A DIFFERENTIAL REFRACTOMETER OF HIGH SENSITIVITY

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Summary

The refractometer is of the Jamin type. The positions of the main and fiduciary fringes are determined by means of a pair of photomultiplier tubes, the outputs of which are fed to a balanced amplifier. A change in optical path of 1/15,000th of a fringe can be detected, and the instrument is stable to within 1/5000th of a fringe over 30 min periods. Examples are given of its use in the measurement of small differences in refractive index for liquids and gases.

I. INTRODUCTION

The invention of the photomultiplier tube has greatly extended the range of light intensities which can be detected with the aid of relatively simple equipment. In particular the intensity in the various regions of the fringe systems produced by interference methods can be readily measured. In the present paper a description will be given of a highly sensitive interference refractometer using these tubes as detectors.

The Jamin refractometer appears to be the most suitable type for this purpose because a relatively large source can be used and the fringe spacing can be easily varied. With the simpler Rayleigh refractometer the source slit is very narrow, giving rather faint fringes, and the fringes are very close together. Because of changes in the intensity of the source and drifts in the positions of the fringes with time it is essential to provide a fiduciary system of fringes with which the main system can be compared. It is still quite commonly claimed that such a system is a prerogative of the Rayleigh refractometer, but in point of fact a fiduciary system is readily obtained with the Jamin refractometer (Guest and Simmons 1953). Attention should also be drawn to a refractometer employing quite different principles designed by Ingelstam (1953), in which the cell containing the fluids is imaged in phase contrast. This instrument also employs photomultiplier tubes as detectors, and an accuracy of 1/1000th of a fringe is obtained.

Up to the present the refractometer described here has only been used for the measurement of small differences in refractive index—mainly those due to impurities in water samples. Such measurements can be undertaken in an ordinary laboratory provided the room temperature does not fluctuate very rapidly. In measuring large differences in refractive index it would be necessary

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to maintain the temperature very accurately constant. The cell length must also be known very accurately. Unfortunately, because of lack of funds, it has not been possible to extend the range of the instrument so that large differences in refractive index can be measured.

The drift of the refractometer over the period necessary to complete a reading is less than 1/5000th of a fringe. The accuracy obtainable in the refractive index difference $\Delta\mu$ for the two substances being compared is about 1×10^{-8} for water samples, using a cell of length 1·3 cm. For gases a sensitivity of 1×10^{-9} is obtained with a cell of length 20 cm. The accuracy for the intercomparison of air and a gas such as oxygen is lower by a factor of 50 because of the difficulty in measuring and maintaining constant the pressure and the temperature.

II. Description of the Refractometer

A schematic diagram of the refractometer is given in Figure 1. The two Jamin plates J_1 and J_2 are 1 cm thick, and the spacing between the two interfering beams is therefore also about 1 cm. A small value of plate thickness and beam separation reduces the effect of temperature gradients in the refractometer. However, a slightly greater plate thickness (perhaps up to 2 cm) would permit

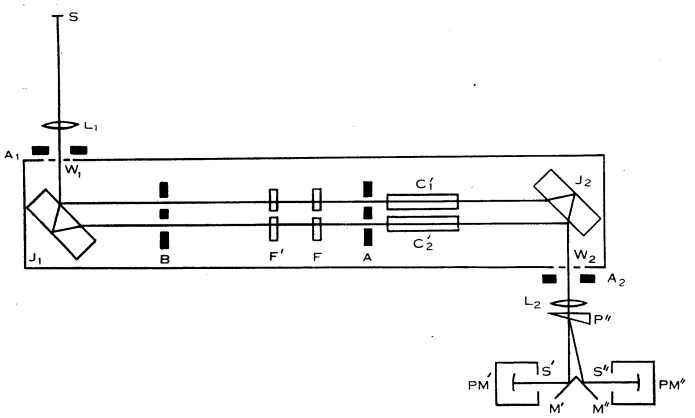

Fig. 1.—Schematic diagram of the refractometer. Components marked with a prime superscript are in the lower beam only, those with a double prime in the upper beam only.

a wider separation of the cells C_1' and C_2', which would simplify the problem of isolating the two cells from one another. Screws are provided for tilting the plates about horizontal and vertical axes. The plates are spaced 50 cm apart to allow cells of various lengths to be used. The entire path traversed by the interfering beams is shielded by a wooden cover to eliminate air currents, the light entering and leaving by the windows W_1 and W_2.

