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Refractive Index Increments to Calculate the Refractive Index of a Single Solute in a Buffer Solution: An Experimental Course

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Abstract

An experimental protocol for BSc students is proposed in which the refractive index increment at the wavelength corresponding to the sodium D line (λ=589 nm) of solutions containing different isomers of a solute is proposed. The used molecules are the isomers of dihydroxy benzene at pH = 5, namely 1,2-dihydroxybenzene (catechol), 1,3-dihydroxybenzene (resorcinol) and 1,4-dihydroxybenzene (hydroquinone). But in principle the experiments could performed with other isomers of a molecule in a suitable solvent ensuring perfect solubility of the chosen solute. The obtained refractive index increments are then used to calculate the refractive index of the solute (at this particular wavelength) knowing its density. The results are compared with the literature data and related to molecular properties like the polarizability and dipole moment. Error calculation are proposed followed by a discussion about statistical differences or not between the refractive index of the three investigated substances.

Keywords: Abbe Refractometer, Refractive Index Increment, Refractive Index of a Solute

Introduction

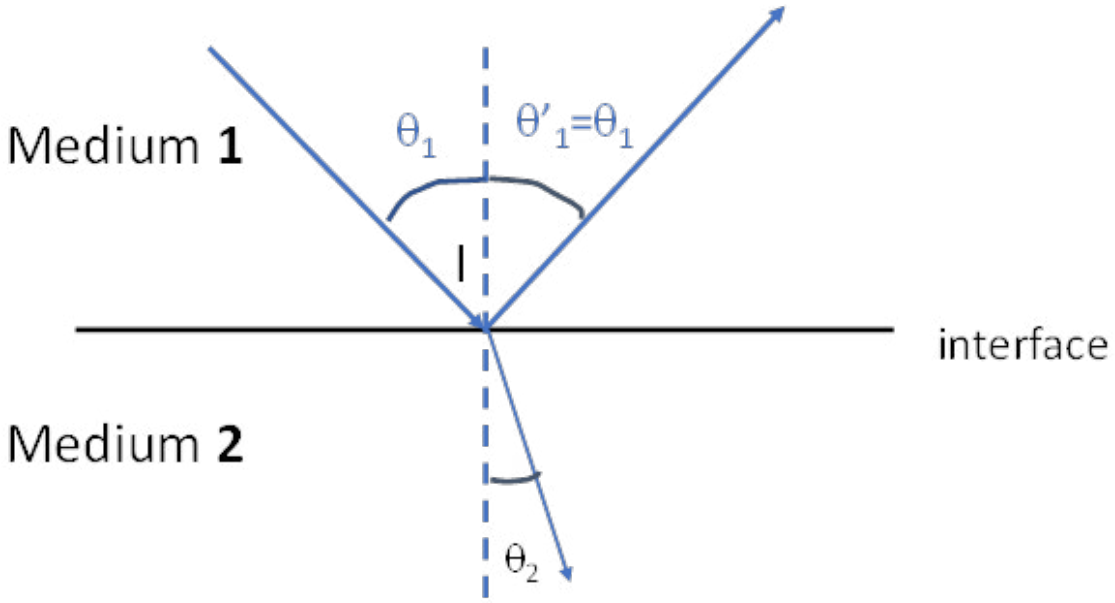
The refractive index of a phase, a homogeneous medium, is defined as the ratio of the speed of light in vacuum divided by its speed in the considered medium. It depends on the wavelength of the used monochromatic light as well as on the temperature. The first dependence is called a dispersion relationship. For instance, the refractive index of water at 20°C is equal to 1.330 at 589 nm (at the wavelength of the sodium D line) but amounts to 1.340 at the same temperature and at 434 nm [1]. Measurements of refractive indexes are often a first qualitative characterization of a medium and are widely used in the food industry for example. The refractive index of a homogeneous medium is measured with a refractometer relying on the principle of refraction. Indeed, when a light beam propagating in medium 1, is reflected at the interface with a second medium 2, part of the incident radiation can be reflected back in medium 1 and the complementary part is refracted in medium 2 (Scheme 1). The incidence angle of a beam with respect to an interface is defined as the angle between that beam, propagating as a straight line in a homogeneous medium, and the normal to the interface traced at the incidence point (I in Scheme 1).

