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STANDARD CONDITIONS FOR PRECISE PRISM REFRACTOMETRY

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ABSTRACT

Air as a standard reference medium for precise refractive-index measurements is discussed with respect to the precision necessary in the control and measurement of its temperature, pressure, humidity, and carbon-dioxide content. Particular attention is given to the selection of provisional values for α, the optical temperature coefficient for air; and the preparation of accurate correction tables for the reduction of refractive-index observations to standard conditions of reference is described and exemplified.

The approximate range of temperature effects on absolute refractive index is indicated; also the range of pressure effects on liquids. A new (empirical) relation between index and density is derived from Pockels' optical data on elastically deformed glass and a basis for quantitative treatment of permissible stress-birefringence is given. For glasses, the character of annealing and the permissible degree of striation are considered; and for several media the requisite constancy in wave length of light source is determined.

Tolerance equations are given for all requirements that are quantitatively discussed and it is concluded that both precision and accuracy to within ± 2 or 3×10^{-6} can be attained in determining refractive index by the classical method of minimum deviation.

CONTENTS

I. INTRODUCTION

In the practice of precise refractometry a desirable degree of approximation to the ideal physical and chemical conditions of measurement is seldom realized. Although the necessity for control of some of the physical conditions is more or less well known, only a comparatively small amount of the published index data is accompanied by adequate references to the conditions under which the measurements were actually made or to the conditions which are considered as standard.[1]

The tolerances for variations in air temperature, pressure, and humidity have not been explicitly and precisely evaluated, and the effects of temperature and pressure on the absolute indices of various media are not adequately known. Moreover, the question of the effect of heterogeneities in the sample has not hitherto been discussed in connection with refractive-index measurements. On the other hand, it appears that no attempt has been made to justify or to disprove the commonly accepted opinion that even a moderate amount of birefringence in a medium may make precise index measurements useless.

Certain refractive-index measurements of high precision, that are being made in the refractometric laboratory at the National Bureau of Standards, have made it necessary to determine the precision with which all of the working conditions must be controlled or, in some instances, quantitatively observed. It has seemed advisable to differentiate clearly between the effects of such conditions on the reference medium and on the sample to be measured and, wherever possible, to specify on a quantitative basis the requirements and tolerances relating to these working conditions; also, to set forth in detail a system of accurate corrections to standard reference conditions. However, when considering such matters as heterogeneity of the sample and the permissible degree of its birefringence, the treatment is necessarily limited to simple approximations.

For convenience of reference, the definitions of various symbols that are used and explained in this paper are summarized here as follows:

$\alpha \equiv$ temperature coefficient of expansion of air at constant pressure; also (negative) temperature coefficient of refractivity;

$\beta \equiv$ pressure coefficient of volume change at constant temperature (often called compressibility), that is

$\beta = -\frac{1}{V_0}\left(\frac{dV}{dP}\right)$; also, for air, the pressure coefficient of refractivity;

$C \equiv$ total (volume) proportion of CO_2 in atmosphere;

$C', C'', C''' \equiv$ constants of proportionality in various equations expressing index-density relationship;

$c \equiv$ excess of CO_2 above the normal proportion, that is, $c = C - 0.00035$;

$d \equiv$ density;

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[1] Brief historical references have been made in a former paper, BS J.Research 2, 912-915 (1929) RP64.

$E \equiv$ Young's modulus of elasticity;

$\epsilon = 179 \times 10^{-6}/(\mu_o - 1)$;

$\gamma = 41 \times 10^{-6}/[760(\mu_o - 1)]$;

$K \equiv$ modulus of volume elasticity or "bulk modulus", that is, $K = 1/\beta$;

$\lambda \equiv$ wave length of light;

$m \equiv$ mass;

$\mu \equiv$ index of refraction of air, the general subscripts t, p, v, and c referring to the temperature, pressure, humidity, and carbon-dioxide content, respectively, while the subscript 0 indicates standard conditions of 0° C and 760 mm pressure and D specifies a wave length of 5893 A;

$n \equiv$ relative (to air) index of refraction of a medium;

$\bar{n} \equiv$ absolute (or vacuum) index of refraction of a medium;

$P \equiv$ pressure of air;

$p \equiv$ excess in mm of Hg over 1 atmosphere of air pressure, that is, $p = (P - 760)$;

(p'/v') and $(q'/v') \equiv$ the Pockels experimental constants for certain glasses, v' being the velocity of light in the unstressed glass;

$s \equiv$ proportion by volume of striae in glass;

$\sigma \equiv$ Poisson's ratio;

T and $t \equiv$ temperatures on absolute and centigrade scales, respectively;

$T_{\Delta t_a} \equiv$ tolerance in air temperature control and measurement that corresponds to an error of $\pm 1 \times 10^{-6}$ in (relative) refractive index;

$T_{\Delta p_a} \equiv$ tolerance in air-pressure control and measurement that corresponds to an error of $\pm 1 \times 10^{-6}$ in (relative) refractive index;

$T_{\Delta v} \equiv$ tolerance in absolute humidity that corresponds to an error of $\pm 1 \times 10^{-6}$ in (relative) refractive index;

$T_{\Delta c} \equiv$ tolerance in abnormal proportion (by volume) of CO_2 in the atmosphere that corresponds to an error of $\pm 1 \times 10^{-6}$ in (relative) refractive index;

$T_{\Delta P} \equiv$ tolerance in hydrostatic-pressure variations corresponding to $\pm 1 \times 10^{-6}$ in refractive index of liquid and solid media;

$T_{\Delta n_b} \equiv$ tolerance in absolute stress-birefringence corresponding to an error of $\pm 1 \times 10^{-6}$ in refractive index (for the transverse ray if $n < 1.8+$);

$T_{\Delta \lambda} \equiv$ tolerance in wave length of source corresponding to an error of $\pm 1 \times 10^{-6}$ in refractive index;

$V \equiv$ volume; and,

$v \equiv$ pressure of water vapor in the atmosphere in mm of Hg.

II. AIR AS A STANDARD MEDIUM OF REFERENCE

The great majority of all measurements involving light velocities are made while using the earth's atmosphere as the practical standard medium of immersion or reference. Since the velocity of light in air is a function of chemical composition and also of the temperature and pressure of air, it is necessary to specify CO_2, moisture content, and other factors with appropriate precision in order that the measurements may have definite value.

The composition of CO_2-free dry air has been discussed in a former paper.[2] Although this composition appears constant to a high degree when air is chemically analyzed, it has long been estimated that variations in the normal density of air are as large as 5 or 10 parts in 10,000 and for this reason air is no longer considered a suitable reference medium for accurate specific gravities of gases. Statistical analysis of existing data indicates, likewise, that the refractive index of air at standard conditions is not constant but varies over a range perhaps as large as $\pm 12 \times 10^{-7}$ from a general average value of 1.0002925 for $\lambda = 5893$ A. Consequently all relative indices of refraction may be subject to an inherent uncertainty which can be estimated as

$$\Delta n = \pm 12 n \times 10^{-7} \tag{1}$$

unless accompanied by reliable measurements on air itself.

In reducing relative indices to absolute values when direct measurements on air are lacking, it is probable that this uncertainty is statistically diminished by using for μ, the index of air, a value properly computed[3] from dispersion data and from an equation that gives the sodium-lines index of air for 0° C and 760 mm pressure as

$$(\mu_D - 1) \times 10^7 = \mu_{S=0} - kS \tag{2}$$

where S is the relative annual sunspot number (for the year in which the relative indices were measured) as given in the Wolf-Wolfer series of sunspot observations. For use in this equation the parameters $\mu_{S=0}$ and k should be determined from the best available data on the refractive index of air for the period in question. Provisional values obtained by the writer for the whole interval 1857 to 1934 are, respectively, 2932.2 and 0.148; whereas for the limited interval 1912 to 1934, during which a number of very important observations have been made, the corresponding values of the parameters are 2927.5 and 0.079. With either of these sets of values for the parameters, however, the probable errors of estimates of index interpolated by use of equation 2 are large, namely ± 5 and $\pm 3 \times 10^{-7}$, respectively, and it is readily seen that for certain years within the interval 1912 to 1934 two estimates can actually differ by 5×10^{-7}. Extrapolations will probably be even less reliable and consequently it appears (see equation 1) that uncertainties of ± 1 or 2 units of the sixth decimal place of index can not be entirely excluded when refractivities of optically dense media are measured in CO_2-free dry air. From evidence at present available it does not seem likely, however, that such differences can occur over periods of time measured in days or weeks but rather that such possibilities should be remembered when comparing absolute determinations separated by or extending over a period of years.

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[2] L. W. Tilton, BS J. Research **13**, 111 (1934) RP695.

[3] See equation 22 of this paper.