The source slit S, in the focal plane of the lens L_1, is a few millimetres square. Its size is limited by the necessity for preventing the beam from spreading too much in its passage through the refractometer. The lenses L_1 and L_2 both have a focal length of 25 cm. A_1 and A_2 are vertical slits which block off multiply reflected beams. The apertures, of diameter 2 mm, in the

opaque screen A select the four beams, the lower pair passing through the cells and the upper pair being used to produce a fiduciary fringe system.

Immediately behind the lens L_2 is a prism P'', whose angle is about 20°. This prism is only in the upper beam, and it deviates this beam on to the mirror M''. The lower beam falls on the mirror M'. S' and S'' are horizontal slits of adjustable width in the focal plane of the lens L_2, where the fringe systems are formed. Portions of each fringe system pass through the slits and fall on the cathodes of the photomultiplier tubes, which are enclosed in light-tight holders.

Two pairs of fringe-shifting plates, F and F', are shown in the diagram. Both are of the Jamin type, the two plates having a constant angle of separation and rotating together on a common shaft. The plates F are in both the upper and lower beams, and are employed to test whether the two systems of fringes are coincident (see Section IV below). The plates F' are in the lower beams and hence move only the main set of fringes, leaving the fiduciary system unaltered. These plates are turned by a micrometer screw at the end of a pivoted bar, so that small rotations can be accurately measured. The pitch of the screw is 0·5 mm, and the length of the bar 30 cm. A drum fitted to the head of the screw is divided into 100 divisions, and the angle between the plates is chosen so that one division corresponds to a fringe movement of about 1/4000th of the fringe spacing.

B is a shutter which can be used to block off one or other of the pairs of beams, so that the intensities of the upper and lower beams reflected from the front of J_1, or from the back of J_1, can be compared. This provides a check on the stability of the equipment.

The cells C_1' and C_2' contain the fluids being compared. For liquids a stainless steel block 1·3 cm thick was ground and polished so that its surfaces were flat and parallel. Grooves were cut for the cells, and the ends were closed with optical flats which were wrung to the steel. This design is simple, and is satisfactory for the comparison of very dilute water solutions, but it is not certain that the two cells are completely isolated from one another. For gases, glass tubes 20 cm long have been used, the end windows being cemented to the glass.

A white light source may be used when the refractive index difference is very small and the dispersion is not important. However, a monochromatic source is much more suitable. A standard high pressure mercury lamp of the type used for street lighting is very convenient, the green mercury line being isolated by a monochromator and a gelatin filter. With such a high intensity source the photomultiplier voltages can be kept quite low (60–70 V per stage), and this reduces the random fluctuation in the output current. The only disadvantage of such a source is the breadth of the line, which limits the optical path difference to a small number of wavelengths. It is quite possible to use a laboratory type " Osira " lamp at somewhat higher values of photomultiplier gain (with voltages of about 90 per stage) in cases where the broadening effect might be important. With weaker sources the fringe spacing is made very wide and the slits S' and S'' are opened so that all the light in the image falls on the photomultiplier cathode.

III. The Electronic Circuits

The photomultiplier tubes are of the 931A type. Figure 2 shows the circuit for the photomultiplier power supply. The rectifier uses two 5R4GY tubes and a transformer with a 385–0–385 V secondary in what might be described as a "voltage one-and-a-halfer" circuit giving 1500 V D.C. output. This circuit was used because a commercial radio transformer of this type was readily available, but a simple circuit using a 1000 V transformer would be equally satisfactory. This D.C. voltage is applied to a conventional electronic regulating circuit. The screen voltage of the 6J7G tube is obtained from a divider across the unregulated side of the supply, and by adjustment of this divider the regulation may be made perfect for changes in the mains input voltage.