If the incidence angle in medium **1** is equal to θ_1, the reflection angle is equal to θ_1' and the refraction angle (in medium **2**) is equal to θ_2 (Scheme 1) these three angles are related through the Snell-Descartes equations:

$\theta_1=\theta_1'$ (1)

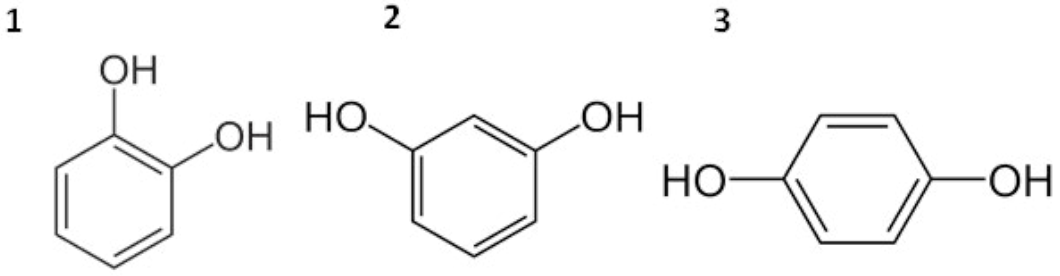
and: $n_1 \sin\theta_1=n_2 \sin\theta_2$ (2)

Relation (2) means that knowing the refractive index of a reference material, for instance the vacuum (with n1=1 by definition) one can calculate n_2 for any medium **2** by simply measuring θ_1 and θ_2. This is the basic working principle of any refractometer. Note that the well-known Snell-Descartes relationships can be easily demonstrated from the basic principles of optics, namely the Fermat principle stating that the optical path between two points is stationary. The demonstration can be found in any textbook of elementary physics and is not given here. But the students involved in the one day experimental course proposed herein should be able to make the demonstration.



Scheme 1: Representation of the interface between two (transparent) media **1** and **2** and the incident, reflected and refracted light beams. I represent the incidence point of the incident beam propagating as a straight line in medium 1. The angles θ are defined in the main text.

However, it is most often not possible to determine the refractive of a pure organic or inorganic material when it is in the form of a powder, because it is non homogeneous in these conditions. The investigated material has then to be solubilized in a well suited solvent to yield a homogeneous solution. It is the aim of the proposed practical course to allow for BSc students to determine the refractive index of a substance from its solution. As an example, it is proposed to determine the refractive index of the three isomers of dihydroxy benzene (Scheme 2).



	1 : catechol	2 : resorcinol	3 : hydroquinone
pKa_1	9.4	9.2	10.0
pKa_2	13.7	10.9	11.1
Solubility (mg/mL) at 20°C	430	1100	59
Dipole moment (D)	2.07±0.02	2.62±0.03	1.4±0.1

Scheme 2: Structure of the three isomers of dihydroxy benzene investigated in this experimental course. Their two *pKa* values at 25 °C are listed in the two first lines of the Table. The values of their solubility in water at 20 °C are taken from Wikipedia. The dipole moments are taken from reference [2].

The supervisor of this experimental course should spend a few minutes to explain the aim of the course and ask the students' opinion if the refractive index of the three isomers is the same, or not. At first glance one could believe their refractive index to be identical because of their identical chemical composition. But their structure is also different meaning changes in the local electronic density and expected small changes in their refractive index. The second question to be asked is to discuss about the water solubility of the three compounds listed in Scheme 2. Indeed, the mother solution to be prepared should be homogeneous…if some precipitate is present in the flask the molecules inside it will not contribute to the solution's refractive index. The solvent to be chosen will be water in which the solubility of **2** is higher than that of **1** and **3** (Scheme 2) which is pretty surprising owing to the decreasing dipole moment from **1** to **3** [2]. The solubility in water of **2** in indeed higher than that of **1** at 20 °C, owing to the possibility of **1** to form intramolecular hydrogen bonds due to the close proximity of the two hydroxyl groups impeding the formation of hydrogen bonds with water molecules. The students should also be invited to consider the fact that the experimental dipole moment of 3 is different from zero as would be naively expected on the basis of symmetry reasons. The answer for that can be found in ref. [2]. The experiments presented herein will be performed in 50 mM sodium acetate buffer. But, they could also be performed in any kind of buffer having a pH lower than 8. In this case, owing to their lowest *pKa* value, none of the three investigated molecules is deprotonated and they all remain in the uncharged form.

