

# Determination of Absolute Values of Refractive Index of Liquids Using an Interferometric Method

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A novel interferometric technique for measuring the refractive index of transparent liquids to a high degree ( $10^{-5}$ ) of accuracy is presented. This technique permits studying transparent solutions, such as aqueous solutions of salts, biological agents, organic solvents etc. The measuring principle is based on the comparison of two interferometric measurements of mirror displacements, one of which is performed in the liquid and the other one in air. Sources of experimental error are discussed and technical details are described so that the apparatus can easily be constructed at low cost in a modest laboratory.

## 1 Introduction

The refractive index plays a vital role in many branches of physics, biology and chemistry. Knowledge of the refractive index of aqueous solutions of salts and biological agents is of crucial importance in applications of evanescent wave techniques in biochemistry<sup>1</sup>. Chemical modifications may be detected by measurements of refractive index. Among the many possible applications is the control of adulteration of liquids.

Different methods have been developed to measure the refractive index of liquids. The most common type of refractometer measures the refractive index of the samples by detecting the critical angle of total reflection<sup>2</sup>. Many kinds of interferometric methods for determining the refractive index of materials have also been developed<sup>3-5</sup>. Rayleigh refractometer, Mach-Zehnder, Jamin, Michelson and Fabry-Perot interferometer can be used. Interferometric refractometers have a great potential for high precision. Some of the proposed interferometric methods are suitable for measurements of the absolute value of the refractive index and others can only measure changes of refractive index<sup>6,7</sup>. In this paper we are measuring the absolute index with a desired degree of accuracy typically of the order of  $10^{-4}$  to  $10^{-5}$ . The emphasis is on achieving high precision using only simple and low cost equipment. An example of measured index values of solutions of NaCl in water as a function of concentration and temperature at the wavelength of  $\lambda = 632.8$  nm is given.

## 2 Principle of the method and experimental setup

The method for measuring the refraction index  $n$  at a fixed temperature is based on two simultaneous interferometric measurements of mirror displacements. One measures the displacement with a laser beam traveling in air and the other

one measures the same displacement with a second beam from the same laser travelling in the liquid sample. During the mirror displacement the resulting light intensities oscillate in time. The ratio of counted interference oscillations of the two beams is then equal to the ratio of refractive index of the sample  $n$  and of ambient air  $n_{AIR}$ .

In order to determine  $n$  with precision of the order of  $10^{-5}$  the index of air cannot be considered to be one. The following empiric formula (Edlen's formula<sup>8,9</sup>) was used to determine  $n_{AIR}$

$$n_{AIR} - 1 = A \cdot P \frac{1 + P[B - C(T - T_0)]}{1 + D(T - T_0)} - EP_{H_2O}, \quad (1)$$

where  $P$  is the ambient air pressure,  $T$  is the ambient temperature and  $P_{H_2O}$  is the partial pressure of water in the ambient air. The constants  $A$  to  $E$  and  $T_0$  are

$$A = 3.782218724 \times 10^{-7} \text{ Torr}^{-1} \quad B = 0.817 \times 10^{-6} \text{ Torr}^{-1}$$

$$C = 1.33 \times 10^{-8} \text{ Torr}^{-1} \text{K}^{-1} \quad T_0 = 273.15 \text{ K}$$

$$D = 3.6610 \times 10^{-3} \text{ K}^{-1} \quad E = 5.722 \times 10^{-8} \text{ Torr}^{-1}$$

The index of ambient air was determined from measurements of  $P$ ,  $T$  and  $P_{H_2O}$  with typical error smaller than  $\delta n_{AIR} \approx 2 \cdot 10^{-7}$ .

