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THE USE OF A REFRACTOMETER WITH VARIABLE REFRACTING ANGLE

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The precise determination of refractive indices above $n=1.8$ constitutes a problem that is frequently vexing to the petrographer. The difficulty is due primarily to two causes: (1) the actual determination of the index of refraction, and (2) the lack of suitable immersion media that will not dissolve or react chemically with the substance under investigation.

In the actual determination of indices of refraction, and particularly the higher indices, the refractometer with variable refracting angle has proved to be a valuable instrument. The examination of liquids with indices beyond the range of the Abbé refractometer, constitutes a use for which the instrument is especially well fitted. Its range of application is unlimited and extends from $n=1$ to $n=\infty$.

LITERATURE

The literature describing the operation of the refractometer with variable refracting angle is lacking in many important details. When examining solids, the principle involved is similar to that of the prism method of F. Kohlrausch,¹ but the design of the apparatus is so different that the similarity of principle is not readily evident. In the limiting case the method becomes that of grazing incidence and normal emergence, and it is possible to take advantage of this simplified procedure in determining the index of refraction of fluids. The method of application of the refractometer with variable refracting angle, as used in the examination of fluids, has been described in the literature of Carl Zeiss, Jena.² The essence of this description is included here for the sake of completeness.

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¹ F. Kohlrausch, *Wiedemann's Ann.*, XVI, 603, 1882.

² Optische Ausrüstungen für mineralogische Untersuchungen, *Mess 449*, 26-28. This publication has been translated into English.

The application of the refractometer to solids involves a much more complicated procedure, and the existing literature on this subject is entirely inadequate.

EXAMINATION OF FLUIDS

The fluid is enclosed between two plane-parallel glass plates and the refracting angle of the prism thus produced may be varied as desired. One of the glass plates (*G* in Figure 1) serves as the horizontal floor for the cell which contains the fluid *F*. The other glass plate *T* is permanently attached to a telescope, below the objective lens, in such a manner that the plane-parallel ends are exactly normal to its optical axis. Actually this "plate" has the form of a slightly tapering cylinder, the lower end of which dips into the fluid.

Monochromatic light entering the plate *G* by grazing incidence, because of its plane-parallel sides is transmitted to the fluid *F* in a manner equivalent to grazing incidence. The ray consequently follows the critical angle r of total reflection in its course through the fluid *F*. When the optical axis of the telescope, or the normal to the plate *T*, is so oriented that it coincides with the direction of the limiting ray passing through the fluid, the critical angle r of total reflection is equal to the angular rotation of the telescope from the vertical position. The index of refraction of the fluid *F* is therefore

$$n = \frac{1}{\sin r}.$$

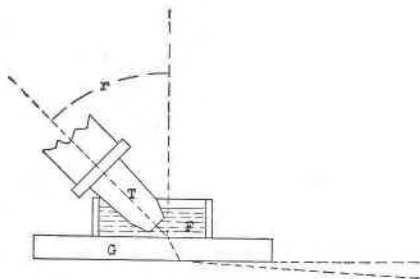


FIG. 1

Since the method of grazing incidence is always employed in the operation of this refractometer, it is not necessary to know the refractive indices of plates *G* and *T*. In the construction of these plates it is possible to use glass that is highly resistant to chemical corrosion.

Control of the temperature of the fluid, as in the double variation method, may be obtained by substituting a hollow glass cell for the plate *G* and allowing water to flow through it. Care must be taken that the walls of the cell are constructed from plane-parallel glass plates and that the assembled cell also has parallel upper and lower surfaces. It is also possible to apply the monochromatic light by grazing incidence at the upper surface of the cell or plate *G*, provided that one end of the plate or cell has been polished in order to allow the passage of the incident rays.

The refractometer is not well adapted to the determination of indices of highly volatile liquids because it is not feasible to cover them.

