An Investigation of the Refractive Index of Selected Liquids in the Ultraviolet

Robert Bruce Eaton
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AN INVESTIGATION OF THE
REFRACTIVE INDEX OF SELECTED
LIQUIDS IN THE ULTRAVIOLET

by

Robert B. Eaton

A Thesis submitted to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
August 1967
ACKNOWLEDGEMENTS

I wish to express my gratitude to all whose suggestions and guidance have been so helpful. In particular, special thanks are due Dr. Stanley K. Derby, Dr. Nathan L. Nichols, and Dr. Larry D. Oppliger, the members of my advisory committee.

Mr. Richard Durbin deserves recognition for his assistance during the construction of the equipment.

Finally, I wish to thank my wife Karen for her patience and understanding during the progress of this work.
Master's Thesis

EATON, Robert Bruce

AN INVESTIGATION OF THE REFRACTIVE INDEX
OF SELECTED LIQUIDS IN THE ULTRAVIOLET.

Western Michigan University, M.A., 1967
Physics, general

University Microfilms, Inc., Ann Arbor, Michigan
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CHAPTER I
INTRODUCTION

The refractive indices of a large number of substances have been precisely determined at wavelengths throughout the visible spectrum, particularly for the Fraunhofer H, G', F, D2, and C lines. Few refraction measurements have been made in the ultraviolet because so many substances exhibit strong ultraviolet absorption bands. Many gases and some solids, particularly quartz, silica, and the crystalline halides, are more transparent to ultraviolet radiation, so their refractive indices have been investigated. The recent development of a stable, high pressure, xenon arc lamp has provided the high intensity ultraviolet source needed for measurement of refractive indices within the strong ultraviolet absorption bands.

Several methods may be used to determine \( n \), the refractive index. A few of the more common ways will be mentioned for purposes of comparison, even though they are not suitable for ultraviolet measurements of \( n \) for liquids.

Measurements of the principal angle of incidence and the principal azimuth angle for light reflected from the surface of the substance may be used to calculate \( n \). The method works well near strong absorptions because of the high reflectivity associated with them, but it is generally limited to use with solids because of the flat, unobstructed surface needed for reflection from the substance.
Various ways of determining $n$ by measuring the critical angle of incidence have considerable application to liquids in the visible region, but each requires the use of a measuring plate or prism for which the dispersion is accurately known. Problems with absorption by the plate or prism and the difficulty of locating images in the ultraviolet make these methods impractical for ultraviolet measurements of $n$.

A precise way of determining $n$ for liquids or solids uses a prism which is either hollow to contain the liquid or is constructed of the solid to be examined. Determinations of the angle of minimum deviation and the prism angle provide the information necessary to calculate $n$. This method is frequently used to determine $n$ for solids in the ultraviolet, but specially made thin, hollow prisms are needed if $n$ is to be measured for liquids near absorption bands.

The most precise methods of determining $n$ use interferometric principles. These employ various means of introducing known thicknesses of the substance to be investigated into one or both of the optical paths of the interfering light beams. The resulting alteration of optical path length due to the different phase velocity of light, $v = c/n$, in the substance shifts the interference pattern by a number of fringes, $\Delta m$, according to:

$$\Delta m = \frac{(n - 1) t}{\lambda}$$  \hspace{1cm} (1)
where \( t \) is the difference in thicknesses of the substance placed in the two light beams and \( \lambda \) is the wavelength of the monochromatic light used. Interferometric methods require extreme precision in producing and positioning the components of the system to provide a significant increase in measurement precision over other methods. Light of high spectral purity is required to produce the distinct interference fringes required for accurate counting. These methods are especially suitable for use with gases or for measuring small changes in refractive index.

A direct application of Snell's law\(^1\):

\[
n_1 \sin \theta_1 = n_2 \sin \theta_2
\]

(2)

to the refraction of light transmitted through a parallel-sided slab of the substance provides a simple, precise method of determining \( n \) for liquids.

Figure 1 illustrates the principle of this method. The three optical paths are shown superimposed for the conditions; unobstructed light beam, light beam through empty container, and light beam through container filled with the liquid. The relation between the separation \( s \) of the two deviated light beams and the refractive index \( n \) of the liquid is given by;

\[
s = \left[ 1 - \frac{\cos i}{(n^2 - \sin^2 i)^{1/2}} \right] d \sin i
\]

(3)
A - Path if container is filled with a liquid
B - Path if container is empty
C - Path of undeviated beam
S - Separation of A and B

Path Deviations of a Light Beam by a Container with Parallel Sides

Figure 1
where \( i \) is the angle of incidence and \( d \) is the thickness of the liquid in the container. This equation is discussed in Appendix I.

