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A New Method of Measuring Small Refractive Index Differences

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A modification of the Rayleigh interference refractometer, characterized by the production of an optical image of the light source slit in one dimension only and an optical image of the cell in the other dimension, was described by Calvet [1–3] and by Philpot and Cook [4]. The new instrument and its application to diffusion and electrophoresis has since been the object of a number of investigations [5–13] which show that it is an extremely valuable tool in physico-chemical measurements. The present paper deals with still another application, the measurement of small refractive index differences.

The measurement of such differences, *e.g.* that between a solution and the solvent, is a frequently performed operation in chemical laboratories as an accurate and convenient way of determining the concentration of the solution. A direct measurement of the refractive index difference is superior to two separate measurements of absolute refractive indices for several reasons. First, the time required is less, and the accidental error is smaller in one measurement than in two, Second, a number of systematic errors are automatically eliminated in the direct procedure.

The differential refractometers that have been described in the literature are, in general, based on the measurement of the angular deflection of light in a double-prismatic cell, or on interferometric measurement of optical thickness in white light. While the interferometric method is superior in accuracy, the result is sometimes obscured by the fact that the optical path length compensator does not have the same colour dispersion as the solutions under investigation. In addition, the result obtained does not refer to any specified wave-length and is thus a little undefined. With coloured solutions, the white light interferometric method often fails altogether.

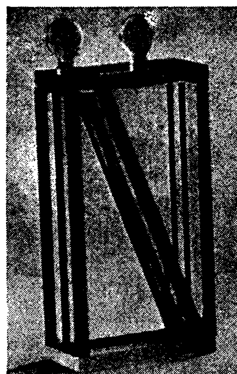


Fig. 1. The double-prismatic cell.

The present differential refractometer makes use of a double-prismatic cell, but in conjunction with a Rayleigh-Calvet-Philpot interference refractometer operating with monochromatic light. In this way, the high accuracy characteristic of the interferometric method is guaranteed at the same time as the above-mentioned difficulties have been removed.

CELL CONSTRUCTION

The cell used is shown in Fig. 1. It has a parallelepipedic form with the outside dimensions of 31 × 57 × 14 mm. The smaller vertical walls as well as the diagonal partition wall are each made of one piece of high-precision optical glass. Consequently the two side walls are composed of triangular pieces cemented between the afore-mentioned walls. All three optical walls extend a distance outside one of the side walls. When the cell is traversed by light, this wall will subdivide the aperture defined by the cell into two portions, both having exactly equal thicknesses of glass in the light paths. In the roof piece of the cell, there are two small conical holes with glass stoppers, for filling and emptying the cell. Since this cell is used in a water-bath, the two prismatic chambers to the right are not covered. When it is immersed into the water, the latter will automatically fill these spaces. For a cell to be used in air, equality between the optical path lengths inside and outside the cell would have to be guaranteed by other means.

The two halves of the cell are filled with the two solutions to be compared. The smaller chamber, with the tip of the triangle towards the bottom, is suitably used for the solution, which is generally not available in quantity. Its total volume is 4.5 ml, but measurements can be carried out with any smaller volume. Reduction of the volume by a factor of 4 will only reduce the accuracy to 1/2 since it is the height of the liquid column that defines the accuracy.

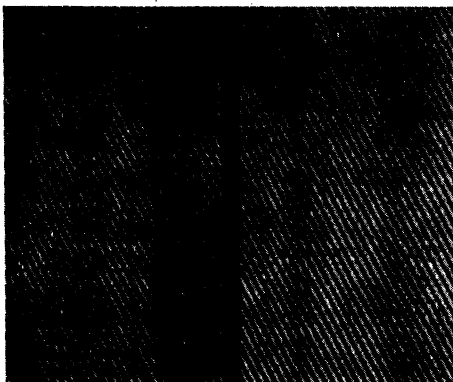


Fig. 2. Rayleigh interferogram obtained with distilled water and a one per cent sugar solution in the two chambers of the double-prismatic cell. The number of fringes per unit length in a direction parallel with the black line is proportional to the refractive index difference.

