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SOURCES OF ERROR IN PRECISE COMMERCIAL REFRACTOMETRY

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ABSTRACT

Exclusive of compensators, the mechanical requirements for accurate refractometry to a few units of the fifth decimal place in index are difficult but not impracticable. Optical requirements are high because the symmetrical use of all apertures is, in general, not possible. If it is necessary to distinguish between index of sample referred to air at t or at t_0, this usually can be done by choice of a relative or an absolute temperature coefficient when correcting for temperature of the refractometer block. For an error of 1×10^{-5} in index of solids, the permissible prism of contact liquid is one-third fringe per centimeter as viewed in the exit pupil of the telescope. The requirements for minimum shielding of critically refracted rays, for absence of certain interference fringes in the field of view, and for surfacing of the illuminating prism are so related with reference to measurements on small samples of liquid that compromises are necessary in the design of precision refractometers.

CONTENTS

I. INTRODUCTION

Critical-angle methods of refractometry offer interesting possibilities of obtaining great sensitivity over a limited range in refractive index on specially designed instruments with carefully determined constants, as is shown by discussions such as those of Guild,[1] Simeon,[2] Smith,[3] Schultz,[4] and Straat and Forrest.[5] Various types of refractometers have been in use for many years in connection with the routine and control analysis of a wide variety of products. Specialized instruments have been developed for the more or less direct

[1] J. Guild, Proc. Phys. Soc. (London) **30**, 157–189 (1918) or Nat. Phys. Lab., Collected Researches **14**, 273–296 (1920).
[2] Frederick Simeon, Proc. Phys. Soc. (London) **30**, 190–203 (1918).
[3] T. Smith, Nat. Phys. Lab., Collected Researches **14**, 297–300 (1920).
[4] H. Schultz, Z. tech. Physik **3**, 90–93 (1922); Z. Instrumentenk. **48**, 26–30 (1928).
[5] H. W. Straat and J. W. Forrest, J. Opt. Soc. Am. **29**, 240–247 (1939).

determinations of such specific substances as sugar, butter, milk, and oils. Such instruments include both the Abbe and the dipping types, but the Abbe type with water-jacketed prisms predominates. This instrument has been more or less standardized and is the most commonly used instrument for measuring refractive indices of liquids and solids.

All these instruments have achromatizers that permit the use of a white-light source, and in this respect they differ from the Pulfrich refractometer,[6] which is much used in the optical-glass industry. The Pulfrich is designed for use with a spectral-line source and is somewhat more suitable for work on solid media than on liquid samples. Formerly it was customary to use Pulfrich or dipping refractometers whenever precise refractive indices were desired, but as a result of the greater convenience of the Abbe type with double prisms, the manufacturers have improved the design of these instruments and to some extent have simplified them so that they can now be used in precision measurements. The chief changes have been finer scale rulings, better bearings, and the omission of achromatizers in some instances. Certain details regarding the careful use of Abbe-type refractometers were recently discussed in another paper.[7] The high precision obtainable in using these instruments has prompted these further investigations of possible sources of inaccuracy.

II. INSTRUMENTAL AND OBSERVATIONAL ERRORS

It is difficult but not impracticable for a manufacturer to standardize and control his product within approximately the tolerances corresponding to ± 0.00005 in refractive index. This is demonstrated by the ability of some manufacturers to approximate these requirements in some instances, especially when concerned with precision refractometers. They have, as a rule, not attempted this high degree of standardization in making the usual type of Abbe refractometer, but even there such accuracy is sometimes approximated. Table 1 gives an idea of the optimum performance that is occasionally found for fourth-decimal-place Abbe refractometers. These examples are selected from numerous tests and represent the product of five manufacturers. In some cases, however, in order to get such good performance it was necessary to eliminate the maladjustment that results when the test slab that accompanies an instrument is incorrectly or inadequately marked. In all cases the scale settings were estimated to better than 0.1 division, and numerous settings and readings were averaged.

When in 1874 Ernst Abbe described the refractometer that now bears his name, he discussed [8] in a direct and simple manner the effects of erroneous constants adopted for a given instrument. Also the above-mentioned papers [9] by Guild, Simeon, Smith, Schultz, and Straat and Forrest cover, to some extent, the same subject. From Abbe's work, and from some of the other papers cited, it is evident that an error of ± 0.00005 in measurement of refractive index of the sample can be caused if the index of the glass block (refracting prism) of the refractometer differs from its supposed value by only ± 0.00006;

[6] A valuable paper by J. Guild on refractometers, with particular reference to the Pulfrich type, was published in 1918. See footnote 1.
[7] L. W. Tilton, J. Opt. Soc. Am. **32**, 371 (1942).
[8] See Gesammelte Abhandlungen von Ernst Abbe, **II**, 136 (Gustav Fischer, Jena, 1906).
[9] See footnotes 1 to 5, p. 311.

also if the refracting angle of the block is in error by about ±10 seconds.

TABLE 1.—*Correction data on exceptionally good Abbe refractometers of the usual type, with achromatizers, that permit readings, by estimation of tenths, to the fourth decimal place of index*

[The product of five manufacturers, including the domestic corporations Bausch & Lomb Optical Co., Industro-Scientific Co., and the Spencer Lens Co., is represented, but in each case the adjustment approximates the optimum and was made irrespective of the particular test plate that accompanied the instrument.]

Line of scale	[a] Required corrections ×10⁵				
	A	B	C	D	E
1.333	0	+6	+1	+1	+7
1.392				+8	
1.395	−3				
1.434	0			+9	
1.459	+2	−4		0	
1.461	+2		0		−6
1.479		−4			
1.480	+1				
1.490				−2	
1.504	−1	−1	−3	−8	
1.515				−8	
1.519	−1		−1		+4
1.522			−1		
1.569	−6	−4	0	−9	+3
1.612	+2	−1	−1	−2	+2
1.656	−4		+1		
1.672	−1	−1	+2	−8	−4

[a] Corrections for water, 1.333, are more often positive than negative because of the negative errors that are likely to be caused by shielding (section VI) or by fringes (section VII).

On a refractometer with an index range 1.3 to 1.7 and for an unfavorable case, a determination of the relative orientation of the telescope and the refracting prism must be accurate to within about ±15″, or for one with index range 1.3 to 1.5 a determination must be accurate to within about ±20″, in order that a resulting error in index of the sample shall not exceed ±0.00005. With reference to most instrumental matters, such as the bearings and the scale rulings of refractometers, the accuracy of orientation and its determination within 15 or 20″ presents no serious problem. For Abbe refractometers of the usual dimensions this accuracy of 15″ in the evaluation of prism orientation means that many lines of the scale must be correctly positioned along the arc within about 10 microns, and for an unfavorable case the axis of rotation of the prism must intersect the sector center within about 25 microns.

