

## NOTES ON MINIMUM-DEVIATION REFRACTOMETRY

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### ABSTRACT

Minimum-deviation refractometry problems are presented at the maximum precision level likely to be required by mineralogists. Using a medium-precision spectrometer equipped with a Gauss ocular for auto-collimation, it is concluded that for solids the probable error of a single determination should not exceed  $\pm 2$  or  $3 \times 10^{-5}$ . For liquids, where temperature coefficients are relatively high, probable errors between  $\pm 1 \times 10^{-4}$  (for methylene iodide) and  $\pm 4 \times 10^{-5}$  (for water) need not be exceeded. Tests of the accuracy of this spectrometer, using a Bureau of Standards calibrated glass prism, check within  $\pm 2 \times 10^{-5}$ . It is emphasized that the level of precision of index determination of a liquid used in the immersion procedure should ideally be much higher than the precision of index determination aimed at for the solid. Under any circumstances, however, an estimate of the error in index of the liquid should accompany the statement of index error assumed for solids determined by the immersion method.

### INTRODUCTION

It is generally agreed by competent authorities (Tilton, 1929) that the minimum-deviation method of refractive index determination is inherently superior to any other. For solids, single determinations with a probable error of  $\pm 2$  or  $3 \times 10^{-6}$  are routine and precision can be improved if replicate measurements are made. For liquids, on the other hand, which have relatively high refractive index variation with temperature, a precision of  $\pm 1 \times 10^{-5}$  is about the limit obtainable, and for ordinary work with open, hollow cells a considerably lower goal of precision must be faced. As a major use of the minimum-deviation method in mineralogical work is in calibrating liquids for the immersion method of refractive index determination, it is important to know what precision is obtained under given conditions. The immersion method assumes particular importance in investigations of rock-forming minerals because of the impossibility of obtaining fragments large enough for preparation of oriented prisms to be used on a spectrometer. Since there is always an unavoidable random error in matching a grain with its embedding liquid, it is only common sense to devote considerable care to the calibration of the liquid being used as the standard. Depending on the nature of the problem, a degree of precision may be required which makes advisable calibration of a liquid beyond the precision limit ( $\pm .0002$ ) of the ordinary Abbe refractometer. This can not be done, as is usually attempted in mineralogical laboratories, by pressing into service a one-circle crystal goniometer, since auto-collimation is not provided on these instruments

and sufficiently precise prism angle determinations can not be carried out. A spectrometer designed for the purpose must therefore be used. The author uses a medium-precision Gaertner instrument (Type LIII) which reads directly to 20 seconds and by interpolation to 10 seconds. It is provided with a Gauss ocular (for auto-collimation) which can be illuminated by any small concentrated light source such as a Penlite battery lamp. A sodium-vapor lamp supplies monochromatic radiation<sup>1</sup> for the minimum-deviation measurements.

Temperature control is provided by a constant-temperature assembly supplied by American Instrument Co. Temperature in the supply tank is controlled to .05° C., but is probably not better than .1° C. elsewhere in the circulating system. Air temperature is checked by a thermometer suspended directly above the prism table.

#### TOLERANCES IN MEASUREMENT

Tilton (1929, 1931, 1933, 1935) has thoroughly investigated the sources of error in minimum-deviation refractometry and has established tolerances based on a probable error of  $\pm 1 \times 10^{-6}$  in refractive index. Table 1 lists most of the errors discussed in his papers and gives, for selected refractive index values, the larger tolerances based on a probable error of  $\pm 1 \times 10^{-5}$ , which is the goal under consideration here.

All the sources of error may be either positive or negative except errors in prism orientation, which, from the mechanics of the method, can be positive only. As noted in the table, most of the tolerances are large enough in terms of measurement and control that the desired error of  $\pm 1 \times 10^{-5}$  need not be exceeded. Exceptions are (1) the prism angle determination, where the observed tolerance (see Table 2) is commensurate with a refractive index error of  $\pm 2 \times 10^{-5}$  rather than  $\pm 1 \times 10^{-5}$ , and (2) the control of temperature for organic liquids, where the tolerances are too small for ordinary control equipment. This matter will be discussed on a later page.