Materials and Methods

Chemicals and Safety

The used chemicals, catechol (C9510), resorcinol (ref. 398047) and hydroquinone (ref. H9003) were all purchased from Sigma-Aldrich and used without further purification. Note that the degree of purity is important because the solution concentration will be determined on the basis of weighing a given amount of compound and dissolving it in the buffer solution inside a precision volumetric flask, herein (100.0 ±0.1 mL). The products used herein had a purity higher than 98 %. All the compounds were dissolved in 50 mM sodium acetate buffer which pH was adjusted to 5.0 using concentrated hydrochloric acid. The *pH* was measured with a calibrated *pH* meter (Hannah Hi221 pH meter calibrated with buffer solutions at *pH* = 10.0, 7.0 and 4.02). The mother solutions prepared herein never exceeded 8.0 mg/mL which lies far below the solubility of the investigated compounds (See the Table provided in Scheme 2). The students should check the MSDS (materials safety data sheets) files of the used compounds (on the website of Sigma Aldrich) before starting any solution preparation. The used solutions should not be put in the sink at the end of the experiments. The students should wear gloves and a chemist's coat all along their experiments.

Preparation of the Diluted Solutions to be Characterized by Refractometry

Once the mother solutions are prepared and their nominal concentration calculated, they should be diluted to some proper ratios typically between 2 and 20 using precision vessel like graduated pipettes and precision flasks. Cascade dilutions should absolutely be avoided because they can induce *some systematic errors* in the concentration determination of the solute. For instance, the mother solution diluted by a factor of 5 should be prepared independently from the mother solution diluted by a factor of 10. All the diluted solutions have to be homogenized to ensure a uniform concentration and kept hermetically closed before the measurement of their refractive index in order to avoid evaporation of water which would induce an overestimation of the solute's concentration.

Used Refractometer

In this investigation we used an Abbe refractometer of the RFM 340 type from Belligham –Stanley Ltd (Figure 1A) giving the refractive index at λ=589 nm, the sodium D line. Any other commercial Abbe refractometer may be used. They usually give the refractive index value up to a precision of 10^{-5}. But it should not be forgotten that the refractive index of a solution decreases by about 10^{-5} $C^{\circ-1}$. This means that the temperature at which the measurements are performed should be recorded (many modern refractometers are fitted with a thermometer) and ideally the temperature should change by less than 0.1°C during the characterization of a data set comprising many dilutions of the mother solution of an investigated solute.

