Table of Contents

Merely transcribe ΔD from this data log to the Calibration Summary. You need a data log like this for each solution.

6. Plot and analyze the data in the calibration table as as Δn vs ΔD. The lines will be given by:

$$\Delta n = B_{cal,\lambda_o} + K_{\lambda_o} \cdot \Delta D$$

The intercept, B_{cal}, should be near–zero and the data should fall almost perfectly on a line with a linear correlation coefficient like 0.9999 or perhaps even better. The optical constant of the BP instrument for a given wavelength is K_{λ_o}, and its uncertainty is $\sigma_{K_{\lambda_o}}$.

7. The calibration plots for each wavelength, together with the best fit lines, INCLUDING UNCERTAINTIES AND LINEAR CORRELATION COEFFICIENTS, should be saved together with the appropriate Calibration Table in a lab notebook by glueing or taping in the sheets. The calibration is very important and it should last for a given user as long as the machine isn't bumped.

Measuring Actual Samples

1. As for the KCl calibration, the first step in measuring samples is to measure solvent against solvent. To do so, flush both components of the dn/dc cell several (3 or 4) times with the solvent to be used. If it is incompatible with the water used in the preceding step, it may be necessary to exchange the water slowly. E. G., for toluene after a water measurement, rinse with alcohol, then acetone or THF, then finally toluene.

IN NO CASE SHOULD YOU REMOVE THE CELL TO POUR OUT THE WATER.

2. Measure D_o, i.e. $(d_2 - d_1)$ for solvent vs. solvent.
Obtain D_o at each and every wavelength. As always, make several trial readings. The dn/dc Blank Form shown above is again to be used.

3. Measure ΔD for each solution at each wavelength, using one dn/dc Measurement Form for each solution.

4. Compile the data from the dn/dc Measurement Forms into a Measurement Summary, like this:

Measurement Summary

Solvent: _____ Solute: _____

Sol'n #	c (gm/ml)	λ_o: $D_{o\lambda_o}$: ΔD_{λ_o}	λ_o: $D_{o\lambda_o}$: ΔD_{λ_o}	λ_o $D_{o\lambda_o}$: ΔD_{λ_o}	λ_o: $D_{o\lambda_o}$: ΔD_{λ_o}
1	_____	_____	_____	_____	_____
2	_____	_____	_____	_____	_____
3	_____	_____	_____	_____	_____
4	_____	_____	_____	_____	_____
5	_____	_____	_____	_____	_____

5. For each wavelength, plot ΔD vs. c. The lines have the equations:

$$\Delta D = B_{meas,\lambda_o} + A_{\lambda_o} \cdot c$$

6. The plots and the linear fit data (interepts B_{meas}; slopes A_{λ_o}, correlation coefficients AND ERROR ESTIMATES, $\sigma_{A_{\lambda_o}}$) should be saved and taped into a lab book, together with all the raw data in the dn/dc Measurement Forms and the Measurement Summary.

7. The mean dn/dc value for the solute at λ_o is given as:

$$(dn/dc)_{\lambda_o} = A_{\lambda_o} \cdot K_{\lambda_o}$$

8. The error estimates for dn/dc at each wavelength can be obtained in one of 2 ways:

$$\sigma \approx (A_{\lambda_o} + \sigma_{A_{\lambda_o}}) \cdot (K_{\lambda_o} + \sigma_{K_{\lambda_o}}) - (\text{mean value of dn/dc}).$$

or...

$$\sigma_{dn/dc} = (K^2\sigma_A^2 + A^2\sigma_K^2)^{1/2}$$

Foreword

The Brice–Phoenix differential refractometer, based on the 1953 design of Brice & Hawler, relies on exceptionally linear optics to determine the difference in refractive index with respect to concentration of solution, i.e. dn/dc.

The instrument in the Russo lab was built in 1963 and renovated in 1987. Modern differential refractometers include one manufactured by C. N. Wood, which is essentially the same design as the Brice Phoenix but in a more compact form, and the Chromatix, which is a laser–based instrument. The Chromatix can only measure at 632.8 nm. The Wood or Brice designs are preferable for our work, because they can measure at multiple laser wavelengths simply by including laser line filters immediately after the source, which is an ordinary tungsten filament lightbulb. Despite its age, the Brice Phoenix (BP) is an excellent differential refractometer, and is still widely used in some of the most successful labs worldwide.

Appendix 1 of this "manual" includes the original manual supplied long ago with the instrument. Some changes are necessitated because we use laser wavelengths, but the original manual is still the best place to start reading. You should read it now.