Pyramidal error of the Amici prisms in Abbe refractometers causes index readings to differ for a given sample, depending on which of two possible settings of the achromatizer is used. Because of the way in which the two Amici prisms are mounted and rotated, the combined components of the lateral deviations are, in the direction of the resultant dispersion, oppositely directed for the two achromatizing positions, as shown in figure 1, and the mean of the index readings is free from influence of the pyramidal error.

More insidious are the effects of deviations of sodium light by a compensator in the direction of the principal planes. See figure 2. Even in Abbe's time it was considered that critical workmanship could, with certainty, hold this deviation by an Amici prism to within 1′ of arc, and he pointed out the merit of combining prisms having deviations with opposing signs, so that the consequent error in refractive index need never reach 2×10^{-4}. Control of deviation within 30″ is now considered practicable. Nevertheless, in the course of criticial studies on numerous refractometers, including instruments of foreign and of domestic manufacture, the writer sometimes finds instruments of the Abbe type that have a total compensator deviation variation appreciably in excess of 2×10^{-4}, and occasionally it is as high as 2×10^{-3}. In such cases the labor of a precise calibration of the instrument is excessive. Figure 3 shows approximate calibration

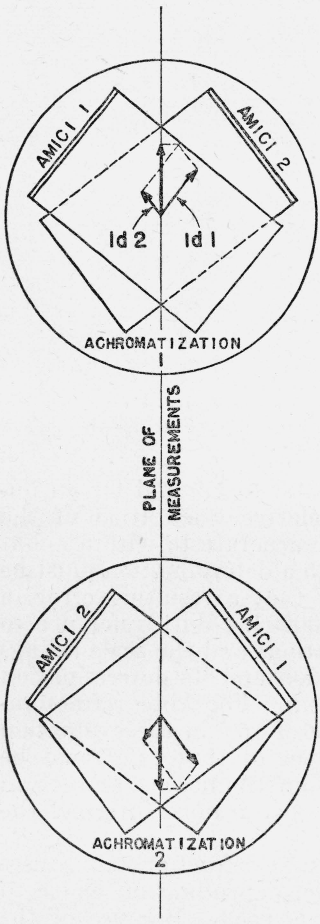

FIGURE 1.—*Effect of lateral deviation (ld) by Amici prisms.*

Mean readings taken after opposite settings of the compensator are free from effects of pyramidal error. See text of this paper; also L. W. Tilton, J. Opt. Soc. Am. **32**, p. 373–74 (1942).

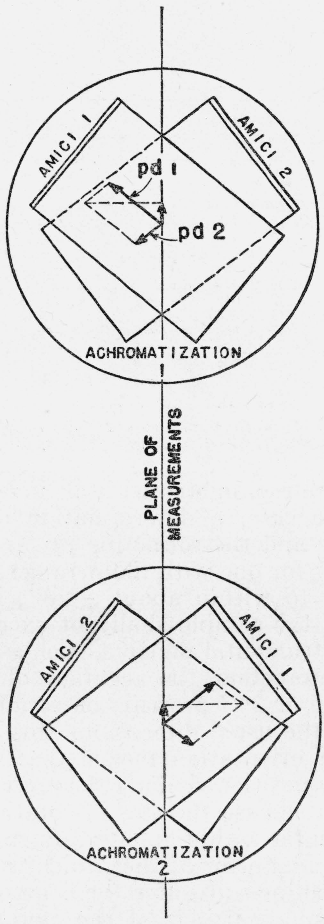

FIGURE 2.—*Effect of principal plane deviation (pd) by Amici prisms.*

Mean readings are free from compensator deviation only if the manufacturer has properly paired the Amici prisms, so that *pd* 1 = −*pd* 2.

curves for an instrument having excessive compensator deviation variation. These curves are averages for the two possible achromatizations that have approximately equal numerical drum readings.

The difficulty of making good compensators for critical-angle refractometers reading to the fifth decimal of index is an important reason for the present tendency to substitute monochromatic sources for white light. However, as a result of his experience with refractometers having specially built compensators, the writer believes that it is not necessary to abandon the use of a white-light source when measuring only *D*-lines index and seeking an accuracy of say ±0.00004 in index. Practically, the cost of making compensators sufficiently accurate for the purpose may be excessive.

The only important observational errors, aside from maladjustment or failure to adjust the instrument to a proper reading for the test

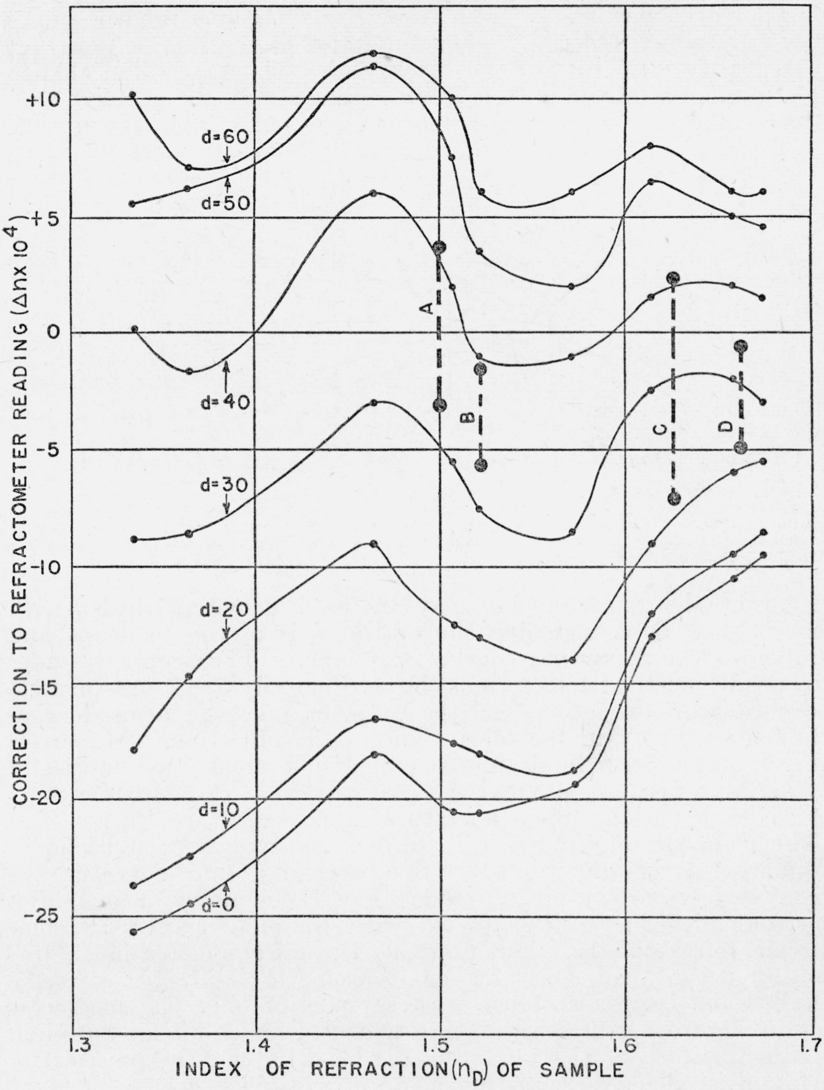

FIGURE 3.—*Calibration curves for refractometer having a defective compensator.*

The required corrections are functions of index and also of the compensator drum reading, *d*. The length of line *A* shows the difference in correction for benzene, which achromatized at a drum reading of 32, and for a sample of glass having exactly the same index, which, however, achromatized at 41. Similarly, lines *B*, *C*, and *D* show, respectively, the differences in correction for tung oil, carbon disulfide, and monobromnaphthaline, as compared to glasses of identical refractivity.

slab, are those committed in setting the refracting prism with respect to the telescope axis and in determining that angular relationship. Certainly the *precision* of setting cross hairs on the critical border is always ample if a reasonably sharp dividing line is obtainable. The writer has found that such optical settings can be made with a probable error of $\pm 6''$ when using a refractometer telescope magnifying only about 2 times, even when the objective is stopped down to an aperture 1 mm in diameter.

The *accuracy* of optical settings is a different matter. The effective telescope apertures used on Abbe refractometers are sometimes necessarily small, especially when the index of the sample does not differ greatly from that of the block. Also, since it is desirable to use a minimum of contact liquid for solid samples, the effective area is often of irregular shape. Thus it is probable that the optical

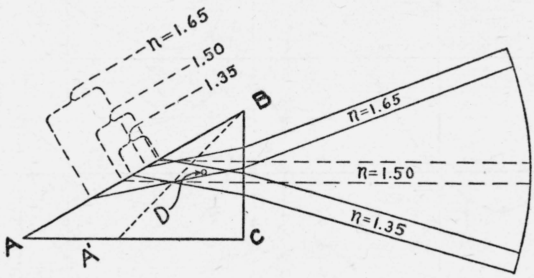

FIGURE 4.—*Mounting of refractometer block with respect to axis of rotation.*

If the image $A'B$ of the AB surface, after refraction by the BC surface, is very near the axis, D, the differences in location of the effective contact areas for various samples are very small, but the telescope aperture may not be filled for high-index samples. If the BC surface is very near the axis, the effective emergent areas coincide approximately, but the contact areas differ. As the effective areas approach A the shielding angle (see fig. 6) increases.

system of the refractometer may be used unsymmetrically with respect to a plane including the optical axis of the telescope and parallel to the refracting edge of the prism. For accuracy under such conditions the telescope must be satisfactorily free from spherical and chromatic aberration, and the eyepiece must be focused accurately for imagery in the focal plane of the objective. Moreover, the refracting prism and the Amici prisms must have optically flat surfaces because, otherwise, there will exist variable refracting angles when various prism aperatures are used.

The principle of symmetrical use of all apertures,[10] so useful in eliminating errors due to aberration, focusing, and curvature of prism surfaces when making index measurement by means of a spectrometer, can not be applied with complete success in commercial refractometry. For example, the refractometer block (refracting prism) can, even for monochromatic light, be correctly installed for symmetrical use with samples of only one particular index. Figure 4 is drawn to facilitate consideration of this question. If either surface of the refractometer block is slightly spherical, a variation in effective refracting angle of the block occurs as slight changes are made in the location of the sample on the face of the block. If at the circumference of an area 1 cm in diameter on the block surface the departure from a plane tangent at the midpoint of the area is only $\lambda/4$, the change in angle can be fully $\pm 10''$ (equivalent to $\pm 5 \times 10^{-5}$ in index of sample) if the displacements of effective aperture can amount to ± 5 mm. This is a matter often

[10] J. Guild, Dictionary of Applied Physics **4**, 113 (MacMillan & Co., Ltd., London, 1923).
L. W. Tilton, BS J. Research **11**, 25–57 (1933) RP575.

overlooked, especially for the small surface of the block from which the rays emerge to the compensator. Since spherical departures from planeness vary as the square of the displacement along a surface, it follows that for equally curved surfaces the prism should be so mounted with respect to the axis of rotation that approximately

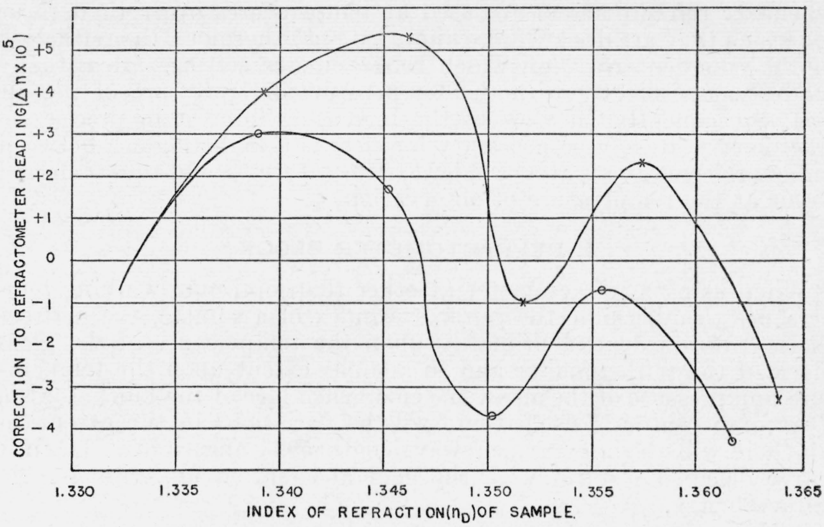

FIGURE 5.—*Correction curves showing the systematic nature of small errors in performance of very good dipping refractometers.*

Each curve is an average for the "*A*" prism of three instruments made by the same manufacturer.

equal displacements of effective aperture shall occur at each polished face of the block. Fortunately, there are some chances of compensating effects. For example, if both prism-surface apertures shift equal distances in opposite directions with respect to the refracting edge, there will be no change in refracting angle, provided the surface curvatures are of like sign and are equal in magnitude.

It seems possible that effects attributable to asymmetrical or extra-axial use of apertures may account for certain systematic errors in the performance of some instruments such as dipping refractometers that have focal-plane scales. The errors for the best dipping refractometers are such that corrections of $\pm 4 \times 10^{-5}$ in index are required as shown in figure 5 for the product of two different manufacturers.

III. TEMPERATURE EFFECTS

It is well known that the average decrease in refractive index of liquids is about 4×10^{-4} per degree centigrade increase in temperature, and it is recognized that temperature must be controlled at the required values, within ± 0.1°C, in order to reduce the direct temperature errors to $\pm 5 \times 10^{-5}$ in index. Otherwise, proper corrections must be applied for the direct errors in index measurements that are caused by the differences between observed and required temperatures. The refractive indices of glasses and other solids are also, although less sensitively, functions of temperature, and thus one cannot entirely neglect temperature control or correction for the direct errors that occur in their measurement.

Of importance also, but seldom mentioned, is the effect of temperature on the blocks or prisms of glass that are the essential parts of refractometers. In this way, somewhat indirect errors are caused whenever refractometers are used at temperatures other than those for which they are designed or calibrated. Futhermore, the refraction of the emergent rays, on which refractometer settings are actually made, varies slightly with the temperature and pressure of the air and, consequently, in view of the increasing interest in precise refractometry, it may be necessary for clearness to distinguish between indices referred to air at a standard temperature, t_0, and those referred to air at the temperature of observation, t.

1. REFRACTOMETER BLOCK

When using a refractometer at other than optimum working temperature to determine the refractive index of a sample, the indirect thermal errors depend primarily upon the temperature of the glass block of the refractometer and to a slight extent upon the temperature and pressure of the air at the emergence face of the block. Also, if a compensator is used, there will be variations in the extent to which it will deviate rays of wavelength 5893 angstroms. Quantitative discussion starts with the general equation for critical-angle refractometry,

$$\overline{n}=\sin A\sqrt{\overline{N}^2-\mu^2\sin^2\vartheta_2'}+\mu\cos A\sin\vartheta_2', \tag{1}$$

where $\overline{n}$ is the absolute index of the sample; A and $\overline{N}$ are, respectively, the refracting angle and absolute index of the block; μ is the index of the air at the emergence face; and ϑ_2' is the emergent angle (positive if emergence be toward the refracting edge). The relative (to air at $t°$ C) index of refraction, $n=\overline{n}/\mu$, for a sample is expressed as

$$n=\sin A\sqrt{N^2-\sin^2\vartheta_2'}+\cos A\sin\vartheta_2', \tag{2}$$

which is merely equation 1 after division by μ, the index of air at $t°$ C, and replacement of $\overline{N}/\mu$ by N.

From equation 2, after partial differentiation with respect to N and neglecting higher orders, there may be obtained, for finite differences, the equation

$$\frac{\Delta n}{\Delta N}=\frac{N\sin A}{\sqrt{N^2-\sin^2\vartheta_2'}}, \tag{3}$$

from which one may compute the error Δn in the relative (to air at $t°$ C) index, n_t, caused by taking readings from a refractometer table or scale that is correct for N at a standard temperature t_0 and not for the existing $N+\Delta N$ at temperature t. Note that the observed ϑ_2', dependent on N and μ, which change with t, corresponds automatically to the existing $N+\Delta N$ at temperature t and to the existing μ. Thus the assumption of constancy for ϑ_2' with respect to N is justified, and with respect to μ the constancy is justified if the air at the emergence face is also at t. The ratio $\Delta n/\Delta N$ has its minimum value, namely

$\sin A$, for a sample with $n=N\sin A$ (which is the condition for normal emergence, namely $\vartheta_2'=\vartheta_2=0$ and $\vartheta_1'=A$) and since, for the usual Abbe-type refractometer, ϑ_2' does not exceed approximately $\pm 25°$, the ratio $\Delta n/\Delta N$ never exceeds $\sin A$ by more than a few parts in a hundred. Consequently, this important error in determining the relative index of any sample at temperature t with respect to air at the same temperature is fairly well represented as

$$\Delta n=\sin A(t-t_0)\Delta N, \tag{4}$$

provided ΔN is now the temperature coefficient of relative index of the refractometer block.

From equation 1, after partial differentiation with respect to N and setting $\mu^2=1$, there is obtained the equation

$$\frac{\Delta\overline{n}}{\Delta\overline{N}}=\frac{\overline{N}\sin A}{\sqrt{\overline{N}^2-\sin^2\vartheta_2}}, \tag{5}$$

from which one may compute the error, $\Delta\overline{n}$, in the absolute index, or the error, Δn_{at_0}, in the relative (to air at t_0) index, n_{at_0}, caused when using a refractometer at t °C. Here the index of the sample at t is referred to air at t_0 (thus its temperature coefficient of index, Δn_{at_0}, is identical with $\Delta\overline{n}$, the temperature coefficient of absolute index of the sample) and the fact that ϑ_2' may be measured in air not at t_0, but perhaps at t, has been ignored. Apparently this is the basis on which it is sometimes customary to write and use values of $\Delta\overline{N}$ rather than ΔN in the practical application of equations such as 4 or 5.

For the Pulfrich refractometer, equation 5 becomes $\Delta\overline{n}=(\overline{N}/\overline{n})\Delta\overline{N}$, and the manufacturers have recommended temperature corrections computed as $\Delta n_{at_{20}}\equiv\Delta\overline{n}=(N/n)\Delta\overline{N}(t-20)$. If, however, it is desired that the measured indices refer to air at t, then values of ΔN should be used instead of $\Delta\overline{N}$. In table 2, on lines designated by roman numerals, there are listed (positive) values of ΔN and $\Delta\overline{N}\times 10^5$, for the spectral lines C, D, F, G', and h, that apply to the three 90° blocks that are customarily used on the Pulfrich refractometer. Other listings relate to 60° blocks on Abbe-type refractometers and to similar glasses. Approximate values for other wavelengths may be obtained by linear interpolation. These data should be used, in the absence of more specific information, when applying equations 4 or 5 for estimating corrections to refractometer readings made at t °C. It should be noted that glasses having similar indices and dispersions do not necessarily have similar temperature coefficients of index.

2. AIR AT EMERGENCE FACE

In order to investigate the extent to which it is permissible to ignore the temperature and pressure of the air at the emergence face of the prism, equation 1 is differentiated, partially with respect to μ, and after dividing the right-hand member by μ, one may write

$$\frac{\Delta\overline{n}}{\Delta\mu}=\frac{n\cos A-\sin\vartheta_2'}{n\csc\vartheta_2'-\cos A'}, \tag{6}$$

TABLE 2.—*Temperature coefficients*[a] *of relative* (ΔN) *and absolute* ($\Delta \overline{N}$) *index of refraction (units of fifth decimal) for refractometer blocks and similar glasses at room temperatures*

Highest index measurable	Block		$\frac{t+t_0}{2}$	λ=6563 A		λ=5893 A		λ=4861 A		λ=4340 A		λ=4047 A	
	N_D	ν*		ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$	ΔN	ΔN	ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$
	1.5045	64.7	30°	0.29	0.16	0.32	0.19	0.38	0.25	0.44	0.31	------	------
	1.5175	64.2	35°	.16	.03	.17	.04	.22	.09	.25	.12	0.28	0.15
1.50	1.5220	58.5	28°	.17	.04	.19	.06	.24	.11	.27	.14	.30	.17
	1.5202	59.6	30°	.34	.21	.35	.22	.40	.27	.44	.31	.48	.35
(I_b) 1.613	1.6220 R, Z	35.9	55°	------	.24	------	.28	------	.39	------	.50	------	------
	1.6227	55.6	33°	.33	.19	.34	.20	.38	.24	.44	.30	.48	.34
	1.6561	33.2	35°	.44	.30	.46	.32	.60	.46	.75	.61	.92	.78
1.70	1.7167	29.4	28°	.66	.51	.74	.59	.94	.79	1.14	.99	1.33	1.17
(II_b) 1.713	1.7474 R, Z	27.8	57°	------	.70	------	.78	------	1.05	------	1.31	------	------
(II_c) 1.746	1.7548	27.6	30°	.77	.62	.85	.70	1.12	0.96	1.36	1.20	------	------
	1.7537	27.6	30°	.70	.55	.81	.66	1.09	.93	1.34	1.18	------	------
1.75	1.7619	27.1	26°	.77	.62	.86	.71	1.17	1.01	1.43	1.27	------	------
(III_b) 1.899	1.9068 R, Z	21.7	?	------	1.03	------	1.21	------	1.71	------	2.26	------	------
(III_c) 1.910	1.9180	21.0	30°	1.12	0.95	1.30	1.13	1.83	1.66	2.44	2.27	------	------

[a] With the exceptions noted, the coefficients were determined with the apparatus described in J. Research NBS **17**, 389 (1936) RP919.

R, Z These coefficients of $\Delta \overline{N}$ as listed on p. 37 of Refraktometrisches Hilfsbuch, by W. A. Roth and F. Eisenlohr (Leipzig, 1911), are almost identical with those recommended by Carl Zeiss for their Pulfrich refractometer. For block I these values are those found by C. Pulfrich, Ann. Physik **45**, 609–65 (1892), for Jena glass O. 544 over the range 11° to 99° C; similarly for block II, they list Pulfrich's values for glass O. 165 over the range 14° to 100° C. Their values for block III agree with interpolations between those found by J. O. Reed, Ann. Physik **65**, 707–41 (1898), for glasses O. 163 and S. 57.

*Abbe's value, $\mu=(N_D-1)/(N_F-N_C)$, is the reciprocal of the relative mean dispersion.

from which it can be shown that index of sample, as observed by use of a refractometer, is independent of the air at the emergence face when $\vartheta_2'=0$, and also for the unimportant case when $\overline{n}=N$. For refractometers with $A=60°$ and for extreme cases with $\vartheta_2'=\pm 30°$, equation 6 becomes

$$\frac{\Delta \overline{n}}{\Delta \mu}=\frac{n-1}{4n-1} \text{ or } -\frac{n+1}{4n+1}, \tag{7}$$

and the ratio $\Delta \overline{n}/\Delta \mu$ varies from $+0.12$ to -0.37 as n varies from approximately 1.7 to 1.3. Since $\Delta\mu=-0.94\times 10^{-6}$ per degree centigrade at room temperature, it is evident that changes of less than $\pm 88°$ in air temperature at the emergence face of the prism on the usual type of Abbe refractometer cannot cause error in excess of $\pm 1\times 10^{-5}$ in measuring samples with indices of 1.7. A corresponding change of $\pm 29°$ C applies for samples with indices of 1.3

For refractometers having blocks with larger refracting angles the tolerances are somewhat less liberal. With a 90° block, as on the Pulfrich refractometer, the right hand of equation 6 becomes $-(\sin^2 \vartheta_2')/n$. Evidently for a ϑ_2' of $-74°$, which occurs when measuring a sample of index 1.30, or 1.47, or 1.66, depending on the particular block that is used, the corresponding tolerances in air temperature at the emergence face are $\pm 15°$, $\pm 17°$, and $\pm 19°$ C, respectively.

To some extent, then, an Abbe-type refractometer, for which $\vartheta_2'=0$ at or near the middle of its index range, is more nearly independent of room temperature than is the Pulfrich type. As a practical matter it is probable that the effect of temperature of air at the emergence face of a refractometer prism is always negligible when one uses a water jacket that partially surrounds the block but not the whole instrument. If the warmer or cooler air can be considered as distributed in successive parallel layers adjacent to the emergence face of the block, then the effective observed ϑ_2' will be determined by room temperature. This view is in accord with the customary practice of using $\Delta\bar{N}$ rather than ΔN in equation 4; thus obtaining a correct n at t referred to air at or near t_0. It is not clear, however, why n should be expressed in this manner. Such relative indices are lower than indices referred to air at t by approximately 1×10^{-5} for every 7° of the excess of t over t_0.[11]

3. COMPENSATOR

The effect of temperature on the compensator of an Abbe refractometer is seldom mentioned. For sodium-lines indices read on Hilger refractometers of the Abbe type at temperatures other than 20° C, the manufacturers recommend a correction, R, expressed in units of the fifth decimal place, as

$$R=r_1(t_1-20)+r_2d(t_2-20), \tag{8}$$

where t_1 and t_2, are, respectively, the temperatures of the Abbe prisms and of the compensator prisms in degrees centigrade, and d is the achromatization reading on a compensator drum having in each quadrant 25 unequal graduations proportional to the cosine of the angular orientation of the compensator. Hilger's accompanying tabulated values of r_1, are the values of $\Delta\bar{n}$ for sodium light that can be computed from equation 5 of this paper. The tabulated values of r_2 vary from 0.062 to 0.018 as n varies from 1.30 to 1.70 and thus, according to the Hilger recommendation, and assuming unusual cases with maximum drum readings of 25, a correction of 10×10^{-5} in index should be added for each temperature rise of from 7° to 22° C of the compensator.

4. ELIMINATION OF COMBINED EFFECTS

There may be some uncertainty in obtaining a suitable value of ΔN, even with the aid of table 2, for use in equation 4 or 5 and, nearly always, there is considerable doubt about values of r_1, r_2, and t_2 for equation 8. Also, there are other sources of uncertainty when using refractometers at other than room temperatures. The temperature distribution in the block may not be uniform and, in addition to causing a variable N, the temperature gradients may temporarily change the refracting angle of the block in an almost unpredictable manner to an extent that may nullify or double the computed corrections. Consequently, it is advisable in precise critical-angle refractometry at other than room temperatures to use a comparison series of standard refractive-index samples for which the indices are known over a range of temperatures and to correct all results on unknowns according to experience with the known samples.

IV. EFFECTIVE WAVELENGTH OF SODIUM LINES

For the most accurate work on a carefully calibrated Pulfrich or other spectral-line refractometer, separation of the D_1 (λ=5896 A) and D_2 (λ=5890 A) lines should, whenever possible, be obtained by

[11] Changes in temperature of air of index μ result in changes in relative index n of a referred medium, according to the equation $\Delta n=\bar{n}\alpha(\mu-1)(t-t_0)/(1+\alpha t_0)$, where $\alpha=1/270$. See J. Research NBS **14**, 397-400 1935) RP 776.

using a slit or knife-edge provided for such purposes, and either D_1 or D_2 may be measured as desired.[12] Obviously, either the tables used or the scale of the instrument must apply to the particular line measured; otherwise corrections must be known or determined. It should also be remembered that the relative positions of D_1 and D_2 in the field of view are reversed whenever the dispersion of the sample exceeds that of the block.

When the D lines are easily resolvable but not separated with a slit or knife-edge, the critical border at the edge of the dark part of the field usually corresponds to D_1 for samples having smaller dispersions and always corresponds to D_2 for samples having larger dispersions than that of the reference block.[13] Ordinarily, however, the critical edges for D_1 and D_2 are not separated by use of a slit or knife edge and often they are so near the limit of resolution that they are seen as a blurred or soft region instead of a sharp edge. Then, according to Guild, one sets on something intermediate between D_1 and D_2. The exact results obtained probably vary with the observer and with the nearness of approach to the limit of resolution, but it would seem that tables usually furnished by the makers, and probably approximately correct for the arithmetic mean of the D lines (D_m, $\lambda=5893$ A), are suitable for use with readings made under these circumstances. The fact that refractometers are used for substances having various dispersions, some larger and some smaller than that of the refractometer block, adds weight to the argument that the scales and tables should be computed for D_m, especially if only one scale or table is provided with a given instrument.

Conditions are more complicated in using white light to measure D-lines indices with an Abbe refractometer or with some of its variants, such as the dipping or immersion type. In all standard Abbe instruments reading by estimation to the fourth decimal place, the whole matter is irrelevant because the index difference (D_m-D_1) seldom if ever exceeds 1×10^{-4} for media having indices of 1.7 or less. A corresponding statement is true for dipping refractometers with index ranges below 1.5 approximately. On the upper index ranges of Abbe refractometers reading to the fifth decimal and on dipping refractometers with high-index prisms, the actual setting for the nominal D-line index is, strictly speaking, influenced slightly by the way in which the compensator functions. It is very difficult to make the combined Amici prisms nondeviating for sodium light with sufficient accuracy for fifth-decimal-place measurements. Fortunately, the question of whether a compensator is more nearly nondeviating for D_1, D_m, or D_2 is not as important as it is to know just which of these wavelengths was used in computing a scale or table of equivalents and then to adjust and use the instrument accordingly. The actual deviation is of less importance because, first, not all of the deviation of a compensator gives rise to effective error,[14] and second, a portion of the effective error is tantamount to a change in length of a scale

[12] See discussion by J. Guild, Proc. Phys. Soc. (London) **30,** 162 (1918) or Nat. Phys. Lab., Collected Researches **14,** 276 (1920).

[13] If the ratio $(n_F-n_C)/(N_F-N_C)$ is lower than the ratio $(N\tan A)/[n\tan A+(N^2-n^2)^{1/2}]$, then the critical border corresponds to D_1. The second of these ratios reduces to n/N for a sample that yields normal emergence from the refractometer block.

[14] Sometimes only relatively small orientations of the compensator are required in order to effect achromatizations for a wide variety of samples, and in other instances the particular class of samples to be measured may achromatize within a very narrow range of drum readings.

and thus is compensatable in making the scale or the table of equivalents.

V. CONTACT LIQUID

The permissible degree of prism in the contact liquid between sample and refractometer block can be conveniently specified in terms of interference fringes. For two successive fringes separated by any distance, a, in a prismatic layer of liquid having a very small refracting angle, ϕ, and refractive index, n_1, the difference in optical path differences is expressible as $\lambda = 2n_1 \Delta t \cos\theta$, where λ is the wavelength in air, $\Delta t = \phi a$ is the difference in thickness for any distance a, and θ is the angle of refraction in the film. Hence, an expression for the number of fringes per unit length of the film is $1/a = (2n_1\phi \cos\theta)/\lambda$. Guild has quantitatively discussed the relation of film angle to the error, Δn, in refractive-index measurement of a sample and finds $\phi = \Delta n/n_1(1-n^2/n_1^2)^{1/2}$. Consequently, the general expression for tolerance in number of fringes per unit length corresponding to an error of 1×10^{-5} in refractive-index measurement is

$$T_{(fringes)} = \frac{2\times10^{-5}\cos\theta}{\lambda(1-n^2/n_1^2)^{1/2}}. \tag{9}$$

If fringes are formed by light that enters the film at nearly normal incidence, $\cos\theta$ is essentially 1, and the number of fringes per unit length is greater than for other conditions. Also, the number of permissible fringes, when formed in this manner, increases as n_1 is chosen more nearly equal to n. Thus, for example, if an observer uses monobromnapthalene as contact liquid when measuring the index of lithium fluoride, 1.39, or of borosilicate crown glass, 1.52, the maximum tolerances in permissible fringes per centimeter when applying the sample to the refractometer block are 0.6 and 0.8 fringes, respectively, for an error of $\pm1\times10^{-5}$ in index measurement. If, however, one chooses a light oil with index of 1.45 when measuring the lithium fluoride, and ethylene bromide with index 1.54 when measuring the crown glass, then the tolerances per centimeter become 1.2 and 2 fringes, respectively.

In best practice, however, the light enters at grazing incidence, the angle of refraction is critical, $\sin\theta = n/n_1$, and thus from equation 9 the tolerance in number of fringes as viewed in the exit pupil is found to be constant for a given wavelength, namely, one-third fringe per centimeter for yellow light.

The possible effect of contact liquid on the cement that holds the refracting prism in its metal water jacket must be considered in precise refractometry. Accumulating evidence indicates that dimensional changes in the cement can cause fluctuating variations in the angular relationship between prism and scale that render the fifth decimal place in refractive index of no value. Since this type of error was first noticed by the writer, reports from another laboratory seem to confirm this opinion. When using successive solid samples it is probable that various degrees of partial saturation can exist in the cement, and thus the resulting errors in index readings are variable. On the other hand, when measuring the index of liquids it is probable that saturation reaches approximate equilibrium, especially after requisite purity in situ has been maintained by repeated samplings and consequent thorough leeching of the cement.

These views are in accord with the possibility of a short-term repeatability for liquids that may explain a growing demand for calibrations and standardizations with liquid samples, regardless of their very high temperature coefficients, ease of contamination, and possible instability. Actually, however, it seems that liquids having identical index, but differing in their effects on the cement, might give different index readings. Thus the accuracy of results with liquids is even more questionable than has previously been supposed, unless a solid sample is used before, during, and after successive saturations and dryings of the cement. Obviously, since various contact liquids may differ in their effects on the cement, it is advisable to use caution in changing from one to another during a given calibration or series of measurements, and it is desirable to ascertain what contact liquids have minimal effects on the cement used on a particular instrument. Also, it is evident that the cements used by manufacturers on precision refractometers should be carefully selected for minimum susceptability to dimensional changes.

VI. SHIELDING

When using solid samples the rays at truly grazing incidence in the sample may not exist because of improper extent or location of the source, improper preparation of sample, excess of contact liquid, or because the contact surfaces are below the level of the adjacent cement or metal.

Shielding of the rays that might be critically refracted can occur even when working with liquids. Since the liquid layer of the sample must have finite thickness and also be limited in its extent, the limiting rays cannot be truly grazing but are necessarily shielded in some degree, as illustrated in figure 6. Abbe shows that when the actual angle of incidence in the liquid is $[(\pi/2)-E]$ the index determined is erroneously low by $nE^2/2$. Thus with a shielding angle $E=25'$ (i. e., 0.0073 radians) and for $n=1.7$, the resulting error is less than 5×10^{-5}. Assuming the layer of sample is as thick as 0.10 or 0.15 mm, the shielding angle cannot be as large as 25′ provided the ray paths in the sample are as long as 14 and 21 mm, respectively.[15] To reduce this error to 1×10^{-5} when using those thicknesses, the corresponding ray paths must be 29 and 43 mm. Possibly, however, there is sufficient multiple internal reflection and scattering to produce some illumination at truly grazing incidence. Otherwise it would seem necessary, or at least advantageous, in the design of refractometers for precise measurements, to provide ample length of the hypotenuse faces of the Abbe prisms. In any case it is advisable to use sufficient liquid to permit transmission over a goodly portion of the prism face even though the effective aperture is small.

VII. HERSCHEL FRINGES

A troublesome phenomenon in precise refractometry of liquids is the production of Herschel interference fringes in the thin layer of liquid between the Abbe prisms. These fringes are observable in the telescope as narrow dark bands in the light half of the field, and there is danger that some of them may be so close to the critical border

[15] A corresponding shielding error ascribable to the curvature of the contact surface of solid samples is almost negligible if the contact surface merely approximates optical planeness.

as to appear continuous therewith. The consequent errors are maximal for lowest index liquids.

Originally, both prisms of the Abbe refractometer had polished surfaces and Abbe[16] relied entirely on adequate prism separation for the avoidance of these interference fringes. Later, Pulfrich[17] in-

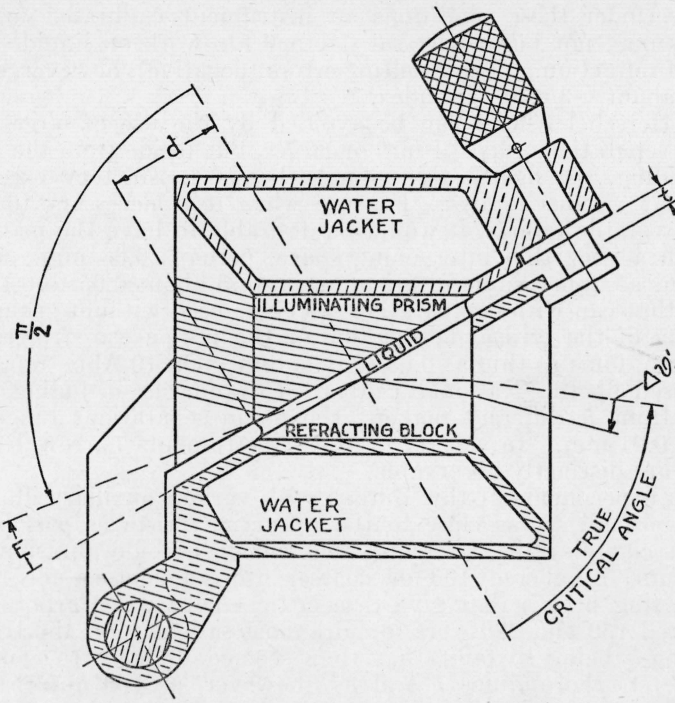

FIGURE 6.—*Geometrical shielding of critical rays caused by separation of Abbe prisms.*

For a sample thickness, *t*, of 0.10 mm (greatly exaggerated here) the distance, *d*, from effective aperture to edge of ground-glass surface must be 14 mm or more in order that the shielding angle, *E*, shall not exceed 25′, and the resultant error in emergent rays, ϑ'_2, shall not exceed 5×10^{-5} in refractive index.

troduced a modification by fine-grinding the surface of the illuminating prism in order to avoid well-defined and disturbing images of the source and also to avoid the interference fringes with which he associated the name of Mascart.

If, however, the surface of the illuminating prism is too finely ground, or if it lies too near the polished surface of the refracting prism when the two prisms are clamped together for use with liquid samples, then Herschel interference fringes may still be visible in the light half of the field near the critical edge or border. These fringes are formed by interference between directly transmitted light and light that is multiply reflected between the prism surfaces at angles very near the critical value. The finer the grinding, the sharper is the contrast between the light and dark fringes.[18] The closer the prism surfaces and the lower the optical density of the intervening liquid

[16] Gesammelte Abhandlungen von Ernst Abbe, **II**, 149, 150 (Gustav Fischer, Jena, 1906).
[17] Z. Instrumentenk. **18**, 107 (1898).
[18] See E. Gehrcke, Handbuch der Physikalischen Optik **1**, 392 (Johann Ambrosius Barth, Leipzig, 1927).

layer, the greater is the distance between successive bright fringes and from the true edge to the first bright fringe. The width, separation, and visibility of the fringes varies, also, with the degree of inclination of the prism surfaces. Consequently, in many refractometers of the double-prism type the true edge is masked and cannot be distinguished from the edge of the first or some succeeding bright fringe. Under these conditions an instrument calibrated for solid samples may not be equally satisfactory for work on liquids of low index of refraction. The resulting errors (negative), however, seldom exceed about -3×10^{-4} in index.

The Herschel fringes can be avoided by the use of large prism-surface separations, say 0.1 mm or larger, but (aside from the danger of shielding, see fig. 6) this is not always satisfactory except for somewhat viscous liquids. For use when it is necessary to retain thin or volatile liquids, it would be desirable to have the prism pair set with a very thin intervening space, perhaps 0.03 mm. Abbe [19] mentions as upper limits of prism separation about 0.05 to 0.10 mm; values that can with comparative safety be used without geometrical shielding of the critical border line or the presence of fringes. He used, also, films as thin as 0.03 to 0.05 mm. On 10 Abbe refractometers used at the National Bureau of Standards, including instruments from 5 different makers, the prism separations range from 0.02 to 0.21 mm. In several of these instruments narrow Herschel fringes are distinctly observable.

From experiments at this Bureau with various auxiliary illuminating prisms, all set as close to the refracting prism as was possible without clamping, it was found that silicon carbide abrasives (carborundum) numbered 100 or coarser are satisfactory for making illuminating prisms that give true critical borders. Carborundums numbered 150 and 220 were found almost satisfactory, the traces of the fringes being so faint that they seemed unlikely to cause any trouble. Carborundums *F* and *FF*, however, proved unsatisfactory for such extremely close prism settings. Likewise, emery in sizes numbered 140 and 200 (standard mesh) and 302 and 304 (Am. Optical Co.) were tried without success in seeking a fine-ground flat surface that can be set very close to the refracting prism without the production of fringes or other shielding effects to an extent that is fatal for accurate fifth-decimal-place refractometry.

Coarsely ground surfaces are, however, somewhat objectionable in this connection, because they are not easily and thoroughly cleaned between successive applications of a series of liquid samples. Trials with concavely surfaced lenses as illuminating prisms showed that the character of the fringes was favorably changed by slight curvatures, perhaps because the greater glass separations permitted greater thickness of the liquid layer at the effective aperture. Consequently, the use of concave surfaces made with the finer abrasives was tried. With emery numbered 140, 200, and 302, cylindrical surfaces with axes lengthwise of the illuminating prism and with radii of 525 mm, were successively ground and found entirely satisfactory. Also, with emery 302 a similar surface having a radius of 1,050 mm was made and found almost satisfactory. The prism width used in these experiments was 18 mm, and the maximum prism separations along

[19] Gesammelte Abhandlungen von Ernst Abbe, **II**, 150. (Gustav Fischer, Jena, 1906).

the axes of the surfaces are therefore approximately 0.08 and 0.04 mm for the curvatures mentioned.

After the above-described preliminary experiments the prism of a fifth-decimal-place refractometer was ground with 150 emery on a cylindrical tool with a 700-mm radius and the lateral edges flattened for a width of 1.5 mm on each side. This illuminating prism was set so that when clamped the flattened lateral edges were about 0.02 or 0.03 mm from the polished face of the refracting prism. The maximum separation along the axis of the ground surface was then about 0.05 mm, or 0.002 in. While this value is perhaps a little greater than desired when the ground surface is flat, it is found to be more or less satisfactory under these conditions for briefly retaining liquids such as ether, alcohol, and hexane, provided a sufficiently large sample of the liquid be applied. However, with small samples, or after partial evaporation takes place, no satisfactory edge is obtained.

VIII. SUMMARY

Those sources of error that have been quantitatively treated in this paper are briefly summarized in table 3, together with tolerances that correspond in each individual case to an error of $\pm 1 \times 10^{-5}$ in refractive index of sample (instead of $\pm 5 \times 10^{-5}$ that has been frequently used in the text). Sources numbered 1, 2, 5, 6, 7, and 12 are primarily of interest in the construction of refractometers. Number 9 can, almost always, be neglected. The user should, at least once, consider 7, 12, and also the possibility of compensator defects, for each instrument that he uses. Those requiring almost constant attention are 3, 4, 8, 10, 11, and, of course, the possibility of the shielding of those rays that alone can correspond to critical-angle phenomena.

TABLE 3.—*Summary of sources of refractometer error that have been quantitatively discussed*

Page of this paper	Source number	Quantity evaluated or controlled			Plus or minus tolerances for various indices of sample ($\Delta n = \pm 1 \times 10^{-5}$; Abbe-type refractometer, $A=60°$ and $N=1.75$, unless otherwise noted)			
		Name	Symbol	Unit	$n=1.3$	$n=1.5$	$n=1.7$	Provisory remarks
312	1	Index of block	ΔN		0.00001	0.00001	0.00001	
313	2	Angle of block	ΔA	Seconds of arc.	1.8	2.3	5.0	For all values of A.
313	3	Zero adjustment	Δn		0.00001	0.00001	0.00003	Test slab of $n=1.5$.
313	4	Prism orientation	$\Delta \vartheta'_2$	Seconds of arc.	3	4	10	
313	5	Position of scale ruling		Microns	1.9	2.3	5.6	12-cm scale arm.
313	6	Linear eccentricity		do	5		11	Correct adjustment at $n=1.5$.
316	7	Block surface sagitta [1]		λ	0.04	0.05	0.10	±5-mm displacements.
319	8	Block temperature	Δt_N	°C	1.5°	1.5°	1.4°	
320	9	Air temperature	Δt_a	°C	29°	Very large	88°	Abbe; $A=60°$; $N=1.75$.
320	9	do	Δt_a	°C	15°	17°	19°	Pulfrich; $A=90°$; $\vartheta_2'=74°$.
321	10	Compensator temperature	Δt_c	°C	0.64°	0.85°	2.2°	Hilger; maximum compensation.
323	11	Contact wedge	ϕ	Fringes/cm	.3	.3	0.3	Viewed in exit pupil.
324	12	Shielding angle	E	Minutes of arc.	13.5	12.5	12	

[1] For an area 1 cm in diameter.

After careful experiments extending over a period of years and involving much testing and other precise work on numerous refractometers of various kinds and makes, including the Pulfrich and the dipping types, the writer is unable to say that he has attained an accuracy better than ± 2 or 3×10^{-5} in critical-angle refractometry of solid samples on commercial instruments.[20] In fact, speaking only of precision, it has often seemed impossible to do better than ± 1 or 2×10^{-5}, even when merely repeating observations with the same solid sample on a given instrument after independently resetting the fringes for the elimination of wedge effect in the contact liquid. These statements do not relate entirely to "single observations" but sometimes refer to the means of four or more scale readings (the number depending on the sensitivity of the particular instrument) made after as many settings of the cross hairs on the critical border. Thus these estimates of accuracy and precision are to a large extent independent of the ordinary accidental errors of settings and readings. Moreover, they refer to work done with considerable care in order to eliminate systematic error. More or less attention has at times been given to temperature effects, nature of contact liquid, shielding effect of excess contact liquid, orientation of fringes, width of fringes, location of effective area of contact on face of block, curvature of sample surface, curvature of block faces, curvature of faces of Amici prisms, chromatic parallax, spherical aberration, etc., without finding that any one of them seemed especially pertinent to the problem at hand. Probably, then, it is the combined effect of a number of these sources of error that occasionally can cause sufficient trouble to prevent the consistent attainment of a higher precision and accuracy that sometimes seems almost within reach.

WASHINGTON, February 12, 1943.

[20] The errors and imprecisions experienced in the refractometry of very small samples of liquid are, on the average, larger than those found for work on solid media. This is probably because of the higher temperature effects and the difficulty of preventing contamination.