Obviously, it is seldom convenient to use as a reference medium pure air having a standard temperature and pressure, and free from CO_2. Usually it is advisable to allow these conditions to vary continuously and to keep adequate records during index determinations. In investigating the relationships involved, a unit error of 1×10^{-6} will be considered as was done in former papers[4] discussing the geometrical aspects of prism refractometry.

1. TOLERANCES IN MEASUREMENT AND CONTROL OF REFERENCE MEDIUM

The most obviously important effects of varying air conditions on measured relative indices are those arising from the changes in air density through changes in pressure, P, and in air temperature, T (absolute). The relationship between the index of air and its density, d, is usually assumed to be that constancy expressed by Gladstone and Dale's law as $(\mu-1)=Cd$. Then, in accordance with the ideal gas law, $PV=RT$, it is customary to write for any given wave length

$$(\mu-1)_{TP}=(\mu_0-1)\left(\frac{273}{760}\right)\left(\frac{P}{T}\right) \tag{3}$$

where μ_0 is a value for standard conditions of 0° C and 1 atmosphere pressure, and P is measured in mm of Hg; or, defining p as the excess in mm of Hg over 1 atmosphere of pressure, $p=(P-760)$ and

$$(\mu-1)_{tp}=(\mu_0-1)\frac{(1+\beta p)}{(1+\alpha t)} \tag{4}$$

where t is the temperature on the centigrade scale, β is the pressure coefficient of volume change of a gas at constant temperature (namely 1/760 for a 1 mm change at a pressure of one atmosphere) and α is the temperature coefficient of expansion of air at constant pressure. The value of α would be $0.00366=1/273$ for a change of 1° C, at a temperature of 0° C, if air behaved like a perfect gas, but 0.00367 if the results of experiments on the expansion of air are considered. The only published references to computed reductions or corrections for indices measured in air at other than standard conditions have been based on these or on similar assumptions.

Since at constant temperature the proportionality between $(\mu-1)$ and d has been found to hold without serious discrepancy over a pressure range of many atmospheres, it is safe to assume that the pressure coefficient of refractivity is identical with β for such small variations in atmospheric pressure as those which occur during index measurements and also, for variations which exist between various places on the earth's surface. Concerning α, however, the similar assumption does not seem equally reliable. According to generally accepted theories of dispersion, a change in the temperature of a medium affects the resonance frequency as well as the mass per unit volume. As a result there is a change or "shift" of the effective wave length of the absorption band, and for each given wave length a different secondary temperature influence on index is superposed on that which is directly ascribed to the change in density. Thus it is

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[4] L. W. Tilton, BS J. Research **6**, 59 (1931) RP262; **11**, 25 (1933) RP575.

not necessarily true that values of $\partial\mu/\partial t$ can be accurately obtained by differentiating equation 4 with respect to t and solving for

$$\frac{\partial\mu}{\partial t}=-\frac{\alpha(\mu-1)_{tp}}{1+\alpha t} \tag{5}$$

with a constant value of α determined from the expansion of air or even from index data for a single wave length. Instead of such a constant "optical temperature coefficient",[5] the measurements on air by W. F. Meggers and C. G. Peters [6] yield an α varying with wave length from 0.00367_4 at 7500 A to 0.00373_8 at 3500 A.

Table 1 summarizes the results of direct determinations of this constant for air. The Gylden value was deduced from astronomical observations. Mascart's value should not be considered because of a systematic inconsistency in results obtainable from his data.[7] Scheel's α is very high, but his temperature interval is much lower than that used by the others. He selected $\alpha=0.00367_4$ for reducing his own index of air from 16 to 0° C. Cheney's temperature interval is much higher than that used by the others. A close analysis of his published numerical data shows that a low value of $\alpha=0.00364$ fits as well or better than the conventional value which he considered verified. Von Lang's α is too low for serious consideration and no great accuracy was claimed for the Barus data.[8]

TABLE 1.—*Optical temperature coefficient for air*

(Visible range of frequencies)

Observer	Reference	Temperature interval on Centigrade scale	$\alpha\times10^5$
Gylden	Mém.acad.St.Petersburg **10,** no. 1 (1866); **12,** no. 4 (1868)	Seasonal range	369
L. Lorentz	K.Danske Videnskab.Selskabs Skrifter [5] **10,** 485 (1875)	1 to 17°, 100°	367
Von Lang	Pogg.Ann. **153,** 463 (1874). (This α is given as computed by Benoit).	2 to 95°	303
Mascart	Compt.Rend. **78,** 617–679 (1874); Ann.Sci.École Normale Supérieure [2] **6,** 9–78 (1877).	5 to 38°	382
Benoit	Travaux et Mémoires Bur. Int. Poids et Mesures **6,** 102 (1888).	1 to 80°	367
Walker	Trans.Roy.Soc. (London) **A201,** 454 (1903)	10 to 100°	360
Scheel	Verhandl.deut.physik.Ges. **9,** 24–36 (1907)	−192 to 0°	373
Barus	Carnegie Inst.Wash.Pub.no. 249–I, page 137 (1916)	22 to 100°	361
Meggers and Peters	See page 735 Bul BS **14,** (1918) S327	0 to 30°	$368._8$
Pérard	J.phys.radium [6] **6,** 223 (1925)	0 to 100°	$371._6$
Cheney	Phys.Rev. [2] **29,** 292–298 (1927)	25 to 300°	367

Considering the amount of data taken, particularly the number of temperatures used, the results by Benoit and by Pérard are probably entitled to special consideration. They used the same method (Fizeau dilatometer) and to some extent the same apparatus. If their values are averaged one has $\alpha=0.00369$ which agrees closely with the average value of $\alpha=0.00368_8$ that is obtained from the Meggers

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[5] From inspection of equation 5 one finds that α can be regarded as the (negative) temperature coefficient of index of refraction of air per unit of "excess refractivity", as determined for $t=0°$ C and $p=0$.

[6] Bul. BS **14,** 697 (1918) S327.

[7] If from the experiments which he conducted when investigating temperature effects one discards those for temperatures below the middle group, which averages 14.4° C for t, the writer finds that $\alpha=0.00395$ is indicated. On the other hand, when the observations at temperatures above those of the middle group are discarded an $\alpha=0.00356$ is obtained.

[8] It is of interest to note that Barus' qualitative conclusion concerning the decrease of α for high temperatures is consistent with the trend which has been mentioned for some of the data of table 1, particularly the high value which Scheel found in the very low temperature interval that he used, and the low value which the writer would recommend from Cheney's data.

and Peters data for those particular wave lengths [9] which Pérard used. Thus it seems certain that the optical temperature coefficient is appreciably larger than the coefficient of expansion which has been so generally used. Since the Meggers and Peters values of α are based on data for such a large number of wave lengths, and since their average for the visible region is in excellent agreement with the average α from the Benoit and the Pérard data, the Meggers and Peters values are therefore recommended for all intercomparisons between precise relative-index data taken at markedly different temperatures.

The wave-length variation in α is of importance chiefly in the ultraviolet region; but even for the visible region, especially for the shorter wave lengths, it is in some cases preferable to use the variation in α when reducing six- and seven-decimal-place indices to certain reference conditions. In particular, when relative indices are used as a basis for computing temperature variations in the absolute index of a medium, it is desirable to consider the most accurate data available on air.

(a) TEMPERATURE OF AIR

Whether α is regarded as constant or as varying with wave length, a formal expression for the error in relative index caused by air-temperature variations is readily written after considering the definitive relation

$$n \equiv \frac{\bar{n}}{\mu} \tag{6}$$

which exists between the relative index, n, of a medium and its absolute index, $\bar{n}$. Since the latter is necessarily independent of air temperatures and μ^2 is approximately unity

$$\frac{dn}{dt} = -\bar{n}\frac{d\mu}{dt} \tag{7}$$

and consequently, using equation 5, it is found that changes in air temperature result in index variations of like sign according to the equation

$$\Delta n = \frac{\bar{n}\alpha(\mu-1)_{tp}}{(1+\alpha t)}\Delta t_a \tag{8}$$

from which precise index corrections may be computed for the whole wave-length interval 2218 to 9000 A by using the Meggers and Peters values [10] of α, which they approximately expressed by the equation

$$\alpha = 0.00367 + \frac{3\times 10^{-6}}{\lambda^3} \tag{9}$$

where λ is to be used in microns.[11]

For the purpose of establishing practical tolerance limits in temperature control and measurements, $\bar{n}$ is essentially equivalent to n, and α for the visible region is approximately the ratio 1/270. Moreover, it happens that the refractivity of air at temperatures between 0 and 50° C varies only from about 24 to 30×10^{-5} over the range of

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[9] Pérard used only five wave lengths, all within the visible region, and the data do not seem sufficiently concordant either to confirm conclusively or to disprove the variation of α with wave length.