A schematic of the experimental setup is shown in Figure 1. A light beam from a linearly polarized He-Ne laser ( $\lambda = 632.8$  nm) is split into two parallel, vertically separated beams by means of a glass plate with enhanced surface parallelism. The upper beam is reflected by a glass plate, which is mounted outside the sample holder on a slide, and by the outer surface of the entrance window of the sample

holder. The intensity corresponding to the sum of these reflections is registered as the reference signal. The reference light is prevented from entering the sample by scratching the inner surface of the upper half of the entrance window with sand paper. The lower beam is reflected by the surface of the entrance window and by a mirror, which is mounted on the same slide and that hangs into the sample. The interference signal of these reflections is registered as sample signal. These signals are registered by a data acquisition system as a function of time while the slide is slowly being pulled by a clockwork (velocity  $\approx 1$  cm/min). The measu-

red intensities oscillate in time and the number of oscillations is then counted including fractions of oscillations at the beginning and end of the measuring interval.

It is important to use a polarized laser. Lasers with random polarization result in intensity fluctuations generated at the beam duplicator.

The detection of light intensities does not require expensive, calibrated, large area detectors. A simple phototransistor (for instance TIL 78 or TIL 81) together with an amplifying circuit is sufficient. Fig. 2 shows the electronic circuit used for light detection and data acquisition.

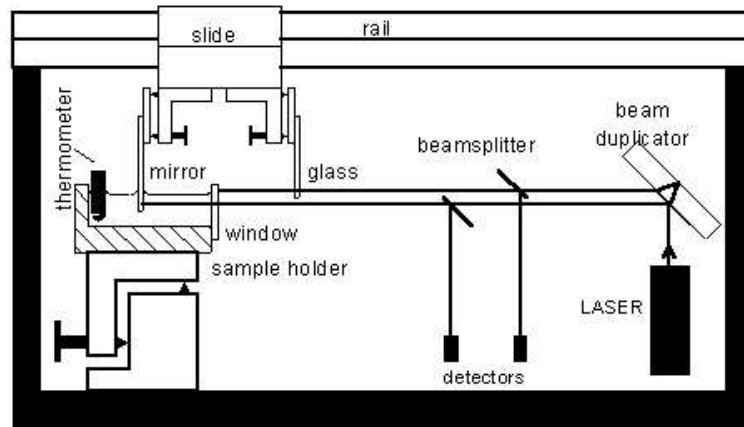


Figure 1. Double interferometer with sliding mirrors.

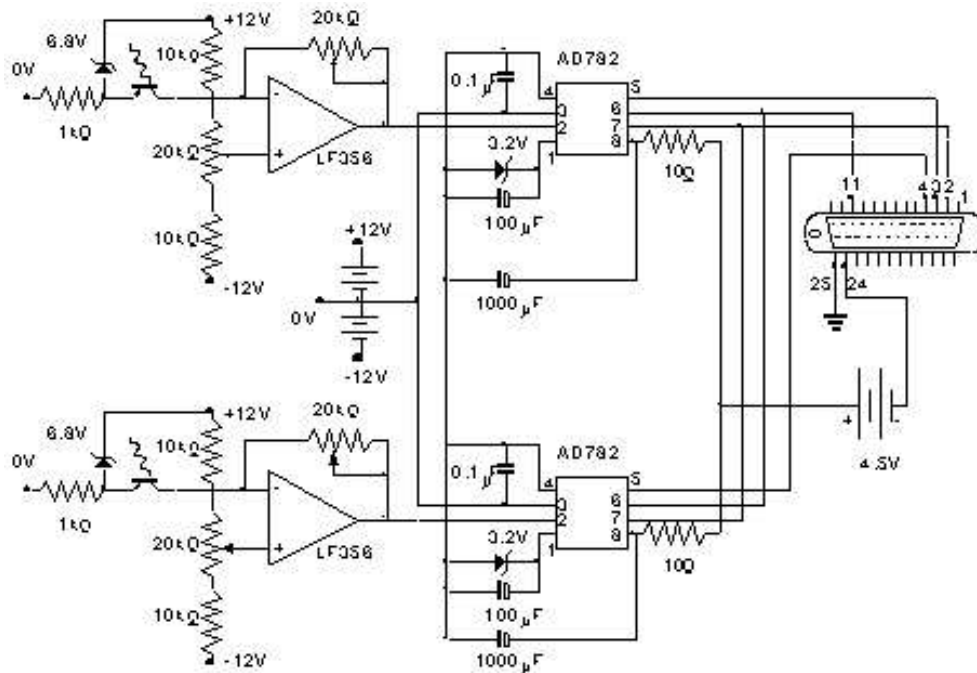


Figure 2. Detector and data acquisition circuit.