Figure 2 shows an experimental arrangement used to apply this principle. Two sets of collimating slits limit the light from the monochromator to a thin beam which passes, unobstructed, to the cells. One "empty" cell contains only air, and the other cell contains the liquid to be examined. The empty cell walls deviate the light a small amount, as shown, but the full cell deviates the beam to a greater extent. The two beams emerge from the cells parallel to the undeviated reference beam.

Measurement of the deviation is accomplished by using a precision dial indicator to determine the distance traveled by a set of slits moving from one beam to the other. An ultraviolet sensitive photomultiplier phototube indicates when the slits are centered on a beam. An alternate method of measuring the beam separation using a mechanical chopper is discussed in Appendix III.

The precision obtainable by this method is independent of the light intensity if the intensity is stable and high enough to be detected by the photomultiplier. Lenses and mirrors which would reduce the intensity by absorption and reflection are absent. An intensity reduction by reflection does occur at each of the cell wall faces which must be set at an angle to the incident light in order to produce a significant separation of the light beams.
A System for Measuring Index of Refraction of Liquids

Figure 2
However, reflections at the interior faces of the filled cell are greatly reduced because the cell walls and the liquid have similar refractive indices.
CHAPTER II
MECHANICAL CONSTRUCTION

A refractometer of the type shown in Figure 2 was constructed for the purposes of determining the dispersion curves of liquids in the visible and ultraviolet regions of the spectrum. Figure 3 is a cut-away drawing illustrating the mechanical features of the measuring apparatus.

One set of slits is mounted on each side of a 1" thick magnesium alloy plate which is grooved to slide along a set of rails mounted vertically in the frame. The photomultiplier tube, which is not shown, mounts directly on the last set of measuring slits and moves with them. The measuring slits are moved from one light beam to another by rotating the adjustment shaft which is threaded into the measuring slit slide. Stiff coil springs between the slide top and the frame eliminate backlash to give the adjustment a more positive motion. The collimating and measuring slits are each made of a pair of stainless steel injector razor blades fastened to the slit holders with small screws. The upper edges of the collimating slits are mounted on dovetail slides to make the slit opening adjustable. Small angular adjustment of the measuring and collimating slits is possible for alignment purposes. (see Appendix II)

The cell holder is machined from magnesium alloy to be a
Refractometer Assembly

Figure 3
sliding fit for two cells placed side by side. A hole is drilled through the holder adjacent to one of the cells to allow a reference beam to pass unobstructed to the measuring slits. The angle of incidence may be adjusted by rotating the cell holder shaft mounted on ball bearings in the frame.

The frame itself is made of 1" magnesium alloy plate, grooved to insure proper positioning of the collimating slits.

A flat spiral coil of 3/16" copper tubing is mounted on the bottom cover and connected to cold, running water to provide cooling and temperature stability.

When the top cover is in place, no light can enter except through the collimating slits. The interior, except the cell holder, is lined with black felt to absorb scattered light. The cell holder is painted a dull black and is fitted with a mask to block light transmitted edgewise through the unused sides of the cells.
CHAPTER III

ELECTRONIC CONSTRUCTION

The electronic circuitry is an adaptation of a photometer circuit developed by Sweet\(^2\) to give a logarithmic response to changes in light intensity. This type of circuit provides high sensitivity to low levels of light intensity and allows the use of high intensity without overloading the circuit components. No calibration to measure intensity levels is necessary because the circuit is used only to facilitate adjustment of the measuring slits to a position at the center of a light beam.

Figure 4 is a circuit diagram of the electronic apparatus used. Figure 5 is a simplification useful in presenting the principles of operation as a type of bridge circuit. When no light is allowed to strike the photocathode of V2, the anode dark-current from V2 and the grid current from V1 produce approximately 50 volts drop across resistance RL. The NE-32 maintains a constant 55 volts between resistance RB and the cathode of V1, so the grid of V1 is biased about 45 volts positive with respect to the cathode. A current of 8.3 milliamperes flows through the V1 cathode circuit, under these conditions, to produce an 1125 volt drop across resistance RB. Correct adjustment of potentiometer RS balances the circuit, so that the microammeter M reads zero current.

If low intensity light is allowed to strike the photocathode of
Logarithmic Photomultiplier Amplifier

Figure 4
Simplified Photomultiplier Bridge

Figure 5
V2, a small rise in the anode current of V2 occurs, increasing the voltage drop across resistance RL and reducing the positive bias on the grid of V1. This results in a lower V1 cathode current and a decreased voltage across resistance RB. The decrease of the V2 dynode voltages lowers the sensitivity of V2 until its anode current is back to the original, no-light value. The voltage drop across RB remains at a lower value to offset the effect of the light. Sweet has shown that the change in RB voltage drop is logarithmically related to the change in light intensity.