[10] See page 735 Bul. BS **14** (1918) S327.

[11] For precise refractometry the angstrom is generally favored by the writer as the appropriate unit of wave length, but the micron is often more convenient in the writing and using of dispersion equations.

the visible spectrum, and ordinary atmospheric-pressure changes of $p=\pm 30$ mm do not materially increase this variation. Therefore, with an accuracy of approximately ± 10 percent, the tolerance corresponding to $\pm 1\times 10^{-6}$ in refractive-index measurement is

$$T_{\Delta t_a}=\pm n^{-1}(1+\alpha t) \text{ degrees C} \tag{10}$$

or, for work on media having indices of 1.9 and 1.3, respectively, the air-temperature changes of $\pm 0.53°(1+\alpha t)$ and $\pm 0.77°(1+\alpha t)$ are equivalent to errors of $\pm 1\times 10^{-6}$ in the measured relative indices. Thus it is evident that a neglect of seasonal changes in air temperatures may easily affect the fifth decimal place of relative-index work on any medium, even though its temperature coefficient of absolute index is negligibly small.

(b) PRESSURE OF AIR

For the purpose of arriving at similar correction and tolerance equations for air pressures, one differentiates equations 4 and 6 with respect to p and finds that an increase in air pressure results in a decreased value of the measured relative index of other media according to the equation

$$\Delta n=-\frac{\overline{n}\beta(\mu-1)_{tp}}{(1+\beta p)}\Delta p \tag{11}$$

from which precise corrections to measured indices can be satisfactorily computed.

Again approximating, as was done with equation 8, equation 11 reduces to the practical working tolerance in air pressures

$$T_{\Delta p_a}=\pm 2.8n^{-1}(1+\beta p)\text{mm} \tag{12}$$

which is written for an error of $\pm 1\times 10^{-6}$ in refractive index and, obviously, for the usual small values of p only one term is needed. Thus for media having indices of 1.9 and 1.3, respectively, the air-pressure changes of 1.5 and 2.2 mm are equivalent to variations of unity in the sixth decimal place of measured relative index of refraction. For many localities, therefore, it is apparent that the fluctuations in barometric pressure within a single working day should not be neglected in precise measurements of relative index, and it is certain that the air-pressure variations that occur over somewhat longer periods affect the fifth decimal of such indices.

(c) HUMIDITY OF AIR

The proportion of water vapor in air is such a variable factor, depending on locality and weather conditions, that it is a difficult matter to decide upon any definite proportion as a satisfactory normal moisture content of the atmosphere. Consequently it is probably better to treat moisture as an impurity and refer all refractive-index measurements to dry air as a standard reference medium.

L. Lorenz [12] gives, for sodium light, a value of $\mu_D=1.0002500$ as the index of refraction of water vapor at a concentration of 1 mol in 22.4 liters. Comparing this with his index of dry air for equivalent conditions, he gives a correction of $\Delta\mu_v=-0.000041\ v/760$ to be applied to his results on dry air when it is desired to obtain indices for moist

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[12] Ann. Physik [3] **11,** 91 (1880).

air containing water vapor of v mm pressure. The Cuthbertsons [13] and others [14] have confirmed the magnitude of this correction and, for the region 4779 to 6708 A, have shown that the dispersion of water vapor is closely comparable with that of air. It seems, in fact, from experimental evidence, that the coefficient of this Lorenz correction, namely, 41×10^{-6}, should not vary more than $\pm 1 \times 10^{-6}$ throughout the visible spectrum.

Since the pressure of water vapor in the air seldom exceeds a small fraction of an atmosphere, it seems permissible to assume the equivalence of optical temperature coefficients for water vapor [15] and for air, and to use the Lorenz humidity correction for all ordinary temperatures by writing for the whole visible range of frequencies

$$(\mu_t-1)_v=(\mu_t-1)_{v=0}(1-\gamma v) \tag{13}$$

where $\gamma=185\times10^{-6}$ is used to replace $41\times10^{-6}/[760\ (\mu_0-1)]$. This equation is written for a pressure of 760 mm, but is applicable at all ordinary atmospheric pressures. Differentiating equation 13 with respect to v gives

$$\frac{d\mu}{dv}=-\gamma(\mu_t-1) \tag{14}$$

and, referring to a similar differentiation of equation 6, it is evident that an increase in the moisture content of the air results in an increased relative index of a medium which is being measured therein, the error equation being

$$\Delta n=+\bar{n}\gamma(\mu_t-1)\Delta v \tag{15}$$

for use in precise computations of refractive index of the medium which is measured in air.

For an error of unity in the sixth decimal of index, and with sufficient accuracy for many purposes, equation 15 yields

$$T_{\Delta v}=\pm\ 20n^{-1}\text{mm} \tag{16}$$

which shows that the unit tolerances in absolute humidity vary from approximately ± 10 to ± 15 mm of vapor pressure. These figures apply to measurements of relative index on media having indices of 1.9 and 1.3, respectively. Vapor pressures of 10 and 15 mm correspond at 50° C to 10 and 15 percent in relative humidity and at 30° C to 30 and 45 percent, respectively. Thus it is evident that humidity corrections are not negligible in sixth-decimal-place refractometry, especially when working in air at temperatures somewhat higher than those of ordinary room conditions or whenever there is danger of humidities approaching the saturation point (because, for example, of leaks in water-jacketed housings used for temperature control).

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[13] C. and M. Cuthbertson, Trans. Roy. Soc. (London) **A213,** 16 (1913).

[14] J. Wüst and H. Reindel, Z. physik. Chem. **B24,** 176 (1934). See, also, P. Hölemann and H. Goldschmidt, page 204 of same volume.

[15] From the Hölemann and Goldschmidt data (see footnote 14) on water vapor, considered together with published densities of steam, one may deduce a tentative value α=0.0035 to compare with 0.0037 for air.

(d) CARBON-DIOXIDE CONTENT OF AIR

After water vapor the next atmospheric constituent of recognized importance, so far as its variability is concerned, is carbon dioxide. Although the range in its fluctuations is known to be much smaller than in the case of water vapor, there is a prevalent opinion that when using air as a reference medium for measurements of highest precision one should eliminate either the CO_2 itself or the effects of its variations. While there are on record some presumably reliable analyses of air showing a carbon-dioxide content as high as 0.3 percent by volume, such samples were taken under exceptional circumstances, such as in very crowded theaters of an obsolete and most unfavorable type, or in rooms with no ventilation, and they have no interest in the present connection. Boothby and Sandiford[16] reported that outdoor air sampled under favorable conditions varies in its CO_2 content by only a few thousandths of one percent from a normal value of 0.036 percent. Similarly, F. G. Benedict[17] found that outdoor air does not vary in this respect more than a few thousandths from an average value of 0.031 percent, but Hann[18] states that the percentage of CO_2 varies from 0.033 to 0.043 in the air of cities. Consequently, in view of these small variations, it seems permissible and somewhat preferable to adopt some value, say 0.00035, as the normal volume proportion of CO_2 in air rather than to favor the more stringent requirement that a standard reference medium must be entirely free from carbon dioxide.

Precise index measurements are, of course, seldom made in outdoor air, but in any well ventilated modern laboratory it is unlikely that the carbon-dioxide content ever exceeds two or three times the normal value. In air from the Boston and New York subways, sampled just after the rush hours, Benedict found only twice the normal CO_2 content. Moreover he found that an increase in CO_2 is accompanied by an equal volume decrease in O_2, and consequently it is the difference in the refractivities of carbon dioxide and of oxygen which must be considered in making corrections to indices measured in air having an abnormal CO_2 content.

The averages of a number of published[19] values of the refractive indices of CO_2 and O_2 are 1.000450 and 1.000271, respectively, for sodium light, a temperature of 0° C and a pressure of 760 mm. Hence a correction of

$$\Delta\mu_C = +0.000179(C-0.00035) \tag{17}$$

should be applied to the measured index of normal air (containing the proportion 0.00035 of CO_2) at 0° C and 760 mm pressure when it is desired to obtain the index of air containing the total proportion C of carbon dioxide.

A comparison of the dispersions of oxygen and of carbon dioxide shows that the correction given by equation 17 varies only 1 percent or less for the visible-spectrum region. Proceeding as with the water-vapor correction (part c of this section) and writing $c=C-0.00035$ to represent excess CO_2, one finds for all ordinary temperatures

$$(\mu_t-1)_C = (\mu_t-1)_{c=0}(1+\epsilon c) \tag{18}$$

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[16] Am. J. Physiol. **55,** 295 (1921).

[17] The Composition of the Atmosphere, Carnegie Inst., Wash., Pub. no. 166., pages 110–114 (1912).

[18] J. von Hann's Lehrbuch der Meteorologie, page 5 (1915).