### 3 Error sources

The precision of this method is limited by three opto-mechanical imperfections:

1) The orientation of the sample holder and the moving mirrors (including the glass plate) is carefully adjusted such

$$s_{REF} = s_1 + n_{AIR} \left\{ \frac{2x}{\cos \theta} - 2xtg\theta \sin \theta \right\} = s_1 + n_{AIR} 2x \cos \theta \quad (2)$$

$$s_{SIGNAL} = s_2 + n \frac{2y}{\cos \alpha} - n_{AIR} 2y tg\alpha \sin \theta' = s_2 + n 2y \cos \alpha \quad (3)$$

where  $\theta$  and  $\theta'$  are the incidence angles of the reference and signal beam,  $\alpha$  is the inner incidence angle of the signal and  $x$ ,  $y$  are the distances between reflections (compare Fig. 3). The constants  $s_1$  and  $s_2$  represent contributions from glass plates which will not enter the final result. The incidence angles  $\theta$  and  $\theta'$  may be different because of a possible

non-parallelism of the surfaces of the beam duplication plat  $\theta' = \theta + \beta$ . During a displacement of the mirrors the distances  $x$  and  $y$  change by the same amount,  $\Delta x = \Delta y$ , and one gets the following relation between index  $n$  and the number of counts  $N$  (fringe order):

$$\frac{n}{n_{AIR}} = \frac{N_{SIGNAL}}{N_{REF}} \frac{\cos \alpha}{\cos \theta} = \frac{N_{SIGNAL}}{N_{REF}} \frac{\sqrt{1 - \left( \frac{n_{AIR} \sin \beta'}{n} \right)^2}}{\cos \theta} \quad (4)$$

Expanding this expression up to quadratic terms in the angles one gets:

$$\frac{n}{n_A} \approx \frac{N_{SAMPLE}}{N_{REF}} \left( 1 + \frac{\theta^2}{2} \left( 1 - \left( \frac{n_{AIR}}{n} \right)^2 \right) - \theta\beta \left( \frac{n_{AIR}}{n} \right)^2 + \frac{\beta^2}{2} \left( \frac{n_{AIR}}{n} \right)^2 \right) \quad (5)$$

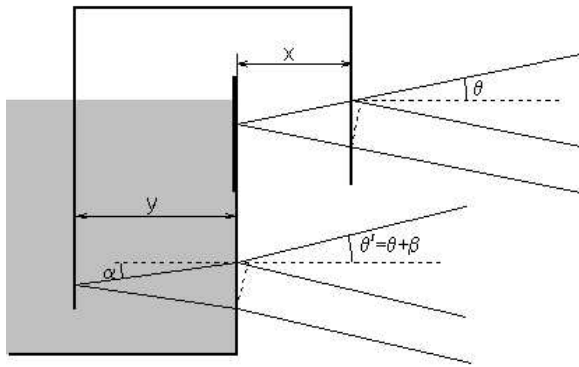


Figure 3. Schematic representation of beam geometry. Ideally the incidence angles  $\theta$  and  $\theta'$  should be zero.

The experiment is evaluated considering  $n = n_{REF} N_{SIGNAL} / N_{REF}$ . Therefore the terms proportional  $\theta^2$ ,  $\beta\theta$  and  $\beta^2$  are errors. One sees that it is necessary to keep these angles smaller than  $10^{-3}$  in order to obtain results of the desired precision. The beams should travel right back

into their origin. In the equations (2) and (3) we have not taken into account a possible angle between the Fabry-Perot mirrors. The angle between the Fabry-Perot mirrors is adjusted up to the point where one observes only a single light spot and no longer any fringes. In fact convergent lenses ( $f = 20\text{mm}$ ) are used to amplify the fringe pattern.