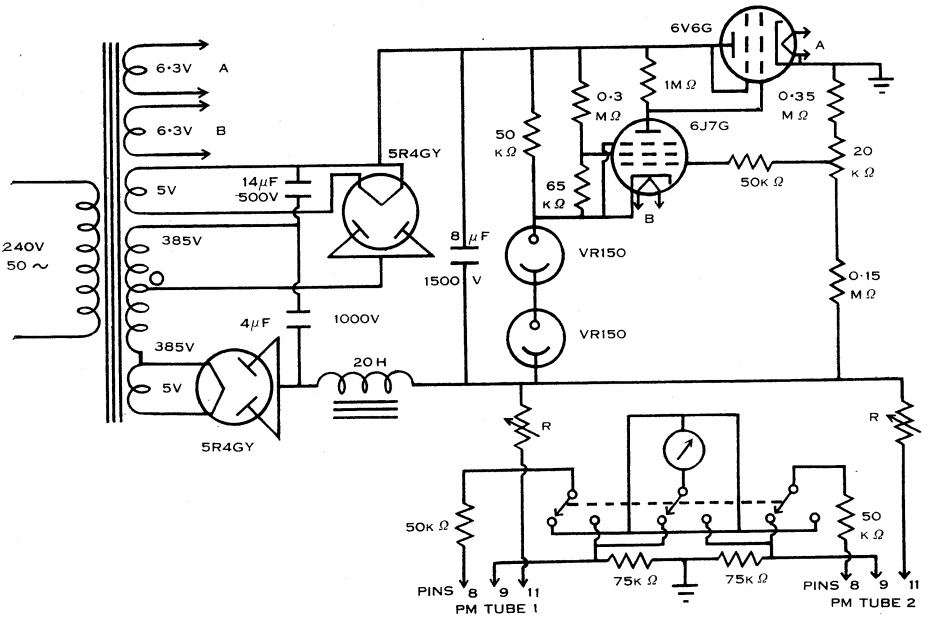

Fig. 2.—Photomultiplier power supply.

The positive side of the regulated output is earthed. The voltages for the dynodes are obtained from a series of 50,000 Ω resistors between pins 11 (cathode) and 9 (final dynode). These resistors are mounted in the 931A tube holders and are not shown in the diagram. The resistance R between pin 11 and the negative side of the supply consists of a switch for inserting resistances and a variable 50,000 Ω wire-wound rheostat. These provide the coarse and fine controls for adjusting the "volts per stage" for the 931A tubes.

The current from the network supplying the dynode voltages is applied through a switch to a calibrated meter on which the volts per stage for either tube may be read. The network is completed by a 75,000 Ω resistance to ground, and the final anode is returned to ground through the amplifier load resistance. This connection is by means of a separate shielded lead clipped

directly on to the pin, the corresponding lug on the tube socket being removed to minimize leakage currents.

The D.C. amplifier shown in Figure 3 is based on a circuit described by Scroggie (1952). As used here it is completely symmetrical. The photomultiplier currents are fed through 10 MΩ load resistances connected to the grids of the EF37A tubes, and they return to earth through the small resistances in the EF55 cathode circuits. The two EF37A tubes have a common cathode resistance and the circuit behaves as a balanced amplifier. The output meter is connected between the cathodes of the two EF55 cathode followers. The EF37A may be replaced by the more modern EF86, while the two EF55 tubes may be replaced by a single 12AT7 or ECC81 double triode.

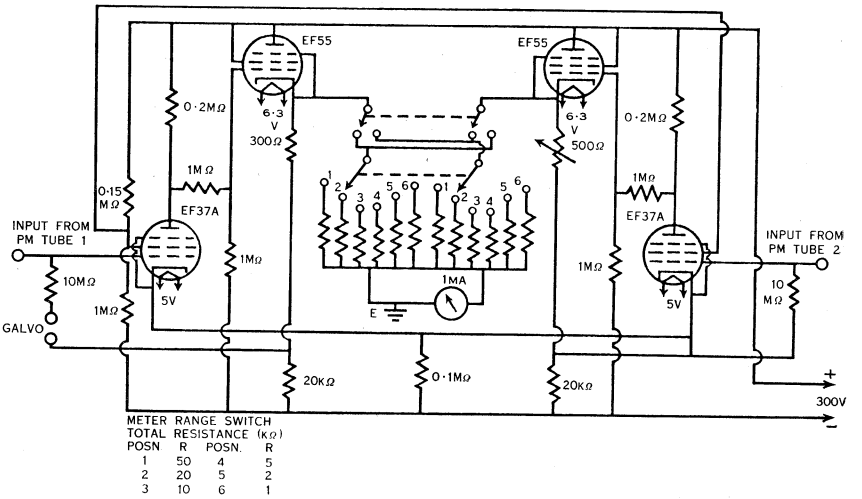

Fig. 3.—Balanced D.C. amplifier.