THEORETICAL

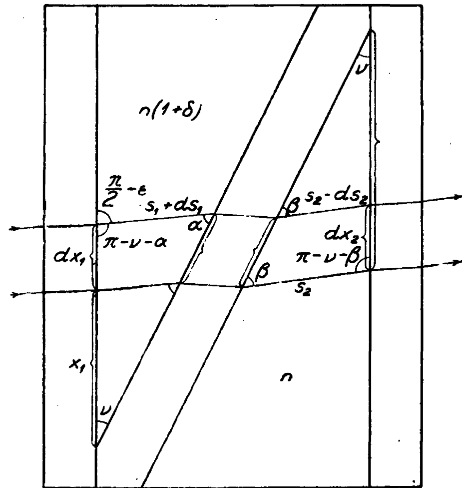
It is easy to realize that the optical thickness of the cell along a horizontal line will be a linear function of the height coordinate, while the optical thickness of the comparison cell is independent of this coordinate. When the cell is put in place into the optical system of the Rayleigh-Calvet-Philpot interferometer, therefore, the resulting interferogram will contain a number of equidistant fringes which make a certain angle with the cell axis and which are more closely spaced along this axis, the greater the refractive index difference in the cell. Fig. 2 shows such an interferogram obtained with distilled water and a one per cent sugar solution in the cell, and with the modification of the interferometer described in reference [12]. The vertical black line is the optical image of a vertically suspended thread which is superposed on the interferogram and serves as a reference line.

In an exact theory of such a cell as this, one has to take into account the fact that the light does not travers it in a horizontal direction, and that the optical path length has to be computed along the actual course of the ray. Fig. 3 shows a drawing of the cell and two mutually parallel rays of light traversing it. The notation used is evident directly from the figure. The difference in optical path length between these two rays is:

$$ds = n(1 + \delta)\ ds_1 - n\ ds_2 \tag{1}$$

but the relations:

$$\frac{ds_1}{s_1} = \frac{dx_1}{x_1} \text{ and } \frac{ds_2}{s_2} = \frac{dx_2}{x_2} \tag{2}$$



give:

$$ds = n\ (1 + \delta)\ \frac{s_1}{x_1}\ dx_1 - n\ \frac{s_2}{x_2}\ dx_2 \tag{3}$$

According to the sine theorem, we have:

$$\frac{s_1}{x_1} = \frac{\sin\ v}{\sin\ \alpha}\ \text{and}\ \frac{s_2}{x_2} = \frac{\sin\ v}{\sin\ \beta} \tag{4}$$

$$\frac{dx_1}{dl} = \frac{\sin\ \alpha}{\sin\ (v + \alpha)}\ \text{and}\ \frac{dl}{dx_2} = \frac{\sin\ (\text{v} + \beta)}{\sin\ \beta} \tag{5}$$

This gives the equation:

$$\frac{ds}{dx_2} = n\ (1 + \delta)\ \frac{\sin\ v\ \sin\ (v + \beta)}{\sin\ \beta\ \sin\ (v + \alpha)} - n\ \frac{\sin\ v}{\sin\ \beta} \tag{6}$$

Since x_2 and $x_2 + dx_2$ are the exit coordinates, they are directly related to the coordinates on the photographic plate by the magnification factor; the cell and the plate being corresponding image planes. Equation (6), therefore, gives after division by the cell magnification directly the fringe density along the vertical line on the photographic plate.

With the aid of the relation:

$$\frac{\pi}{2} - \varepsilon = \alpha + v \tag{7}$$

equation (6) can also be written in the form:

$$\frac{1}{n}\frac{ds}{dx_2} = (1+\delta)\frac{\sin v \sin(v+\beta)}{\sin\beta \cos\varepsilon} - \frac{\sin v}{\sin\beta} \tag{8}$$

