OPTICAL HETEROGENEITY OF A FUSED QUARTZ DISK

By L. W. Tilton and A. Q. Tool

ABSTRACT

In preparing a refractive index standard of fused quartz, having the form of a 60° prism, it was considered advisable to investigate carefully the optical density of this glass since appreciable variations might be present because of nonuniform heat treatment or other factors. With this in view the standard, together with nine small auxiliary prisms, was cut from a disk 52 mm in diameter and 13 mm thick. The indices of these prisms were measured, for five different wave lengths, to an accuracy of a few units in the sixth decimal place. As a result, the standard is adjudged uniform within the limits of $\pm 4 \times 10^{-6}$ in its index of refraction. The optical heterogeneity distribution found within the whole disk is in accord with the hypothesis that the variations are caused mainly by temperature gradients which exist during the annealing or which change during the cooling procedures.

CONTENTS

I. RELATIVE VARIATIONS IN CERTAIN PROPERTIES OF FUSED AND CRYSTALLINE QUARTZ

Quantitative data showing that the refractivity and certain other properties of optical glass are affected by the character of the annealing have been obtained by Tool and others.[1] Although no such definite information concerning fused quartz (or quartz glass) appears to be available, both Dorsey [2] and Merritt [3] have observed a difference between the thermal dilations of quenched and annealed samples. Merritt has also reported that in a specimen of fused quartz a change in size occurred when it was held at a constant temperature slightly above 1,020° C. From these results it may be inferred that differences occurring in the rates of cooling which are employed for this material

[1] A. Q. Tool and E. E. Hill, Trans. Soc. Glass Tech., **9**, pp. 185–207; 1925. A. Q. Tool, L. W. Tilton, and E. E. Hill, Meeting Opt. Soc. Am., Ithaca, N. Y.; 1925 (abstract in J. Opt. Soc. Am. and Rev. Sci. Inst., **12**, pp. 490–491; 1926). Fritz Eckert, Trans. Soc. Glass Tech., **9**, pp. 267–272; 1925; Zeitschr. f. Tech Phys., **7**, pp. 282–287; 1926. A. A. Lebedeff, Revue d'Optique, **5**, pp. 1–30; 1926; Die Glas Industrie, **35**, pp. 6–9; 1927.

[2] H. G. Dorsey, Phys. Rev. **30**, pp. 271–272; 1910.

[3] G. E. Merritt, J. Am. Ceram. Soc., **7**, pp. 803–808; 1924. See also R. B. Sosman, The Properties of Silica, pp. 408–411 (New York); 1927.

may also produce appreciable changes in the optical density. Furthermore, if the cooling is sufficiently rapid it may cause this property to vary within a single piece of the glass. If the properties of transparent fused quartz are affected by cooling rates to an appreciable degree, wider variations in such properties should be found among samples of the glass than among the crystals from which it is made. Concerning density this relative magnitude of their variations certainly obtains, for according to figures given by Sosman,[4] who has critically examined the numerous published data, the definitely established variations in density for various samples of this glass having optical quality are approximately ten times as large as the corresponding variations for specimens of crystalline quartz.

Additional evidence of the same nature is afforded by an inspection of the measurements of refractive indices. In this case, Sosman [5] concludes from the published data that the variations in the refractive index of clear crystalline quartz of optical grade are certainly as large as 2 and possibly amount to 10 units in the fifth decimal place. In fused quartz of optical quality there is, on the other hand, some indication that such interspecimen variations may reach 300×10^{-5}. The latter figure, however, is subject to question. It depends on several measurements, but only three or four of them appear of sufficiently high accuracy to yield convincing results and these show a much smaller total variation. For the purpose of a further critical comparison, some of these values are given in Table 1, together with results both for the disk, which is the chief subject of discussion in this paper, and for another sample previously measured. This restricted list of values shows a difference in index of approximately 20×10^{-5} when either one of the latter two samples is compared with the fused quartz used by Trommsdorff or with that measured by Gifford. This spread is considerably larger than that hitherto found among precisely measured samples, and it brings the interspecimen variation for fused quartz to a value which, as in the case of density determinations, is ten or more times as great as that reliably established for crystals of quartz.