[19] See Landolt-Börnstein Tabellen.

where $\epsilon=0.612$ replaces $179\times10^{-6}/(\mu_0-1)$. Differentiating equation 18 with respect to c gives

$$\frac{d\mu}{dc}=+\epsilon(\mu_t-1) \tag{19}$$

whence, again using equation 6, it is apparent that the presence in laboratory air of CO_2 in abnormally high proportions results according to the equation

$$\Delta n=-\overline{n}\epsilon(\mu_t-1)\Delta c \tag{20}$$

in decreased values for such relative indices as are measured in the laboratory.

For unit error in the sixth decimal place of refractive index the corresponding tolerance in volume proportion of abnormal CO_2 content of air is

$$T_{\Delta c}=\pm\ 0.006n^{-1} \tag{21}$$

with sufficient accuracy for all purposes. Evidently no consideration whatever need be given to CO_2 content of air in sixth-decimal-place refractometry. Even for the extreme case when a medium of index 1.9 is being measured, the excess proportion of CO_2 must reach the high value of 0.003, or nine times the proportion normally present in fresh air, in order to produce an error of -1×10^{-6} in relative index. For seventh-decimal-place index work, however, it may be ascertained from these results that the normal CO_2 content of fresh air causes a lowering of approximately 1×10^{-7} in the measured relative indices of very dense media as compared with the use of a standard reference air containing no carbon dioxide. Consequently, it may be safely inferred that, in general, indices of laboratory air, or relative indices measured in such air, are not likely to have any precision whatever in the eighth decimal place unless simultaneous CO_2 determinations are made.

2. CORRECTIONS TO STANDARD REFERENCE CONDITIONS

If the working conditions affecting the reference medium are not maintained constant at the desired standard values or controlled within the tolerance limits as specified above, then it becomes necessary to observe the existing conditions and make the proper corrections to the results actually obtained. When it is necessary to correct sixth-decimal-place indices to standard conditions, or to convert them to absolute indices, the use of slide-rule corrections is often lacking in adequate precision and correction tables for these purposes are advisable. Their preparation in detail is a profitable preliminary whenever numerous data are to be reduced for a limited number of spectral lines. For highest precision such tables are especially desirable because certain refinements in precision of correction need be considered explicitly only during their original preparation.

The writer recommends the use of logarithms in the computation of indices, and the evaluation of all corrections in terms of log n. One of the first requirements is a double-entry table of barometer corrections with barometer temperature and barometer reading as arguments. With the temperature reductions [20] to be listed in this table the barometer calibration corrections (for a given instrument)

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[20] Temperature reductions for use with a Fortin-type barometer and brass scale are given in tables 46 and 47 of the 4th revised edition, Smithsonian Meteorological Tables.

are combined and then all entries are modified to reduce pressures from local[21] to standard gravity, $g=980.665$ dynes.

Another requirement is a series of double-entry tables (or their equivalent), with air pressure and temperature as arguments, giving the positive corrections which, when applied to log n, will yield log $\bar{n}$, of which the antilog is absolute index. The various members of such a series of tables relate to the different spectral lines that are to be frequently used for index measurement and these member tables will differ principally because of the dispersion of air. (There is also a slight additional difference because of the nonconstancy of α, the optical temperature coefficient of index. See discussion in part 1 of section II.) As an example of a member table of such a series, table 2 is abstracted (by decimation in each argument) from a usefully detailed tabulation for the hydrogen line, $\lambda=4861$ A.

TABLE 2.—*Data for converting from relative to absolute index* ($\lambda=4861$ A) *by the equation* $\log\ \bar{n}=\log\ n+\log\ \mu$

P≡air pressure (in mm of mercury)	Values of $10^8\times\log\ \mu_F$ for dry air at various temperatures (with normal CO_2 content)				
	0° C ($\Delta P=0.06$)	10° C ($\Delta P=0.13$)	20° C ($\Delta P=0.24$)	30° C ($\Delta P=0.44$)	40° C ($\Delta P=0.77$)
730	12295	11857	11449	11069	10713
740	12464	12020	11606	11220	10859
750	12632	12182	11763	11372	11006
760	12800	12344	11920	11524	11153
770	12969	12507	12077	11675	11300
780	13137	12669	12234	11827	11446

NOTES

1. For each 10 percent of relative humidity subtract tabulated values of ΔP from air pressure before entering this table.
2. Tentatively it may be advisable to reduce log μ by 5 or 10 parts in 10,000 for each increase of 20 in relative annual sunspot number above average $S=46$.
3. If it is desired to use these data for wave lengths other than 4861 A, modify air temperature according to table 4 before entering this table.

In preparing such correction tables in this laboratory, the temperature and dispersion data as given by Meggers and Peters[22] have been combined with the average value of refractive index, $\mu=1.0002926$ (for $\lambda=5893$ A, $t=0°$ C and $P=760$ mm), which is obtained by considering all published data[23] and adding a very slight correction for normal CO_2 content. Since the ratio of log μ to $(\mu-1)$ is very nearly constant over the whole range in μ that is involved in temperature and pressure reductions and corrections, the actual computation of air indices is unnecessary except for 0° C and 760 mm pressure. The values of log μ for all ordinary temperatures and pressures may be directly computed (see equation 4 and citations of footnote 22) from the equation

$$\log\ \mu_{tp}=\frac{1+\beta p}{1+\alpha t}\log\left[1+\left(2884.3+\frac{13.412}{\lambda^2}+\frac{0.3777}{\lambda^4}\right)\times 10^{-7}\right] \quad (22)$$

where α varies with wave length as approximately expressed by equation 9, and λ should be written in microns.

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[21] Gravity reductions are discussed on pages XXXV and XXXVI of 4th revised edition, Smithsonian Meteorological Tables.

[22] See pages 722 and 735, Bul.BS **14** (1918) S327.

[23] See page 115, BS J.Research **13** (1934) RP695.

If, in table 2, the values for a standard pressure are subtracted from those for other pressures in the same column, a set of air-pressure corrections to the logarithms of observed indices is obtained. Table 3 gives such corrections for limited ranges in pressure and in temperature variations. Such a table may, of course, be computed directly from the basic values of the logarithms for the indices at standard pressure, $p_0=760$ mm. For this purpose the equation

$$\Delta \log \mu_{tp}=\frac{\log \mu_{tp0}}{760}\Delta p \tag{23}$$

is obtained from equation 22.

TABLE 3.—*Data for referring relative indices to dry air at standard pressure by the equation* $\log n_{760}=\log n_p+\Delta\log n$.

Use tabulated values with negative sign when $P-760$ is negative]

($P-760$ mm) ≡ excess atmospheric pressure	Values of $10^8 \times \Delta \log n$ for various air temperatures		
	10° C ($\Delta P=0.13$)	20° C ($\Delta P=0.24$)	30° C ($\Delta P=0.44$)
20	325	314	303
19	309	298	288
18	292	282	273
17	276	267	258
16	260	251	243
15	244	235	227
14	227	220	212
13	211	204	197
12	195	188	182
11	179	173	167
10	162	157	152
9	146	141	136
8	130	125	121
7	114	110	106
6	97	94	91
5	81	78	76
4	65	63	61
3	49	47	45
2	32	31	30
1	16	16	15
0	0	0	0

NOTE.—For each 10 percent of relative humidity subtract tabulated values of ΔP from air pressure before entering this table.

Although the direct use of table 2 is strictly limited to the correction of indices for the F line of hydrogen, table 3 is applicable over a very wide range in the spectrum. In fact, for pressure corrections as large as 30 mm the use of table 3 may be extended over the whole visible range of frequencies without errors exceeding $\pm 5 \times 10^{-8}$ in the logarithmic corrections so determined.

As they are written, tables 2 and 3 both relate to dry air and must be modified because of the presence of water vapor. From equations 11 and 15 it is evident that any given increase in moisture can be represented as an equivalent decrease in pressure, and thus it is possible to find a simple system of modifying the actual corrected pressures to fictitious or pseudo pressures which, when used as actual pressures, permit tables 2 and 3 to serve for moist as well as dry air. Hence the ΔP equivalents which appear in the column headings of tables 2 and 3.

If for any reason it is objectionable to prepare a complete series of log μ tables, similar to the single example given as table 2, one may use a relationship between $\Delta\mu/\Delta\lambda$ and $\Delta\mu/\Delta t$ for extending to other wave lengths the use of a table written primarily for one particular wave length. For this procedure it is found advantageous to regard temperature as the fictitious argument, and table 4 gives the particular corrections of this type that should be algebraically applied to actual air temperatures before entering table 2 for wave lengths other than 4861 A.