If it is desired to find tolerances for other values of refractive index error, the relations are linear throughout except for prism orientation error, where a second power relation obtains (see Table 1).

The flatness of the prism faces is critical because of its influence on the tolerances in prism translation, eccentricity of prism-table axis, and collimator focusing. However, it is routine procedure to obtain surfaces deviating from true flatness by less than .25  $\lambda$  per 1 cm. area. Where this holds, these three dependent sources of error acquire large tolerances and may be neglected for work at  $\pm 1 \times 10^{-5}$ .

<sup>1</sup> In addition to the strong doublet (5890 and 5896), lines 6563, 4861, and 4340 may also be used with this lamp.

TABLE 1. TOLERANCES FOR A PROBABLE ERROR IN REFRACTIVE INDEX OF  $\pm 1 \times 10^{-5}$   
PRISM ANGLE ASSUMED TO BE 60°

Source of Error	Refractive Index				Notes	Reference
	1.3	1.5	1.7	1.9		
Prism Angle (A)	5.7 sec.	3.3 sec.	2.2 sec.	1.6 sec.	Tolerances are in general too small for a refractive index error of only $\pm 1 \times 10^{-5}$ . Tolerances large, varying directly with index.	Tilton 1929
Double Deviation (2D)	5.6 sec.	6.2 sec.	8.0 sec.	15.0 sec.		Tilton 1929
Prism Orientation Azimuth at the Minimum Deviation Setting	~6°	~5°	~4.5°	~4°	Error is always positive. $\Delta n \propto (\text{P.E. azimuth})^2$ . Tolerances large.	Tilton 1931
Prism Flatness	2.7λ	1.4λ	.8λ	.4λ	Referred to an area 1 cm. diameter. Tolerances large, varying inversely with index.	Tilton 1933
Prism Translation Eccentricity of Prism-Table Axis					Tolerances dependent on flatness of prism, and are large enough to be ignored if prism flatness $< .5\lambda$	Tilton 1933
Collimator Focussing						
Air Temperature	8° C	7° C	6° C+	6° C-	For $\lambda = 5893$ and room temperature. Tolerances cannot be ignored.	Tilton 1935
Air Pressure	22 mm. Hg.	19 mm. Hg.	16 mm. Hg.	15 mm. Hg.	Tolerances are fairly critical.	Tilton 1935
Temperature of Solids	Sylvite $\sim .3^\circ \text{C}(-)$ , $n_e$ Calcite $\sim .1^\circ \text{C}(+)$ Fused quartz $\sim 1^\circ \text{C}(+)$ Light Flint Glass $\sim 2^\circ \text{C}(+)$ Water $0.1^\circ \text{C}(-)$ Most organic liquids about $.025^\circ \text{C}(-)$ Methylene iodide $.015^\circ \text{C}(-)$				For $\lambda = 5893$ . Coefficients positive or negative. Tolerances ample.	Tilton 1935
Temperature of Liquids					For $\lambda = 5893$ . Tolerances too small (water excepted) for $\pm 1 \times 10^{-5}$ probable error. Coefficient always negative.	Tilton 1935
Wavelength of Light Source	Water 1.0 Å	Fluorite 1.3 Å			For $\lambda = 4000$ . Tolerances ample when using sodium, mercury, etc., vapor lamps	Tilton 1935