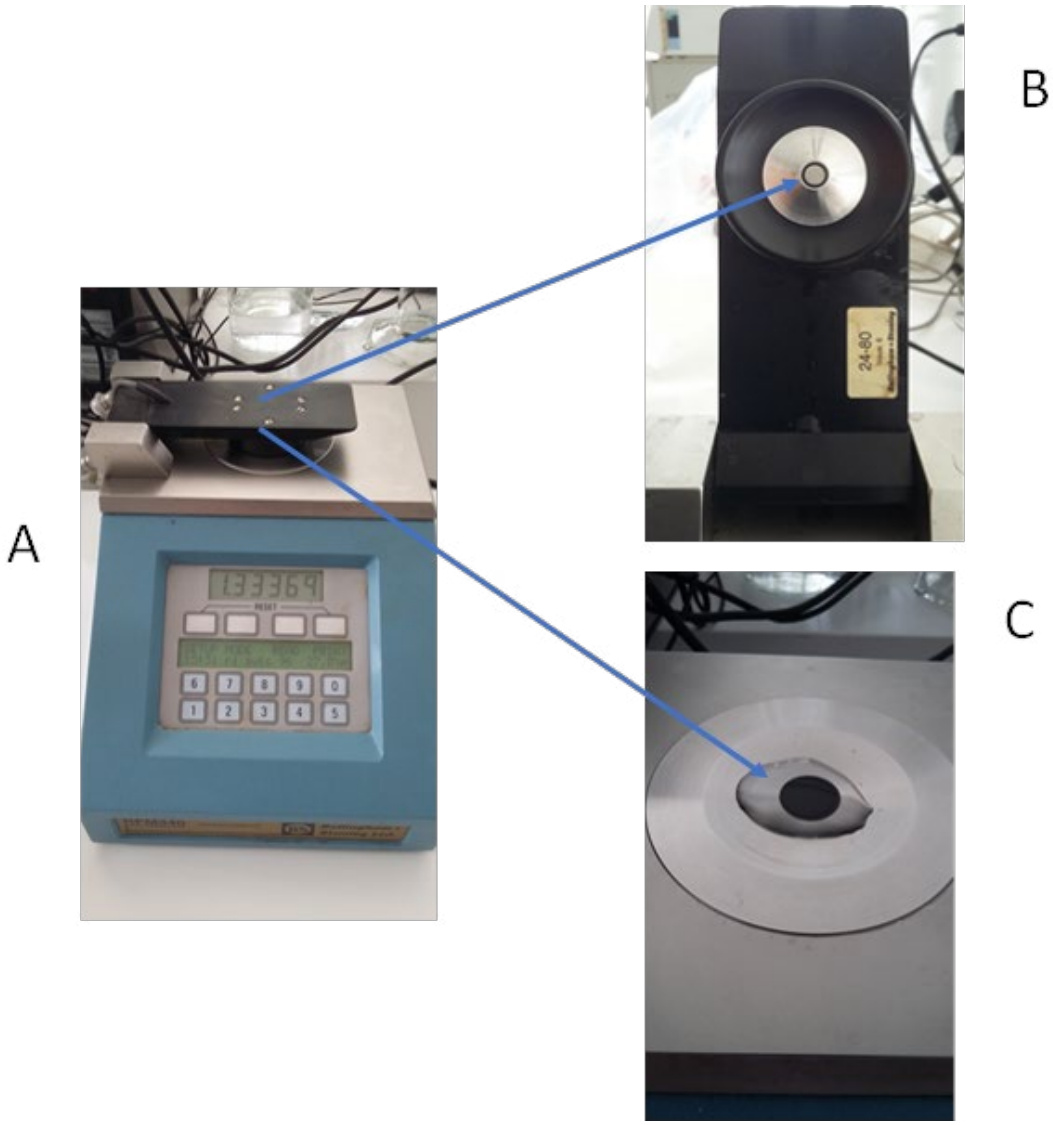


Figure 1: A: Picture of the Used Abbe Refractometer.
B: Upper Part of the Measurement Chamber.
C: Solution to be Characterized and Deposited on the Lower Part of the Measurement Chamber.

The measurement plate of the refractometer should be cleaned with distilled water and carefully dried before each measurement (the presence of some water will induce a dilution of the investigated solution and hence a reduction in its refractive index). For each compound, *the solutions should be measured from the most diluted to the mother solution* also to avoid some systematic errors which will be more important if a small drop of concentrated solution (or dried solute) remains on the lower plate of the refractometer (Figure 1C). When the solution to be measured is deposited on the lower part of the measurement chamber, the upper part of the chamber (Figure 1B) can be lowered and the measurement performed.

Results and Discussion

The students will find that the refractive index of the different solutions increases with the solute concentration according to a linear law (Figure 2).