TABLE 4.—*Auxiliary data for extending use of table 2 to various wave lengths*

$\lambda \equiv$ wave length (in angstroms)	Values of Δt for modification of air temperatures		
	0° C	20° C	40° C
4000	−3.18	−3.30	−3.43
4100	−2.70	−2.80	−2.91
4200	−2.25	−2.33	−2.42
4300	−1.83	−1.90	−1.98
4400	−1.45	−1.50	−1.56
4500	−1.10	−1.14	−1.18
4600	−0.76	−0.79	−0.82
4700	−0.45	−0.47	−0.49
4800	−0.16	−0.17	−0.18
4900	+0.11	+0.11	+0.12
5000	+0.36	+0.38	+0.40
5200	+0.81	+0.84	+0.87
5400	+1.21	+1.26	+1.31
5600	+1.57	+1.63	+1.69
5800	+1.88	+1.96	+2.04
6000	+2.17	+2.26	+2.35
6200	+2.42	+2.52	+2.63
6400	+2.65	+2.76	+2.88
6600	+2.86	+2.98	+3.10
6800	+3.05	+3.18	+3.31
7000	+3.21	+3.36	+3.50

III. REQUISITE CONSTANCY AND UNIFORMITY FOR REFRACTIVE MEDIA

Uniformity of reference conditions is a necessary but by no means a sufficient condition for high precision in refractometry. Even the absolute indices of refraction of optical media are ratios which may, for divers reasons, vary from time to time or with respect to coordinates within the media. Temperature and pressure are obviously important factors and, in the case of optical glass, heat treatment may introduce not only a variation of index with direction of travel of the light, but also a marked physico-chemical change[24] in index that often varies from point to point in the glass although it is not a function of orientation. Moreover, the writer has found that striae in glass, when they exist in well-stratified layers, can affect measurements of index and of dispersion in a systematic manner that may prove misleading in some investigations. Therefore, for consistent results in index determinations, it is necessary carefully to consider the conditions which cause real or apparent changes in the optical density of media that are subject to measurement.

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[24] A. Q. Tool and C. G. Eichlin, J.Opt.Soc.Am. **4,** 359 (1920); BS J.Research **6,** 525 (1931). A. Q. Tool L. W. Tilton, and E. E. Hill, J.Opt.Soc.Am .and Rev.Sci.Inst. **12,** 490–491 (1926). L. W. Tilton, J.Wash' Acad.S ci. **20,** 12–13 (1930).

1. EFFECTS OF TEMPERATURE ON REFRACTIVE MEDIA

Comparatively little recent progress has been made in the theory of temperature effects on absolute index. It is considered, however, that this effect consists of at least two well-defined components which may, and often do, have opposite signs. The more frequently mentioned component is the direct result of thermally produced changes in density and its sign is always as indicated by the equation

$$\frac{\partial \bar{n}}{\partial t} = f(\bar{n}) \frac{dd}{dt} \tag{24}$$

where $f(\bar{n})$ is a positive function, which may be variously approximated (for example as $\bar{n}-1$, $\bar{n}^2-1$, $\frac{\bar{n}^2-1}{\bar{n}^2+2}$, etc.). Consequently, for media which expand when heated, this change in index is negative as temperature increases, and this effect of temperature is not a function of wave length but relates primarily to conditions for infinite wave length. As mentioned for air in part 1 of section II, the second component is ascribed to changes in the resonance frequencies of the media. The increase in volume which usually takes place with rising temperature is often accompanied by a capacity for absorbing radiation of longer wave length. Thus, under such circumstances, ultraviolet absorption bands are "shifted" toward the longer wave lengths of the visible region while the long wave lengths of infrared bands become still longer. Obviously, then, these absorption components of temperature coefficients of index are functions of wave length.

The velocity of propagation of radiation of a wave length longer than that corresponding to the effective absorbing frequency is decreased, while that of shorter wave length is increased. Consequently, for media whose principal effective absorption bands lie in the ultraviolet, this total absorption-band component of refractive index usually increases as temperature increases, while the reverse is true for media with predominant infrared absorption. In most optical glass the index change (in and near the visible spectral region) that is ascribable to the ultraviolet absorption bands predominates over the combined effects of the directly produced density change and the change caused by shifting of the infrared bands. For some crown glasses, however, the opposing tendencies are about equal in absolute value, and the index sensitivity to temperature is quite negligible. For a few crowns of very low index and somewhat unusual chemical composition the density and infrared effects predominate and negative temperature coefficients of absolute index are found, especially for the longer wave lengths of the visible spectrum.

(a) THERMAL COEFFICIENTS OF ABSOLUTE REFRACTIVE INDEX

For a few optical glasses temperature coefficients of absolute index are readily available through the work of C. Pulfrich [25] and of J. O. Reed.[26] Also, such coefficients can be readily computed from coeffi-

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[25] Ann.Physik **45**, 609–665 (1892).

[26] Ann.Physik **65**, 707–744 (1898).

cients of relative index that have been determined by C. S. Hastings,[27] G. Müller,[28] H. Fizeau,[29] and J. W. Gifford;[30] or they may be estimated from the graphs published by C. G. Peters.[31] From a critical examination of these data, and also from unpublished results obtained in this laboratory, it is inferred that chemical composition is a predominantly important factor in determining this thermo-optical relationship for glass. Accordingly, it is difficult to make concise general statements, with a useful degree of precision, about the quantitative effects of temperature variations on the refractivity of glasses.

At usual room temperatures the values of $10^6 \times \Delta\bar{n}/\Delta t$, for the sodium-lines indices of flint glasses vary from approximately 0 for some light flints containing barium to +14 for those with highest lead content. For low-index glasses it is often considered that the temperature coefficients of absolute index are small and that they lie within a narrow range as compared with flint glasses. Available data confirm this view for the optical crowns in frequent use, the range in their coefficients being −1 to +3. Measurements in this laboratory show, however, that certain fluor crowns have values of −3 while for Pyrex and fused-quartz glasses of similar refractivity the coefficients are +5 and +9, respectively.

For crystals the range in refractive-index sensitivity to temperature is greater than for glasses. It is sufficient to mention sylvite, which, at room temperature, has a coefficient of approximately -34×10^{-6}, and calcite with its value of $+11 \times 10^{-6}$ for the extraordinary ray.

Numerous published data concerning the temperature coefficients of refractive index of liquids show that such values are all negative (direct density effect predominating over that of the absorption shift in the ultraviolet) and very much larger in numerical value than those for most solids.[32] It is useful to remember, however, that the percentage variations among such temperature coefficients for different liquids are, in general, relatively small compared with similar variations for solids. For a large number of transparent and semitransparent liquids (including numerous oils) the value of $\Delta\bar{n}/\Delta t$ is approximately expressed as -4×10^{-4}, although a number of organic liquids have values ranging from −4 to -6×10^{-4}. Water with a value of -1×10^{-4} is a most important exception and, on the other hand, there are some optically dense liquids which have unusually high (negative) temperature coefficients of index, such, for example, as −7 and -8×10^{-4} for methylene iodide and carbon disulphide, respectively.

(b) APPROXIMATE RANGE IN TEMPERATURE TOLERANCES FOR SOLIDS AND LIQUIDS

When considering temperature tolerances for general refractometry it must be remembered that one may have no prior knowledge of the media and their temperature coefficients of index. From the values given above it is evident that even for glasses known to be the usual crowns and light flints, the temperature of the sample during refrac-

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[27] Am.J.Sci. [3] **15**, 269-275 (1878).

[28] Publicationen Astrophysikalischen Observatoriums Potsdam **4**, 149-216 (1885).

[29] Ann.chim.phys. [3] **66**, 429-482 (1862).

[30] Proc.Roy.Soc. (London) **A91**, 319-321 (1915); **A100**, 621-626 (1921-22).

[31] BS Sci.Pap. **20**, 635 (1926) S521.

[32] The absolute value of the ratio between temperature coefficients of liquids on the one hand and of glasses and common optical crystals on the other may be very roughly expressed as 100. Consequently, for liquids, coefficients of relative and of absolute refractive index are practically identical, whereas for glasses and crystals they frequently are quite different and may be of opposite sign.

tive-index determinations must be known within the limits of approximately ± 0.3° C to correspond to a limiting error of $\pm 1 \times 10^{-6}$ in index. For Pyrex glasses and for fused quartz the corresponding temperature tolerances are ± 0.2 and ± 0.1° C, respectively. Possibly, precision and accuracy in temperature measurement within approximately these limits can with care be obtained when a glass prism is mounted on a spectrometer table and exposed to the air of a room in which the temperature is constant or changes but slowly. When, however, the denser flint glasses are considered, it is found that the tolerances are reduced to ± 0.07° C (and even to ± 0.03° C for determinations with the shorter wave lengths of the visible spectrum).