In this application, the decrease of voltage across resistance RB unbalances the bridge circuit, producing a current flow through the microammeter. Large changes in light intensity require adjustment of potentiometer RS to keep the current within the range of the meter.

The response time of the circuit is quite low, so fluctuations in light source intensity cause sporadic motion of the meter needle unless a large capacitor C is placed in parallel with the meter to integrate the current readings. This also eliminates the effects of electrical noise. Changes in light intensity still produce annoying instabilities if the changes are large or more than a second in duration.

The 1P28 photomultiplier phototube (designated V2 in figures 4 and 5) is especially suitable in this application because it is designed for high sensitivity and low noise. The S-5 spectral response of the 1P28 limits its use to wavelengths between 200 and 650.
millimicrons with a maximum response at 340 millimicrons. Light enters the 1P28 through the cylindrical side of the ultraviolet transmitting glass envelope. The photocathode size is 5/16" by 15/16", adequate to accommodate all three light beams.
CHAPTER IV
ASSOCIATED EQUIPMENT

The light source used is a high pressure xenon arc lamp, model 614, available from O. C. Rudolph and Sons, Incorporated. The arc produces a continuous spectrum from below 200 μm to above 700 μm, operating from a 22,000 to 25,000 volt, 60 cycle ac supply. The arc current remains fairly constant after a 15 minute warm-up period, though the arc is not as stable as desired. The main cause of instability is the tendency for the arc to shift position between the electrodes, either in an oscillatory manner or as a complete change of path. The best stability occurs for arc currents between 8.1 and 8.2 amperes, but a slight alteration of the current is helpful in curing the oscillatory instabilities. No measurement of the spectral intensity distribution was made, but according to Flach the intensity maximum occurs at 420 μm, decreasing only slightly to 700 μm, but fading to an intensity of about 0.5% maximum at 200 μm.

The monochromator is mounted in alignment with the light source by means of a 1½ inch diameter tube, flanged at both ends for attachment to the lamp lens holder and the monochromator entrance slit holder. The length of the tube is 4 inches so that the monochromator entrance slits are positioned in the focal plane of the light from the xenon arc.

A Jarrel-Ash 0.25 meter Ebert monochromator, model 82-410, is
used to select the wavelengths of the light passed to the measuring equipment. Two 1180 groove/mm reflection gratings are supplied, blazed for 600 μm and 300 μm. They are mounted back to back within the instrument so that the more efficient grating may be used for the wavelength desired. The precision of the three digit wavelength dial is ± 1 μm. When 100 μm entrance and exit slits are used, the bandwidth, focused at the exit slit, is 1 μm.

A problem arises in matching the output from the vertical monochromator slits to the horizontal collimating slits of the refractometer. The collimating slits must be horizontal because the liquids cannot be conveniently changed after being sealed in the refractometer cells for use in a horizontal position with vertical collimating slits. The xenon arc lamp must be operated vertically and is most suitable for use with vertical monochromator slits.

This mis-match is resolved by using the mirror arrangement shown in figure 6. Light from a vertical slit striking the upper mirror is reflected to the lower mirror where its projection appears as a horizontal line. The lower mirror reflects the light which enters the refractometer as though from a horizontal slit. The assembly is mounted in a housing attached to the monochromator exit slit holder.

A 1025 volt regulated dc power supply designed by Flach for use with a 1P28 photomultiplier tube was altered to produce 1200 volts regulated dc. Alterations were also made to provide complete isolation of the high voltage from the chassis. The circuit diagram of
Slit Orientation Convertor

Figure 6
the resulting power supply is shown in figure 7.

The cells used to contain the liquid during calibration and measurement are Scientific Cell Company precision spectrophotometer cells, type 400, obtained as a matched pair. The two optical faces of each cell are formed of a type of fused quartz, positioned to be very parallel, 1.000 cm apart on the inside. Each wall is 1.24 mm thick. The outside dimensions are 12.5 mm square by 45 mm long.

A Bryant model B-70 dial indicator is mounted on the refractometer frame to measure the displacements of the measuring slits. The 1.5 inch diameter dial is calibrated in thousandths of an inch, but it is capable of greater precision and may be read consistently within 0.0002 inches. A 0.05 inch displacement of the indicator actuating plunger contacting the top of the slit slide results in one full revolution of the indicating needle. The calibrated scale may be rotated without otherwise disturbing the indicator setting. The range of this instrument is 0.375 inches.
Figure 7
Regulated High Voltage Power Supply