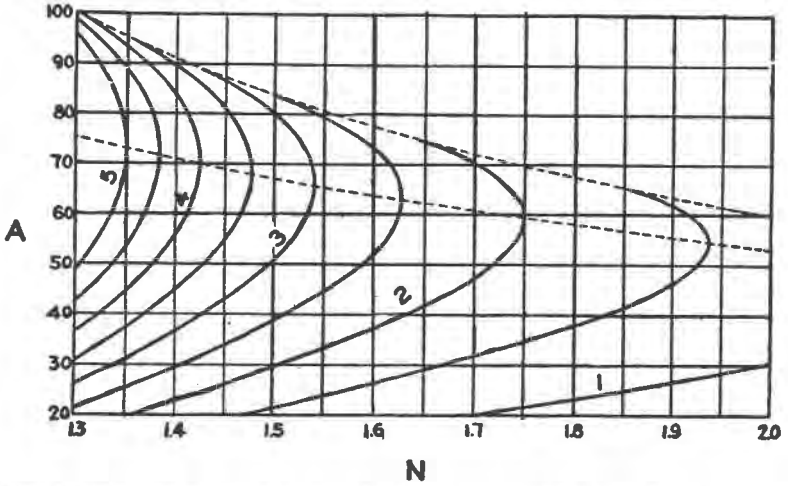


FIG. 1. Iso-tolerance curves (in seconds) for various combinations of prism angles  $A$  and refractive indices  $N$ , based on an arbitrary error of  $\pm 1 \times 10^{-3}$ . The merit of using prism angles close to  $60^\circ$  (for this range of indices) is indicated by the broken line connecting the crests of the curves. The upper broken line shows the largest prism angle which could possibly be used for various refractive indices. Modified from Tilton (1929).

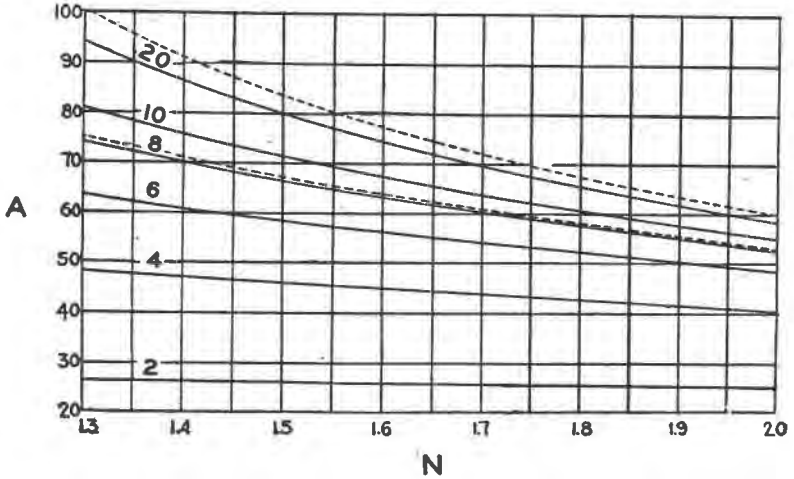


FIG. 2. Similar to Fig. 1, but drawn to show tolerances (in seconds) in the double-deviation angle  $2D$ . The broken lines are identical with those in Fig. 1. Note the larger tolerances compared with prism angle tolerances. Modified from Tilton (1929).

The tolerances for prism angle determinations are shown in Fig. 1. The general merit of using  $55\text{--}75^\circ$  prisms is evident from the broken line connecting the peaks for each curve. The tolerance varies inversely with index.

Figure 2 applies to errors in double-deviation. The tolerances vary directly with prism angle and refractive index. The broken lines have the same positions as in Fig. 1.