2) If the direction of translation is not parallel to the light beams the light spots move on the slide mounted mirrors during translation. In case the glass plates used as mirrors do not have high optical surface quality this movement introduces additional displacements  $\delta\Delta x$  and  $\delta\Delta x_{REF}$ , which are not necessarily equal for the signal and reference beam. We minimized this kind of error using a sliding rail that is much longer than the translation distance used. Parallelism of translation and incident light was then carefully adjusted with translations of about 50 cm and using electronic light detection instead of visual adjustment.

3) The translation of the slide is not a pure translation but may involve some small rotation due to geometrical imperfection of the sliding rail. Let  $\vec{\varphi}$  be the rotation vector of this rotation, i.e. a vector pointing along the rotation axis

and having modulus of the angle. Let  $\hat{n}$  be a horizontal unit vector that is perpendicular to the light beams. Then the displacements  $\Delta x$  and  $\Delta y$  are not equal but differ, to first order, by  $d \hat{n} \cdot \vec{\varphi}$ , where  $d$  is the distance of the upper and lower beam. This gives an additional error for the index ratio

$$\delta \frac{n}{n_A} = \frac{N_{SAMPLE}}{N_{REF}} \frac{d \hat{n} \cdot \vec{\varphi}}{\Delta x} \quad (6)$$

In our experiment the ratio  $d/\Delta x$  is approximately 0.3 so that the resulting relative error of refractive index is  $0.3 \hat{n} \cdot \vec{\varphi}$ . Aiming at an overall error of the order  $10^{-5}$  one would like to keep this contribution smaller than say  $5 \cdot 10^{-6}$ , which means  $\hat{n} \cdot \vec{\varphi} < 1.7 \times 10^{-5}$  rad, which is a tight requirement for the straightness of the rail. An elevation of only 1 micron at a distance of 1 cm corresponds to an angle of  $10^{-4}$  rad! Fortunately the overall error resulting from the contributions 2) and 3) can be measured easily by substituting the liquid sample by air. In this case the deviation of  $N_{SAMPLE}/N_{REF}$  from the expected number 1 measures the error. The way we controlled the third kind of error, which results from imperfections of the sliding rail, was simply to look systematically for a portion of the sliding rail where the air to air error was minimal. Fig. 4 shows the beginning and end of the interference signals of an air to air measurement where the overall error was  $1.7 \cdot 10^{-6}$ . The instances of the intensity maxima were determined with the help of quadratic fits around the desired maxima. This method gives, with the number and quality of our data points, a precision of approximately 2% of the oscillation period. This way the error of data analysis in 50355 oscillations is  $2 \times 0.02/50355 \approx 8 \times 10^{-7}$ , which is small enough for our purpose.

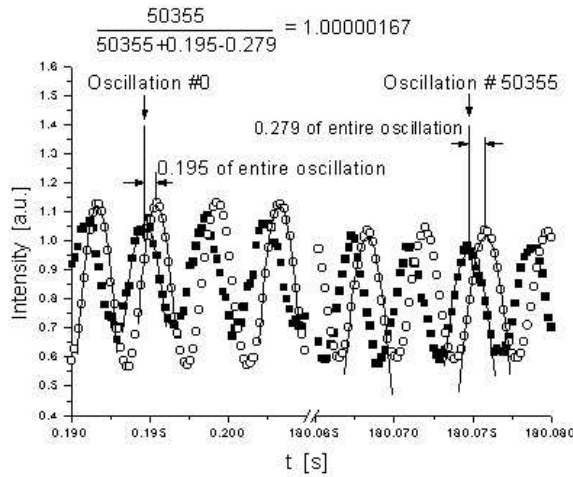


Figure 4. Interferometric signals from an air to air measurement.