1200 VDC

8 - VR150s

2x2

NE51 47K

NE51 47K

4K 4K

40K 20w

2M

115 VAC
CHAPTER V

CALIBRATION

After alignment (see Appendix II), the only calibration necessary is an accurate adjustment of the incident angle. This must be done prior to each series of measurements. The refractive index of the liquid can generally be found in a handbook with a specification of the wavelength and temperature for which the index is valid, usually 589 mµ and 20°C. The beam separation corresponding to this value of n must then be determined using the known sample thickness and the desired incident angle. (see Appendix I for a discussion of this calculation)

The filled cell and the empty cell are positioned in the refractometer and allowed to attain an equilibrium temperature of 25°C. The flow of cold water through the cooling coil requires occasional adjustment to correct deviations from this temperature. The temperature is monitored by a thermistor probe taped to the frame near the cells. Actual measurement of the temperature is done by placing the bulb of a mercury thermometer on the cells before and after a series of index measurements. When the temperature has stabilized at 25°C, the calibration proceeds. A coarse adjustment of the incident angle is achieved by rotation of the cell holder shaft until an angle of 45° is indicated on the dial. The monochromator is then set to the wavelength for which n
is known and the measuring slits are moved toward the empty cell beam until a maximum photomultiplier amplifier current reading is obtained, indicating that the measuring slits are centered on the empty cell beam. The scale of the dial indicator used for measurement of the slit travel is then rotated until the indicator needle points to zero. The calculated separation corresponding to \( n \) is the distance the measuring slits must be raised to center them on the full cell light beam, so the slits are raised until the dial indicates a displacement equal to the calculated separation. A small adjustment of the incident angle is then necessary to center the slits on the full cell light beam. Alternate zeroing and angle adjustment are continued until no further corrections are necessary.

When values of \( n \) near the operating temperature for other wavelengths are available, they are checked as a further test of the calibration and corrections are made until there is agreement with all of the available calibration information.

Once the dial indicator zero has been set correctly, recalibration of the incident angle for other series of measurements is simplified because the position of the empty cell light beam is constant for a constant incident angle. This zero reading is also found to be valid for any wavelength between 220 m\( \mu \) and 650 m\( \mu \).

Three series of measurements conducted to determine the wavelength dependence of the zero setting revealed no more than a random scatter of readings within 0.0003 inches of zero throughout the range of the refractometer. The absorption curve supplied by the cell...
manufacturer agrees with the absorption curve for Suprasil, a special type of fused quartz, but no dispersion curve for Suprasil could be found. Calculations based on the dispersion curve for ordinary fused silica predict a change of 0.0022 inches in the zero reading between 220 m\(\mu\) and 650 m\(\mu\).

If the liquid to be examined has no listed refractive index or if the listed temperature is not consistent with the 25°C operating temperature, the refractometer may be calibrated using some other, more convenient liquid. After calibration, the liquid to be examined is introduced into the previously empty cell and allowed to attain equilibrium. The empty cell is needed only during calibration.

The empty cell may also be filled with the same liquid as the other cell if more transmitted light intensity is desirable. This is frequently done, although it is not necessary. The measurements made using one and two filled cells show no difference larger than the normal measuring uncertainty. The use of two cells does allow more rapid measurements because the logarithmic circuit decreases the effects of light source fluctuations when higher intensities are used. On the other hand, too much transmitted intensity results in a reduced sensitivity to small variations of intensity, making the adjustment of the slits to the center of the light beam more uncertain. Medium transmitted light intensities produce the least scatter in the measurements.

The undeviated reference beam is used only when measurements are
made to determine the deviation produced by the empty cell. This deviation is 0.0035 ± 0.0002 inches throughout the wavelength region 220 mμ to 650 mμ.
CHAPTER VI
MEASUREMENTS

The calibrated refractometer is used to determine the light beam separation as a function of wavelength by using the microammeter as an indicator to center the measuring slits on the full cell light beam at each wavelength setting of the monochromator. The resulting dial indicator readings are then used to determine the refractive index at each wavelength. A series of determinations of \( n \) for wavelengths between 220 m\( \mu \) and 650 m\( \mu \) provides the dispersion curve for the liquid in that region.

Whenever practical, both entrance and exit slits are used in the monochromator. However, one or both of the slits must be removed when measurements are made at wavelengths for which the liquid shows strong absorption or at wavelengths near the performance limits of the 1P28 and the xenon arc lamp. This is necessary because the light intensity transmitted by the liquid becomes insufficient to produce a significant microammeter reading. The higher intensity light allowed to reach the liquid by removing the monochromator slits provides sufficient transmitted light. The slit removal should result in an undesirable increase in the wavelength band width leaving the monochromator. Two conditions help compensate for this. The xenon light remains focused at the position of the removed entrance slit and the refractometer collimating slits limit the band width reaching the
liquid by passing only the light focused by the monochromator near the position of the removed exit slit. Measurements made with and without one or both of the monochromator slits in regions of high dispersion and adequate intensity show a tendency toward higher readings with the slits in place. This is noticed at wavelengths for which the liquid has high dispersion but not where there is low dispersion. The probable reason for this is the fact that the highest indices occur at the edge of the absorption bands where the intensity of transmitted light is becoming weak and the dispersion is high. Slit removal allows longer wavelengths with higher intensities to enter the refractometer where a smaller deviation is produced by the liquid, corresponding to the smaller index at the longer wavelength. The higher intensity, less deviated light overrides the weaker, more deviated beam to produce an apparent beam position slightly lower than correct for the monochromator setting. Wavelengths shorter than the monochromator setting would also enter the refractometer, but they would be low intensity because of their proximity to the absorption band. The uncertainty in n produced this way is approximately 0.75%. Instances for which this was unavoidable are noted with the results.