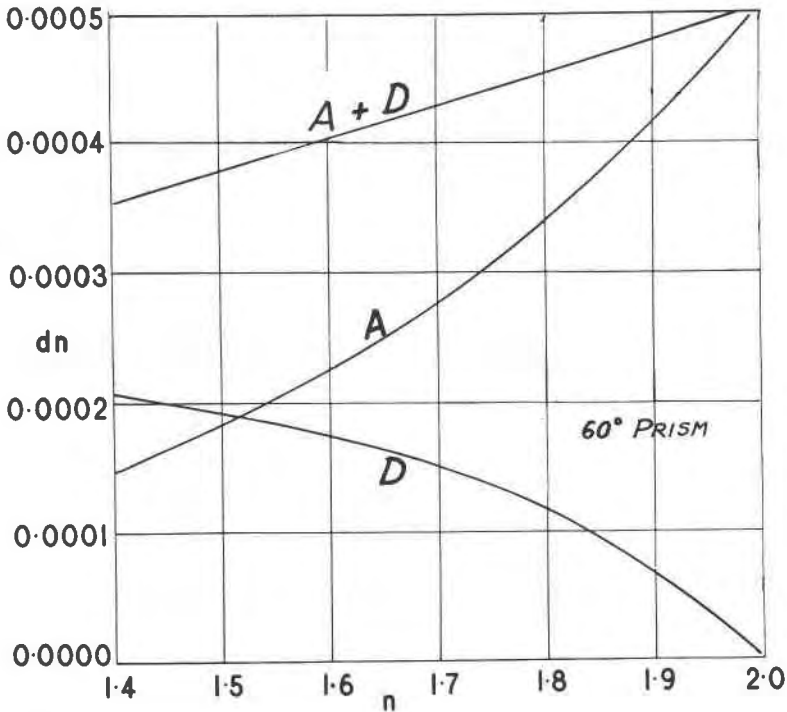


FIG. 3. Diagram showing relative trends of error in prism angle  $A$  and deviation angle  $D$  for a fixed prism angle. The opposing trends in the  $A$  and  $D$  curves show the need for particular care in determining  $A$ . From Fairbairn and Sheppard (1945), based on a maximum error of 1 minute in measuring  $A$  and  $D$ .

Figure 3 shows, for a 60° prism, the opposing trend of errors in prism angle and double deviation. Except for low-index materials, tolerances are less liberal for prism angles than for double deviation angles, thus emphasizing the requirement of auto-collimation in prism angle determination.

#### TESTS WITH A STANDARD GLASS PRISM

In order to test the precision and accuracy of the present spectrometer, measurements were made with a glass prism furnished by the Optics Section, National Bureau of Standards. Two determinations of its prism angle are stated to differ by less than one second and the refractive index varies less than 3 units in the sixth decimal place. Table 2 gives a sum-

mary of measurements made for comparison with the Bureau of Standards data. The probable error of 5 seconds in the prism angle computed for one set of measurements is about twice the tolerance given in Fig. 1 for an index error of  $\pm 1 \times 10^{-5}$  and is therefore commensurate with an error of  $\pm 2 \times 10^{-5}$ . The double-deviation error on the other hand is well within the limits set by Fig. 2. This contrast in the two errors is striking, but nevertheless normal, and points up the fact that even with the auto-collimation method, prism angle determination is a much greater source of error than the double-deviation determination.

TABLE 2. SUMMARY OF TESTS WITH STANDARD PRISM

Prism Angle Data (A)			Double Deviation Angle Data (2D)				Refractive Index
Angle	Probable Error	No. of Trials	Angle	Probable Error 2D	Probable Error D	No. of Trials	
60°14'55"	5 sec.	5	87°51'48"	2 sec.	1 sec.	4	1.57205
60°14'50"	n d	3	87°51'56"	n d		2	1.57211
60°14'50"	n d	2	87°51'50"	n d		2	1.57209
60°14'50"*			87°51'53"*				1.57210*

\* Data supplied by Optics section, Bureau of Standards, Washington, D. C. Two determinations of prism angle varied  $< 1$  second. Refractive index varied about 3 units in the sixth decimal place and is here rounded off to five places. Compare with corresponding data immediately above.

The flatness of the glass prism is about  $.25 \lambda$ , well within the tolerance range given in Table 1, and also below the threshold value of  $.5 \lambda$  where dependent errors due to prism translation, eccentricity of the prism table axis, and collimator focussing would be significant.

Data on relative values of air temperature and pressure at the Bureau of Standards and in our laboratory are not available. However, in view of ordinary room temperature ranges, it is unlikely that the corresponding tolerances given in Table 1 have been exceeded. The tolerances for air pressure are slightly more critical and the present measurements may be affected beyond  $\pm 1 \times 10^{-5}$ , but not above  $\pm 2 \times 10^{-5}$ .

The prism is a light flint glass having a tolerance of about  $2^\circ \text{C}$ . for our arbitrary index error of  $\pm 1 \times 10^{-5}$ . As the writer's measurements were made at somewhat higher room temperature ( $2-4^\circ \text{C}$ .) than the standard  $20^\circ \text{C}$ . used at the Bureau of Standards, the index error limit may need to be raised to  $\pm 2 \times 10^{-5}$ . Any correction applied would be negative (see Table 1 for details for various solids).