Consequently, without considerable prior knowledge concerning a particular transparent solid, it is not advisable to attempt sixth-decimal-place refractometry unless temperature is controlled and measured to within ± 0.1° C or better. It is, therefore, highly desirable to provide a constant-temperature prism housing, even for work in a constant-temperature room, and to determine all indices with respect to a stirred air bath surrounding the prism.

Tolerances in temperature control and measurement during refractive-index determinations on liquids to within one unit of the sixth decimal place are so strict that there seems to be no published account of a serious attempt to reach such precision. The requirements are ± 0.01° C for water at room temperature, and approximately ± 0.002° C for liquids of average thermo-optical sensitivity.

2. EFFECTS OF PRESSURE ON REFRACTIVE MEDIA

L. Zehnder [33] found that water under pressure increases in absolute index by 15×10^{-6} per atmosphere at 20° C, and he favored the Gladstone and Dale relation, the constancy of $(n-1)/d$, when the density of liquids is varied by pressure. W. C. Röntgen and L. Zehnder [34] give data on similar increases in index for several other liquids. Although they do not choose between the Gladstone and Dale relation and that of Lorenz-Lorentz, their results are in general somewhat more favorable to the former.

F. Pockels [35] investigated the effects of unidirectional pressure on seven kinds of glass, using Neumann's equations for expressing the influence of elastic deformation on the propagation of light, and he found the Newton relation, $(n^2-1)/d$, somewhat more nearly constant than that of Gladstone and Dale or of Lorenz-Lorentz. L. H. Adams and E. D. Williamson [36] also have published results on the relation between birefringence and stress in various types of glass and have confirmed Pockels' results where comparisons can be made.

There is, however, a general lack of direct experimental evidence relating to the effect of atmospheric-pressure variations on the absolute refractivity of transparent media, and particularly so for optical glasses. Both Hovestadt [37] and Adams and Williamson have mentioned the conputation of such effects from Pockels' work and the equations of Neumann but, unfortunately, the necessary constants

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[33] Ann. Physik [3] **34,** 91-121 (1888).
[34] Ann. Physik [3] **44,** 49-50 (1891).
[35] Ann. Physik [4] **7,** 745-771 (1902); also, for important corrections, see **9,** 221 (1902,) and **11,** 652 (1903).
[36] J. Wash. Acad. Sci. **9,** 609-623 (1919).
[37] H. Hovestadt, Jena Glass, appendix H, page 409 (Macmillan and Co., London, 1902).

characteristic of different media are known only for the seven glasses used by Pockels, and two [38] of these are unusual alumino-borates.

(a) VARIATIONS IN ATMOSPHERIC PRESSURE

Some indications concerning the effects of atmospheric-pressure changes on liquid and solid refractive media may, however, be obtained from a consideration of the index-density relationships together with the published data on β, the compressibility at constant temperature, and on its reciprocal, K, the "bulk modulus" or modulus of volume elasticity. If, in accord with Pockels' results for glass, the Newton form $(n^2-1)=C'd$ is written to express the index-density relation for a medium having a modulus $K=-V\,dP/dV$, and a density $d=m/V$, then

$$d\overline{n}=\frac{(n^2-1)}{2nK}dP \tag{25}$$

is obtained as the differential relation between refractive index and pressure. Or, if the index-density relation is $(n-1)=C''d$, one finds according to this Gladstone and Dale premise

$$d\overline{n}=\frac{(n-1)}{K}dP \tag{26}$$

as an alternative index-pressure relationship. Similarly, from the Lorenz-Lorentz expression

$$d\overline{n}=\frac{(n^2-1)(n^2+2)}{6nK}dP \tag{27}$$

would be written.

In view of the analysis which Pockels made from his experiments on glass under pressure, equation 25, rather than 26 or 27, is preferable for solids, while from the work of Zehnder and of Röntgen and Zehnder with pressure applied to liquids it may be inferred that equation 26 is more suitable for liquid media. The writer has found, however, that Pockels' data agree with an index-density relation

$$\left(\frac{n^2-1}{n^2+2}\right)^5=C'''d^3 \tag{28}$$

much more closely than with the Newton relation, and consequently the differential equation

$$d\overline{n}=\frac{(n^2-1)(n^2+2)}{10nK}dP \tag{29}$$

is preferable to equation 25. Since $K=E/[3(1-2\sigma)]$, where E is Young's modulus of elasticity and σ is Poisson's ratio, equation 29 may be written

$$d\overline{n}=\frac{3(1-2\sigma)(n^2-1)(n^2+2)}{10nE}dP \tag{30}$$

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[38] The Pockels glass listed as 0.428, $n=1.5123$, was not, as originally supposed, an alumino-borate like his two other crown glasses but, according to subsequently published corrections (see footnote 35, p. 409), was a borosilicate glass. The revised data are free from peculiarities which marked the original exhibit. Nevertheless the errors continue to be propagated in the literature or, as in the International Critical Tables, 2, page 106, this important glass is omitted from consideration.

or, the change in index may be computed approximately from

$$\Delta\bar{n}=\frac{0.15(n^2-1)(n^2+2)}{nE}\Delta P \tag{31}$$

if the constant value $\sigma=0.25$ is used instead of experimentally determined values [39] which with few exceptions lie within the range from 0.21 to 0.27.

Equation 26 has been used in computing $\Delta\bar{n}$ for water, ethyl ether, ethyl alcohol, benzene, and carbon disulphide, using for $1/K$ averages of several published values for the compressibility of these liquids. The results agree within the limits of ± 10 percent with published experimental values. Equation 29, which is based on the new index-density relation, has been used in computing $\Delta\bar{n}$ for Pockels' glasses when subjected to changes in hydrostatic pressure, and the results lie within approximately ± 5 percent of those computed from the actual experimental constants in the manner suggested by Pockels. These 5 percent differences compare with 15 and 20 percent differences that are obtained when a similar computation is made by equation 25, which is based on the Newton index-density relation as favored by Pockels. If, however, the approximate form (equation 31) is used instead of equation 29 the differences are as large as 15 percent.

From equation 26 the tolerance in atmospheric- or other hydrostatic-pressure changes for work on liquid media is

$$T_{\Delta P}=\pm\frac{0.000001}{(n-1)\,\beta} \tag{32}$$

for a limiting error of $\pm 1\times10^{-6}$ in refractive index. For ethyl ether or carbon disulphide the limits ± 12 mm are found, and for ethyl alcohol or benzene they are ± 17 mm. Consequently, pressure corrections of this nature should not be entirely neglected. The less compressible liquids water and glycerin have the correspondingly more liberal tolerances of ± 47 and ± 72 mm, respectively, and they require corrections only for extremes of pressure variations or for reductions to standard conditions after measurements are made where the prevailing barometer level is appreciable different from 760 mm.

From equation 31 one may write

$$T_{\Delta P}=\pm\frac{0.000007nE}{(n^2-1)(n^2+2)} \tag{33}$$

as the tolerance in ΔP for sixth-decimal-place refractometry of glass. The values of E seem to range within ± 10 percent of the average 0.72×10^6 atmospheres for borosilicate glasses not containing lead oxide or phosphoric acid,[40] and except for a few extremes all other glasses seem to have values of E which lie within ± 10 percent of 0.58×10^6 atmospheres. Hence, considering only the absolute index of glass, it is evident that the tolerance in measurement or control of air pressures is seldom if ever [41] less than about 1/2 atmosphere, and therefore of no moment.

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[39] R. Straubel, Ann. Physik [3] **68**, 409 (1899); or see page 193 of reference cited in footnote 37, page 409.

[40] See page 159 of reference cited in footnote 37, page 409.

[41] Glasses containing approximately 74 percent of PbO may perhaps be exceptions. See part b of this section.

In connection with the subject of pressure effects on absolute index it should be remembered, however, that corrections of this nature should be considered if one attempts a precise comparison between relative indices and those observed under actual vacuum conditions. In the case of liquids, it becomes imperative, even for accuracy in the fifth decimal place, to distinguish between values actually measured in a near vacuum (under their own vapor pressure) and those which are reduced from relative measurements by considering only the effect of pressure on the ambient air.