EXAMINATION OF SOLIDS

The determination of the index of refraction of a solid body involves a more complicated procedure, but the principle is similar to that of the prism method devised by F. Kohlrausch.³

It is necessary to construct a prism from the substance whose index of refraction is to be determined, and to accurately measure the angle θ of this prism. The prism is then placed upon a plane-parallel glass plate *G*, using a drop of water or oil between them. (See Figures 2 and 3.) The critical line of total reflection is observed through the viewing telescope as in the case when examining fluids, and the angle *R* is obtained from the scale on the refractometer.

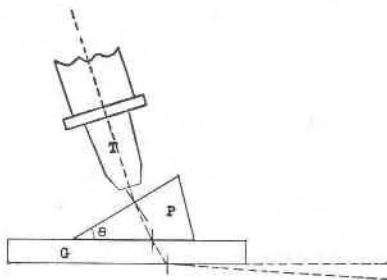


FIG. 2

In the limiting case where *R* happens to equal the prism angle θ , we have the condition of grazing incidence and normal emergence and consequently $n = \frac{1}{\sin R}$. In all other cases the method of calculating the index of refraction may be derived as follows:—

³ F. Kohlrausch, *Wiedemann's Ann.*, XVI, 603, 1882.

In the general case in which a ray S (Figure 3) passes from a medium whose index of refraction is N , and enters a prism whose index of refraction is denoted by n , we have the following relations:

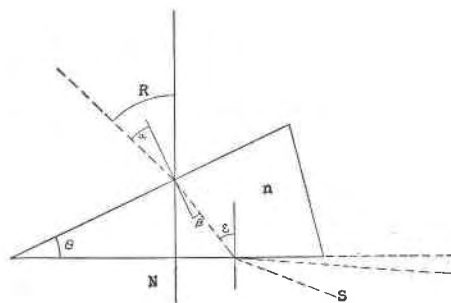


FIG. 3

$$n = \frac{\sin \alpha}{\sin \beta} = \frac{N}{\sin(\theta \pm \beta)}$$

when $R > \theta$, then $\epsilon = \theta + \beta$ and

$$\begin{aligned} N \sin \beta &= \sin \alpha \sin(\theta + \beta) \\ N \sin \beta &= \sin \alpha \sin \theta \cos \beta + \sin \alpha \cos \theta \sin \beta \\ \frac{N \sin \alpha}{n} &= \sin \alpha \sin \theta \sqrt{1 - \frac{\sin^2 \alpha}{n^2}} + \frac{\sin \alpha \cos \theta \sin \alpha}{n} \\ \frac{N \sin \alpha}{n} &= \frac{\sin \alpha \sin \theta \sqrt{n^2 - \sin^2 \alpha}}{n} + \frac{\sin \alpha \cos \theta \sin \alpha}{n} \\ N \sin \alpha &= \sin \alpha \sin \theta \sqrt{n^2 - \sin^2 \alpha} + \sin \alpha \cos \theta \sin \alpha \\ N &= \sin \theta \sqrt{n^2 - \sin^2 \alpha} + \sin \alpha \cos \theta \end{aligned} \quad (1)$$

Similarly when $R < \theta$, then $\epsilon = \theta - \beta$ and

$$N = \sin \theta \sqrt{n^2 - \sin^2 \alpha} - \sin \alpha \cos \theta. \quad (2)$$

Since the source of light for the refractometer always enters the prism by grazing incidence, the sine of this angle is equal to unity.

Therefore, when $R > \theta$

$$\begin{aligned} 1 &= \sin \theta \sqrt{n^2 - \sin^2 \alpha} + \sin \alpha \cos \theta \\ 1 - \sin \alpha \cos \theta &= \sin \theta \sqrt{n^2 - \sin^2 \alpha} \\ (1 - \sin \alpha \cos \theta)^2 &= \sin^2 \theta (n^2 - \sin^2 \alpha) \\ 1 - 2 \sin \alpha \cos \theta + \sin^2 \alpha \cos^2 \theta &= n^2 \sin^2 \theta - \sin^2 \alpha \sin^2 \theta \\ n^2 &= \frac{1 - 2 \sin \alpha \cos \theta + \sin^2 \alpha \cos^2 \theta + \sin^2 \alpha \sin^2 \theta}{\sin^2 \theta} \end{aligned}$$

$$n^2 = \frac{1 - 2 \sin \alpha \cos \theta + \sin^2 \alpha (\cos^2 \theta + \sin^2 \theta)}{\sin^2 \theta}$$

$$n = \frac{\sqrt{1 - 2 \sin \alpha \cos \theta + \sin^2 \alpha}}{\sin \theta} \tag{3}$$

