Determination of the refractive index with the refractometer

Aims of the experiment

- To learn about the function of a refractometer
- To produce a calibration curve for the determination of concentration
- To determine the refractive index of an ethanol-water mixture

Principles

Light travels at different speeds through different media. The phase velocity of light in a vacuum is 299,792.458 km.s^{-1}. In comparison, the phase velocity in air at 299,705.518 km.s^{-1} is somewhat slower and in water at 225,000.000 km.s^{-1} considerably slower. Furthermore, the wavelength of light changes at the boundary between two surfaces with different optical densities. Depending on the angle of incidence, the waves are deformed in the process and, because of this, change their direction of motion. This phenomenon is known as light refraction. Refraction at the boundary between two media with different optical densities is described by Snell's law of refraction.

$$\frac{\sin(\alpha)}{\sin(\beta)} = \frac{n_1}{n_2}$$

α and β are the angle of incidence and the angle of refraction of the light beam, n_1 and n_2 are the refractive indices of the two media. The refractive index n of a medium is defined as the ratio between the velocity of light in a vacuum c_0 to the velocity of light in the medium being considered c_x.

$$n = \frac{c_0}{c_x}$$

On passing from an optically denser to an optically less dense medium, the light beam is refracted away from the normal. In this way, for a given angle of incidence of the light, an angle of refraction can result that is greater than 90°. In this case, the light will no longer enter the other medium. Instead, it is totally reflected from the surface. Here one speaks of total internal reflection.

The critical angle of total internal reflectionγ can be calculated using Snell's law of refraction. In this case it corresponds to the angle of incidence α:

$$sin(90\,°) = 1$$

$$\frac{\sin(\alpha)}{1} = \sin(\alpha) = \frac{n_1}{n_2}$$

If the refractive index of one of the two media is known, the refractive index of the second medium can be determined by finding the critical angle for total internal reflection.

In an Abbe refractometer, however, the reverse beam path (from an optically less dense medium to an optically denser medium) is used (see Fig. 2). In this case, the beam is refracted towards the normal. The maximum angle of incidence of almost 90° results in an angle of refraction that corresponds to the critical angle for total internal reflection γ.

In the optically denser medium, an illuminated zone is created which covers an angle of 2γ and is sharply delineated from

Fig. 1: Refractometer

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the darker zone into which no light falls. The dark-bright interface can be moved into the cross-wires of the field of vision via an adjustable mirror. The refractive index can then be read off directly on a scale.

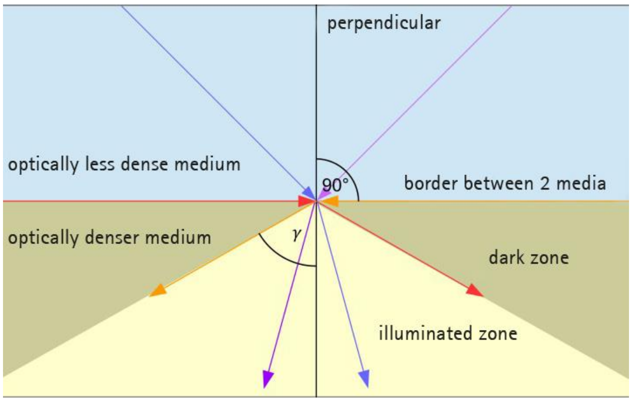

Fig. 2: Beam path of an Abbe refractometer

One important aspect is the dependency of the refractive index on the wavelength of the light beam. This is also called dispersion. It is different for all substances. Refractive indices are therefore stated for monochromatic light of wavelength 589 nm, corresponding to the sodium D line.

If the Abbe refractometer is used with daylight, a coloured fringe can be recognised at the light-dark interface which prevents accurate measurements. However, the Abbe refractometer possesses a correction mechanism which minimises the coloured fringe. To correct the dispersion, two Amici roof prisms in line can be rotated against one another using an adjustment screw in such a way that the refraction of the red and blue-green wavelengths can be progressively corrected while the yellow light remains unaffected. By turning the adjustment screw for dispersion correction, the coloured fringe can be made to disappear. The refractive index thus obtained is with reference to the sodium D line.

Apart from the wavelength, the refractive index also depends on the density and therefore also on the temperature of the medium being investigated. Refractive indices are usually quoted at a temperature of 20 °C. The prisms of the refractometer can be brought to the desired measurement temperature using a recirculating thermostat and a Peltier element. This prevents the sample being heated up during the measurement.

Frequent applications for the determination of refractive index include purity testing of substances in the pharmaceutical industry, the authentication of gemstones and the determination of concentration of binary mixtures.

For the determination of concentrations in binary mixtures, first a calibration curve is produced based on the refractive indices of a series of samples with known substance amount of the two components. Then the refractive index of the binary mixture with unknown substance amount is determined. Assuming that the sample is not contaminated with a third component, the substance amount in the sample can be read from the calibration curve.

In the experiment presented here, calibration curves will be produced for binary mixtures of ethanol and water at two different temperatures. The purpose of this is to demonstrate the temperature dependency of the refractive index.

The curves can subsequently be used to determine the substance amount in an unknown mixture of ethanol and water with the help of the refractive index. In this way, for example, the ethanol concentration of the distillates from the experiment C 2.4.3.1 "Distillation of red wine" can be determined.

Risk assessment

As ethanol is a flammable liquid, the experiment should not be carried out in the vicinity of sources of ignition. Protective goggles and a lab coat should be worn.

Ethanol	
 **Signal word:** **Hazard**	**Hazard statements** H225: Highly flammable liquid and vapour. **Precautionary statements** P210: Keep away from heat/sparks/open flames/hot surfaces and other sources of ignition. No smoking.

Equipment and chemicals

1 Laboratory refractometer 667 359
1 Compact balance 440-3N, 200 g: 0.01 g...... 667 7977
2 Beaker, Boro 3.3, 100 ml, squat 602 022
1 Wash bottle, PE, 500 ml 661 243
2 Graduated pipette 10 ml 665 997
1 Pipetting aid 10 ml 666 002
10 Flip-flap glass, 20 ml 661 251
1 Dropping pipette, 150 x 7 mm, set of 10....... 665 953
1 Rubber bulbs, 10 pcs. 665 954
1 Ethanol, solvent 1 l 671 9720
Also required:
Distilled water
Waterproof pen
Recirculating thermostat, e.g.:
1 Peltier thermostat PT 30.............................. 667 3551
2 Tubing 8 mm Ø, 1 m, (transparent) 307 70

Set-up and preparation of the experiment

Preparing the solutions

To produce the calibration curve, the refractive indices of 10 solutions with different substance amounts of ethanol and water are determined (see Table 1). 10 g of each solution are prepared in sealable flip-flap glasses. For this, the required amount of ethanol is weighed out and water added to produce 10 g. The flip-flap glasses are marked with a waterproof pen and sealed to prevent evaporation.

Table 1: Prepared solutions

Percent ethanol by weight	Amount of ethanol in g
0	0
20	2
40	4
60	6
70	7
75	7.5
80	8
85	8.5
90	9
100	10

Connecting up the refractometer

First insert the thermometer into the provided opening of the refractometer (m in Fig. 3). Attach the illumination equipment by inserting one of the two diodes into the provided opening of the illumination prism (d). The second diode serves to illuminate the measurement scale. This is directed into the illumination window (l) and screwed to the refractometer housing. The scale brightness can be varied by altering the direction of the diode.

To achieve a constant measurement temperature, it is recommended to use a Peltier thermostat. This can be connected to the refractometer with tubing. Three pieces of 8 mm diameter tubing are required. The length of the inlet and outlet tubing can be freely chosen, depending on the distance between the refractometer and the thermostat. The connecting piece between the illumination prism and the refracting prism should be at least 30 cm long to prevent the tubing from kinking. Connect the outlet of the thermostat to the inlet of the illumination prism (h). The 30 cm long piece connects the illumination prism with the refraction prism. Connect the outlet of the refraction prism (e) to the inlet of the thermostat. Demineralised water should in any case be used in the thermostat to avoid the formation of limescale.

Calibration of the refractometer

To test whether a calibration is required, set the thermostat to a temperature of 20 °C and switch the water recirculation on. Check the temperature on the thermometer of the refractometer. As soon as thermal equilibrium has been reached, determine the refractive index of distilled water. For this, place a few drops of distilled water onto the refraction prism (g) and fold down the illumination prism (c). Bring the light-dark interface onto the cross-hairs of the field of view using the adjustment screw (i). Adjust this using the dispersion correction adjustment screw (j) until it is sharp. The refractive index can now be read on the scale. The refractive index of distilled water at 20 °C is 1.3330. If the value measured differs from this, preset the value initially to 1.3330 with the adjustment screw (i). Using a cross-head screwdriver, turn the calibration screw (k) so that the light-dark interface is exactly on the cross-hairs of the field of view.