The average refractive index of the three trials reported in Table 2 (1.57208) agrees very closely with the standard value of 1.57210. A probable error based on so few determinations would not give a very significant statistic and no computation has been made. However, in assessing the magnitude of such errors it must be kept in mind that practically all the component sources of error may be either positive or negative. This compensating factor tends to reduce the magnitude of the combined probable error in refractive index. Tilton (1935) states that high precision determinations in the Bureau of Standards laboratory have a probable error of about  $\pm 2$  or  $3 \times 10^{-6}$ . In view of the evaluation of errors of measurements made in the writer's laboratory, a probable error not greater than  $\pm 2$  or  $3 \times 10^{-5}$  may be assumed. The Gaertner instrument may therefore be considered adequate, both from the standpoint of precision and accuracy, for refractive index determinations correct to at least four decimal places and approximate in the fifth.

#### *Tests with a Hollow Prism*

Calibration of the spectrometer with solid prisms gives a sound basis for tests with hollow prisms.<sup>2</sup> As is well known, hollow prisms are subject to two inherent defects (1) non-parallelism of the inner and outer surfaces, and (2) curvature of the prism faces. For satisfactory work, therefore, a good grade of optical glass should be obtained. Glass recently used by the writer deviates from true parallelism by 6 seconds and from true flatness by 2 rings ( $= 1 \lambda$ ) per 1 cm. diameter. It would be possible for given orientations of the symmetry planes related to the wedging and curvature of the glass to work out an assembly for the hollow prism in which these defects are minimized. It is simpler, however, to proceed empirically and to calculate a cell "constant" for the particular prism used. For example, from trials with distilled water as a reference liquid, the writer determined a systematic excess in its refractive index, at the temperature used, amounting to .00005. For unknown liquids this value is therefore subtracted from the calculated refractive index. If a new cell is assembled its "constant" must be independently determined.

If the cell is built as in Fig. 4, it may turn out that no "constant" need be used. This would be the case if error from the flatness of the surfaces was negligible and if the "wedging" of the glass was so small that the tolerance for prism translation (Table 1) was not exceeded.

As already stated on a previous page (see also Table 1) the temperature of liquids is a critical parameter and the limits of control must be known. In the writer's laboratory thermometers are installed in the

<sup>2</sup> Same design as illustrated by Butler (1937).

pump-driven bath circuit at equal distances on each side of the hollow cell. These read to  $0.1^\circ$  and had previously been checked against each other. Since temperature control in the bath is rated at  $\pm 0.05^\circ\text{C}$ ., it is probable that the fluid flowing through the cell does not vary more than  $\pm 0.1^\circ\text{C}$ .

For purposes of calibration it is a fortunate circumstance that the temperature tolerance of distilled water is about five times larger than that of the organic liquids used for immersion refractometry of minerals. Its tolerance of  $0.1^\circ\text{C}$ . is of the same order of magnitude as the probable temperature variation of the circulating fluid and makes possible determination of a cell "constant" as already outlined. It also permits investi-

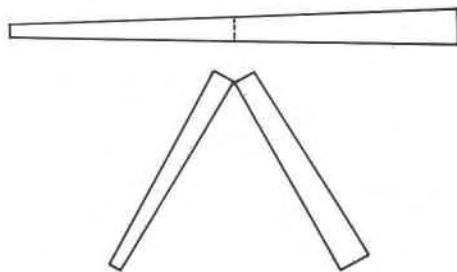


FIG. 4. Sketch showing preferred method of reducing error due to non-parallelism of glass plates in construction of a hollow cell.