The method of looking systematically for a good portion of the sliding rail works well with sufficiently imperfect surfaces such as rails covered with stripes of float glass. Who prefers to use a machined precision rail should avoid a construction where the rail is suspended at the ends. Of

course, the whole construction should be rigid and well isolated against vibrations. The pulling clockwork should not be mounted on the optical table. In our experiment a homemade clockwork moved by a suspended weight and eddy current velocity control was used.

## 4 Temperature

Precision of  $10^{-5}$  of refractive index of a liquid sample would simply be meaningless if the temperature of the sample was not known with high accuracy. As the temperature coefficients of most liquid samples are of the order of  $\partial n/\partial T \approx 10^{-4} \text{ K}^{-1}$  a measured index with 6 significant digits is only meaningful if the temperature is declared with precision of the order of  $\delta T \approx 0.01 \text{ K}$ . The temperature was measured with a F3141 platinum resistor using a four wire configuration with the multimeter HP34401Av<sup>10</sup>. The thermometer had been calibrated with a triple-point cell.

The idea is to measure the absolute value of refractive index of a sample at a fixed but arbitrary temperature and, with an independent differential measurement, to determine the temperature dependence of refractive index afterwards. This way no active temperature control was needed. However, the real situation is more complicated. In our measurements the sample was kept in a stainless steel vessel of approximately 6 mm thick walls and the sample surface was exposed to ambient air. Evaporation at the sample surface can create considerable temperature gradients in the sample. These gradients show up once the slide is being pulled so that the immersed mirror mixes liquids of different temperatures leading to fluctuations of the measured temperature. To minimize these effects we cooled the sample holder approximately to the temperature at which liquid water would be in equilibrium with the atmospheric partial water pressure. This was done by wrapping the sample holder with wet pieces of cloth. This way the evaporation at the sample surface was minimized. With this setup the measured temperature stayed stable during the 3 minutes measurement time better than  $3 \cdot 10^{-3} \text{ K}$ . The time constant of the thermometer was  $\tau = 20 \text{ s}$ .

## 5 Results and Conclusion

In order to show what degree of precision may be obtained in experiments where concentrations and temperatures are varied, we measured the refractive index of solutions of NaCl in  $\text{H}_2\text{O}$ . As masses are easier to measure with high precision than volume, the concentration  $K$  was measured in terms of mol of NaCl per mass of solution. This is an unusual measure of concentration. We could have used molality (mol of solvendum / kg of solvent), however the index shows a fairly linear dependence with  $K$  but not with molality. A total of 40 measurements were performed with concentration  $K$  and temperature varying from 0 to 4 mol/kg and 20,4 °C to 23°C respectively. The resulting data points were fitted by the following polynomial with 11 parameters