The range switch inserts resistances in series with the meter, which has a 1 mA movement. The centre point of the meter circuit is earthed. The meter zero position is adjusted by a 500 Ω rheostat in the cathode of one EF55 tube. The output current is a measure of the difference between the currents in the two photomultipliers. Terminals are provided for a galvanometer (sensitivity about 2 cm/μA) to measure the current flowing in one of the photomultipliers.

The electronic equipment has been in operation for a period of more than two years. During that time the only trouble encountered was a change in the zero setting of the balanced amplifier, due to aging of the 1 MΩ resistors coupling the plate of the EF37A tube to the grid of the EF55. These resistors should preferably be of the high stability type.

IV. Adjustment of Fringes to Coincidence

The galvanometer is used to measure the current produced by the fiduciary fringe system. The gain of the photomultiplier tube is adjusted till the current at the fringe maximum is 2·5 μA.

In Figure 4 are drawn typical curves of current against fringe position for the two systems as the fringes are moved across the photomultiplier tubes by the fringe-shifting plates F. In Figure 4 (b) the minima are coincident and the differences in amplitude—and hence the currents in the balanced amplifier—at positions such as those labelled 1 and 2 are the same. In Figure 4 (a) the minima are slightly displaced and the amplifier current is greater at position 1 than at position 2. In Figure 4 (c) the minima are displaced slightly in the opposite sense and the amplifier current is greater at position 2. This then provides a method for detecting when the main system of fringes is coincident with the fiduciary system, the main system being moved by means of the fringe-shifting plates F' until the amplifier currents in positions 1 and 2 are the same.

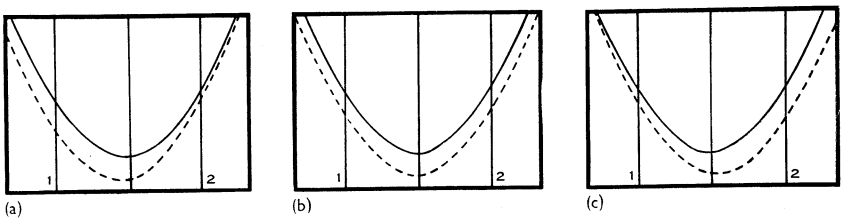

Fig. 4.—Curves of photomultiplier current against fringe position. Solid curves refer to the fiduciary system, dotted curves to the main system. In diagram (b) the minima are coincident, in the other two diagrams they are displaced.

The test positions 1 and 2 are located by moving the plates F until the galvanometer current reaches a definite value—say 1 μA. Clearly the magnitude of the main fringe current will not affect the equality at positions 1 and 2 in Figure 4 (b). However, it is an advantage to have the current difference at these positions close to that at the minimum, for then the current difference will not vary greatly as the plates F are rotated and it will not be necessary to set the galvanometer current accurately to 1 μA.

The procedure for determining the setting of F' for which the fringe systems are coincident is then as follows. The fringe systems are moved by F from a position corresponding to a fiduciary current of 1 μA through the minimum till the current is again 1 μA. The difference between the balanced amplifier currents at these two positions is noted. This difference is reduced to zero by rotating F'. When the fringes are coincident the gain of the photomultiplier tube in the main fringe system may be varied till the current at the minimum is the same as at the two test positions 1 and 2. The adjustment of the gain is not at all critical and need only be performed occasionally.

Because of screw backlash it is not easy to set the fringe-shifting plates F' exactly on the coincident position. It has been found best to move the screw through intervals of one division at a time, observing the amplifier current difference for positions 1 and 2 and stopping when this difference changes sign. The correct setting can then be found by interpolation.