The light used in the wavelength regions below 240 μm and above 600 μm is considered impure because of spurious reflections within the monochromator. The long wavelength region is contaminated by short wavelengths, so a filter is employed to transmit only wavelengths above 615 μm to the refractometer. No filter or other means could be
found to purify the light in the 220 μ to 240 μ region.

Most measurements were made with the liquid at a temperature of 25°C. The calibration values of \( n \) specified for 20°C could not be used without introducing a systematic error into the measurements. The values of \( n \) used in the calibration were reduced by 0.002 from the 20°C value in an attempt to compensate for the temperature discrepancy. A negative temperature coefficient is reasonable for \( n \) because of the decrease in density of the liquid with rising temperature. The value chosen corresponds to the differences in \( n \) for benzonitrile, the only liquid for which refraction data could be found at both 20°C and 25°C. In this respect, benzonitrile was assumed to be representative of the other monosubstituted benzenes tested.
CHAPTER VII

SAMPLES

The fourteen liquids examined were each based on the six carbon ring structure of benzene with the exception of water. Of these, all but benzene and cyclohexane were monosubstituted benzene derivatives. The benzene derivatives were chosen because of their relatively strong ultra violet absorption spectra and because they represent a closely related class of liquids. The absorption spectrum of each resembles that of benzene, but differences arise because each has a different addition to the benzene ring.

The organic liquids were all of reagent quality and no additional purification was attempted. Styrene is believed to contain a small impurity, probably hydroquinone, diphenylamine, or tertiary butyl catechol, which act to inhibit polymerization. A benzene impurity in each of the benzene derivatives is likely. No actual analysis was available except for benzene which contained 0.02% water as the major impurity. No solvent was added to the liquids to dilute them for use. The water sample was distilled and then deionized by means of a resin deionizing bed.

The samples showed no cloudiness or precipitates, and all were colorless except nitrobenzene, aniline, and acetophenone. Nitrobenzene was yellow, as it should be when pure, but acetophenone and aniline should be colorless. Aniline is oxidized by contact with air
and the oxidation products produce a brown discoloration noted in the sample. The acetophenone sample had a slight yellow tinge. This is also believed to be caused by oxidation products. No better samples were available and the discolorations were weak in both cases, so the samples were used.
CHAPTER VIII
RESULTS

Figures 9 through 22 show the dispersion curves plotted from measurements made on the refractometer. Included with each dispersion curve is the absorption curve for the same liquid. The absorption curves were drawn from curves found in the literature as noted. Several values of the refractive index taken from the literature are also shown.

The measured refractive indices are plotted against wavelengths in m\(\mu\). The absorption curves are plotted as \(\epsilon\), the molar extinction coefficient, against the wavelength \(\lambda\). The molar extinction coefficient is defined by:

\[
\epsilon = M \frac{\log_{10} \frac{I_0}{I}}{d \cdot c}
\]

Where:
- \(M\) = molecular weight
- \(I\) = transmitted light intensity
- \(I_0\) = incident light intensity
- \(d\) = sample thickness
- \(c\) = concentration in gm/ml.

The different sets of independent measurements for each liquid are denoted by the symbols; •, Δ, X, O, and □. In many instances, two or more of these symbols coincide. The known values of \(n\) taken from the literature are marked by the symbols * or by * and + if two
different sources or temperatures are quoted. The absorption curves are drawn with a dashed line, while a solid line is sometimes used to connect parts of the dispersion curve.

The dispersion curves all exhibit normal dispersion where there is negligible absorption. The refractive index decreases sharply where the absorption begins to increase. This is similar to the behavior exhibited by the dispersion curves for gases and crystalline solids near strong absorption lines. The refractive index of any substance which has a small number of distinct, well separated absorption lines should behave in a way similar to that shown in figure 8.

