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

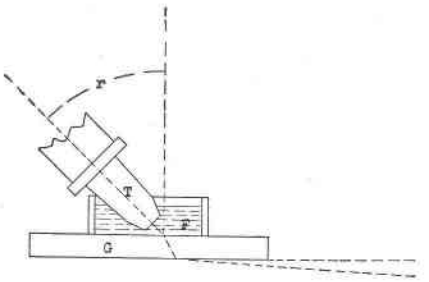

Fig. 1

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.

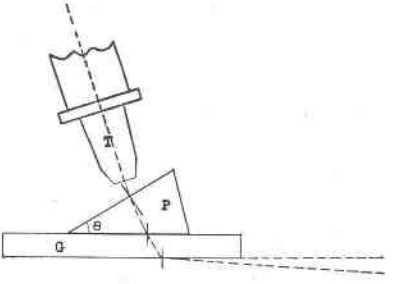

Fig. 2

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:

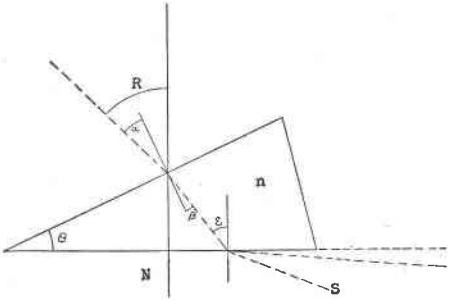

FIG. 3

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

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

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

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

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

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 $R>\theta$

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

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

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

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

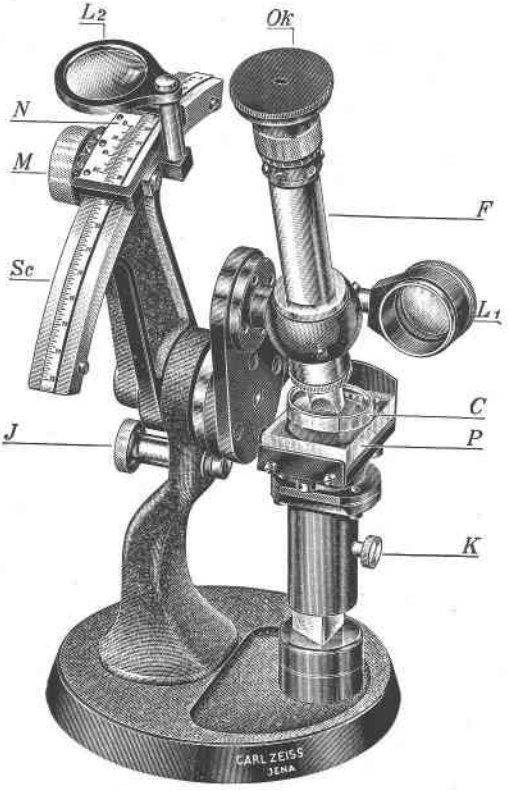

Fig. 4

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.

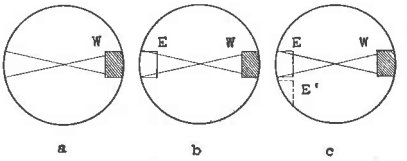

FIG. 5

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 rememberd 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.

RECIPROCALS OF SINES

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

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