Basic Considerations

1. All differential refractometers must be calibrated. The standard reference is usually a series of KCl salt solutions. The KCl should be dried prior to weighing. The true dn/dc varies with wavelength and, to lesser degree, temperature. KCl solutions were measured long ago at 25°C for the mercury lines, and these data are provided in the original Brice–Phoenix (BP) manual. The values of dn/dc at common laser lines have been obtained by extrapolation & interpolation. They are listed below (and in Appendix 2).

REGARDLESS OF THE TEMPERATURE YOU WISH TO MEASURE YOUR POLYMER SAMPLES AT, THE CALIBRATION SHOULD BE DONE AT 25°C.

REGARDLESS OF THE WAVELENGTH YOU PLAN TO GATHER YOUR ZIMM PLOT AT, STANDARD PRACTICE IN THIS LAB IS TO OBTAIN dn/dc DATA FOR FOUR WAVELENGTHS: 488 nm (argon blue); 514.5 nm (argon green); 589 nm (yellow Na D line); 632.8 nm (HeNe red).

2. An ordinary (not differential) refractometer operates by Snell's law deflections of light through a liquid sample in contact with a glass or quartz flat, which works fine for medium–resolution work. The major limitation of such refractometers is the difficulty of adequate temperature control. The BP operates by deflecting light through a divided (two compartment) cell. The deflection is measured by reading a drum that positions a crosshair to coincide with a slit image (see below).

The compartments are separated by a slanted glass wall. This eliminates (mostly) the temperature drift problem, since the solution of interest (usually a dilute solution; i.e., mostly solvent) drifts with the temperature about the same amount as the reference (pure solvent). The cells are supposed to be made to the original design specs of Brice & Hawler, but they vary somewhat. You must select which cell to use. (Note: they are numbered on an opaque side). If you intend to use a volatile solution, use the teflon capped cell. If your sample is to be solvated in a hydrocarbon or water, use the open faced cell. Note: you must calibrate the instrument with

the same cell that you intend to use!

3. For best results, you still have to be pretty careful with the temperature. Each time you change samples you should allow at least 15 minutes before taking a reading.

MAKE SURE THE HOUSING CAP IS IN PLACE DURING T EQUILIBRATION AND DURING ALL READINGS. Believe it or not, the gaudy cap makes a substantial T difference. At 25°C the water bath will keep the cell housing to 25.0 ± 0.01°C. At 20°C or 30°C, there is approximately a 1°C T lag. If you intend on working at these T's, adjust the water bath T to a higher value (@ 30°C) or lower (@ 20°C) T and then measure the actual T at the cell with a thermometer.

4. The exquisite glass cells are crudely clamped in place—someday we will fix this. You must securely (but gently) lock the cell of your choice in place and take care not to bump it. The cell must be approximately centered.

THE CELL SHOULD NOT BE REMOVED OR BUMPED AT ANY TIME DURING ALIGNMENT OR MEASUREMENT. IF IT IS, YOU MUST START OVER.

5. The required volume is at least one ml. Use pipets for filling. For the open cell, it is best to empty with a plastic–tipped Pipetman as this minimizes the chance of scratching the cell walls. Excess solution can then be blotted up with some OPTICAL tissue. KIMWIPES are NOT optical tissues. For the capped cell, you have two choices. One is to use a Dispo pipet. CAUTION: this choice can be dangerous to your health! It would be very easy to scratch one of the cell walls with a glass Pasteur pipet. If the cell becomes scratched along the optical path, it will be destroyed. In this case, Paul Russo will likely kill you. He would be justified; the cells are extremely expensive (several hundreds of dollars, depending on design). A better choice is to use a syringe with needle coated with insoluble medical tubing to avoid scratching.

6. The BP is a brilliantly simple optical design, but very poorly executed in the mechanical sense. Its gimpy post–mounted optics are easily bumped and thrown out of alignment. Someday when we have absolutely nothing better to do, we should beef up these mounts; meanwhile, the user is advised to always approach the instrument carefully and gently. Also, do not set it up where it is likely to be bumped by yourself (bad) or another labmember (worse, because you may not know it happened).

Measurement Steps

A complete measurement consists of calibration, followed by actual reading of the samples.

Calibration

1. As with any experiment, the first step is to correctly measure "nothing". In the BP, this means measurement of water vs. water. When both compartments are filled with H_2O (good quality water), the slit image (which should be sharply focussed and as narrow as you find convenient for your eyes) should fall nearly on 5. There should be little or no deviation in the reading when the cell is turned 180°. This is a quick way of testing for proper alignment. If the image does not fall near 5, or the rotation through 180° does not yield approximately the same reading, then usually adjusting the setscrews which limit the cell rotation will rectify the situation. If the instrument has been brutally manhandled, other adjustments may be required

(see P. Russo).