(b) STRESS AND BIREFRINGENCE

In addition to hydrostatic-pressure effects there should also be considered those effects which are due to unequally distributed stresses within media. Such stress distribution is caused, for example, by improper annealing of glass and by the improper mounting or tight clamping of optical components, especially under varying temperature conditions. The birefringence that is produced in this manner is commonly used as a measure of the internal stress and it seems desirable, if possible, to use birefringence as a measure of that change in refractive index which accompanies the stresses.[42]

From Pockels' [43] work it is possible to express the ratio between the change in index, Δn_y or Δn_z, and the absolute birefringence, $\Delta n_y-\Delta n_z$. For the ray which vibrates parallel to the axis of stress

$$\frac{\Delta n_y}{\Delta n_y-\Delta n_z}=\frac{2\sigma}{1+\sigma}-\frac{(1-2\sigma)\frac{q'}{v'}}{(1+\sigma)\left(\frac{p'}{v'}-\frac{q'}{v'}\right)}\tag{34}$$

and for the transverse ray

$$\frac{\Delta n_z}{\Delta n_y-\Delta n_z}=\frac{2\sigma}{1+\sigma}-1-\frac{(1-2\sigma)\frac{q'}{v'}}{(1+\sigma)\left(\frac{p'}{v'}-\frac{q'}{v'}\right)}\tag{35}$$

where p'/v' and q'/v' are experimentally determined constants for a given medium and σ is Poisson's ratio. For glass in the index range 1.5 to 1.75 the Pockels' data lead to higher absolute values for the transverse ray ratio, while for his glass of $n=1.96$, equation 34 gives the larger ratio. Consequently, it may be said that the tolerance in absolute stress-birefringence $\Delta n_b=(\Delta n_y-\Delta n_z)$, in millimicrons per centimeter, for sixth-decimal-place measurements of refractive index is at least as large as

$$T_{\Delta n_b}=\pm\frac{10}{f\left(\sigma,\frac{p'}{v'},\frac{q'}{v'}\right)}\ \text{millimicrons per cm}\tag{36}$$

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[42] For clearness it may be necessary to mention that any piece of unannealed glass in which such stresses exist is a balanced system involving both tensions and compressions so that the index changes which are produced are of opposite sign and offset each other. (See L. H. Adams, J. Franklin Inst. **216**, 39–71 (1933).) Nevertheless, portions of the glass may show an average birefringence of a given sign and therefore experience a correspondingly changed index. Such limited portions of the medium should be individually considered because such a procedure corresponds closely to conditions under which optical-glass components are often measured and used, namely, at partial rather than at full apertures.

[43] Ann.Physik [4] **7**, 745–771 (1902); also for important corrections, see **9**, 221 (1902), and **11**, 652 (1903).

where the denominator is computed according to equation 35 for glasses of index $<1.8+$ and by equation 34 for glasses of index >1.9, approximately.

Equation 36 with each of these denominators written in turn, has been used in computing the corresponding values of this tolerance for the seven Pockels glasses, and figure 1 shows the chief results. It does not seem clear where the curves of this figure should cross [44] and accordingly they are not drawn in full. In any event, it is evident that stress-birefringence differs greatly in the degree of sensitivity with which it can serve to measure the variations in index which may exist because of the stresses in various kinds of glass. For flints it is obvious that the birefringence present should be much lower than for crowns, and consequently the annealing requirements and schedules for flints should not be too readily neglected because of the comparative ease with which their stress-birefringence seems to be reduced. Nevertheless, remembering the Rayleigh limit of one-quarter wave

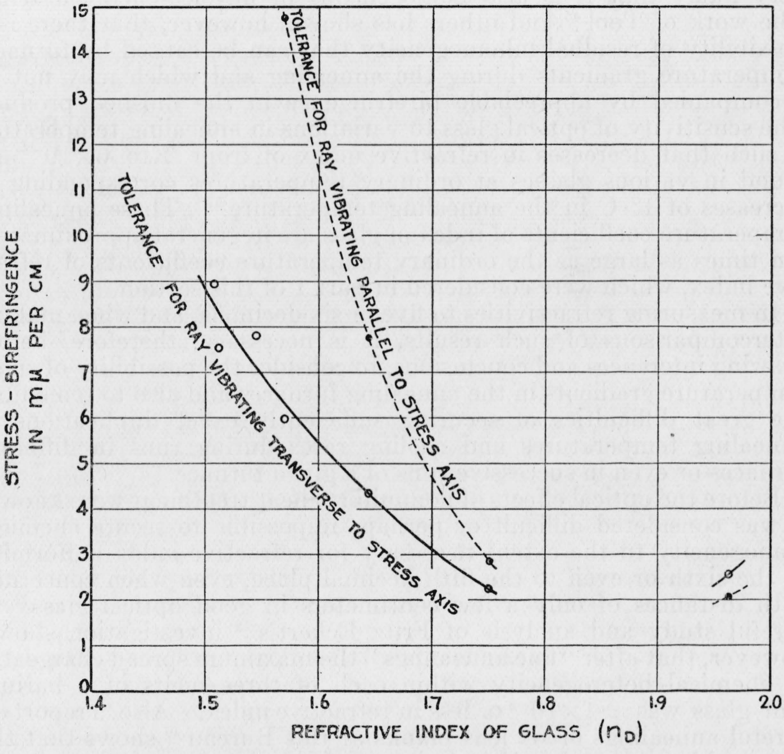

FIGURE 1.—*Tolerances in stress-birefringence for optical glass on which refractive index is measured to* $\pm 1 \times 10^{-6}$.

Where the orientation is indefinite, the safer tolerance is obviously that indicated by the lower curve.

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[44] Pockels concludes that p' must equal q' for some glass containing about 74 percent of PbO (index 1.8+) and consequently from equations 34, 35, and 36 it seems that for p' and q' not zero the crossing of the curves of figure 1 should occur at zero tolerance (at least for all values of σ other than 0.5, which is the limiting value for the case of an incompressible medium). On the other hand, for $\sigma=0.5$ when $p'=q'$, or whenever $p'=q'=0$, the ordinate of the point of crossing appears indeterminate as judged from these equations.

length of permissible phase difference and the resulting requirement [45] that optical glass be uniform in index within ±0.000007 per cm, it seems that tolerance limits of from 5 to 10 mμ birefringence per cm are of a proper order of magnitude for most of the requirements of optical glasses.

3. HEAT TREATMENT, CHEMICAL HETEROGENEITY, AND STRIATION OF GLASS

When a piece of glass has been annealed in such manner that the stress-birefringence is within the tolerances shown in figure 1 it is very likely that it is also homogeneous in physico-chemical sense. The work of Tool [46] and others has shown, however, that there is a possibility of residual inhomogeneity that can be caused by furnace-temperature gradients during the annealing and which may not be accompanied by appreciable birefringence in the finished product. The sensitivity of optical glass to variations in annealing temperature is such that decreases in refractive index of from 2 to 6×10^{-5} are found in various glasses at ordinary temperatures corresponding to increases of 1° C in the annealing temperature.[47] These annealing-temperature coefficients of index of glass are in general approximately ten times as large as the ordinary temperature coefficients of refractive index, which were considered in part 1 of this section.

In measuring refractivities to five or six decimals, and when making intercomparisons of such results, it is necessary, therefore, before drawing inferences and conclusions, to consider the possibility of small temperature gradients in the annealing furnaces and also to remember the great difficulties of securing sufficiently exact duplications of annealing temperatures and cooling rates during runs in different furnaces or even in successive runs of a given furnace.

Before the optical effects of nonuniform heat treatment were known, it was considered difficult or perhaps impossible to secure chemical homogeneity to the extent necessary for refractive-index uniformity to the sixth or even to the fifth decimal place, even when concerned with distances of only a few centimeters in good optical glass. A careful study and analysis of Fritz Eckert's [48] investigation shows, however, that after "fine annealings" the maximum spread chargeable to chemical heterogeneity within each of three melts of a barium flint glass was $\pm1\times10^{-5}$ or less in refractive index. Also, a report on careful annealings of six lens blanks at this Bureau [49] shows that the chemical heterogeneity, if any, was confined entirely to a few units of the sixth decimal place of refractive index.

Such gross and intensely localized heterogeneities as striae do not occur to any large extent in the best optical glass, but it is sometimes desirable to extend minimum-deviation measurements to less perfect glasses. Consequently, it would be of interest to know the extent to which striation can be present without seriously affecting index measurements. Unfortunately little definite information is available.

Striae commonly exist in two well-known forms—as "cords" or "veins" and as sheet striae or "ream." Their optical properties are,

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[45] See page 720 of BS Sci.Pap. **22,** (1928) S572.

[46] A. Q. Tool and C. G. Eichlin. J.Opt.Soc.Am. **4,** 359 (1920); BS J.Research **6,** 525 (1931) RP292.

[47] A. Q. Tool, L. W. Tilton, and E. E. Hill, J.Optical Soc.Am. and Rev.Sci.Inst. **12,** 490–491 (1926). L. W. Tilton, J.Wash.Acad.Sci. **20,** 12–13 (1930). See also Annual Report of the Director of the Bureau of Standards, U. S. Department of Commerce, pages 11, 23, 21, and 25, of years 1925, 1927, 1928, and 1929, respectively.

[48] Z.tech.Physik **7,** 282–287 (1926).