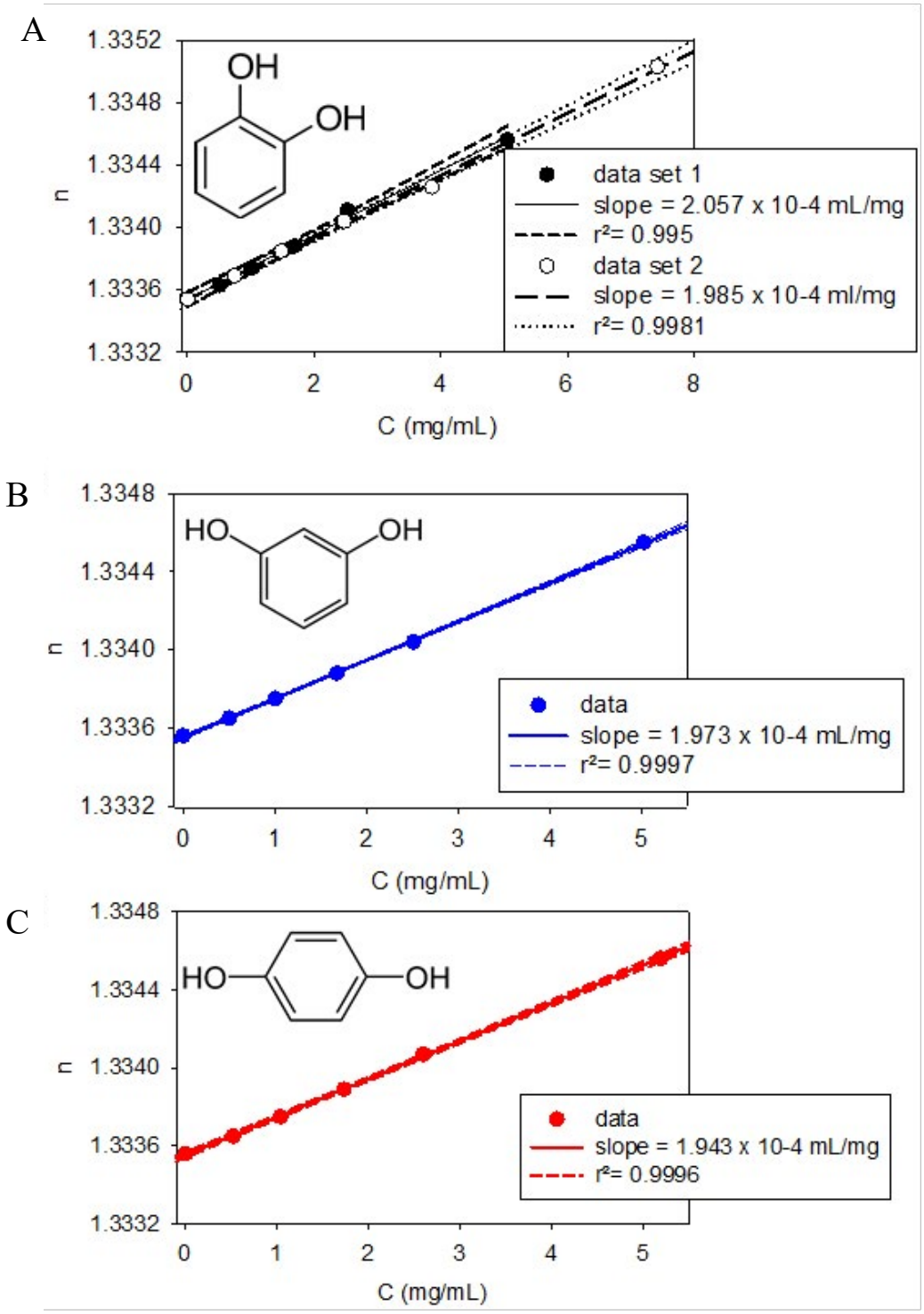


Figure 2: Variation of the refractive index (n) with the solution concentration (C) for the three isomers of dihydroxy benzene. A: catechol (2 independent data sets are given), B: resorcinol, C: hydroquinone. A linear fit was adjusted to the data and the dotted lines represent the limits of the 95 % confidence interval. The values of the slopes, corresponding to the refractive index increment (*dn/dc*) values and the linear correlation coefficients are given in the inset of each plot.

A linear regression, with linear correlation coefficients higher than 0.995 in all cases, was used to calculate the slope of the straight line (insets in Figure 2). The students should remember that on a straight line the slope is constant and corresponds to the same value of the curve derivative at each point along the curve. When plotting *n* versus *C*, the derivative is dn/dc, which is the refractive index increment of the investigated solutions. Note that two independent data sets are given in the case of catechol (Figure 2A). By independent data sets, it is meant that the diluted solutions are made from two independently prepared mother solutions. The students should also perform at least two independent data sets for each other solute in order to determine the standard deviations on the *dn/dc* values.

From the experimental data (Figure 2), equation (3) is used to fit the data:

$n=n_0+dn/dc.C$ (3)

where n_0 is the refractive index of the buffer solution without added solute. The refractive index of the solution is also the average of the refractive index of the solvent (herein the buffer), n_0, and the refractive index of the solute, n_s, where the refractive index values are pounded by the molar fraction of the solute, x, and the molar fraction of the solvent, 1-x. Hence:

$n=(1-x).n_0+x.n_s$ (4)

which rearranges in:

$n=n_0+x.(n_s-n_0)$ (5)

The comparison between equation (3) and equation (5) yields:

$c.dn/dc=x.(n_s-n_0)$ (6)

and hence:

$dn/dc=x/C.(n_s-n_0)$ (7)

When the concentration is expressed in weight per volume, as in the present experiments (Figure 2), x/C is the partial specific volume of the investigate solute, namely the reciprocal of its specific density, ρ (the students should verify the homogeneity of the relation: $1/\rho=x/C$, remembering that *x* is a molar fraction).

