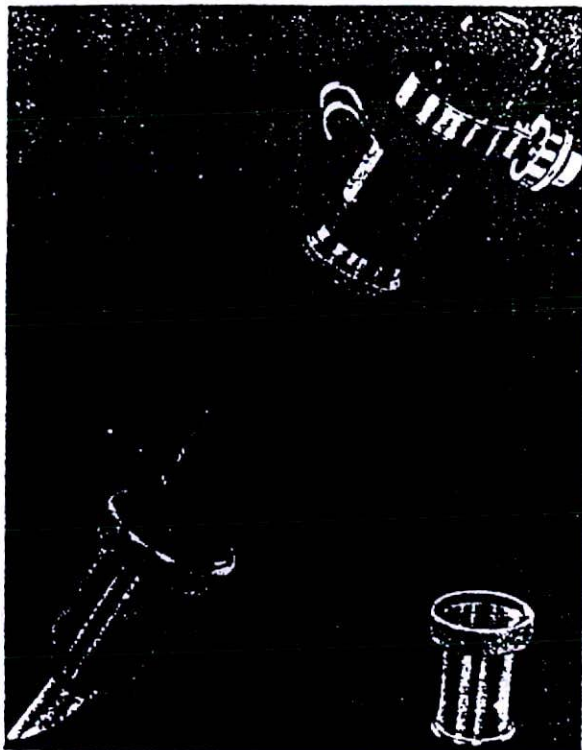


FIGURE 11.5: Bausch & Lomb dipping refractometer.

analyze gases, *e.g.*,  $\text{CO}_2$  in air, in the analysis of dilute solutions and small changes in the composition of mixtures.

Precision spectrometers may be used to measure refractive index. In these instruments the material to be measured is formed into a prism, which is placed at the center of a large, precisely ruled circle of metal. Monochromatic energy is focused through a slit and passed through the sample prism. The

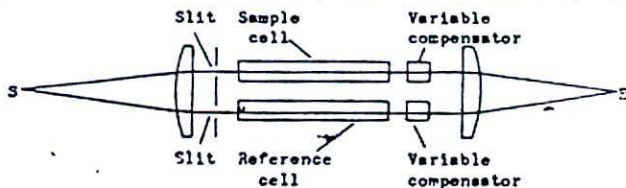


FIGURE 11.6: Schematic diagram of a typical Rayleigh refractometer.  $S$  = light source;  $E$  = eyepiece.

angular setting of the displacement of the image of the slit is a measurement of the index of refraction of the substance at the particular wavelength and temperature. This type of refractometer can yield good precision,  $\pm 1 \times 10^{-4}$  units of  $n$ , and is most versatile. Wavelengths in the ultraviolet and infrared regions of the spectrum may be used and there is no limit on the value of  $n$ , since any angle of refraction can be determined. However careful angular measurement and close temperature control are necessary to obtain precise measurements and these instruments are not generally suitable for routine laboratory analyses.

A type of image-displacement refractometer which may be used for a very rough measurement of refractive index is the *Jelley-Fisher* refractometer. As with the prism-spectrometer type, the sample liquid is formed into a prism by the beveled edge of a glass slide. The operator looks through this liquid sample prism at a graduated illuminated scale containing a slit. The refractive index is read by observing the refracted slit image formed by the eye focused in the plane of the scale. Using the most yellow part of the dispersed white light of the slit image, it is possible to estimate a refractive index within  $\pm 0.002$  units of  $n$ .

## 11.7 APPLICATIONS OF REFRACTIVE INDEX MEASUREMENTS

Refractive index measurements may be used as physical constants for the identification of substances. For example, in pharmaceutical analysis refractive index may be used as a means for the identification and detection of impurities in volatile oils. The standard Abbe refractometer usually has sufficient range and precision for the comparison of pharmacopoeial materials.

Refractometry may be employed as a convenient method of measurement and evaluation of the separation of complex materials by physical means such as chromatography, distillation, electrophoresis, and extraction.