We will now regard the right-hand side of this equation as a function of the two independent variables δ and ε and derive the second-degree approximation of this function according to the formula:

$$F(\delta,\varepsilon) = F(0,0) + \delta\frac{\partial F(0,0)}{\partial\delta} + \varepsilon\frac{\partial F(0,0)}{\partial\varepsilon} +$$

$$+\frac{1}{2}\left[\delta^2\frac{\partial^2 F(0,0)}{\partial\delta^2} + 2\delta\varepsilon\frac{\partial^2 F(0,0)}{\partial\delta\partial\varepsilon} + \varepsilon^2\frac{\partial^2 F(0,0)}{\partial\varepsilon^2}\right] \tag{9}$$

It is then to be remembered that β is also a function of these two variables according to Snell's law:

$$(1+\delta)\sin(v+\varepsilon) = \cos\beta \tag{10}$$

Its partial derivatives are:

$$\frac{\partial\beta}{\partial\delta} = -\frac{\sin(v+\varepsilon)}{\sin\beta} \tag{11}$$

$$\frac{\partial\beta}{\partial\varepsilon} = -\frac{(1+\delta)\cos(v+\varepsilon)}{\sin\beta} \tag{12}$$

For $\delta = \varepsilon = 0$ they assume the values $-\tan v$ and -1, respectively, since β is then $= \pi/2 - v$.

The partial differentiation of the function $F(\delta,\varepsilon)$ gives the result:

$$\frac{\partial F(0,0)}{\partial\delta} = \tan v \quad \frac{\partial F(0,0)}{\partial\varepsilon} = 0 \tag{13}$$

$$\frac{\partial^2 F(0,0)}{\partial\delta^2} = \tan^3 v \quad \frac{\partial^2 F(0,0)}{\partial\delta\partial\varepsilon} = 0 \quad \frac{\partial^2 F(0,0)}{\partial\varepsilon^2} = 0 \tag{14}$$

The second-degree approximation of $F(\delta,\varepsilon)$ can thus be written:

$$\frac{ds}{dx_2} = n\delta\tan v + n\frac{\delta^2}{2}\tan^3 v \tag{15}$$

From the disappearance of ε in this expression we conclude that the fringe displacement is independent of the angle of incidence. This means that a vertically extended light source slit or grating can be used without obscuring the result. Compare in this respect reference [8].

The δ^2 term in (15) allows us to compute the deviation of the fringe density from the linear dependence on δ expressed by the simple formula:

$$\frac{ds}{dx_2} = n\ \delta\ \tan\ v \tag{16}$$

If we require the second term not to exceed 10^{-6} in refractive index, we get for this cell, with $\tan v = 0.4$, the condition:

$$\delta < 0.00485 \text{ and } \Delta n = n\ \delta < 0.00647 \tag{17}$$

for water solutions. We should thus expect an exactly linear dependence of the fringe density on the refractive index difference up to $\Delta n = 650 \cdot 10^{-5}$, which corresponds to about 4.5 per cent sugar and 3.5 per cent protein solution. Consequently the simple equation (16) can be used in the majority of practically occurring cases.

If greater refractive index differences than (17) have to be measured, the cell with $\tan v = 0.4$ is unsuitable, not only due to the non-linear dependence, but also because the fringe density becomes too high for ordinary photographic material to resolve. The useful refractive index range of the instrument, however, can be increased at will by constructing other cells with smaller values of $\tan v$.

The accuracy to be expected from this new method and instrument can easily be computed. If the availabie height (the height of the cell, or the height of the liquid column if the cell is not completely filled) is h cm, the effective thickness of the cell becomes $h \tan v$, and the difference in optical thickness between top and bottom of the cell $h \tan v\ \Delta n$ cm $= h\ \Delta n \tan v/\lambda$ wavelengths. According to experience gained in the references [5–13], it is possible under favourable conditions to localize a fringe to within 1/50 of the separation between fringes. We thus get the following expression for the ultimate limit of accuracy of this method:

$$\Delta n = \frac{\lambda}{50\ h\ \tan\ v} \tag{18}$$

With the numerical figures of the actual cell, $h = 4.5$ cm and $\tan v = 0.4$, and with $\lambda = 5461 \cdot 10^{-8}$ (the green mercury line), we get $\Delta n = 0.6 \cdot 10^{-6}$.

