

# Refractivity of Lithium Fluoride With Application to the Calibration of Infrared Spectrometers<sup>1</sup>

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The refractivity of lithium fluoride was measured from 0.4 to 5.9 microns and expressed for 23.6° C by a four-constant dispersion formula by which an interpolation table was prepared for included wavelengths. The temperature coefficient was determined as  $-1.63 \times 10^{-5}$  (constant within  $\pm 0.05$ ) for the visible region and a table of indices made for 20° to 60° C at equal intervals of  $\lambda$  from 0.4 to 0.7 micron. Most of the observed indices agree with the tabulated values within  $\pm 3 \times 10^{-6}$  for the visible region and  $\pm 3 \times 10^{-5}$  in the infrared. In calibrating an infrared spectrometer simple empirical relationships between drum reading,  $D$ , and wavelength are not entirely reliable. Three steps are recommended: (1) the expression of  $D$  in terms of  $E$ , the emergent angle of energy from the prism; (2) expression of  $E$  in terms of refractive index; and (3) the obtaining of the indices or their expression as a function of  $\lambda$ . The first step requires at least two constants, one for angular equivalent of the screw and another for the particular Littrow-mirror orientation for  $D=0$ . The second requires knowledge of the refracting angle of the prism and its orientation with respect to the incident energy. The adequate expression of index as a function of wavelength usually requires four constants.

Lithium fluoride is preferable to calcium fluoride for use in prismatic form in the infrared to about  $6\mu$  because of its much greater dispersion. Synthetic lithium fluoride has been available for 20 years or more, and data on its indices of refraction have been published by Littman [1]<sup>2</sup> for the visible and to  $3\mu$ ; also by Hohls [2] to 3 and 4 decimals from 0.546 to  $12\mu$ . The 4-decimal indices by Gyulai [3] are chiefly for the ultraviolet region.

Formerly, the making of lithium fluoride was carried out completely in an atmosphere of air, whereas more recently a vacuum technique has been used, with a concomitant change in some of the optical, mechanical, and thermal properties of the product [4]. Thus some question has arisen regarding possible differences in the refractivity of various specimens of this material. No final answer should be made at present, but it can be said that only small variations in the fifth decimal of refractive index have been found at this Bureau among six or more prisms of synthetic lithium fluoride that have been carefully measured in the visible region, including one that has been on hand for about 12 years and used as a secondary standard.

On this NBS standard prism refractive-index measurements were made in the visible region for five wavelengths in four groups of experiments at temperatures that averaged 28.6°, 31.6°, 52.6°, and 59.9° C. On two other prisms, at seven wavelengths, dispersion measurements were made at temperatures near 25° C and represented by a four-constant Ketteler-Helmholtz dispersion formula with the parameters adjusted by least squares. These prisms were lower in index than the above mentioned

standard by only  $1.4 \times 10^{-5}$ , and no differences in dispersion could be detected. From these data, by the process of graduation, table 1 of the average refractivity of lithium fluoride was prepared at 5-deg intervals from 20° to 60° C at intervals of 100 Å in wavelength from 4000 to 7000 Å.

These data in the visible region yield tentative values for the temperature coefficient of refractive index. The average found for data on five wavelengths and for a very small temperature interval near 30° C is  $-16.4 \times 10^{-6}$  per 1° C, and similarly for a small temperature interval near 56° the average is  $-17.5 \times 10^{-6}$ . Some of the same data yield an average value of  $-16.3 \times 10^{-6}$  for the interval 31.6° to 52.6° C. For red light the values are somewhat larger than for violet, perhaps 5 percent larger. These values agree well with the coefficient of  $-16.67 \times 10^{-6}$  published by Littman, and are plotted in figure 1 for comparison with similar values reported by Radhakrishnan [5].

The coefficients in the right-hand columns of table 1 were obtained from differences smoothed in such manner that the results approximate average values for the derivatives. The change in index with wavelength applies almost equally well at all listed temperatures. The change with temperature is more nearly valid at the mid temperature of 40° C.

The refractive-index measurements herein reported for the infrared region were made on a prism with faces about 6 by 8 cm and a refracting angle,  $A$ , of  $72^{\circ}2'24''$  as ground and polished by the Perkin-Elmer Corp. of Glenbrook, Conn. The first work was done on a minimum-deviation spectrometer for several wavelengths in the visible region in order to compare its refractivity with that of lithium fluoride prisms that had been previously measured. These index values proved to be intermediate with respect to, and closely an average of, those previously determined for other specimens. They are expressed with approximately sixth-decimal-place precision in

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<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

TABLE 1. *Refractivity of lithium fluoride at various temperatures in the visible region*

$$\left[ \text{The column for } 25^\circ \text{ C was computed as } n^2 = 1.9261590 - 0.00705034\lambda^2 + \frac{0.00471433}{\lambda^2 - 0.0094731} \right]$$