This method of setting to coincidence is not affected by absorption in the fluids. A second method of measurement has been used occasionally when the difference in absorption of the standard and unknown fluids is very small.

The fringes are set in some position such as 2 in Figure 4 (*b*) and the gains and the plates F' adjusted till a movement of the fringe systems about this position leaves the amplifier current unaltered. The two curves have then the same slope in the region about position 2, and the amplifier current is unaffected by simultaneous drifts of the two sets of fringes. It is, however, affected by changes in the photomultiplier sensitivities and by zero drift in the amplifier, and these must be allowed for. If the pair of beams reflected from the front of the plate J_1 is blocked off by the shutter B, the pair reflected from the back of the plate will provide an indication of the changes mentioned above. The intensity of the current due to a single beam is about one-quarter of the peak fringe intensity, and, if the single beams are to be used as a reference, it is desirable that the fringe currents at the working position should also be of this order of magnitude. The change in the amplifier current when the unknown fluid is substituted for the standard can then be corrected by subtracting the corresponding change with one pair of the beams blocked off by the shutter. It is clear that this method cannot be used if the fluids differ appreciably in absorption. The change in amplifier current can be calibrated to read directly small shifts of the fringes, an advantage if the refractive index is varying rapidly.

It should be mentioned that the presence of the plates F' in the lower beam causes the distance between neighbouring fringes in the focal plane of the lens L_2 to be slightly different in the two systems. For the very small angular separation of the plates F' used here this effect is barely noticeable. Both the methods of measurement described above ensure that the difference in fringe spacing has no effect on the readings. For visual observations, however, the plates F' will usually be at a larger angle and the difference in the fringe spacing may be quite marked. This difference in spacing may be eliminated by placing in the upper beam a pair of plates similar to the pair F' in the lower beam.

V. Performance of the Refractometer

(*a*) *Calibration of the Jamin Compensator*

It is first necessary to determine the displacement of the fringes produced by the fringe-shifting plates F'. The displacement for a Jamin compensator is not strictly proportional to the angle of incidence i, but varies according to the expression (Hansen 1930)

$$\sin i\left[1-\frac{\cos i}{(\mu^2-\sin^2 i)^{\frac{1}{2}}}\right], \qquad \ldots\ldots\ldots\ldots \quad (1)$$

where μ is the refractive index of the glass. Thus as i increases the rotation of the compensator plates required to produce a given fringe-shift decreases. In the present equipment the rotation is produced by a micrometer tangent screw bearing against a pivoted bar, and so, if x is the screw setting and L the length of the bar, the rotation is equal to $\tan^{-1}x/L$. A maximum shift of a little more than one-half of a fringe in each direction is provided, the integral part of the fringe-shift being assumed known from less accurate measurements.

It is preferable to calibrate the compensator rather than to rely on expression (**1**). The shaft carrying the plates is arranged so that it can be rotated independently of the tangent screw. Thus the rotation necessary to shift through

one fringe (e.g. from one minimum to the next) can be determined for the four fringes surrounding the working position, and, using finite differences, a formula can then be found for the fringe-shift in terms of the rotation. This can then be converted into a formula giving the fractional shift f in terms of the screw movement x. Fortunately, the non-linearity introduced by the expression (**1**) largely cancels that introduced by the inverse tangent term. The final expression for the fractional fringe-shift f is found in the present apparatus to be

$$f=\frac{x}{45\cdot683}(1-0\cdot00179f). \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

Since x can be read to better than $0\cdot003$, the sensitivity is better than 1/15,000th of a fringe.

This expression was determined at a temperature of 23 °C, most of the measurements being made in the vicinity of this temperature. If x is large and great accuracy is required, it may be necessary to recalibrate the screw at the working temperature. For measurements on gases the pressure may be adjusted so that x is always small.

The screw may also be calibrated by varying the pressure in a short air cell.

(*b*) *Stability*

A stability of better than 1/5000th of a fringe over a period of 20–30 min is claimed for the instrument. Table 1 shows a typical series of readings of the setting x of the tangent screw at which the fringes coincide. These were taken with liquid cells containing water, $1\cdot3$ cm in length, in the interfering beams.