Since the more modern development of ultraviolet, infrared, and nuclear magnetic resonance spectroscopy and mass spectrometry, refractive index measurements are not as important as they once were in qualitative organic analysis. However refractometric data may still be of aid, as a nondestructive method, in the determination of molecular structure.

The precision and accuracy of quantitative refractometric measurements depend on the type of refractometer used and the temperature control. Often it is necessary to prepare accurate calibration curves using pure components since refractive index composition curves are not always linear over the range of concentrations to be determined. Quantitative refractometry has been used for serum, sugar, fat, oil, and petroleum analyses.



## EXPERIMENTS

- E11.1. Qualitative and quantitative analysis of liquids using the Abbe refractometer. (a) Read and note the laboratory directions for the instrument. Determine the refractive index of water at a constant temperature of 20 or 25°C. Take five readings and determine the average. The refractive index of water at 25°C,  $n_D^{25}$ , = 1.3325 and at 20°C,  $n_D^{20}$ , = 1.3330.
- (b) Determine the refractive index of a pure liquid obtained from the instructor. Compare your value with the literature value. Take five readings in either direction on the Amici compensator. With the value for the refractive index and the compensator value, calculate the dispersion of the substance using the dispersion table supplied with the instrument. Using the reported density of the substance, calculate specific dispersion. Use your observed value of refractive index to calculate molar refraction from the Lorenz-Lorentz equation. Calculate the molar refraction from a table of atomic and group refractivities and compare the result with the Lorenz-Lorentz equation.
- (c) Determine the percentage of sucrose in samples of syrup supplied by the instructor. (If the instrument is not supplied with a sugar scale, a calibration curve must be constructed with standard solutions of sucrose.)
- E11.2. Determination of alcohol content using the Pulfrich immersion refractometer. Determine the percentage volume to volume of ethyl alcohol in the preparation supplied by the instructor according to the procedure of the *British Pharmacopoeia*, 1968, Appendix XII H, p. 1278.

## QUESTIONS

- Q11.1. Define the following terms and describe how they are applied to the measurement of refractive index:
- dispersion
  - isotropic light
  - grazing incidence.
- Q11.2. How many measurements of refractive index be used in quantitative analyses?
- Q11.3. Briefly and qualitatively describe the relationship between the refractive index and absorption coefficient of a substance.
- Q11.4. Atomic refractivities of some elements and structural units may be used to calculate the refractive index of a particular structure. In some instances the calculated refractive index may be quite different from the observed refractive index. Explain.

## PROBLEMS

- P11.1. Calculate the molar refraction of triethanolamine;  $n_D^{20} = 1.4852$ ,  $d_4^{20} = 1.1242$ . Compare the results with the theoretical molar refraction calculated by a summation of atomic and group refractivities.
- P11.2. Calculate the molar refraction of nicotine;  $n_D^{20} = 1.5820$ ,  $d_4^{20} = 1.0097$ . Compare the result with the theoretical molar refraction calculated by a summation of atomic and group refractivities.

- P11.3. The molar refraction of limonene (dipentene)  $C_{10}H_{16}$  is 45.25. Calculate the refractive index if its density is 0.840, using the Lorenz-Lorentz equation. Compare the result with the literature value.
- P11.4. What is the composition of a mixture of *n*-hexane ( $n_D^{20} = 1.3751$ ) and cyclohexane ( $n_D^{20} = 1.4264$ ), which has a refractive index of 1.3800 at 20°C? Assume a linear relationship between mole fraction and refractive index.
- P11.5. Calculate the weight per cent of 50 ml of a mixture of morpholine and pyrrole if the density of the mixture is 0.9880 and  $n_D^{20} = 1.4920$ . Pure pyrrole has a  $d_4^{20}$  of 0.9691 and  $n_D^{20}$  of 1.5085. Morpholine has a density of 0.9994 and  $n_D^{20}$  of 1.4545.

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