Similarly when $R < \theta$

$$n = \frac{\sqrt{1 + 2 \sin \alpha \cos \theta + \sin^2 \alpha}}{\sin \theta} \tag{4}$$

Occasionally the writer measures the angle θ of the prism by mounting it on the horizontal revolving stage of the petrographic microscope. A pin-point of light from an arc light source is allowed to fall upon one of the refracting surfaces of the prism and its reflection on the distant wall of the darkened room is marked. The stage is then rotated until the reflection from the other prism surface coincides with the mark, and the prism angle is determined from this angular rotation as in crystal goniometry.

It is usually more accurate, however, to measure the prism angle θ directly on the refractometer, and when any imperfections exist in the prism it is particularly desirable to determine both R and θ without disturbing the position of the prism.

The angle α is equal to R minus θ , or θ minus R , depending on which of these has the greatest magnitude. The index of refraction of any solid prism can therefore be computed by means of equations (3) and (4).

ACCURACY

The accuracy of the refractometer with variable refracting angle necessarily decreases as the index of refraction increases. In the following table n represents the index of refraction, r the critical angle, and dn the error in the value of the index of refraction in terms of the fourth decimal figure corresponding to one minute of error in the determination of r .

n	1.3	1.5	1.7	1.9	2.1
r	50° 17'	41° 49'	36° 2'	31° 45'	28° 26'
dn	3.1	4.8	6.8	9.0	11.5
n	2.3	2.5	2.7	2.9	3.1
r	25° 46'	23° 35'	21° 44'	20° 10'	18° 49'
dn	14.3	16.9	19.7	23.1	26.4

In the examination of solid substances the accuracy of the determination of R is at a maximum when the values of θ and R are equal or nearly equal.

THE ZEISS REFRACTOMETER WITH VARIABLE
REFRACTING ANGLE

The Zeiss refractometer with variable refracting angle is shown in Figure 4.* Attached immovably to the base of the instrument and supported on a pillar is a vertical graduated sector divided into half degrees from 0° to 75° . On one side of this rigid sector a

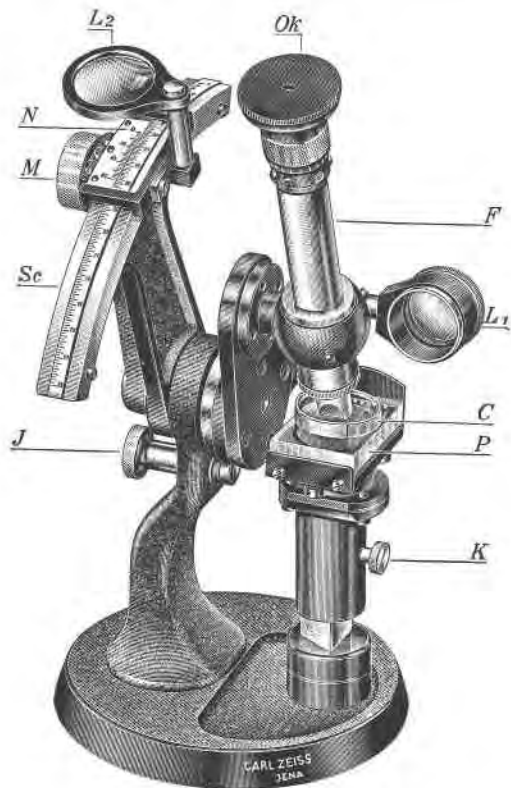


FIG. 4

radial arm rotates on a horizontal axis. The position of this radial arm, upon which is mounted a vernier giving readings accurately to $1'$, is controlled by a gnarled knob which operates a rack and pinion. An adjustable magnifier for reading the vernier is attached