TABLE 1

STABILITY OF THE REFRACTOMETER

Time	Tangent Screw Reading, x	Drift Between Readings	
		$\Delta x(\times10^3)$	$\Delta f(\times10^4)$*
1420	0·437		
1440	0·443	+6	+1·3
1500	0·447	+4	+0·9
1520	0·440	—7	—1·5
1540	0·443	+3	+0·7
1600	0·436	—7	—1·5
1620	0·430	—6	—1·3
1640	0·437	+7	+1·5
1700	0·436	—1	—0·2
1720	0·428	—8	—1·8
1740	0·430	+2	+0·4

* Calculated from equation (**2**), Section V (*a*).

For the readings in Table 1 the maximum deviation from the mean of the set ($0\cdot437$) over the period of 200 min corresponds to a change in f of $2\cdot2\times10^{-4}$. The long-term stability is not always as good as this if the room temperature is varying rapidly.

(*c*) *Reproducibility of Measurements with Liquids*

The design of the refractometer is not ideally suited to the measurement of liquid indices. The lid of the box shielding the refractometer from draughts has to be removed and then the cell cover, when the liquid is being changed. The liquids are inserted and removed by a dropper. It is necessary to wait for a period of 10–20 min to allow the system to return to temperature equilibrium. A separate refractometer for liquids with much shorter beam paths would probably give better results.

It appears that the readings of x are reproducible to better than 1/2000th of a fringe. Table 2 shows a set of successive values of x obtained by removing the liquid from the cell and inserting fresh liquid from the same sample.

TABLE 2

DRIFT ON REPLACING LIQUID

Time	Tangent Screw Reading, x	Drift	
		$\Delta x(\times 10^3)$	$\Delta f(\times 10^4)$*
1750	0·884		
1805	0·880	—4	—0·9
1820	0·883	+3	+0·7
1835	0·887	+4	+0·9
1850	0·904	+17	+3·7
1905	0·912	+8	+1·8

* Calculated from equation (**2**), Section V (*a*).

(*d*) *Refractive Index Differences for Liquids*

The refractive index difference $\Delta\mu$ is given by $(\lambda/t)\Delta f$, where λ is the wavelength and t the cell thickness. On substituting the values $\lambda = 0{\cdot}54623 \times 10^{-4}$ cm and $t = 1{\cdot}3080$ cm, and using equation (**2**),

$$\Delta\mu = 91{\cdot}41 \times 10^{-8}\Delta x. \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

It is usually best to take a set of three readings—standard, unknown, standard—the central reading being then subtracted from the mean of the other two. This guards against possible errors due to disturbance of the apparatus or contamination of the liquids, and also compensates for drifts of the fringes which may occur if there are large temperature gradients present. To obtain greater accuracy a more extended set of readings may be taken. Table 3 shows a typical set for two samples of water (labelled A and B).

The successive differences are not independent, but the mean is the most easily calculated estimate and appears to be reasonably efficient. An estimate s_m of the standard error of the mean can be found from the residuals v, the formula being

$$s_m^2 = \left[\frac{4(4n-11)}{6n^3-52n^2+148n-136}\right]\Sigma v^2,$$

where n is the original number of readings. A discussion of the statistics would be out of place here.

A good check on the reliability of the measurements is afforded by the mutual intercomparison of three liquids. For three water samples identified as A, B, and C, the following differences were obtained:

$$\text{A–B}, \quad 10^8\Delta\mu = 28\cdot7 \pm 0\cdot3;$$
$$\text{B–C}, \quad 10^8\Delta\mu = 24\cdot8 \pm 0\cdot7;$$
$$\text{C–A}, \quad 10^8\Delta\mu = 3\cdot5 \pm 0\cdot8.$$

The general experience has been that the error in a single determination of refractive index difference of this magnitude is almost always less than 2×10^{-8}, while a more extended set of observations enables the difference to be determined to at least 1×10^{-8}.