Finally, one gets from equation (7):

$dn/dc=1/\rho.(n_s-n_0)$ (8)

The obtained refractive index increments for the three isomers of dihydroxy benzene allow hence to calculate the refractive index of each of this solute provided its specific density ρ is known. The ρ values are easily accessible through the *CRC Handbook of Chemistry and Physics* or even via Wikipedia, and are given in the first line of Table 1. The average value of n0 we get in three independent experiments is equal to (1.33354 ± 0.00001). The *dn/dc* values and the calculated refractive indexes (from equation (8) are gathered in the second and third line of Table 1 respectively.

Table 1: Experimental values of the refractive index increments and the calculated values of the refractive indexes for the three isomers of dihydroxy benzene. a: data taken from Wikipedia.

	1: catechol	2: resorcinol	3: hydroquinone
ρ(g.cm^{-3}) at 20°C a	1.344	1.280	1.358
dn/dc (cm3.g-1)	0.2057 (first data set) 0.1985 (second data set)	0.1973	0.1943
ns calculated from the experimental data	1.610 (first data set) 1.600 (second data set)	1.586	1.597
ns at the sodium D line 1	1.604 ± 0.003	1.578 ± 0.001	/

The refractive indexes obtained by this method are extremely close to the values found in Wikipedia and should be a satisfaction for the students with respect to the simple experiments performed in this lab course. They should then think on the experimental errors and the standard deviations on the mean. Are the refractive indexes of catechol, resorcinol and hydroquinone (third line in Table 1) significantly different? One possibility is to perform statistical tests, which could be way to use knowledge acquired from a lecture in statistics. Herein, I propose to estimate the experimental errors affecting the values of n_s.

According to equation (8), the experimental error on n_s is given by:

$\Delta n_s=\Delta(\rho.dn/dc)+\Delta n_0$ (9)

This comes from the fact that the *absolute* error on a sum is equal to the sum of the absolute errors on each term of the sum. And:

$\Delta(\rho.dn/dc)/(\rho.dn/dc)=\Delta\rho/\rho+\Delta(dn/dc)/(dn/dc)$ (10)

Which comes from the fact that the *relative* error on a product is equal to the sum of the relative errors on each term of the product.

The values of the specific densities are given with a precision of 3 digits (Table 1), which implies:

$\Delta\rho$=0.001 $g.cm^{-3}$
with an average value (first line of Table 1): ρ=1.33 $g.cm^{-3}$

For the investigated solutes, the average value of *dn/dc* lies at 0.200 $cm^3.g^{-1}$ (Table 1). The error on the slope of the experimental curves in which the refractive index of the solution is plotted against the solution concentration (Figure 2) originates mainly from the error on the solution concentration, namely from the error on the mass of the solute and from errors on the volume of the volumetric flasks. On average to produce 100 cm3 (1 mL=1cm^3) of the mother solution at around 5 mg.cm^{-3} we have to weigh 500 mg with a precision of about 2mg. The error on the volume for the 100 mL flask is equal to 0.1 mL (as indicated on the volumetric flask). The relative error on the solution concentration is then overestimated to 6 x 10^{-3} which also corresponds to the relative error on the refractive index increment if we neglect the relative error on the refractive index (the absolute error on the n values amounts to 10-5 for an average value of 1.334). Hence according to equation (10):

$\Delta(\rho.dn/dc)/(\rho.dn/dc)$=0.001/1.33+0.006/0.2≤0.031 (11)

Hence with $\rho.dn/dc$=1.33x0.20=0.266, we obtain, according to equation [9] and neglecting again Δn_0 :
$\Delta n_s \leq 0.031x0.266 \approx 0.009$ (12)

Having now this overestimation of the experimental error on the ns values, the calculated refractive indexes are now given in Table 2 with their experimental errors.

Table 2: Refractive Indexes of the Three Isomers of Dihydroxy Benzene with Their Experimental Errors

	1: catechol	2: resorcinol	3: hydroquinone
$n_S \pm \Delta n_s$	1.605±0.009	1.586±0.009	1.597±0.009

The obtained values are also represented in Figure 3. Performing Mann-Whitney rank sum tests (the students should have a look in a statistics textbook), it appears that there are no significant differences between any two of the refractive index values.