* The Zeiss refractometer with variable refracting angle described in Mess 449 is no longer manufactured. The new refractometer shown in Figure 4 has recently been placed on the market. The two refractometers, though necessarily similar in principle, are quite different in detail.

to the end of the radial arm. On the other side of the vertical sector and attached to the radial arm by a horizontal shaft is the viewing telescope. Consequently, as the rack and pinion moves the radial arm along the graduated vertical sector, the optical axis of the telescope may be varied from vertical at 0° to an inclination of 75° from the vertical position.

At the lower end of the viewing telescope is mounted a slightly tapering cylinder of frosted glass 28 mm. in length, whose polished plane-parallel ends are at right angles to the optical axis of the telescope. The lower end of the cylinder is beveled in such a manner that the flat polished surface is bounded by parallel straight edges about 6 mm. apart. The cylinder is so adjusted that one of these edges coincides with the axis of rotation of the telescope.

A second pillar attached rigidly to the base of the refractometer, supports the plane-parallel glass plate upon which the prism or fluid-containing cell is mounted. The plane-parallel glass plate rests loosely upon three capstan screws and is bounded on three sides by a fence. The elevation of the upper part of the plate carrier may be adjusted as desired by means of a clamping screw. It may also be rotated on a vertical axis through small angles in order to set the refracting edge of the prism exactly parallel to the axis of rotation of the telescope. The desired position is found by observation of the reversal of the critical line as the plate carrier and prism are rotated to the right or left.

A collimating lens attached to an easily removable and adjustable support, receives the light from a sodium burner, or other monochromatic source, and transmits it to a slit or window at the front end of the plate carrier. The rays which enter the bottom of the plane-parallel glass plate by grazing incidence must necessarily follow the critical angle of the glass in their course through the plate, and leave the upper parallel surface by grazing emergence if the surrounding medium is air. When a liquid occurs in contact with the upper surface of the plate, the direction of these limiting rays is that of the critical angle of the liquid. If the end of the glass cylinder attached to the viewing telescope is immersed in the liquid, it is possible to incline the axis of the telescope until it coincides with the direction of the critical ray. The critical line of total reflection is placed in contact with the junction of the two cross-lines of the telescope and the critical angle of the liquid is read directly on the scale on the graduated sector.

When the index of refraction of a solid prism is to be determined, the latter is mounted on a plane-parallel glass plate, using a drop of water or other liquid between them. The direction of the critical ray as it emerges into air on leaving the prism is determined by setting the critical line in contact with the junction of the cross-lines of the telescope as before.

Before using the refractometer, care must be taken that the plane-parallel ends of the tapering cylinder are normal to the optical axis of the telescope. The lower straight edge of the polished end of the cylinder should coincide with the axis of rotation of the telescope. When the position of the telescope is set at zero on the graduated sector, the surface of the plane-parallel glass plate must be oriented at right angles to the optical axis of the telescope.

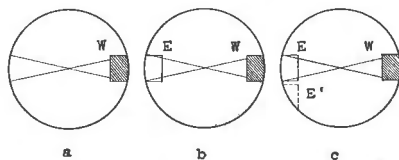


FIG. 5

In order to secure these adjustments, use is made of a small prism or window mounted in the side of the telescope and furnished to illuminate the cross-lines. This projects into the field of the telescope as *W*. (Figure 5*a*). During these adjustments the refractometer is illuminated solely at this small window. If the ends of the glass cylinder are not exactly normal to the telescope axis, an unsymmetrical image of the window will be found at the diametrically opposite side of the field of view. This may be corrected by means of two small capstan screws which produce lateral displacement of the telescope objective. The correct adjustment is secured when the image *E* occupies a position symmetrical to that of the window *W* as in Figure 5*b*.