TABLE 3

REFRACTIVE INDEX DIFFERENCE FOR LIQUIDS A AND B

Time	Liquid	Tangent Screw Reading, x	Mean of Adjoining x	$\Delta x(\times10^2)$	$\Delta\mu(\times10^8)$*
1650	A	0·533			
1705	B	0·230	0·545	31·5	28·8
1720	A	0·557	0·240	31·7	29·0
1735	B	0·250	0·563	31·3	28·6
1750	A	0·569	0·261	30·8	28·2
1805	B	0·272	0·590	31·8	29·1
1820	A	0·612			
Mean				31·4	28·7
Standard error				0·3	0·3
Maximum deviation from mean				0·6	0·5

* Calculated from equation (**3**), Section V (*d*).

(*e*) *The Refractometer for Gases*

The cell length is 20·74 cm, and so for the mercury green line

$$\Delta\mu = 263\cdot4\times10^{-8}\Delta f. \quad \text{..... (4)}$$

In terms of the change in the scale reading x,

$$\Delta\mu = 5\cdot765\times10^{-8}\Delta x. \quad \text{..... (5)}$$

(*f*) *Changes in Atmospheric Pressure*

The refractometer will give a direct indication of short-time variations in the atmospheric pressure. If the refractive index is μ at the pressure p,

$$\Delta\mu = \frac{\mu-1}{p}\Delta p.$$

For standard dry air at t °C,

$$10^3\Delta p = (149\cdot4 + 0\cdot55t)\Delta x,$$

the pressure change being measured in millimetres of mercury. Assuming a limit of 0·01 for Δx, the limit of reading for the pressure change is about 2

microns. If high accuracy is required the humidity of the air should be allowed for. The values obtained for Δp agree with those given by an oil manometer to the limit of reading of the latter (about 10 microns).

The refractometer will also follow very rapid changes in pressure. Its use as a microphone, with a speaking tube attached to one of the cells, provides an interesting novelty. When the EF55 cathode voltage is fed through a power amplifier to a loudspeaker quite good reproduction is obtained, although the noise from the photomultiplier tubes is rather high.

(*g*) *Measurement of Refractive Indices of Gases*

Since it is possible to set the scale reading x to well within 0·01, it should be possible to read the refractive index of a gas to within 5×10^{-10}. However, such an accuracy certainly cannot be obtained outside a standards laboratory, since it requires a very accurate knowledge of the pressure and temperature and of the cell length. Even the dispersion equations for air obtained by the principal standards laboratories give values of refractive index differing by up to 1×10^{-7} (Barrell 1951).

TABLE 4

REFRACTIVE INDEX DIFFERENCE FOR AIR AND COMMERCIAL OXYGEN

Mean temperature, 23·0 °C; mean pressure, 757·5 mm Hg

Time	Difference in Screw Reading, Δx	Difference in Refractive Index, $\Delta\mu(\times10^6)$*
1345	—3·01	18·61
1425	—0·90	18·49
1450	+0·83	18·39
1520	—0·93	18·49
1545	—1·80	18·54
Mean		18·50
Standard error		0·04
Maximum deviation from mean		0·11

* $10^6\Delta\mu=7\times2\cdot634-0\cdot0576\Delta x$.

It seems possible without any elaborate equipment to compare the refractive index of a gas with that of standard air to an accuracy of about 5×10^{-8}. Table 4 gives a series of readings of the change Δx when oxygen (of commercial quality as used for glass-blowing etc.) was substituted for dry air in one of the cells. The value of the integral order—in this case 7—was calculated from refractive index tables. This value was later checked by direct counting of the oscillations of the meter needle as the gases were removed.

The values $\Delta\mu$ show a systematic trend, due at least in part to variations in the atmospheric pressure and temperature, and perhaps also to slight changes in the constitution of the air in the room. The mean value of $10^6\Delta\mu$ was $18\cdot50\pm0\cdot04$. When this is reduced to standard conditions (15 °C, 760 mm),

the value $19 \cdot 08 \pm 0 \cdot 04$ is obtained. Using the value $(277 \cdot 93 \pm 0 \cdot 03) \times 10^{-6}$ for the refractivity of standard air, the refractivity of the oxygen sample is then $(258 \cdot 85 \pm 0 \cdot 05) \times 10^{-6}$.

VI. Acknowledgments

The author would like to express his thanks to Mr. J. Davies of the Physics Workshop, who constructed the refractometer, and to his laboratory assistant, Mr. S. W. Hutchinson, who constructed the associated equipment.

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