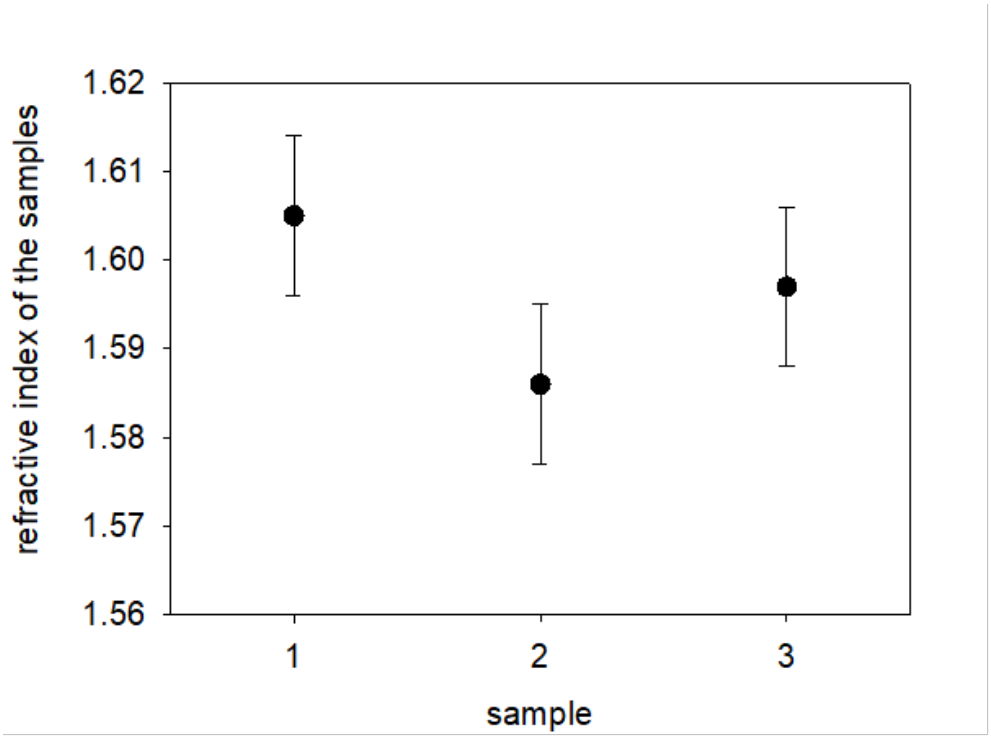


Figure 3: Refractive index of the three investigated isomers of dihydroxy benzene (**1**: catechol, **2**: resorcinol, **3**: hydroquinone) with their experimental errors (equation (12)). There are no significant differences between their values according to Mann-Whitney rank sum tests.

The question to be asked by the supervisor is then the following: if there was a difference between the refractive index of the three isomers of dihydroxy benzene, what would be the origin of it?

The answer lies in the relationship between the relative permittivity of a substance ($\varepsilon_s=n_s^2$), its polarizability (α) and its permanent dipole moment (μ) according to the Clausius-Mossotti equation [3]:

$$(\varepsilon_s-1)/(\varepsilon_s+2)=(\rho.N_A)/(3\varepsilon_0.M).(\alpha+\mu^2/3kT) \quad (13)$$

where N_A, ε_0 and M are the Avogadro number, the permittivity of vacuum and the molar mass of the substance respectively.

The supervisor can discuss with his group of students about close compounds displaying significant differences between their refractive index increments. While not trying to investigate solutions of sodium halides (NaCl, NaBr, NaI) owing to the known increase in polarizability from Cl^- to I^-? In addition, these salts are strong electrolytes in water so there is no contribution from their dipole moment in the Clausius-Mossotti equation (13) and the determination from n_s (via the *dn/dc* values) and hence ε_s allows directly to calculate the polarizability α of the anion. The data are already available in the literature [4].

The experiments that have been performed herein with isomers of dihydroxy benzene could also be performed with cheap proteins like bovine serum albumin or hen egg white lysozyme [5].

Conclusions and Perspectives

An easy experiment, requiring only a precision balance, volumetric flasks and an Abbe refractometry is proposed to determine the refractive index of the three isomers of dihydroxy benzene (other related and pretty cheap compounds could also be chosen instead). The obtained values are compared with tabulated data and some error calculations are proposed to estimate if the refractive index of the different compounds is significantly different. The main goal of this one day experimental course, aimed for BSc students, is to convince them that single experiments in Physical Chemistry allow to relate materials properties to the structure of the constituting molecules.

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