Classical and quantum mechanical approaches differ only slightly in predicting this type of dispersion curve. An application of either method to the case of broad, overlapping absorption bands is complicated because the simplifying assumptions used for well spaced, single absorptions may not be applied. No dispersion formula for polyatomic molecules in liquid phase could be found in the literature. According
to Condon\textsuperscript{6}, a close comparison between experimental measurements of $n$ and the results of the quantum mechanical formulation of the dispersion theory is not practical because of the lack of detailed knowledge of the complicated absorption bands in the ultraviolet.
Figure 9

Cyclohexane

25°C

* 19.5°C, Handbook of Chemistry and Physics

--- Hogness, Zscheile, and Sidwell

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Toluene

$\begin{align*}
26^\circ C & \\
\text{Smithsonian Physical Tables}^8 & \\
\text{Tunnicliff, Brattain, and Zumwalt}^{11}
\end{align*}$

Figure 11
Figure 12

Ethylbenzene

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Bromobenzene

25°C

* 20°C International Critical Tables

--- Azouz, Parke, and Williams

Figure 13
Anisole

25°C

* 16.5°C Smithsonian Physical Tables
+ 20°C Handbook of Chemistry and Physics

--- Williamson and Rodebush

Figure 15
Figure 17

Styrene

25°C

* 17°C International Critical Tables
+ 16.6°C Smithsonian Physical Tables

Rodebush and Feldman

Figure 17
Nitrobenzene

$25^\circ C$

$\epsilon$ 20$^\circ C$ International Critical Tables$^9$

--- Williamson and Rodebush$^{13}$

Figure 21
Figure 22
CHAPTER IX

CONCLUSIONS

A refractometer suitable for use with liquids has been constructed and used to determine the dispersion curves of liquids through the visible and ultraviolet spectrum between 650 μ and 220 μ. The refractometer was found to function well within the strong ultraviolet absorption bands. The good agreement between individual sets of measurements for the same liquid and the observed agreement with the calibration points taken from the literature indicate that the refractometer is capable of a precision within 0.5%. The absence of other experimental or theoretical values for n in the ultraviolet demonstrates the lack of information available for comparison and the need for the measurements made in this study.

The dispersion curves obtained are about what would be expected from the behavior of gases and crystals near absorption lines. An important difference is the apparent tendency toward low values of dispersion within the absorption bands. The curves provide evidence for a slight degree of generalization about the behavior of the refractive indices of simple benzene derivatives.

All thirteen of the organic liquids show normal dispersion as the wavelength becomes shorter. Each organic liquid shows an abrupt decrease in n as the absorption begins to increase. Most of the liquids tested which have similar absorption curves also have similar
dispersion curves, but no generalization can be made on the basis of the differences which do exist. For example, figures 13 and 14, bromo- and chlorobenzene, have similar absorption curves, but quite different dispersion curves. However, it is not difficult to find examples where the absorption and dispersion curves are similar, for example toluene, figure 11, and ethyl benzene, figure 12.

The refractive index of the twelve benzene derivatives rises slightly near 280 mμ, the position of the benzene refraction peak. This may be due to a benzene impurity in each of these liquids, or it may be due to the structural similarities between the derivatives and benzene.

More liquids must be examined before any definite conclusions can be drawn concerning the behavior of the dispersion curve and the structure or absorption curve of the molecule.

No appreciable temperature dependence was noticed for any of the liquids examined, except nitrobenzene. The ultraviolet dispersion curve of nitrobenzene seemed to be quite sensitive to temperature, but no study of the temperature dependence of n was attempted because of the imprecise temperature control method used. A better method of controlling the temperature of the liquid is needed.

The absorption curve for water does not show an appreciable absorption in the wavelength range encountered, but the dispersion curve does show a sharp drop in n as the absorption begins to increase. In the absence of an analysis of the water samples used, it is difficult to attribute the behavior of the dispersion curve
to the behavior of the absorption curve because slight impurities could have a marked effect on both curves.
APPENDIX I

DISCUSSION OF THE WORKING EQUATION

Figure 23

Figure 23 illustrates the terms used in deriving equation 3. The three light paths are shown superimposed for convenience.

The line, NO is constructed normal to both cell walls and is the cell thickness d. It is evident from trigonometry that:

\[ NO = d \tan r' \]  \hspace{1cm} (5)

\[ NA = d \tan r \]

\[ AB = d (\tan r' - \tan r) \]
application of Snell's Law, equation 2, shows that light transmitted through a parallel-sided slab emerges parallel to its original path. The four surfaces of walls 1 and 2 are parallel, so;

\[ r' = \phi = i \]  \hspace{1cm} (6)

The two emerging beams are parallel, so according to Snell's Law, \( A'A \) and \( B'B \) must be parallel. Then;

\[ AB = A'B' \]  \hspace{1cm} (7)

It is evident that \( \theta \) is the supplement of the supplement of \( \phi \). \( A'B' \) is constructed normal to the emerging beams. Therefore;

\[ \theta = \phi \]  \hspace{1cm} (8)