Wave length $\lambda$	Temperature, °C									$\frac{dn}{d\lambda} / A$	$\frac{dn}{dt} / ^\circ \text{C}$
	20°	25°	30°	35°	40°	45°	50°	55°	60°		
4000	1.398772	1.398696	1.398619	1.398541	1.398462	1.398382	1.398301	1.398219	1.398136	$6.18 \times 10^{-6}$	$15.8 \times 10^{-6}$
4100	1.398180	1.398104	1.398027	1.397949	1.397870	1.397790	1.397709	1.397627	1.397544	5.72	15.8
4200	1.397630	1.397554	1.397477	1.397399	1.397320	1.397240	1.397159	1.397077	1.396994	5.31	15.9
4300	1.397118	1.397042	1.396965	1.396887	1.396808	1.396728	1.396647	1.396565	1.396482	4.94	15.9
4400	1.396642	1.396566	1.396489	1.396411	1.396332	1.396252	1.396171	1.396089	1.396006	4.61	16.0
4500	1.396197	1.396121	1.396044	1.395966	1.395887	1.395807	1.395726	1.395644	1.395561	4.31	16.0
4600	1.395780	1.395704	1.395627	1.395549	1.395470	1.395390	1.395309	1.395227	1.395144	4.04	16.1
4700	1.395389	1.395313	1.395236	1.395158	1.395079	1.394999	1.394918	1.394836	1.394753	3.79	16.1
4800	1.394965	1.394946	1.394868	1.394789	1.394709	1.394628	1.394546	1.394463	1.394379	3.57	16.2
4900	1.394677	1.394600	1.394522	1.394443	1.394363	1.394282	1.394200	1.394117	1.394033	3.37	16.2
5000	1.394350	1.394273	1.394195	1.394116	1.394036	1.393955	1.393873	1.393790	1.393706	3.19	16.3
5100	1.394041	1.393964	1.393886	1.393807	1.393727	1.393646	1.393564	1.393481	1.393397	3.02	16.3
5200	1.393749	1.393672	1.393594	1.393515	1.393435	1.393354	1.393272	1.393189	1.393105	2.86	16.3
5300	1.393479	1.393395	1.393317	1.393238	1.393158	1.393077	1.392995	1.392912	1.392828	2.71	16.4
5400	1.393208	1.393131	1.393053	1.392974	1.392894	1.392813	1.392731	1.392648	1.392564	2.58	16.4
5500	1.392958	1.392880	1.392801	1.392721	1.392640	1.392558	1.392475	1.392391	1.392306	2.46	16.5
5600	1.392719	1.392641	1.392562	1.392482	1.392401	1.392319	1.392236	1.392152	1.392067	2.34	16.5
5700	1.392491	1.392413	1.392334	1.392254	1.392173	1.392091	1.392008	1.391924	1.391839	2.23	16.5
5800	1.392273	1.392195	1.392116	1.392036	1.391955	1.391873	1.391790	1.391706	1.391621	2.13	16.6
5900	1.392065	1.391987	1.391908	1.391828	1.391747	1.391665	1.391582	1.391498	1.391413	2.04	16.6
6000	1.391865	1.391787	1.391708	1.391628	1.391547	1.391465	1.391382	1.391298	1.391213	1.96	16.6
6100	1.391673	1.391595	1.391516	1.391436	1.391355	1.391273	1.391190	1.391106	1.391021	1.89	16.6
6200	1.391489	1.391410	1.391330	1.391249	1.391167	1.391084	1.391000	1.390915	1.390829	1.82	16.7
6300	1.391312	1.391233	1.391153	1.391072	1.390990	1.390907	1.390823	1.390738	1.390652	1.75	16.7
6400	1.391141	1.391062	1.390982	1.390901	1.390819	1.390736	1.390652	1.390567	1.390481	1.68	16.7
6500	1.390976	1.390897	1.390817	1.390736	1.390654	1.390571	1.390487	1.390402	1.390316	1.62	16.7
6600	1.390811	1.390738	1.390658	1.390577	1.390495	1.390412	1.390328	1.390243	1.390157	1.57	16.7
6700	1.390663	1.390584	1.390504	1.390423	1.390341	1.390258	1.390174	1.390089	1.390003	1.52	16.7
6800	1.390513	1.390434	1.390354	1.390273	1.390191	1.390108	1.390024	1.389939	1.389853	1.47	16.7
6900	1.390370	1.390290	1.390209	1.390127	1.390044	1.389960	1.389875	1.389789	1.389702	1.43	16.7
7000	1.390229	1.390149	1.390068	1.389986	1.389903	1.389819	1.389734	1.389648	1.389561	1.39	16.7

the visible for a temperature of 23.6° C by the formula

$$n^2 = 1.9262231 - 0.00705034\lambda^2 + \frac{0.00471433}{\lambda^2 - 0.0094731}$$

where, as usual in such equations,  $\lambda$  is to be expressed in microns.