When the scale of the instrument is set at the zero position, the image *E'* of the illuminated window is reflected from the surface of the plane-parallel glass plate. (Figure 5*c*). By means of one or more of the three capstan screws which support the plate, the image *E'* is made to coincide with the image *E*.

If these operations have been carried out with sufficient care the refractometer is now in adjustment and ready for the determination of refractive indices. In the normal position (with the scale

reading zero) and with the plane-parallel glass plate resting on its carrier, the field of view in the telescope is similar to Figure 5*b* with images *E* and *E'* coinciding with each other. The accuracy of these adjustments must be checked by examining a liquid whose index of refraction is known. Distilled water is the most satisfactory liquid for the standardization of the refractometer.

The upper end of the telescope above the eyepiece is permanently mounted with a cap furnished with a stop to eliminate the light rays derived from sources other than the polished end surface of the tapering glass cylinder. By rotating this cap it is possible to bring the cross-lines of the telescope into sharp focus.

CEMENTS

When examining liquids it is necessary to cement a ring to the upper surface of a plane-parallel glass plate, thus forming a cell or container.

Perhaps the most satisfactory, and at least the most durable cement used by the writer is dental plaster of Paris reinforced by litharge and glycerine. The ring is frosted on its outer surface by rubbing it with fine emery cloth. A circular band is similarly frosted on the upper surface of the glass plate. This is accomplished by temporarily cementing the glass ring to the plate with Canada balsam, and rubbing with the outer surface of the ring and the adjoining surface of the plate with fine emery cloth. The ring is then removed by heating the plate and the balsam is washed off with xylene. After thoroughly cleansing the ring and plate, they are cemented together again with the very minimum of dental plaster of Paris. When dry, the excess plaster is removed from the outer margin as well as the inside of the cell by means of a moistened cotton swab. Litharge and glycerine cement is then added to the outer margin of the ring in contact with the frosted surfaces. The particles composing the plaster of Paris, as well as the litharge, should be of semi-colloidal dimensions. When these operations have been carried out properly, the only cement in contact with the liquid in the cell is an exceedingly thin film of plaster of Paris. Bonding strength is furnished by the litharge and glycerine cement and this is not affected by changes in temperature.

A more simple method of cementation involves the use of dental plaster of Paris reinforced with Canada balsam. The minimum of Canada balsam (cooked until brittle when cold) is used to cement

the ring to the plate. Xylene is then placed in the cell to dissolve any excess balsam and partially etch the film between the ring and the plate. Thin plaster of Paris is allowed to flow around the inner margin of the ring, and after removing the excess, a very thin film of plaster remains to coat the inner margin of the balsam. At ordinary temperatures this method of cementation is usually quite satisfactory but its length of service is greatly reduced at higher temperatures.

Regardless of the nature of the materials used to cement the ring to the plate the two most important secrets in the success of the operation are the following:

(1) The surface of the ring must fit the plate with a high degree of accuracy.

(2) In all cases, the very minimum of cement should be used to form the film between the two surfaces.

A properly mounted ring cemented with brittle Canada balsam alone, will retain such solvents as xylene in the cell for a remarkable length of time. A poorly mounted ring may not be able to retain xylene for more than a few minutes.

It is desirable to use cells reinforced with litharge and glycerine as containers for methylene iodide and for alpha-bromnaphthalene. The writer uses one cell exclusively for liquids containing methylene iodide.

COLORED LIQUIDS

When the index of refraction of a liquid is being determined on the refractometer, it is possible to elevate the floor of the cell until it comes in contact with the lower straight edge of the tapering glass cylinder attached to the telescope. Regardless of the depth of liquid in the cell, the thickness of the prism enclosed beneath the end of the glass cylinder is approximately zero at one edge. When the critical line is placed in contact with the junction of the two cross-lines of the telescope, the angle of the prism of liquid enclosed beneath the glass cylinder is equal to the critical angle of the liquid. The higher the index of refraction, the smaller this prism angle will be.