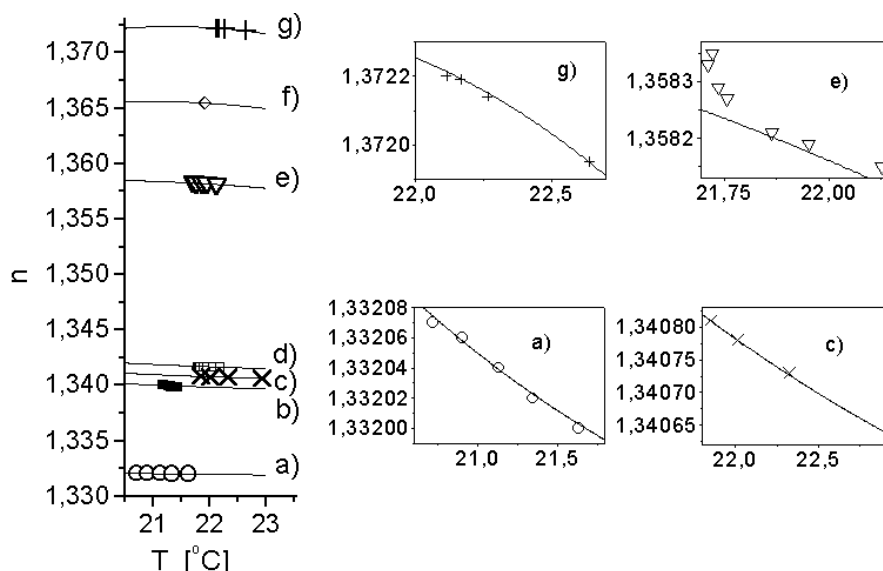


Figure 5. Examples of data points for 7 different concentrations of NaCl in water. a) Open circles  $K = 0$ , b) black squares  $K = 0.77202$  mol/kg, c) crosses  $K = 0.86458$  mol/kg, d) open squares  $K = 0.95447$  mol/kg, e) triangles  $K = 2.57662$  mol/kg, f) diamond  $K = 3.27076$  mol/kg, g) plus signs  $K = 3.90074$  mol/kg, e) continuous lines calculated from equation (7).

$$n(\Delta T, K) = n_0 + L_T \Delta T + L_K K + Q_{TT} (\Delta T)^2 + Q_{TK} \Delta T K + Q_{KK} K^2 + C_{TTT} (\Delta T)^3 + C_{KTT} K (\Delta T)^2 + C_{TKK} \Delta T K^2 + C_{KKK} K^3 + G_{TTKK} (\Delta T)^2 K^2 \quad (7)$$

where  $\Delta T = T - 22.50^\circ\text{C}$ . With parameter values from the following table, 31 measured points showed a discrepancy smaller than  $5 \cdot 10^{-5}$  from the polynomial value, 7 data points had a discrepancy between  $5 \cdot 10^{-5}$  and  $10^{-4}$  and 2 data points between  $10^{-4}$  and  $1.5 \cdot 10^{-4}$ .

These results agree, for example, with reference<sup>11</sup>. Fig. 5 shows some examples of data points. The continuous curves are calculated using equation (7).

A test of reproducibility was also performed by measuring a given sample several times at the same temperature with equal atmospheric conditions. A 0,01 mol/l NaCl solution was measured four times at  $T = (22.29 \pm 0.02)^\circ\text{C}$  and the measured index values had a standard deviation of  $\sigma_{n-1} = 6 \times 10^{-6}$ . A similar set of three measurements of a solution with  $K = 0.772022$  mol/kg measured at  $T = (21.17 \pm 0.02)^\circ\text{C}$  gave a standard deviation of  $3 \times 10^{-5}$ .

In conclusion it was shown that the interferometric measurement of mirror displacements permits precision measurements of refractive indices of transparent liquids with low cost equipment that can be mounted in any optics laboratory. The main difficulties were found to reside in the straightness of the sliding rail and the control of sample temperature.

Table 1 Coefficients from equation (7)

Coefficient	Value
$n_0$	1,3319549
$L_T$	$-4,60 \times 10^{-5} \text{ K}^{-1}$
$L_K$	0,0102180 kg/mol
$Q_{TT}$	$1,00 \times 10^{-5} \text{ K}^{-2}$
$Q_{TK}$	$-1,270 \times 10^{-4} \text{ kg/K mol}$
$Q_{KK}$	$-1,600 \times 10^{-4} \text{ kg}^2/\text{mol}^2$
$C_{TTT}$	$-1,00 \times 10^{-6} \text{ K}^{-3}$
$C_{KTT}$	$3,63 \times 10^{-5} \text{ kg/mol K}^2$
$C_{TKK}$	$-1,67 \times 10^{-6} \text{ kg}^2/\text{mol}^2 \text{ K}$
$C_{KKK}$	$4,47 \times 10^{-5} \text{ kg}^3/\text{mol}^3$
$G_{TTKK}$	$-2,60 \times 10^{-5} \text{ kg}^2/\text{mol}^2 \text{ K}^2$

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