The separation, \( s \), of the empty cell and full cells beams is the length of \( A'B' \), which is given by;

\[ S = A'B' = A'B' \cos \theta \]  \hspace{1cm} (9)

Using equations 5, 6, 7, and 8 in equation 9 produces the result;

\[ S = (\tan i - \tan r) \cos \theta \]  \hspace{1cm} (10)

Snell's Law and trigonometric identities are used in simplifying equation 10 to yield;

\[ S = \left[ 1 - \frac{\cos i}{(n/n')^2 - \sin^2 i} \right] \cos \theta \]  \hspace{1cm} (11)

where \( n' \) and \( n \) are the refractive indices of air and the liquid respectively. This study deals with the indices of refraction of liquids relative to air, \( n/n' \), so this ratio will simply be called \( n \).

\[ S = \left[ 1 - \frac{\cos i}{(n^2 - \sin^2 i)^{1/2}} \right] \cos \theta \]  \hspace{1cm} (12)
This may be rewritten to provide the working equation used to determine $n$ from measurements of $s$.

$$n = \frac{\sin i}{d \sin i - s} \left[ d^2 - 2d s \sin i + s^2 \right]$$

An IBM computer was programmed to tabulate equation 13 as a function of $s$ for the following conditions:

- $i = 45^\circ$
- $d = 1.000 \, \text{cm}$
- $s = 0.080$ to $0.179 \, \text{inches}$
- $\Delta s = 0.0002 \, \text{inches}$

This provided a convenient means for calibration and reduction of the measured separations to refractive indices. Figure 24 is a plot of the tabulated $n$ vs. $s$.

The constant incident angle, $45^\circ$, was chosen and used throughout the measurements because it is large enough to provide a significant beam separation and because it is well removed from the polarizing angle, approximately $57^\circ$. The higher reflection encountered at large angles is also a limiting factor because of the decreased intensity transmitted through the sample.
\[ n = \frac{\sin i}{d \sin i - s \left( d^2 - 2d s \sin i - s^2 \right)} \]

\[ i = 45^\circ \]

\[ d = 1 \text{ cm} \]
APPENDIX II
ALIGNMENT AND TESTING

The measuring slits were visually aligned by clamping the measuring slit slide, face up, to the bed of a precision milling machine with the grooved sliding surfaces parallel to the direction of the longitudinal mill feed. Then, with the two slit blades held in place by light pressure from the fastening screws, the mill cross feed was used to move the slit assembly past a finely pointed indicator held stationary in the mill arbor, very close to one slit edge. Small adjustments in the position of the slit edge were made until the edge to point distance appeared constant along the entire edge when examined through a magnifying glass.

The second edge of the slit was then aligned parallel to the first by the same method except that the edge near the point of attachment to the slide was secured a distance of 100 microns from the first edge. Alignment then proceeded by shifting the other end of the edge blade. The 100 micron setting was determined by measurement with an optical comparator.

The second measuring slit was then aligned in the same way after turning the slit slide over and using the point indicator with the mill's longitudinal feed dial to position the slide so that the bottom slit edge was the same distance from the slide bottom as it was on the first slit.
The measuring slits were then considered to be open 100 microns and correctly positioned perpendicular to the direction of travel used in the refractometer.

The collimating slits were aligned in much the same way.

With all the slits placed in the refractometer and the cells removed, a sodium arc lamp was used in place of the monochromator to check the entire slit system alignment. The collimating slits produced a sharp, thin line at the measuring slits, and adjustment of the measuring slit position produced a uniform cut-off of the line. This indicated that the measuring slits were not tilted with respect to the collimating slits.

Tests with the cells in position showed that the separation measurement does not depend on whether the right or left cell is the one filled with the liquid.

The alignment of the xenon arc and the monochromator is fixed by their coupling tube. This was carefully made and needed no alignment.

Correct positioning of the refractometer in relation to the monochromator was achieved by adjusting the three refractometer supports until a maximum reading could be obtained on the microammeter. This indicated a maximum light intensity reaching the photomultiplier due to correct alignment of the slit system with the monochromator output beam.
Figure 25 is a sketch illustrating how a mechanical chopper may be used to measure the light beam separation, $s$. The chopper, a rigid metal drum with slits mounted at $A$ and cut away at $B$, is revolved at a constant speed by a synchronous motor. The undeviated reference beam from the collimating slits passes through the center of rotation of the chopper. The angles shown are related to the separation and the chopper radius $R$ by:

$$S = R(\sin \theta' - \sin \theta). \quad (14)$$

For small angles;

$$\sin \theta' - \sin \theta \approx \theta' - \theta = \Delta \theta \quad (15)$$
The ratio $s/R$ is small so the angles are small and

$$S = R \Delta \theta \quad (16)$$

$\Delta \theta$ is determined by a knowledge of the rate of chopper revolution, $\omega$, and the time $t$ required for the slit to pass from the full cell light beam to the empty cell beam

$$\Delta \theta = \omega t \quad (17)$$

Equation 15 becomes;

$$S = R \omega t \quad (18)$$

This expression for $s$ is substituted into equation 13 to compute $n$.