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[4] R. B. Sosman, The Properties of Silica, p. 305 (New York); 1927.
[5] R. B. Sosman, The Properties of Silica, p. 616 (New York); 1927.

TABLE 1.—*Variations in index and dispersion of fused quartz glass*

Observer	Conditions of measurement	Measured values			Computed values t=20.0° C., air at 20° C		
		n_D	$(n_F-n_C)\times10^5$	ν	n_D λ=5893	$(n_F-n_C)\times10^5$	ν
H. Trommsdorff	λ=5890 A, t=15° C. (?)	1.45843	677	67.71	1.45847	677	67.7
Dr. Riedel	?	1.45848	677	67.8			
J. W. Gifford and W. A. Shenstone.	λ=5893 A, t=15° C.						
	I. Simple prism	1.458477	675.0	67.92	1.458526	675.3	67.90
	II. Compound prism	1.458483			1.458532		
L. W. Tilton and A. Q. Tool (Table 2 of this paper).	λ=5893 A, t=25.0°C (Corrections to 760 mm. pressure).	1.458808	675.9	67.88	1.458759	675.6	67.90
L. W. Tilton (unpublished data previously obtained on entirely different sample).	λ=5893 A (Corrections to 760 mm. pressure).						
	I. Min. dev. method. t=25.0° C.	1.458765			1.458716		
	II. Wollaston method t=29.6° C.	1.458815			1.458720		

NOTE.—These variations in the optical density of different samples of fused quartz glass are approximately ten times as large as the corresponding variations which are known to exist among different samples of crystalline quartz from which such glass is made. This is regarded as an indication that fused quartz may be optically sensitive to heat treatment. The Trommsdorff measurements (Inaug. Diss. (Jena); 1901. Or, see Physikal. Zeitschr., **2**, pp. 576–578; 1901) were made on a sample from a Jena melt. The temperature mentioned here for his data is that given by Landolt-Börnstein (Physikalisch-Chemische Tabellen (5), Suppl. **1**, p. 485 (Berlin); 1927). Riedel also worked on a Jena melt of quartz glass (see M. Herschkowitsch, Zeitschr. Physikal. Chem., **46**, pp. 408–414; 1903). Gifford and Shenstone (Proc. Royal Soc., London, **73**, pp. 201–208; 1904), however, measured prisms which were made by melting together many fine rods of "vitreous silica." Of the two samples measured at this bureau, at least one was produced by the General Electric Co., Lynn, Mass. The temperature coefficients of relative index which were used in obtaining all of the computed values of this table are those which have been determined for the standard prism (No. 54 of Table 2), viz, +9.7, +9.9, and $+10.3\times10^{-6}$ per 1° C., for the C, D, and F lines, respectively. Direct measurements at 20.0° C. yielded for the last sample listed in this table an index of 1.458715, a value in excellent agreement with the computed result of 1.458716. To the check measurements on this sample by the Wollaston method, no irradiation corrections have yet been applied. (See J. Guild and A. Barbara Dale, Trans. Opt. Soc., London, **22**, p. 151; 1920–21. Or Nat. Phys. Laboratory, Collected Researches, **17**, p. 23; 1922.)

The facts cited above show that in any investigation of the degree of optical homogeneity of quartz glass, it is pertinent to remember the possibility that heterogeneities may be introduced by nonuniform heat treatments of the material during its production, and more especially in the period during which it is in the annealing range. They also indicate that when seeking an especially uniform optical component of this glass it may be advisable to consider the possibility of improving the uniformity of the medium by annealing it under such conditions that temperature gradients may be made as small as required. While this method of treatment has been successfully used for an optical glass,[6] it is realized, in suggesting its extension to fused quartz glass, that great caution will be necessary in the choice of annealing temperatures and periods, and also cooling rates, because of the latter material's tendency to devitrify and, in some cases, to develop discolored regions or filmlike imperfections.

[6] L. W. Tilton, A. N. Finn, and A. Q. Tool, B. S. Sci. Papers, **22** (No. 572), pp. 719–736; 1928.

II. REQUIREMENTS FOR PRISMATIC STANDARDS OF REFRACTIVE INDEX

The refractivity measurements herein reported were made in connection with the preparation of a sample of fused quartz as a refractive index standard for testing refractometers. It is customary for such purposes to prepare standard test pieces having the form of plates or slabs with dimensions approximating 4 by 12 by 25 mm. One face and one end of such a plate are so polished that the face is optically plane and that the end intersects it at an angle of 90°, forming an unbroken edge.

The indices of such plates may be determined on a calibrated refractometer, but their form is not favorable for the use of other methods by which more accurate determinations may be readily made. Accordingly, to permit accurate index measurements by the minimum-deviation method, index standards have in a number of instances been prepared in the form of 60° prisms with their refracting edges so modified[7] (see fig. 1) that one face of such a prism may be applied to the blocks (prisms) of refractometers for testing and calibrating these instruments.

For a test piece of this sort it is preferable, and at times necessary, to attain an accuracy of a few units in the sixth decimal place of the index measurements leading to standardization. This provides only a small factor of safety because with a Pulfrich refractometer a calibration accurate to the fifth place[8] may under certain conditions be required, and even instruments of the Abbe type are sometimes made so that fifth decimal place index readings may be obtained by estimating tenths of a scale division. In determining the effective indices of such test prisms to the requisite degree of accuracy it is obvious that a lack of optical homogeneity may be a serious matter, since only a very thin layer near the contact surface is employed when the piece is used in testing a refractometer whereas approximately its entire volume is involved when the indices are determined spectrometrically.

Current opinion concerning the optical homogeneity within samples of fused quartz is, moreover, not reassuring. It is well known that many specimens show very irregular and peculiar patterns[9] when they are examined either in polarized light or by the "method of striæ" (Foucault Töpler knife-edge test); hence, it is generally considered

[7] Test specimens of this form were originally employed in the refractometric laboratory of this bureau by G. E. Merritt.

[8] J. Guild, Proc. Phys. Soc. London, **30**, pp. 157–189; 1918. Or see Nat. Phys. Laboratory, Collected Researches, **14**, pp. 273–300; 1920.

[9] In some cases these patterns indicate a coarse reticulated structure which is probably similar to that observed by Petit (Carnegie Institution of Washington, Yearbook No. 27, p. 147; 1927–28). It is along the interfaces forming this structure that many of the above noted discolored regions develop during certain heat treatments of this material.

that quartz glass is unsuitable for making high-grade optical components. Quite aside from the question of the presence of a very fine grained structure[10] which is somewhat inimical to best definition but of little or no consequence in the instance under discussion, there is the important possibility of the existence of a grosser type of heterogeneity. In this connection it may also be noted that Buisson[11] has presented evidence that quartz itself, when examined over distances of 5 cm within the limits of a single sample, may vary in index by 5 to 8 units of the sixth decimal place, and is therefore not a homogeneous body with perfectly defined properties.

In view of these facts and considering also that relatively small chemical or physicochemical differences may produce optical heterogeneity affecting the fifth decimal place of index, it seemed quite unwise, in making a test prism of fused quartz, to neglect possible nonuniformities and to rely entirely on the assumption that minimum deviation measurements of index are characteristic of a thin layer at the prism's testing surface. Consequently, in preparing the index standard now to be described it was decided to subject the surrounding portions of the material to a rigorous test of its optical uniformity.

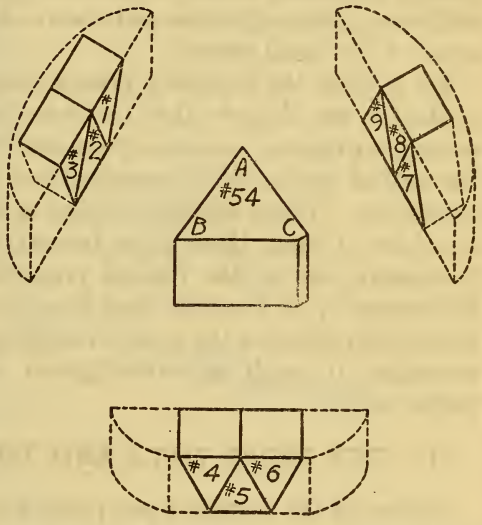

FIGURE 1.—*Relative locations of 60° prisms in disk*

A standard test prism was cut from the center of a disk 52 mm in diameter and 13 mm thick. Nine auxiliary prisms were used in testing the homogeneity of the remaining portions of the disk.

III. PREPARATION OF AN INDEX STANDARD AND THE AUXILIARY PRISMS

The standard test prism was cut from the center of a 13 mm thick disk sawed from a cylinder 52 mm in diameter. From each of the three peripheral segments of the disk, three auxiliary prisms were cut, as shown in Figure 1. Each group of three prisms thus consists of that portion of the material which had been adjacent to one of the faces of the test prism. To the prisms were assigned numbers, and

[10] Lord Rayleigh, Proc. Opt. Convention, pt. 1, pp. 41–46; 1926. L. C. Martin and B. K. Johnson, J. Sci. Inst., 5, p. 338; 1928.

[11] H. Buisson, Compt. Rend., 142, pp. 831–833; 1906.

their outlines and relative positions were indicated on the disk and also recorded on diagrams before any saw cuts were made. The refracting faces of the resulting standard test prism are 12 by 25 and those of the auxiliary prisms 10 by 13 mm, the smaller dimension being in all cases the height. These surfaces,[12] with one or two exceptions, were plane to approximately one-tenth wave length and they formed refracting angles of approximately 60°.

When finished, very few seeds or bubbles were observed, but some double refraction could be detected in these prisms. All gave fair definition, although a few striæ were observed in the standard and in some of the small prisms.

By cutting the auxiliary prisms from the disk in the manner described it was thought that the index measurements would give such complete evidence concerning the disk's degree of heterogeneity that the optical quality of the standard test prism might be safely inferred therefrom. These auxiliary prisms were made, also, with the tentative idea of using them in an investigation of the effect which heat treatment has on the optical properties of fused silica. Had the heterogeneity of the disk been so objectionable as to necessitate an attempt to improve the optical condition of the standard by carefully annealing it, such an investigation would have been a required preliminary.

IV. THE INDEX DATA AND THEIR INTERPRETATION

Indices of the standard test prism were measured for the C, F, and G′ lines of hydrogen and for a mean of the D lines of sodium [13] because it is customary to calibrate Pulfrich refractometers for these wave lengths. For added information on the dispersion of a medium in the range of short visible wave lengths, it is often desirable to use the mercury lines, $\lambda = 4358$ and $\lambda = 4047$ A, and since the conditions and purposes controlling this investigation make it desirable to employ a fairly large number of observations, all of the above lines were included for measuring all prisms, except that the relatively faint G′ line was used only in making measurements on the standard.

The measurements of the indices were made on a spectrometer, by use of the minimum deviation method, while the prisms were immersed in a stirred air bath inclosed in a constant temperature prism housing held at 25.0° C. Corrections were made so that the results correspond to a standard air pressure of 760 mm of mercury and to zero millimeters of absolute humidity. The measurements, of prism angles in particular, were carried out with all the precautions

[12] The prisms were made by E. L. Robinson, of the optical glass shop.

[13] Although a refractometer determination with sodium light is somewhat indefinite and subject to a relatively large personal error unless there is resolution of these lines (see footnote 8, p. 622), it seems in practice that such settings are usually made in the absence of resolution and correspond to some wave length intermediate between D_1 and D_2.

which experience has shown to be consistent with probable errors of a few units in the sixth decimal place of index.[14] In the case of deviation measurements it should be noted that accidental errors made in determining individual indices have little effect in the final analysis of the results because the comparisons between prisms are based on their indices for five wave lengths. It is believed that the combined effect of all errors, whether systematic or accidental, does

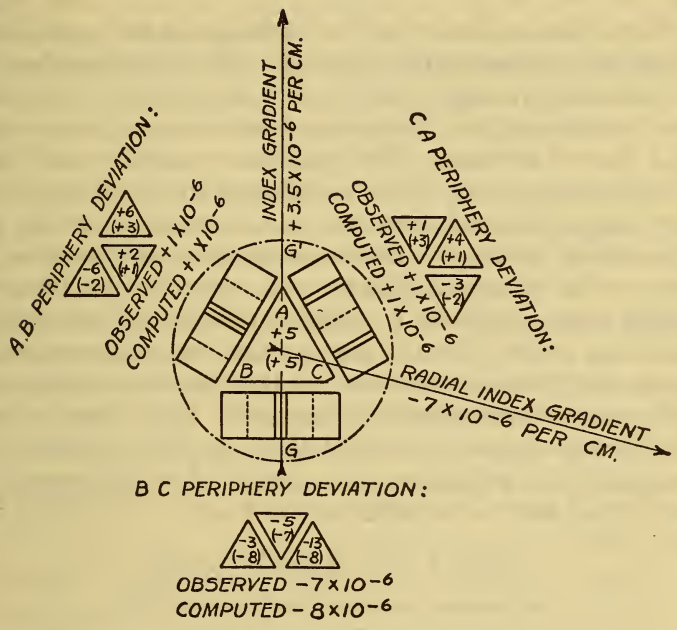

FIGURE 2.—*Observed and computed deviations in index*

The auxiliary prisms are shown in horizontal and also in vertical projection. The values are given in units of the sixth decimal place of index of refraction, and are averages for the five wave lengths which were used. The computed deviations, given in parentheses, are based on the average measured indices, the relative positions of the prisms, and the assumption that uniform index gradients exist as shown by the arrows.

not enter into any index deviation recorded in Figure 2 to an extent greater than $\pm 3 \times 10^{-6}$.

The results of all observations are included in Table 2; that is, none of the data was rejected. Furthermore, no smoothing of values was attempted, although in some instances it may for certain other purposes be advisable. In the few cases where extra observations were made, these determinations were given only equal weight with those which had preceded. The results for the auxiliary prisms, given separately for each wave length, are averages, each of which represents one of the three peripheral groups corresponding to the

[14] For a discussion of some of the goniometrical requirements in index measurements to this degree of accuracy, see L. W. Tilton, B. S. Jour. Research, 2 (RP64), pp. 909–930; 1929.

three faces of the test prism. This averaging was done because the small size of these prisms made it impossible to reach in any other manner the high degree of precision desired for each wave length unless measurements were repeated to a burdensome extent. The general averages used in determining the individual deviations were obtained by giving equal weights to the measured values of the indices of the central prism and to those of each group of three auxiliary prisms.

The final evidence concerning the variations in the optical density within the disk is presented in Figure 2. The deviations shown there were obtained by averaging, for the five wave lengths used throughout, the deviations which the indices of each prism show as compared with the general averages. The maximum variation over the face CA of the standard test prism, as inferred from the results on the auxiliary prisms obtained from that portion adjacent to this surface, is of the order of $\pm 4 \times 10^{-6}$. Furthermore, the results obtained on the test prism when compared directly with those for the three groups of auxiliary prisms, indicate a variation through the standard which is of the same order. Thus it appears that the indices of refraction as determined by the spectrometer for this particular standard prism of fused quartz are sufficiently characteristic of the layer of material near the testing surface to warrant their use when calibrating, with this standard, the refractive index scales of refractometers to an accuracy of one unit in the fifth decimal place.

TABLE 2.—*Optical data for the disk*

(25.0° C., 760 mm air pressure, 0 mm absolute humidity)

Prism No. and disk location	Indices of refraction					Dispersion	
	n_C λ=6563 A	n_D λ=5893 A	n_F λ=4861 A	n_g λ=4358 A	n_h λ=4047 A	$(n_F - n_C) \times 10^6$	$\frac{1}{2}(n_g + n_h) \times 10^6$ minus $\frac{1}{2}(n_C + n_D) \times 10^6$
54 center	1.456778	1.458816	1.463534	1.467105	1.470030	6,756	10,770
1, 2, 3, AB periphery	1.456772	1.458811	1.463533	1.467102	1.470026	6,761	10,773
4, 5, 6, BC periphery	1.456764	1.458800	1.463524	1.467094	1.470020	6,760	10,775
7, 8, 9, CA periphery	1.456773	1.458807	1.463533	1.467102	1.470028	6,760	10,775
General average	1.456772	1.458808	1.463531	1.467101	1.470026	6,759	10,773

NOTE.—The indices tabulated under n_D correspond to settings made on the unresolved sodium doublet. The standard test prism, No. 54, was also measured for the G' line λ=4340 A, with a resulting index of 1.467254. Note that the center of the disk has not only a higher index, but also a lower dispersion than the peripheral portions.

The data give no evidence of a variation in index in a direction parallel to the axis of the disk. Prisms numbered 1, 3, 4, 6, and 8 were cut from a level slightly higher (see fig. 1) than that of prisms numbered 2, 5, 7, and 9, but the general average excess index of the second of these groups is only 1×10^{-6}. Furthermore, separate

measurements were made on the upper and lower halves [15] of the central prism and the resulting index difference between them was only 1×10^{-6}, the larger value corresponding this time to the upper half of the disk.

There is, however, in a plane perpendicular to the axis of the disk, evidence of a slight optical density gradient in the general direction of the dotted arrow, *GG'*, shown in Figure 2, and the average change in index is $+3.5\times10^{-6}$ per centimeter. If, in addition, an outwardly directed radial gradient of -7×10^{-6} per centimeter is considered as superposed, then it is found that the experimentally determined deviations for individual prisms agree, within the limits of $\pm5\times10^{-6}$, with those computed from the average index on the simple assumption that these uniform gradients existed. Such limits are nearly in accord with the estimated errors, whereas from the observed deviations shown in Figure 2 it is not apparent at a glance that the results of the index measurements can have such precision. Neglecting other possible causes of nonuniformities in the material, an explanation of these index gradients is that they occur because the central and the exterior portions of the cylinder were cooled through the annealing range at different rates and likewise because the sides *G* and *G'* were cooled differently. In other words, the assumption that the index of fused quartz varies with different heat treatments is thus confirmed by the fact that, in this disk, the distribution of the heterogeneity is in accord with predictions which could have been made from the known behavior of other glasses, including those containing large proportions of silica. Even after this analysis of the data, however, the conclusion that the test prism is uniform in index to $\pm4\times10^{-6}$ seems to require little or no revision.

As shown in Table 2, there is, also, in addition to these index changes, a slight but probably not fortuitous difference between the partial dispersions of the central portion, as represented by the large prism, and the dispersions of the peripheral regions of the disk. Although the central prism has the higher index, its dispersion is lower. This result has not been accepted without careful review of the data. An association of index and dispersion changes in opposite senses in a given glass is a phenomenon which the authors have observed to a more pronounced degree when investigating other glasses and one which they have in some cases definitely connected with character of heat treatment.

Concerning heterogeneities localized in minute volumes, no conclusive evidence was obtained in this investigation, and it is not known whether in the case of these prisms the slight observed scattering of light was caused by fine structure or by the observed striæ.

[15] The lower half contained no definitely discernible striæ, gave somewhat better definition than the upper half, and appeared noticeably better when examined by the Foucault-Töppler knife-edge test.

Obviously, from the results on this single disk, no definite statements should be made regarding the probable uniformity of other pieces of fused quartz. This specimen was, however, a random sample, not one carefully selected, and it does not appear markedly different under the knife-edge test from some of several other samples which have been examined. Therefore, in addition to yielding the desired particular information, this study as a whole indicates that it is possible at present to obtain fused quartz of optical quality which, at least in so far as the grosser type of heterogeneity is concerned, is sufficiently uniform for use in the production of small optical components of a good grade provided the light path does not greatly exceed a centimeter.[16]

Large components for systems requiring the best definition are desirable, however, not only for certain special purposes, such as replacing the less durable fluor crown glass employed in certain objectives,[17] but also for more general use as a substitute for crystalline quartz, particularly in photography of portions of the ultra-violet region. Under present conditions such components can only be used when a certain amount of scattered light and birefringence can be tolerated.

Although it seems unnecessary to anneal the test prism whose optical condition has been studied, it is quite possible that much larger variations in index are present in other, and especially in larger pieces of this material. Consequently, attention is directed to the desirability of thoroughly studying the problems of fusing and carefully annealing optical quartz glass. Certain difficulties would undoubtedly be encountered but such an investigation should yield valuable information if, as shown to be probable, the properties of this material are, in fact, dependent to some extent on variations in its heat treatment.

Washington, May, 1929.

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[16] For this distance it seems that a one-fourth wave length phase difference would not be introduced by heterogeneities of less than ±0.000007 in index. (L. W. Tilton, A. N. Finn, and A. Q. Tool, B. S. Sci. Papers, 22 (No. 572), p. 720; 1928.)

[17] D. R. P. No. 242.170, Mar. 21, 1910; Brevet français No. 476.882, Mar. 4, 1911, Carl Zeiss.