EXPERIMENTAL

In order to test the performance of the cell and the accuracy obtainable by this method, measurements were carried out on a number of sugar solutions in distilled water of exactly known concentrations. A stock solution was pre-

pared by dissolving 12.5070 g of sucrose (Merck's analytical reagent) in distilled water in a 250 ml calibrated volumetric flask. This gave a concentration of 5.0201 g per 100 ml at 25°. A series of lower concentrations were then prepared by diluting this stock solution, using calibrated pipettes and volumetric flasks. The resulting concentrations are given in Table 1, the first column. Accurate refractive index data for sugar solutions have been presented by Gosting and Morris [14]. Column 2, Table 1, gives the refractive index increments corresponding to the concentrations in column 1, calculated by interpolation from Gosting's and Morris' values.

Table 1.

Sugar concentration g/100 ml	Refractive increment · 10^6	Fringes / cm observed	Fringes / cm calculated	Fringes / cm discrepancy
0.0000	0.0	0.60	0.56	+0.04
0.1000	143.0	4.01	4.03	−0.02
0.2007	287.1	7.48	7.53	−0.05
0.3006	430.1	11.01	11.01	0.00
0.5014	717.4	18.00	17.99	+0.01
1.0028	1434.7	35.43	35.41	+0.02
2.0056	2869.0	70.26	70.26	0.00
3.0094	4304.2	105.13	105.13	0.00
4.0123	5737.7	139.63	139.95	−0.32
5.0201	7178.3	174.62	174.96	−0.34

One of the chambers of the double-prismatic cell was filled with the sugar solution, the other with distilled water. The cell was then put into the water-bath, the temperature of which was kept at 25.0°. After a time period for temperature equilibration, the interferogram was photographed. One photograph was also taken with distilled water in both chambers of the cell. Green mercury light ($\lambda = 5461$ Å) was used.

After developing, the plates were measured in a comparator. They were aligned on the comparator table with the aid of the reference line seen in Fig. 2, and the distance between two fringes, one in each end of the cell, was measured. Finally the number of fringes per cm was calculated. These figures are given in column 3, Table 1.

The figures in columns 2 and 3, Table 1, were then treated by the method of least squares, and the resulting linear relationship between fringe density and refractive index increment was:

$$\frac{ds}{dX} = 0.024296\,\Delta n + 0.556 \qquad (19)$$

From this equation, one should expect the fringe densities given in column 4, Table 1. The discrepancies between these and the observed values, column 3, are given in column 5.

DISCUSSION

The experiments described above show a good agreement with theoretical expectations. In addition, they give an accurate calibration of this particular cell. The constant term in equation (19) indicates a slight optical imperfection of the cell or a slight maladjustment of the optical system, and has to be added to the observed fringe density in every measurement.

The last column in Table 1 shows that the method is capable of an accuracy in the readings of some hundredths of a fringe in the lower concentration range. With the dimensions of this particular cell, this corresponds to one unit in the sixth decimal place in the refractive index. Naturally this accuracy does not persist at higher concentrations simply because the resolving power of the comparator sets a limit at high fringe densities.

The method should, in the first place, be useful for those laboratories where an electrophoresis or a diffusion apparatus with an astigmatic optical system is available. The only thing to be supplied is then the double-prismatic cell itself. That is also the way in which this investigation has been carried out. Should the apparatus not be equipped with facilities for Rayleigh interference observation, but only for *Schlieren*-optical measurements, the cell can still be used on the basis of measuring the angular deflection in the cell. However, some reduction fo the accuracy is then to be expected.

SUMMARY

A method for measuring small refractive index increments based on interferometric measurement of the optical thickness of a double-prismatic cell in monochromatic light has been described. It is capable of a precision of $1 \cdot 10^{-6}$ refractive index units, and the fringe density has been shown to be proportional to the refractive index difference within a wide range, the limit of which has been given mathematically. The method is supposed to be of value for rapid and accurate measurements of concentrations of solutions, especially in laboratories where electrophoresis or diffusion apparatus with astigmatic optical systems are available.

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