Performing the experiment

Following the calibration, measure the 10 samples prepared previously as described above. Place the samples one after the other onto the refraction prism (g). Bring the light-dark interface into the centre of the cross-hairs using the adjustment screw (i) and sharpen the boundary with the dispersion correction adjustment screw (j). Read the refractive index from the scale. After each measurement, remove the previous substance from the refraction prism (g) with a cellulose swab and wait a short time to allow the remaining liquid to evaporate. In order to estimate the reading error, determine a maximum and a minimum value for each measurement. To do this, move the light-dark interface up and down until it is just possible to recognise a deviation from the centre of the cross-hairs.

To investigate the temperature dependency of the measurement, record the calibration curve at two temperatures (here 20 °C and room temperature, about 22 - 23 °C).

After producing the calibration curves, samples with unknown mass ratios can be measured.

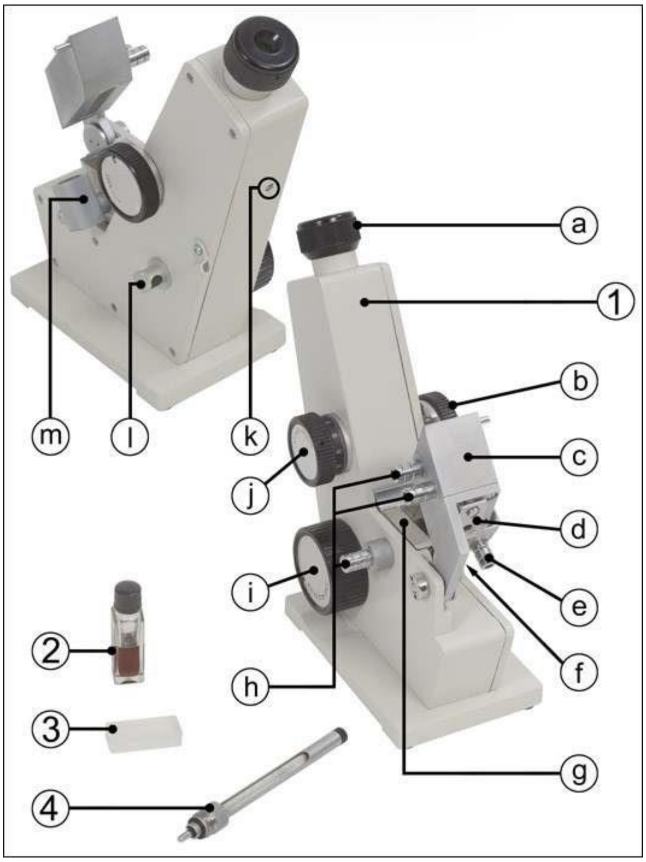

Fig. 3: Overview of the refractometer components

1 Refractometer
- a) Ocular
- b) Locking wheel
- c) Illumination prism
- d) Light inlet of the illumination prism
- e) Water outlet
- f) Light inlet of the refraction prism with mirror flap
- g) Refraction prism
- h) Connections for water circulation
- i) Adjustment screw
- j) Dispersion correction adjustment screw
- k) Calibration screw
- l) Illumination window for scale
- m) Holder for thermometer

2 Contact liquid

3 Calibration block

4 Thermometer

Evaluation

The evaluation is performed using a spreadsheet program. The deviations from the mean value are determined on the basis of the maximum and minimum values. The mean reading error is calculated from this.

Plot the mass fractions of ethanol against the refractive index in a graph. The mean reading error can be added as an error bar. A polynomial trend line is also added.

Results

Two calibration curves were produced: one at room temperature without the use of the illumination equipment and one at 20 °C using the illumination equipment.