gation of the problem of temperature differential between the circulating fluid and the refracting liquid. As the hollow cell is not insulated in any way, the refracting liquid will usually be at a different temperature than that of the circulating fluid unless steps are taken to have the room and bath temperatures the same. As this is rarely possible without a thermally-controlled laboratory, an estimate must be made of the actual temperature of the refracting liquid for known values of room temperature and bath temperature. The thermal coefficient of water, in addition to being relatively low, is also known with greater precision than for other liquids important in immersion work and can, therefore, be used as a standard. A constant volume of distilled water (0.1 ml) was used for the test and refractive indices were determined at bath temperatures varying between  $28^\circ\text{C}$ . and  $51^\circ\text{C}$ . The room temperature varied between  $24^\circ\text{C}$ . and  $28^\circ\text{C}$ . The table in *Handbook of Physics and Chemistry*<sup>3</sup> gives the temperature corresponding to the measured refractive index. These data, plotted as differences, are shown in Fig. 5, with the bath-air differential plotted against the bath-cell differential. Up to  $10^\circ$  bath-air

<sup>3</sup> Chemical Rubber Publishing Co., Cleveland, Ohio.



differential, the relation is unequivocal and reasonably linear; above this range the data are difficult to interpret. This may be due to convection currents in the cell; minimum-deviation angles for example are notoriously less precise for liquids considerably above room temperature.

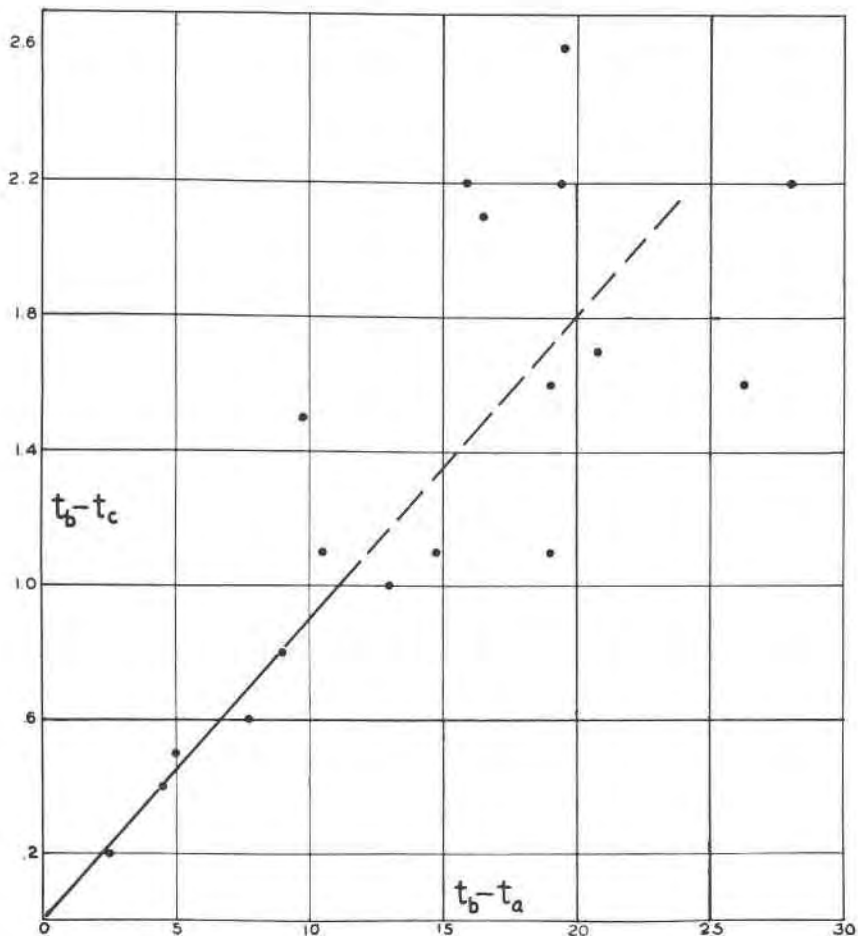


FIG. 5. Diagram showing hollow cell temperature corrections ( $t_b - t_c$ ) required for various room temperatures (shown as a differential  $t_b - t_a$  above temperature of circulating water bath).

However, since air temperature will not normally vary as much as  $10^\circ$  C. from the desired cell temperature, corrections may be read from the graph as needed. If the error in the bath-air differential be taken as  $.2^\circ$ , the corresponding error of the correction (bath-cell differential) would not exceed about  $.02^\circ$  C. and may be neglected.