This formula was used in computing the index 1.39102 of this prism for the cadmium red line,  $\lambda = 6438 \text{ \AA}$ , which is the basic reference point in the index measurements for the infrared region. Also, to insure that the slope of the dispersion curve would be well controlled at the short-wavelength end, the indices computed by this formula were used as "observed" values for seven other wavelengths in the visible region.

The method used for index measurements is the same as that already described for measurements on crystals of thallium bromide-iodide [6] and on a crystal of silver chloride [7]. That is, briefly, the prism was installed with the aid of an auxiliary prism at an angle of known incidence on an infrared spectrometer equipped with a Littrow mirror; a thermocouple was used and a measure of the received energy was recorded on a Speedomax potentiometer. The incidence angle,  $i$ , for which the prism was installed was  $54^\circ 51' 28''$ , which corresponds fairly well to  $(A+D)/2$  at minimum deviation for the cadmium red line. By ray tracing, one computes an angle of emer-

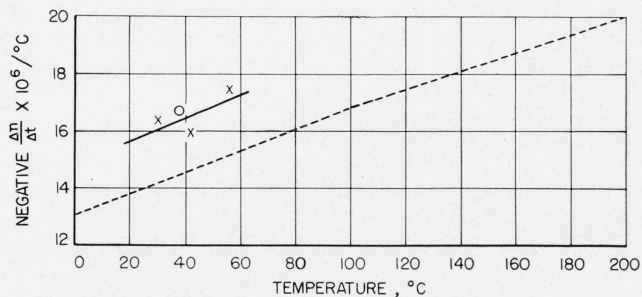


FIGURE 1. *Temperature coefficient of refractivity of lithium fluoride (averages for visible region).*

For red light the values are somewhat larger than for violet, perhaps 5 percent larger. X, NBS; O, Littman ( $n_D$ ); -----, Radhakrishnan.

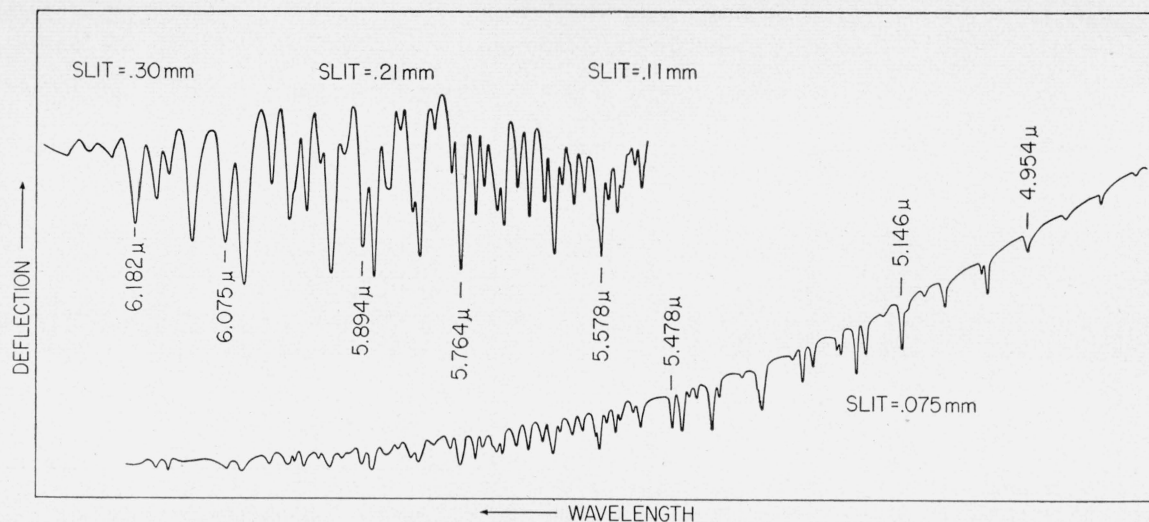


FIGURE 2. Infrared absorption spectrum of water vapor in the 5- to 6- $\mu$  region as measured with a lithium fluoride prism. The upper curve was obtained with automatic slit control for constant radiant energy. The lower curve was recorded with a constant slit.

gence,  $E_0$ , of  $54^\circ 54' 55''$  for the initial conditions at  $\lambda = 6438 \text{ \AA}$ .