REPEAT: ONCE THE CELL AND ROTATING CELL HOUSING ARE PROPERLY ALIGNED, DO NOT REMOVE THE CELL FROM THE CELL HOLDER UNTIL YOU ARE COMPLETELY FINISHED TAKING AND ANALYZING YOUR DATA.

2. Before proceeding further, you should decide, once and for all, which side of the cell will be the solution compartment and which will contain the solvent reference. Conventionally, the solution compartment is the one on the right when the turret handle is pointing towards the lamp (with the operator positioned to look towards the light source). This is the "d1" position, and subsequent steps will follow this convention.

3. With water in both compartments, take several readings in each position (d1 and d2) alternately. For example, put the instrument in position d1 and make a reading. Now put it in d2 and read. Minor differences from 5.000 are tolerable. Repeat the d1 measurement. Repeat the d2 measurement, etc., until you have 5–10 tries each. You accumulate data like this:

(1) 4.997	(1) 5.003
(2) 4.995	(2) 5.005
(3) 4.998	(3) 5.001
(4) 4.997	(4) 5.002
(5) 4.998	(5) 5.004
Avg d1: 4.997	Avg d2: 5.003

Water reading: $D_o = (d2avg - d1avg) = 5.003 - 4.997 = +0.006$

Note the difference between D and d. Our notation doesn't quite follow that of the original BP manual.

YOU MUST REPEAT THIS MEASUREMENT FOR EACH WAVELENGTH. The best way to write down such measuements is with the dn/dc Blank Form below.

dn/dc Blank Form

Solvent: _____

Trial: #1 #2 #3 #4 #5 #6 #7

λ_o:_____ d1:
d2:
D_o,avg:

λ_o:_____ d1:
d2:
D_o,avg:

λ_o:_____ d1:
d2:
D_o,avg:

λ_o:_____ d1:
d2:
D_o,avg:

4. Prepare 5 solutions of KCl (dried in oven first) in clean water. The most concentrated solution should be about 0.02 g/ml; the exact concentration is unimportant, but knowing the exact concentration is! You are advised to use rather large volumetrics for these solutions to improve precision. For each of the five solutions and each of the four wavelengths, compute Δn, using the relationship:

$$\Delta n_{\lambda_o} = c \cdot (dn/dc)_{\lambda_o}$$

The values of dn/dc for KCl at 25°C for various λ_o are shown below. Appendix 2 shows how these values were obtained from the dn/dc values of KCl at Hg wavelengths and 25°C.

λ_o, nm	dn/dc (ml/gm)	comment
632.8 (HeNe red)	0.13409	extrapolation
589.0 (Na D line)	0.13505	interpolation
514.5 (Ar+ green)	0.13727	interpolation
488.0 (Ar+ blue *)	0.13831	interpolation

* An Ar+ laser actually produces several blue lines. 488 nm is the strongest blue line and the only one to approach the output strength of the 514.5 nm green line.

The calculated Δn's should be written into the Calibration Summary shown below. (do not worry about the last column yet). You need data like these at each wavelength!

Calibration Summary

λ_o:_____ (nm) $D_o = (d2–d1)_o,avg =$ _____

Calibration Standard:_____ (e.g., KCl, sucrose, etc.)

Solution #	c (gm/ml)	Δn_{λ_o}	ΔD_{λ_o} $= D - D_o$ $= (d2–d1),avg - (d2–d1)_o,avg$
1	_____	_____	_____
2	_____	_____	_____
3	_____	_____	_____
4	_____	_____	_____
5	_____	_____	_____

5. Now complete the last column of the Calibration Table by measuring each sample. It will be most efficient to leave the sample in place and change wavelengths. Thus, you will need a data log like this:

dn/dc Measurement Form

Solvent: _____ Solute: _____

Solution # _____ Concentration: _____ (gm/ml)

Trial: #1 #2 #3 #4 #5 #6 #7

λ_o:_____

D_o,avg:_____

d1:
d2:
$\Delta D = D_{avg} - D_{o,avg}$:
+/−:

λ_o:_____

D_o,avg:_____

d1:
d2:
$\Delta D = D_{avg} - D_{o,avg}$:
+/−:

λ_o:_____

D_o,avg:_____

d1:
d2:
$\Delta D = D_{avg} - D_{o,avg}$:
+/−:

λ_o:_____

D_o,avg:_____

d1:
d2:
$\Delta D = D_{avg} - D_{o,avg}$:
+/−: