

Interspecimen Comparison of the Refractive Index of Fused Silica*†

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The index of refraction of optical quality fused silica (SiO_2) was determined for 60 wavelengths from 0.21 to 3.71 μ at 20°C. The dispersion equation

$$n^2 - 1 = \frac{0.6961663\lambda^2}{\lambda^2 - (0.0684043)^2} + \frac{0.4079426\lambda^2}{\lambda^2 - (0.1162414)^2} + \frac{0.8974794\lambda^2}{\lambda^2 - (9.896161)^2},$$

where λ is expressed in microns was found to yield an absolute residual of 10.5×10^{-6} . The variation in index between 12 specimens was determined. Dispersive properties of the material and thermal coefficient of index are graphically presented. A comparison with previous NBS index data is discussed.

I. INTRODUCTION

FUSED silica (SiO_2) has been in common use by the optical industry and research laboratories for many decades because of its favorable physical and chemical characteristics. Information on these properties can be found in manufacturers' brochures, Sosman's comprehensive book¹ on the properties of silica, and in a recent publication of the Heraeus Company.² Data on the index of refraction of optical quality SiO_2 have been reported in an earlier NBS publication.³

Recent advances in techniques of purification and quality control have made it commercially possible to produce SiO_2 of high standards of purity and uniformity. This paper is a report on a study of the refractive properties of high-purity, optical-quality fused silica currently manufactured by three domestic companies. A main objective is to determine what degree of uniformity of refractive index can be expected when precise measurements are made on a number of specimens that are considered equally representative of this material. The index of refraction is a fundamental property of a material. Knowledge of this property gives an insight to the purity and reproducibility of a material.

II. SPECIMENS

The companies that submitted material for interspecimen comparison are Corning Glass Works, Dynasil Corporation of America, and the General Electric Company. They identify their brands as Corning code 7940 fused silica, Dynasil high-purity synthetic fused silica, and General Electric type 151. Each company submitted material from four different production

runs.⁴ All specimens are considered to be of comparable optical quality, produced according to the highest standards of purity and uniformity.

Optical homogeneity tests made at the NBS⁵ on random specimens from each brand showed that the maximum refractive index gradient varied from a low value of $0.9 \times 10^{-5} \text{ cm}^{-1}$ to a high of 1.6×10^{-5} for samples 5-cm square and 1-cm thick. Spectral transmission characteristics claimed by each company indicate that the cutoff in transmission is near 0.16 μ in the ultraviolet and 4.5 μ in the infrared for a 1-cm thick sample. Measurements made at the NBS⁶ from 0.2 to 5.0 μ show that, in general, all the brands have nearly identical transmittances for 1-mm thick samples. A maximum high value of about 92% is reached near 0.2 μ and transmittance stays at that level to about 3.5 μ , with exception of the region near 2.7 μ where there is a strong OH absorption band with accompanying weak overtone bands at 2.2 μ and 1.4 μ . At 2.7 μ the transmittance reaches a minimum value of about 10%.

III. REFRACTIVE INDEX DATA

Refractive-index determinations were made for twelve specimens, each in prismatic form, having refracting angles near 60° and faces about 4.5 cm square. Three specimens, one from each company, were measured by means of the minimum-deviation method at controlled room temperatures near 20°C. The measurements were performed on the same apparatus and by identical techniques as described in the earlier NBS paper.³ Indexes were measured at 60 wavelengths over the spectral range 0.2139–3.7067 μ . The wavelengths were selected from the prominent spectra of various emission sources and absorption bands (Table I).

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† Presented in part at the October 1964 meeting of the Optical Society of America [J. Opt. Soc. Am. 54, 1401A (1964)].

¹ R. B. Sosman, *The Properties of Silica* (Chemical Catalog Company, Inc., New York, 1927).

² W. C. Heraeus, *60 Jahre Quarzglas 25 Jahre Hochvakuumtechnik* (GmbH, Hanau, Federal Republic of Germany, 1961). A review of this book has been published in J. Opt. Soc. Am. 54, 1067 (1964).

³ W. S. Rodney and R. J. Spindler, J. Res. Natl. Bur. Std. 53, 185 (1954).

⁴ The author wishes to thank the aforementioned companies for providing specimens of these domestic brands of fused silica for measurement, and for granting the National Bureau of Standards permission to reveal the brand identifications of the data published in this paper. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that any one brand is necessarily the best available.

⁵ F. W. Rosberry (private communication).

⁶ J. W. Schleter (private communication).

TABLE I. Computed refractive index* of fused silica and residuals at 20°C for three specimens.

Wavelength microns	Spectral source	Computed index	C-D-G.E. ^a residual $\times 10^6$	Corning residual $\times 10^6$	Dynasil residual $\times 10^6$	General Electric residual $\times 10^6$
0.213856	Zn	1.534307	-27	-29	-42	-31
0.214438	Cd	1.533722	-2	-11	-21	-22
0.226747	Cd	1.522750	+70	+71	+68	+73
0.230209	Hg	1.520081	-21	-28	-31	-23
0.237833	Hg	1.514729	+1	+13	+23	+19
0.239938	Hg	1.513367	+3	+6	+2	+9
0.248272	Hg	1.508398	+2	+6	-1	+7
0.265204	Hg	1.500029	-29	-32	-25	-13
0.269885	Hg	1.498047	+3	+7	-4	+11
0.275278	Hg	1.495913	-3	+2	+8	+12
0.280347	Hg	1.494039	+1	-4	-9	-11
0.289360	Hg	1.490990	+20	+18	+22	+20
0.296728	Hg	1.488734	-14	-7	-12	-4
0.302150	Hg	1.487194	-4	-9	-2	+4
0.330259	Zn	1.480539	-9	+1	+10	+3
0.334148	Hg	1.479763	-3	-8	-1	+9
0.340365	Cd	1.478584	+6	+9	+2	-8
0.346620	Cd	1.477468	+2	-17	-12	-14
0.361051	Cd	1.475129	+1	+3	-9	-8
0.365015	Hg	1.474539	-19	-11	-15	-21
0.404656	Hg	1.469618	+2	+1	-1	+2
0.435835	Hg	1.466693	-3	+5	+1	+3
0.467816	Cd	1.464292	+8	+5	+3	+6
0.486133	H	1.463126	+4	+6	+5	+7
0.508582	Cd	1.461863	+7	+4	+1	+5
0.546074	Hg	1.460078	+2	+4	+1	-5
0.576959	Hg	1.458846	+4	+5	+3	+4
0.579065	Hg	1.458769	+1	+6	+6	+6
0.587561	He	1.458464	+6	+3	-2	+1
0.589262	Na	1.458404	-4	+6	+3	+7
0.643847	Cd	1.456704	+6	+9	+4	+7
0.656272	H	1.456367	+3	+7	+5	+7
0.667815	He	1.456067	+3	+8	+6	+3
0.706519	He	1.455145	+5	+10	+12	+7
0.852111	Cs	1.452465	+5	+8	+3	+5
0.894350	Cs	1.451835	+5	+11	+5	+10
1.01398	Hg	1.450242	+8	+6	+3	+6
1.08297	He	1.449405	-5	+8	+1	+9
1.12866	Hg	1.448869	+1	+7	+8	+9
1.3622	Hg	1.446212	-12	-6	-14	-12
1.39506	Hg	1.445836	+4	-1	+4	-3
1.4695	Cs	1.444975	-5	+3	+9	+10
1.52952	Hg	1.444268	+2	+8	+6	0
1.6606	TCB ^b	1.442670	-20	-14	-19	-11
1.681	Poly ^c	1.442414	+6	-2	-10	+8
1.6932	Hg	1.442260	0	+7	-6	+1
1.70913	Hg	1.442057	+3	0	+3	-1
1.81307	Hg	1.440699	+21	-7	-7	+6
1.97009	Hg	1.438519	+1	+6	+12	+12
2.0581	He	1.437224	-4	-3	-9	-11
2.1526	TCB	1.435769	-29	-22	-25	-24
2.32542	Hg	1.432928	-18	-10	-3	-6
2.4374	TCB	1.430954	-24	-23	-21	-14
3.2439	Poly	1.413118	+32	+21	+29	+25
3.2668	Poly	1.412505	+25	+20	+30	+25
3.3026	Poly	1.411535	+25	+32	+30	+28
3.422	Poly	1.408180	+20	+40	+42	+37
3.5070	Poly	1.405676	-16	-26	-20	-10
3.5564	TCB	1.404174	-24	-27	-29	-18
3.7067	TCB	1.399389	-19	-22	-14	-9
Average of absolute values of residuals			10.5	11.9	12.2	11.7

* Residuals for arithmetical-mean table of values compiled from experimental data of Corning (C), Dynasil (D), and General Electric (G.E.).

^b TCB = 1,2,4-Trichlorobenzene.

^c Poly = Polystyrene.

Because the refractive indexes of the three prisms were determined to be nearly the same at all the measured wavelengths, an arithmetical-mean table of values was compiled which is representative of the experimental data. These values are plotted as a func-

tion of wavelength in Fig. 1. Index values could not be determined from 2.4 to 3.2 μ , shown by the dashed portion of the curve, because of the strong OH absorption band in that region.

The index values were fitted to the three-term Sell-

meier dispersion equation

$$n^2 - 1 = \frac{0.6961663\lambda^2}{\lambda^2 - (0.0684043)^2} + \frac{0.4079426\lambda^2}{\lambda^2 - (0.1162414)^2} + \frac{0.8974794\lambda^2}{\lambda^2 - (9.896161)^2}, \quad (1)$$

where λ is expressed in microns. The parameters of the equation were adjusted by a least-squares solution performed on an electronic computer. The method is described by Sutton and Stavroudis.⁷ The agreement between observed and computed values is shown by the residuals in column 4 of Table I. For the most part, the largest residuals occur at both extremes of the measured wavelength range. In the ultraviolet they are attributed to the use of wide slits, necessitated by the combined absorptions of the prism material, the envelopes of the emission lamps, and the atmosphere. At wavelength $\lambda = 0.226747 \mu$ where the maximum positive residual occurs, the residual would change to $+28 \times 10^{-6}$ if the wavelength used was $\lambda = 0.226624 \mu$ which is the average of cadmium wavelengths (0.226502μ) and the assigned wavelength. It is significant to note that in this region of the spectrum, where the slope is changing rapidly, a difference of $+0.000123 \mu$ corresponds to an appreciable difference in the sixth decimal place of index. In the infrared, at wavelengths larger than about 2.2μ , the wavelength accuracy is not exactly known since atmospheric water-vapor bands were superposed on the absorption spectra of the wavelength standards used in this experiment. Furthermore, the absorption of the prism and the increase in dispersion with wavelength made the use of wide slits necessary. Therefore the larger residuals may be as much the result of inaccuracies of the wavelength identification as of inaccuracies of the index measurements. In general, considering the whole range of wavelengths, an average absolute residual of 10.5×10^{-6} indicates that values of index may be interpolated by means of the dispersion equation to five significant decimal places.

In order to make an interspecimen comparison the indexes computed by formula were subtracted from the experimental values for each prism. The average absolute residual was about 12×10^{-6} in each case. The results are given in Table I. Because the three brands of SiO_2 appear to be so nearly the same, the computed values of Table I are probably typical for this material.

The indexes of the remaining nine prisms and the three specimens discussed above were then measured at 20°C on a Wild precision spectrometer. An infrared image-converter tube set at the viewing end of the instrument, normally limited to visible-light observation, enabled measurements to be made visually at 18 wavelengths from 0.4047 to 1.08μ . The uncertainty of

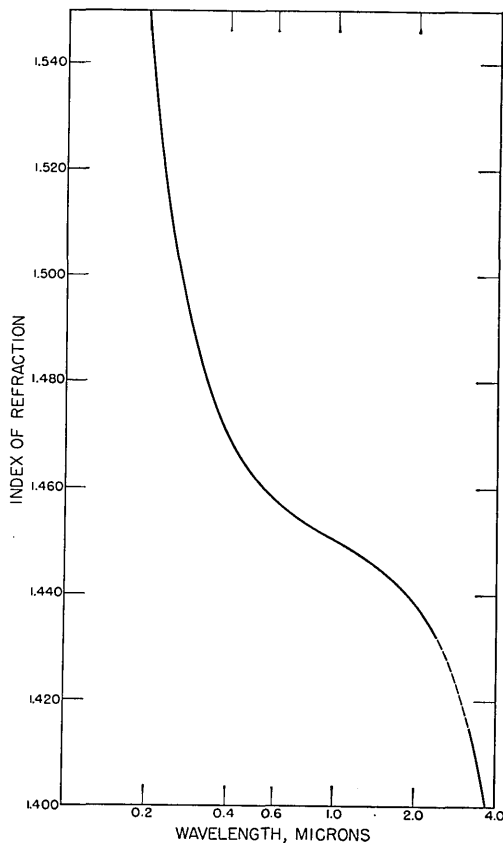


FIG. 1. Refractive index of fused silica at 20°C . The dashed portion of the curve indicates region of strong OH absorption band. The dispersion equation (1) is valid for interpolation to five decimal places over the measured wavelength range.

these determinations is believed to be $\pm 5 \times 10^{-6}$ for 14 visible lines and $\pm 20 \times 10^{-6}$ for 4 near infrared wavelengths. A representative sampling of index data for the 12 prisms is given in Table II. The results are expressed in units of the sixth decimal place and are differences between the measured values and those computed by Eq. (1). The final analysis of the results is based on comparisons between the averages of the residuals (Δn) for the 18 wavelengths that were used.

Certain conclusions about the uniformity of the refractive index of fused silica may be drawn from examination of Table II. First, the maximum index variation for specimens from the same source is 11, 24, and 23 units in the sixth decimal place for Corning, Dynasil, and General Electric, respectively. Second, the interspecimen variations are as low as 4 and as large as 27 units in the sixth decimal place. This spread is considerably smaller than that found for standard optical glasses and crystals. The indexes of specimens No. 1 of Corning and of Dynasil, and No. 3 of General Electric are generally lower than the other intracompany specimens. Since the 12 prisms were measured under identical conditions all the differences cannot be accounted for on the basis of experimental error alone.

⁷ L. E. Sutton and O. N. Stavroudis, *J. Opt. Soc. Am.* **51**, 901 (1961).

TABLE II. Interspecimen variation of the refractive index of fused silica at 20°C from different sources.

λ μ	Corning residual $\times 10^6$				Dynasil residual $\times 10^6$				General Electric residual $\times 10^6$			
	1	2	3	4	1	2	3	4	1	2	3	4
0.4047	11	26	24	20	4	27	21	21	11	12	-12	14
0.4861	16	27	16	21	5	29	19	21	7	15	-7	12
0.5461	14	24	22	17	5	33	25	16	11	12	-13	12
0.5893	12	27	23	27	0	18	20	22	12	13	-8	12
0.6563	12	23	19	19	1	27	22	23	13	10	-7	14
0.7065	17	28	20	18	2	31	23	23	13	15	-11	17
0.8944	11	26	22	19	3	31	19	25	11	12	-8	13
1.014	16	21	20	20	6	30	26	22	14	13	-11	14
1.083	15	24	25	25	7	35	25	25	13	16	-9	12
Av. Δn	13.5	24.9	20.0	21.6	3.5	27.4	20.4	20.5	11.3	12.9	-9.6	13.2
ν -value	67.78	67.78	67.86	67.80	67.78	67.80	67.85	67.85	67.88	67.77	67.82	67.84

NOTE: Numbered columns under each brand indicate individual specimens. The residuals are differences in the sixth decimal place of index between measured values and those computed by dispersion Eq. (1). Each Δn is an average for the 18 wavelengths which were used.

Of the 12 specimens listed above, specimen 1 of each brand is the same reported in Columns 5, 6, and 7 of Table I. Residuals for these specimens are based on results obtained on the Wild spectrometer, whereas the residuals for corresponding wavelengths of Table I are based on results obtained on a Gaertner spectrometer. This accounts for differences in residuals between tables.

The fact that the indexes are lower suggests that the variations are caused mainly by small temperature gradients which exist during the annealing or which change during the cooling procedures, rather than by slight traces of impurities which would tend to raise the index. Finally, the fact that the ν -value, a datum frequently used for calculating chromatic aberration in the visible region, is nearly the same for each prism indicates that the dispersions are the same for all specimens.

IV. DISPERSIVE CHARACTERISTICS

The electronic computer is programmed to compute the refractive index n and the dispersion $-dn/d\lambda$ at small wavelength intervals. From these data the machine computes two quantities that describe the dispersive properties of fused silica as a function of wavelength. The two quantities shown on Fig. 2 may be useful during the early stages of the design of refractive optical systems.

The quantity $(-dn/d\lambda)/(n-1)$ is the ratio of dispersion to deviation and is analogous to $1/\nu$, the dispersive power as defined for the visible region of the spectrum. The shape of the curve shows that the relative dispersion decreases with increasing wavelength, passes through a minimum near 1.3μ , then increases again as it approaches the infrared cutoff. This quantity is also useful for estimating the regions of optimum resolution of a material. Good resolution is characterized by sharp, narrow spectral lines. The width of a line is a function of the refractivity or deviation expressed by the denominator $(n-1)$ as well as the dispersion. Therefore, the ability of fused silica to resolve closely spaced lines should improve in the regions where increasing dispersion is accompanied by simultaneously decreasing values of $(n-1)$. In fact, fused silica is known to have high dispersion accompanied by good resolution in the 2.0 to 4.0μ region when compared to other infrared materials. Obviously, this quantity is a more reliable criterion for estimating dispersion and resolution than the simple dispersion coefficient $-dn/d\lambda$ customarily used for this purpose.

The reciprocal relative dispersion $[(-dn/d\lambda)/(n-1)]^{-1}$ is analogous to the ν -value traditionally used for the calculation of achromatic systems working in the visible region of the spectrum. As the generalized ν -value increases, the contribution to the chromatic aberration of a lens element made of fused silica decreases and reaches a minimum near 1.5μ .

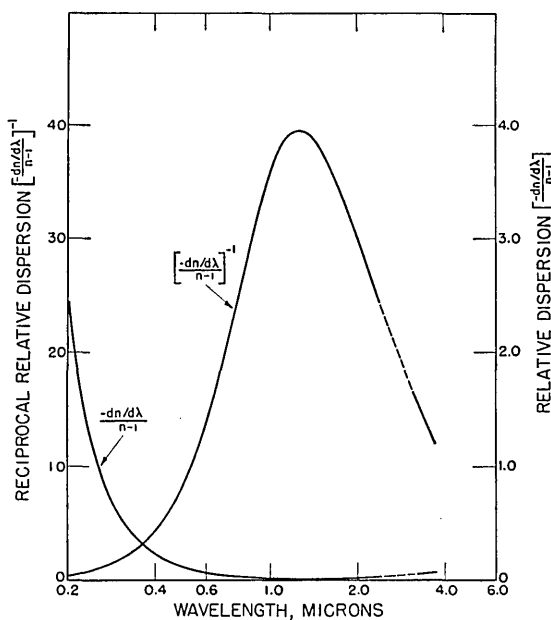


FIG. 2. Dispersive properties of SiO_2 at 20°C. The quantity $[(-dn/d\lambda)/(n-1)]^{-1}$ defines the dispersion relative to deviation at any wavelength λ . The contribution to chromatic aberration decreases as the reciprocal relative dispersion $[(-dn/d\lambda)/(n-1)]^{-1}$ increases.

⁸ L. W. Tilton and A. Q. Tool, J. Res. Natl. Bur. Std. 3, 619 (1929) RP112.

The dispersive quantities, discussed above, graphically demonstrate that for a given material there are optimum regions of the spectrum for dispersion and resolution, and minimal chromatic aberration.

V. THERMAL COEFFICIENT OF INDEX

In order to determine a thermal coefficient of index for fused silica, index measurements were repeated at a controlled room temperature of 30°C for the General Electric sample of Table I. The average values of dn/dt for the temperature range 20°–30°C are shown graphically on Fig. 3. The coefficients are positive over the measured wavelength range. They decrease from about $15 \times 10^{-6}/^\circ\text{C}$ at 0.21μ to about $10 \times 10^{-6}/^\circ\text{C}$ at 0.4μ and stay constant at this value through the visible region. The coefficient slowly increases to about $12 \times 10^{-6}/^\circ\text{C}$ at 2.0μ , then decreases to $10 \times 10^{-6}/^\circ\text{C}$ at 3.7μ . The visible-region values compare favorably with previous NBS^{3,8} determinations of dn/dt , but are higher than the reported value of $4 \times 10^{-6}/^\circ\text{C}$ near the long-wavelength cutoff.