Thus it is seen that even with the weak intensity of the monochromatic light supplied by a sodium burner, the index of refraction of a highly colored liquid may be determined readily.

When reasonably pure, the indices of refraction of all of the liquids commonly used as immersion media, as well as the heavy

liquids, can be determined accurately with the refractometer with variable refracting angle.

When used for gravity separations, methylene iodide may become so highly colored that the determination of its index is difficult. This is not due so much to the inability to observe the critical line as to the problem of adjusting it to coincide with the junction of the cross-lines of the telescope. Recently this problem has been largely overcome by placing a small shaded light near the window or prism used to illuminate the cross-lines. An oblique angle will be found at which the incident light from the small lamp illuminates the cross-lines without masking the critical line.

CONSTRUCTION OF THE PRISM

For the determination of the refractive indices of solid bodies, it is necessary to shape them into the form of a prism. Materials with a low melting point usually can be moulded between glass plates. The latter must be plane-parallel and their thickness must be sufficient to resist distortion due to changes in the volume of the melt on solidification. In most cases, cover glasses are too thin, being warped by the contraction of the solidifying melt. When the shrinkage of the melt is such that it separates from the glass plates, it may be necessary to grind and polish the prism. This procedure is obviously unavoidable in many cases where the determination of the refractive index is to be made directly upon a refractory or infusible substance.

Transparent silica glass plates are satisfactory for the construction of prisms of many solid bodies whose melting point is too high to permit the use of ordinary glass. It is frequently possible to make use of cleavage planes in the construction of the prism.

The writer uses a mould of copper to support the glass plates when making prisms from molten materials. The two plane surfaces of the mould are hinged to enable prisms of any angle to be made. A contact goniometer is used to set the mould at the desired angle, clamps being provided to rigidly maintain that position. Plaster of Paris is used to fill the ends and temporarily cement the edge of the glass plates in order to hold the melt. The mould may be gradually heated somewhat below the melting point of the substance and the fused material poured into it. Fragments of the solid material may be melted directly in the heated mould.

When making prisms from highly colored substances it should

be remembered that only the thinnest part of the prism is sufficiently transparent to permit the determination of the refractive index. In any case, the amount of material required for the determination is very small.

Pure compounds, or solutions possessing an abrupt melting point, tend to give sharper readings on the refractometer than viscous liquids or solid substances with a long softening range.

MEASUREMENT OF THE PRISM ANGLE

The refracting angle θ of the prism can be measured by means of the refractometer, by using the method employed to adjust the plane-parallel glass plate to the normal position. The prism is mounted on the plane-parallel plate, using a drop of water or oil between them. Monochromatic light is supplied by grazing incidence at the lower surface of the plate and the refracting edge of the prism is oriented parallel to the axis of rotation of the telescope. The angle R of the ray emerging from the prism is measured as described in an earlier paragraph. The exact position or orientation of the prism at the time of the measurement of the angle R , is retained and not disturbed during the determination of the prism angle θ .

During the measurement of the prism angle θ , the refractometer is supplied with light solely at the small window on the side of the telescope. The telescope is inclined until the image of the window W reflected from the upper surface of the prism coincides with the image E . (See Figures 5*b* and 5*c*). Since the other surface of the prism is parallel to the glass plate, (the normal position) the prism angle θ is read directly from the scale on the graduated sector.