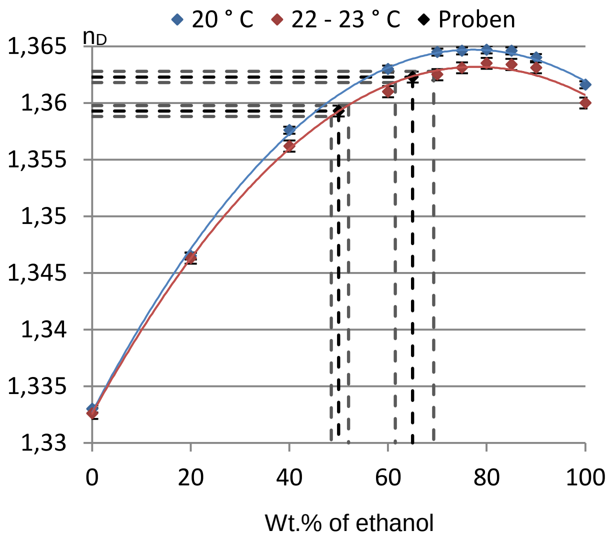

Fig. 3: Calibration curve for 20 °C (blue) and 22 - 23 °C (red)

Comparison of the two curves shows that both curves have a similar shape, with a maximum at about 77% ethanol by weight (Fig. 3). The values measured at 20 °C are higher than those measured at 22 - 23 °C. This is because the refractive index of the medium increases with increased density of the medium. The density of the medium falls with increasing temperature. For this reason, the refractive index falls with increasing temperature.

It is furthermore apparent that the values measured at room temperature show a somewhat greater deviation from the ideal curve form. This can be explained on the one hand by fluctuations in the room temperature, or in the temperature of the prisms, and on the other hand by larger reading errors, as the illumination equipment was not used in this case.

Therefore, for exact measurements, the temperature should be held constant to within a maximum of 0.5 C. It is recommended to use the illumination equipment as far as possible, as it is less strenuous on the eyes than working with only ambient light. The mean reading errors show that this can also have an effect on the accuracy of measurement (Tables 2 and 3). Without illumination equipment, the reading error is about 1.5 times greater.

Table 2: Measurement at room temperature (22 - 23 °C)

Wt. % of ethanol	**Meas-ured value**	**Min**	**Max**	**Deviation**
0	1.3326	1.332	1.3331	0.00055
20	1.3463	1.3456	1.3468	0.0006
40	1.3562	1.3556	1.3567	0.00055
60	1.361	1.3605	1.3615	0.0005
70	1.3625	1.362	1.363	0.0005
75	1.3631	1.3627	1.3635	0.0004
80	1.3635	1.363	1.364	0.0005
85	1.3634	1.363	1.3638	0.0004
90	1.3631	1.3626	1.3635	0.00045
100	1.36	1.3596	1.3604	0.0004
			Mean value:	0.00048

Table 3: Measurement at 20 °C

Wt. % of ethanol	**Meas-ured value**	**Min**	**Max**	**Deviation**
0	1.3330			
20	1.3465	1.3461	1.3469	0.0004
40	1.3576	1.3573	1.3578	0.00025
60	1.363	1.3627	1.3633	0.0003
70	1.3645	1.3642	1.3648	0.0003
75	1.3646	1.3643	1.3648	0.00025
80	1.3647	1.3644	1.365	0.0003
85	1.3646	1.3643	1.3649	0.0003
90	1.364	1.3637	1.3643	0.0003
100	1.3616	1.3611	1.3619	0.0004
			Mean value:	0.00031

Both curves can be used as calibration curves for the determination of the concentration of binary ethanol-water mixtures. For this purpose, the refractive index of the sample is determined at the relevant temperature. The mass fraction of ethanol in the sample can then be read from the corresponding curve.

To determine the limits of error of the value read, horizontal lines are drawn through the error bars. The x-values at the intersection of these lines with the calibration curve produce limits of error values in weight percent. It can be seen from Fig. 4 that even small reading errors in the determination of refractive index can lead to large errors in determining the mass fractions. These errors are even larger in an area of the calibration curve with a low gradient. Therefore, for the best possible accuracy in determination of the substance amount, the reading error must be kept as small as possible.

Cleaning and disposal

After finishing the experiment, remove the tubing from the refractometer. Dry the refractometer and clean the refraction prism with a cellulose swab wetted with ethanol.

The remaining ethanol-water mixture can be disposed of down the drain. Residual amounts of pure ethanol should either be stored for future experiments or disposed of in the container for water-miscible organic solvent waste.