An alternative technique was also carried out, based on direct determination of the temperature of the refracting liquid with a thermocouple and precision potentiometer.<sup>4</sup> A larger volume of liquid (cell filled) was used in these experiments. As would be expected with this larger volume, the bath-cell differential temperature is greater than shown in Fig. 5. Measurements on distilled water, methylene iodide, carbitol, and  $\alpha$ -chloronaphthalene are, however, inconsistent, ranging from  $2^\circ$  to  $4^\circ$  ( $t_b - t_c$ ) for a  $t_b - t_a$  of  $10^\circ$  C. A variety of reasons could be adduced for this discrepancy, but until further refinements in the technique are made, the indirect approach by calculation of the refractive index (Fig. 5) is preferable. This correction should be determined with distilled water for each cell for a fixed volume of liquid. The temperature of an equal volume of an unknown liquid in the same cell can then be read from the graph.

As Table 1 indicates, a precision level of  $\pm 1 \times 10^{-5}$  cannot be maintained for minimum-deviation work with organic liquids if the temperature of such liquids can be controlled only to  $.1^\circ$  C. The index errors corresponding to  $\pm .1^\circ$  C. are  $\pm 7 \times 10^{-5}$  for methylene iodide and  $\pm 4 \times 10^{-5}$  for most other organic liquids. Since the probable error of a single index determination of a solid prism has been set at  $\pm 2$  or  $3 \times 10^{-5}$ , the total error for index determination of an organic liquid would in the worst case be  $\pm 1 \times 10^{-4}$  (methylene iodide) and for other liquids somewhat less. Both of these values are appreciably smaller than can safely be assumed for Abbe refractometer determinations, where error in the setting alone will never be less than about  $\pm 2 \times 10^{-4}$ . Addition of the temperature error increases this to almost  $\pm 3 \times 10^{-4}$ .

From the above analysis of error it would therefore seem eminently worth while to take considerable pains to calibrate adequately any liquid intended for precise refractive index work by the immersion method. Where a pure liquid is used, this need only be done once for any particular lot; for mixtures, frequent checks will be necessary, particularly if methylene iodide is one of the ingredients. In all cases, in reporting a refractive index obtained by the immersion method, the level of precision in the index of the embedding medium is a factor which must be considered in assessing the total error of index determination.

#### APPENDIX

A detailed statement of minimum-deviation procedure scarcely needs to be included here, but the writer will be glad to supply instructions to any reader in need of them. There are a number of special points, how-

<sup>4</sup> The writer is indebted to H. S. Yoder for generous assistance with this phase of the investigation.

ever, not covered in the instructions issued by the manufacturer, which are worth enumerating.

1. Since hollow prisms and most prisms of mineral crystals are smaller than the telescope objective aperture, they may be centered on the prism table fairly accurately by observation through the telescope with ocular removed.

2. The prism should be so centered that no re-focusing of the telescope is needed during measurement of the prism angle.

3. The position of the lamp used for illumination of the cross-hairs should not be altered during measurement of the prism angle.

4. If hollow prisms are filled with mercury during measurement of the prism angle the confusing double set of reflected cross-hairs (due to non-parallelism of the walls of the prism) will be resolved into a very strong and a very faint reflection. Use of the former for measurement gives the true internal angle of the hollow prism.

5. In order to utilize the central light rays in the telescope, the prism, after measurement of the prism angle, should be re-centered for minimum-deviation measurement. Possible error through neglect of this re-centering will be greater for high than for low refractive index liquids.

6. When the prism table clamp is loosened preparatory to making the minimum-deviation measurement, observe whether there is any disorientation of the reflected cross-hairs. Re-set the prism (by the auto-collimation procedure) in the unclamped position if the original orientation is not maintained.

7. Maintain a fixed slit width in measuring any given double deviation.

8. In making the minimum deviation measurement set the vernier table approximately at zero as a convenience in finding the minimum-deviation angles on either side. If an approximate refractive index is already known a nomogram such as that prepared by Winchell (1951) may be used to find the approximate minimum deviation position.

9. Interpolate vernier readings to the nearest 10 seconds and use six-place tables in calculating the refractive index.

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