A set of collimating slits and a cell holder were constructed and aligned in much the same way as has been described for the sliding slit method. An 8 cm diameter chopper was machined from a solid piece of bronze and fitted with an adjustable slit. It was balanced so that very little vibration occurred when it was spun at 1800 rpm by a heavy duty synchronous motor.

The 1P28 photomultiplier tube, held stationary, was mounted directly behind the chopper to detect the light beams as they passed through the slit and cut away portion on the back side of the chopper. The photomultiplier was operated with about 100 volts on each dynode. No special amplifying circuit was used. The photomultiplier anode was connected directly to the vertical input amplifier of a Tektronix 535 oscilloscope, calibrated to measure small time differences between the occurrence of electrical pulses.

The device was used by measuring the time separation between electrical pulses produced by the photomultiplier when the chopper
slit passed through the three light beams. Calibration of the incident angle was done by adjusting the cell angle until the time measurements corresponded to known values of the refractive index for the liquid in the cell. A typical measurement of the time separation of the full and empty cell beams is 427 microseconds, corresponding to a refractive index of 1.4600 measured at an incident angle of 45°.

This method proved to be inadequate for measurements at low light intensities. The signal pulse corresponding to the full cell light beam because obscured by electrical noise whenever a strong absorption band was encountered. The device performed reasonably well when the transmitted light intensity was adequate to produce a recognizable signal on the oscilloscope. The time measurement precision resulted in values of $n$ which were not as reproducible as those obtained with the improved device using the measuring slits to directly measure $s$.

Some of the same liquids were examined with the chopper refractometer and the sliding slit refractometer. The benzene dispersion curve is a typical example of the results obtained by the two methods. Figure 26 shows these curves with error bars to illustrate the scatter present in each case. The sliding slit measurements are considered to be much the better of the two because of the sharpness and reproducibility which is associated with them but is absent from the chopper measurements.

The chopper method should be capable of producing better results.
Benzene

--- sliding slit measurements

--- mechanical chopper measurements
than it did. A method of filtering the electrical noise from the signal could greatly improve the performance. A slower rotation would facilitate filtering and would help to eliminate vibrations which influence the position of the slit as the chopper rotates. The small size of the 1P28 photocathode made alignment of the photomultiplier a very critical operation. A small error in the position of the photomultiplier could result in the loss of considerable signal intensity, particularly for high indices of refraction when the light beam falls near the edge of the photosensitive surface.
APPENDIX IV

INFLUENCE OF DIPOLE MOMENTS

The wavelength at which the refraction peak occurs for a particular liquid appears to be related to the permanent dipole moment of the molecules in the liquid as shown in figure 27. Each point is labeled according to the substituent on the benzene ring which it represents. The values of the dipole moment are plotted in units of debyes. One debye equals $3.3 \times 10^{-30}$ coulomb $\cdot$ meter.

The theory of dispersion is evolved in terms of the interaction between the electric field vector of the light and the electronic dipoles induced in the molecule by the electric field vector. The permanent dipole moment appears to play no part in the theoretical development except for long wavelengths where the motion of the atoms or molecule as a whole becomes important. However, the presence of a permanent dipole moment may well influence the energies associated with the electronic dipoles, and so influence their interaction with light. The theoretical development of a satisfactory explanation is considered beyond the scope of this study.
Relationship of Wavelength of Refraction Maximum to the Permanent Electric Dipole Moment for Various Aromatic Compounds

Figure 27
1. W. Snell, Unpublished paper, University of Leyden (1621)

2. M. H. Sweet, Electronics, 19, 105-109 (1946)


4. Loc. Cit., 8

5. Personal communication from R. A. Durbin, Head of the Physics Instrument Shop, Western Michigan University (1966)


7. R. C. Weast (Editor), Handbook of Chemistry and Physics, Forty Fifth Edition, The Chemical Rubber Company, Cleveland, C-267 (1964)

8. W. E. Forsythe (Editor), Smithsonian Physical Tables, Ninth Revised Edition, Smithsonian Institution, Baltimore, 536 (1964)


13. B. Williamson and W. H. Rodebush, Journal of the American Chemical Society, 63, 3021 (1941)


15. R. C. Hirt and F. T. King, Journal of Chemical Physics, 20, 1821 (1952)