[49] L. W. Tilton, A. N. Finn, and A. Q. Tool, BS Sci.Pap. **22,** 719 (1928) S572.

of course, different from those of the adjacent media, and apparently there is a rather abrupt transition [50] at the interfaces. According to prevailing ideas [51] it may perhaps be assumed that in general the principal and only important effect is a scattering of light, which results in loss of contrast and consequent poor definition of the image of the collimator slit. This is probably true if the striae are present mainly as cords and if they do have abrupt boundaries.

On the other hand, when the striae consist of well-stratified layers or extensive sheets of "ream" the conditions are quite different. Unless the planes of stratification are approximately parallel to the light paths, all of the rays traverse striae and suffer a consequent acceleration or retardation, but it is usually found that an image of the slit is fairly well outlined even when one uses prisms in which such striae are very numerous. If the striae are so thin, or the difference in refractive index so small that beams emerging from adjacent kinds of glass differ in phase by less than one-quarter wave length, then the measured deviation produced by such a composite prism corresponds to that for a similar prism having a fictitious index, n_3, intermediate in value between n_1 and n_2, indices of the "normal" glass and the striae, respectively. In fact, if s is the proportion by volume of the striae present, one may write

$$n_3 = n_1 + s(n_2 - n_1) \tag{37}$$

as an estimated condition which seems probable for the case of a quasi regular composite prism of this type.

Since striae may differ in index from the normal glass by 3×10^{-4} (an average of some values which were observed by Smith, Bennett, and Merritt) it seems that the presence of certain types of striae in amounts exceeding 0.3 percent of the whole volume of glass should be considered a potential source of errors that may appreciably affect the sixth decimal place of refractive-index determinations.

IV. REQUISITE PRECISION IN SOURCE OF RADIATION

It is desirable to know to what extent doublets and complex lines may be used in sixth-decimal-place refractometry, and to decide whether or not it is necessary to specify the conditions under which a source of radiation is operated. For such purposes it is sufficient quantitatively to consider the dispersion in relative index for a few highly dispersive substances.

If the simple Cauchy dispersion formula

$$n - 1 = a + \frac{b}{\lambda^2} \tag{38}$$

is written to approximate (with two constants) the result of experiments over a limited spectral interval it is evident that

$$\frac{dn}{d\lambda} = -\frac{2b}{\lambda^3} \tag{39}$$

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[50] A. A. Michelson, BS Sci.Pap. **15**, 41 (1919) S333.

[51] T. T. Smith, A. H. Bennett, and G. E. Merritt, BS Sci.Pap. **16**, 75 (1920) S373. A. Arnulf, Rev. optique **6**, 6–20 (1927).

can be written to show how refractive index varies with wave length within the specified interval. Consequently, one may consider

$$T_{\Delta\lambda}=\pm\frac{5\lambda^3}{b\times10^7} \tag{40}$$

as a suitable tolerance in wave length of source for a limiting error of $\pm1\times10^{-6}$ in index.

For use with wave lengths measured in angstroms the constant b is seldom as large as $+25$ or $+30\times10^5$ (values for carbon disulphide and densest flint glass of index $n_D=1.92$, respectively, computed for the shortest wave-length region of the visible spectrum) and thus any uncertainty or variation in the source of less than ±0.01 angstroms is not of consequence for wave lengths longer than approximately 4000 A. For the great majority of substances on which refractive indices are precisely determined, the tolerance is appreciably more liberal. Water and fluorite, for example, have the corresponding minimum or safe tolerances of ±0.10 and ±0.13 A, respectively.

V. PRECISION AND ACCURACY ATTAINABLE IN MINIMUM-DEVIATION REFRACTOMETRY

In this and in previous papers[52] many of the difficulties of precise prism refractometry, particularly by the minimum-deviation method, have been discussed. The number, N, of sources of error is fairly large. At least nineteen of them have been quantitatively discussed in these investigations and the discussions are briefly summarized in table 5. Several of the errors, say $(N-N_1)$ of them, are easily held within limits which are small compared with $\pm1\times10^{-6}$ in index. In no respect is it found impossible, and in few if any instances does it seem unreasonably difficult to control or correct within that tolerance limit. With the exception of error arising from incorrect prism orientation, practically all contributions to the final error in index are equally likely to have positive or negative signs in any extensive and well-arranged observational program. Consequently the algebraic sum is never large.

If, as an approximation to the worst case, N_1 of the contributed errors are large compared with the rest and are all about equal in absolute value, say 1×10^{-6}, then the probable error in the final index is $\sqrt{N_1}\times10^{-6}$. For several years the individual tolerances corresponding to $\pm1\times10^{-6}$ have been used in this refractometric laboratory and it seems that probable errors in refractive indices precisely determined by the minimum-deviation method seldom exceed ±2 or 3×10^{-6}. Hence the existence of some five or ten fairly important sources of accidental error is inferred. Whenever less precision is obtained after the expenditures of reasonable effort in the use of fairly good equipment, the difficulty is probably to be sought not in any one or two particularly important sources of error but in a combination of several matters which have been overlooked or deliberately neglected as inconsequential.

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[52] See references listed in table 5.

TABLE 5.—*Summary of sources of refractive-index error that have been quantitatively discussed*

References to BS J. Research			Quantity evaluated or controlled			±Tolerances for various refractivities of sample ($\Delta n=\pm 1\times 10^{-6}$, $A=60°$)				
Volume	Page	Formula	Name	Symbol	Unit	$n=1.3$	$n=1.5$	$n=1.7$	$n=1.9$	Provisory remarks [1]
1929										
2	921	8	Prism angle	ΔA	Second of arc	0.57	0.33	0.22	0.16	
2	921	9	Double deviation	$\Delta 2D$	do	0.56	0.62	0.80	1.5	
1931										
6	72	14	Prism orientation	$P.E.i$	Minute of arc	3.9	3.1	2.7	2.4	(Index error always+).
1933										
11	41	23	Prism surface sagitta	s'	Wave length	0.27	0.14	0.08	0.04	1 cm diam. of surface area.
11	42	24	Prism translation	$P.E.e_0$	Millimeter	1.3	0.7	0.4	0.2	$s'=0.02\lambda$.
11	47	33	Eccentricity of prism-table axis.	ϵ	do	0.3	(Very large)	0.2	0.1	s'=tabulated values.
11	52	45	Collimator focusing	ΔF_C	do	2.9	2.0	1.8	2.7	$f_c=400$ mm, $\epsilon=0.2$ mm.
1934										
13	117	------	Air composition	------	Proportion by volume.	(Relatively large tolerances—see reference cited)				CO_2-free dry air.
1935										
14	400	10	Air temperature	Δt_a	Degree C	0.77°	0.67°	0.59°	0.53°	$t=0°$ C.
14	400	12	Air pressure	Δp_a	Millimeter of Hg.	2.2	1.9	1.6	1.5	
14	401	16	Air humidity	Δv	do	15.	13.	12.	11.	
14	403	21	Abnormal CO_2 in air	Δc	Proportion by volume.	0.005	0.004	0.004	0.003	
14	408	------	Temperature of certain glasses	------	Degree C	------	Soda lime 0.3° Fused quartz 0.1°	Dense flint 0.2°	Densest flint 0.07°	$\lambda=5893$ A.
14	408	------	Temperature of certain liquids.	------	do	Water 0.01°	Many oils 0.002°	CS_2 0.001°	------	$\lambda=5893$ A.
14	411	32	Hydrostatic pressure on glass	ΔP	Atmosphere	------	0.5	0.5	0.5	
14	411	33	Hydrostatic pressure on certain liquids.	ΔP	Millimeter of Hg.	Water 47. Ether 12.	Glycerin 72. Benzene 17.	CS_2 12.	------	
14	412	36	Stress-birefringence in glass	Δn_b	mμ/cm	------	9.	3.	2.	(? at $n=1.8+$).
14	415	37	Striae in glass	s	Proportion by volume.	0.003	0.003	0.003	0.003	$n_2-n_1=0.0003$.
14	416	40	Wave length of light source	$\Delta\lambda$	Angstrom	Water 0.10	Fluorite 0.13	CS_2 0.014	Densest flint 0.010	$\lambda=4000$ A.

[1] For explanations and for other pertinent limitations and conditions, see discussions given in references cited in columns 1 to 3.

It is a much more difficult matter to state precisely what accuracy is attainable. Tests of the accuracy of angle measurement by the use of a prism polished on all three faces are of fundamental importance. Torsion and mechanical strains in the goniometer constitute a particularly dangerous source of systematic error which is seldom entirely constant and cannot always be effectively eliminated. Fortunately, those errors which would be systematic if neglected are automatically replaced by residual accidental errors when proper corrections can be and are applied. In this laboratory no reason has been found for suspecting that residual systematic errors in precise index measurement with a spectrometer are materially in excess of the precision which is attained.

WASHINGTON, January 26, 1935.