RECIPROCAL OF SINES

Sin 16°	0'—3.62845 10'—3.59195 20'—3.55619 30'—3.52113 40'—3.48675 50'—3.45304	Sin 23°	0'—2.55951 10'—2.54194 20'—2.52461 30'—2.50815 40'—2.49128 50'—2.47463
Sin 17°	0'—3.41997 10'—3.38753 20'—3.35683 30'—3.32557 40'—3.29489 50'—3.26584	Sin 24°	0'—2.45881 10'—2.44260 20'—2.42718 30'—2.41138 40'—2.39636 50'—2.38095
Sin 18°	0'—3.23625 10'—3.20718 20'—3.17965 30'—3.15159 40'—3.12402 50'—3.09789	Sin 25°	0'—2.36630 10'—2.35128 20'—2.33699 30'—2.32288 40'—2.30894 50'—2.29463
Sin 19°	0'—3.07125 10'—3.04599 20'—3.02024 30'—2.99581 40'—2.97177 50'—2.94724	Sin 26°	0'—2.28102 10'—2.26757 20'—2.25428 30'—2.24115 40'—2.22816 50'—2.21533
Sin 20°	0'—2.92398 10'—2.90023 20'—2.87770 30'—2.85551 40'—2.83366 50'—2.81136	Sin 27°	0'—2.20264 10'—2.19010 20'—2.17770 30'—2.16591 40'—2.15378 50'—2.14179
Sin 21°	0'—2.79018 10'—2.76932 20'—2.74876 30'—2.72851 40'—2.70856 50'—2.68889	Sin 28°	0'—2.12993 10'—2.11864 20'—2.10704 30'—2.09556 40'—2.08464 50'—2.07340
Sin 22°	0'—2.66951 10'—2.65041 20'—2.63158 30'—2.61301 40'—2.59471 50'—2.57666	Sin 29°	0'—2.06271 10'—2.05170 20'—2.04123 30'—2.03087 40'—2.02020 50'—2.01005

Sin 30°	0'—2.00000 10'—1.99005 20'—1.98020 30'—1.97044 40'—1.96078 50'—1.95122	Sin 37°	0'—1.66168 10'—1.65536 20'—1.64880 30'—1.64258 40'—1.63639 50'—1.63026
Sin 31°	0'—1.94175 10'—1.93237 20'—1.92308 30'—1.91388 40'—1.90476 50'—1.89573	Sin 38°	0'—1.62417 10'—1.61812 20'—1.61238 30'—1.60642 40'—1.60051 50'—1.59464
Sin 32°	0'—1.88715 10'—1.87829 20'—1.86986 30'—1.86116 40'—1.85254 50'—1.84434	Sin 39°	0—1.58907 10'—1.58328 20'—1.57778 30'—1.57208 40'—1.56666 50'—1.56104
Sin 33°	0'—1.83621 10'—1.82782 20'—1.81984 30'—1.81192 40'—1.80375 50'—1.79598	Sin 40°	0'—1.55569 10'—1.55039 20'—1.54512 30'—1.53988 40'—1.53445 50'—1.52929
Sin 34°	0'—1.78827 10'—1.78063 20'—1.77305 30'—1.76554 40'—1.75809 50'—1.75070	Sin 41°	0'—1.52416 10'—1.51906 20'—1.51423 30'—1.50921 40'—1.50421 50'—1.49925
Sin 35°	0'—1.74338 10'—1.73611 20'—1.72921 30'—1.72206 40'—1.71497 50'—1.70823	Sin 42°	0'—1.49454 10'—1.48965 20'—1.48500 30'—1.48017 40'—1.47558 50'—1.47080
Sin 36°	0'—1.70126 10'—1.69463 20'—1.68776 30'—1.68124 40'—1.67448 50'—1.66806	Sin 43°	0'—1.46628 10'—1.46177 20'—1.45730 30'—1.45264 40'—1.44823 50'—1.44383

Sin 44°	0'—1.43947	Sin 47°	0'—1.36724
	10'—1.43534		10'—1.36370
	20'—1.43102		20'—1.35999
	30'—1.42674		30'—1.35630
	40'—1.42248		40'—1.35281
	50'—1.41844		50'—1.34916
Sin 45°	0'—1.41423	Sin 48°	0'—1.34571
	10'—1.41004		10'—1.34210
	20'—1.40607		20'—1.33869
	30'—1.40193		30'—1.33511
	40'—1.39801		40'—1.33174
	50'—1.39412		50'—1.32837
Sin 46°	0'—1.39024		
	10'—1.38619		
	20'—1.38236		
	30'—1.37855		
	40'—1.37476		
	50'—1.37099		