VI. COMPARISON WITH PREVIOUS DATA

In 1954 an NBS publication by Rodney and Spindler³ reported refractive-index data for a number of fused-silica specimens commercially available at that time. A comparison of their results with those of earlier investigators was also given. It is worthy of note that the previous and current NBS experiments were performed on the same instrument and by identical techniques. The only significant difference is in the detectors. The early experiment used a lead sulfide detector and a Golay pneumatic detector equipped with a KRS-5 window to measure index at 24 wavelengths from 0.35 to 3.51μ at a temperature of 24°C. The current study

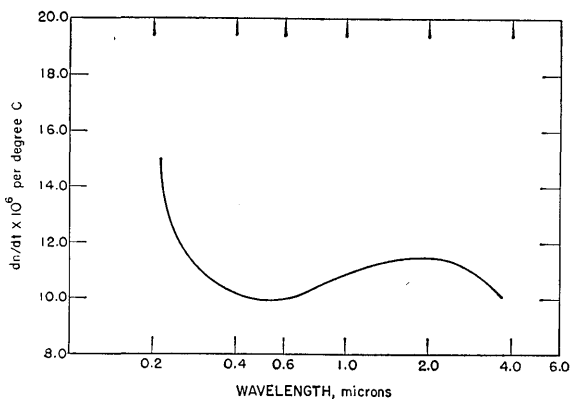


FIG. 3. Thermal coefficient of index of fused silica for a mean temperature of 25°C.

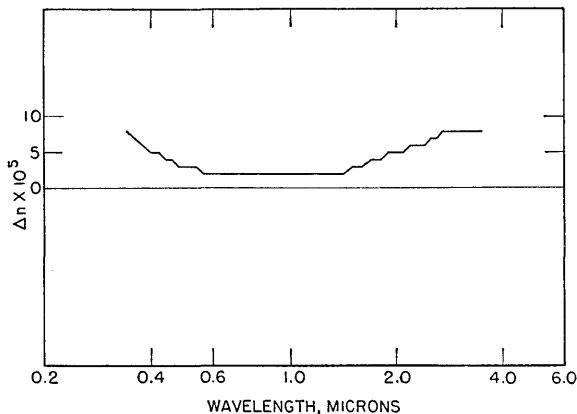


FIG. 4. Comparison of current and previous NBS refractive-index values of fused silica at 20°C. The current values are represented by the line $\Delta n = 0$.

used a single detector, a Golay cell equipped with a CaF_2 window, to measure index from 0.21 to 3.7μ .

Refractive indexes computed by formula were judged by Rodney and Spindler to be, "in general, better than the observed values" and to be the most probable values for fused silica. These values have been adjusted to 20°C by means of the thermal coefficients of Fig. 3 and are compared with corresponding index values computed by means of Eq. (1) which are considered typical for fused silica of recent manufacture. The results are shown graphically in Fig. 4 where the current index values are represented by the line $\Delta n = 0$.

The figure shows that the previous values of index are higher than those determined in this investigation. The largest differences occur near both extremes of the wavelength range. The difference varies from $+8 \times 10^{-5}$ at 0.34μ to a minimum value of $+2 \times 10^{-5}$ that is constant from 0.56 to 1.4μ , then increases to $+8 \times 10^{-5}$ at 3.5μ . In fused silica the influence of impurities can shift both the ultraviolet and the infrared absorption edges and this would tend to raise the refractive index, particularly in the regions near both extremes of the curve.

The quality of an optical material depends upon the purity of the starting material and the technique of preparation. Therefore, the results of this comparison provides evidence that optical-quality fused silica of current manufacture is of higher purity and is produced under improved procedures of fabrication than the material made a decade ago.

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