The angular increments for the Littrow mirror, between the initially and the subsequently recorded energy maxima and minima, when applied to the initial  $E_0$  give approximate values of  $E_\lambda$  for use in computing indices by the equations

$$\left. \begin{aligned} \cot i' &= \cot A + \frac{\sin E}{\sin A \sin i'} \\ \text{and} \\ n &= \sin i (1 + \cot^2 i')^{1/2}. \end{aligned} \right\} \quad (1)$$

If the entrance and exit slits of the infrared spectrometer subtend an angle at the collimating mirror, it is necessary to make appropriate correction for the fact that one-half of the corresponding angle at the face of the Littrow mirror is not constant as wavelength varies. The index-of-refraction measurements were made in the infrared region by the use of a Perkin-Elmer infrared spectrometer. The prism remains stationary, and different regions of the spectrum are obtained by rotation of a Littrow mirror. A new-type thermocouple, developed by the Perkin-Elmer Corp., was used as the detector. It was used with both continuous and modulated radiant energy. Final drum readings, however, were obtained by slow manual control of the drum near the maxima of deflections, in order to avoid errors caused by small time lags in the response of the pen to changes in energy at the detector.

The wavelengths used in the index measurements in the visible and near infrared region were obtained by the use of the radiant energy from an FH-4 mercury-cadmium lamp. Several lines from this source in the visible and near infrared region are sufficiently intense that they may serve as precise standards for determining the relationship of the Littrow mirror angle and wavelength. In table 2

are listed 15 lines of the spectrum of Hg and Cd that have been used for the measurement of the indices of refraction of LiF.

In the region from 2.7 to 6  $\mu$  nine absorption bands of methanol, polystyrene, carbon dioxide, and water vapor were used for the standard wavelengths. The wavelengths of the two absorption bands of methanol were taken from the work of Borden and Barker [8]. The values of indices of refraction experimentally determined by the use of 2.7144- and 4.866- $\mu$  absorptions of methanol differ by  $+7 \times 10^{-5}$  and  $-9 \times 10^{-5}$  from the adjusted values obtained by the use of the empirical equation (2). There may be a small error in the grating determinations of these two wavelengths.

The atmospheric water vapor absorption spectrum was recorded from 4.9 to 6.2  $\mu$ . The wavelengths of the lines were selected from the measurements of Plyler and Sleator [9] and H. H. Nielsen [10]. While there is some doubt as to the correctness of the wavelengths to the fourth decimal place, the accuracy is sufficient for the determination of these indices of refraction of LiF in the 5- to 6- $\mu$  region. In figure 2 there is shown a recording of the water vapor spectrum when medium amplification is used.

The upper curve was obtained when the automatic slit control was in operation, thus making it possible to hold the radiant energy almost constant. Because of the absorption of the prism material and its increase in dispersion with wavelength, it was necessary to increase the slit width by a factor of 3 in going from 5.50 to 6.2  $\mu$ . The lower curve represents the recording of the water vapor spectrum with a constant slit. The wavelengths of some of the lines are marked on the graph. The numerical values are expressed in microns and are given to the third decimal place.

The refractive indices as computed from the observed data by eq (1) were adjusted by least squares through determination of the parameters of a four-

TABLE 2. Observed and computed data on index of refraction of LiF (23.6° C)

Wavelength	Source or absorbing medium	Computed index	(o-c)	Drum reading in turns × 100	
				Observed	Computed
0.4047	Hg	1.39842	+2 × 10 <sup>-5</sup>		
.4358	Hg	1.39678	0		
.4678	Cd	1.39542	0		
.4800	Cd	1.39497	0		
.5086	Cd	1.39403	0	2271.4	2271.1
.5461	Hg	1.39300	0	2244.5	2243.6
.5780	Hg yellow (mean)	1.39226	0	2223.8	2224.0
.6438	Cd	1.39101	+1	2191.8	2191.1
1.0140	Hg	1.38700	-1	2085.5	2085.4
1.1287	Hg	1.38609	+1	2062.3	2062.0
1.5295	Hg	1.38296	0	1980.9	1980.9
1.8131	Hg	1.38052	-1	1917.5	1917.9
1.9701	Hg	1.37904	0	1879.6	1800.0
2.2493	Hg	1.37616	-3	1805.0	1806.2
2.3254	Hg	1.37531	-1	1783.9	1784.6
2.7144	CH <sub>3</sub> OH	1.37056	a+7	1665.5	1666.3
3.2432	Polystyrene	1.36291	-1	1472.0	1473.6
3.5078	do	1.35854	+2	1365.1	1365.9
4.258	CO <sub>2</sub> (center)	1.34410	+3	1015.1	1016.2
4.866	CH <sub>3</sub> OH	1.33001	a-9	680.2	681.4
5.1456	H <sub>2</sub> O vapor	1.32277	0	515.0	515.5
5.4638	do	1.31392	+2	313.5	312.5
5.7637	do	1.30496	-2	110.7	109.3
5.8944	do	1.30086	+3	20.5	17.1

<sup>a</sup> These larger residuals, +7 and -9 × 10<sup>-5</sup>, both for the wavelengths defined by absorption of methanol, would vanish if the wavelengths were in error by +0.0056 and -0.0036 μ, respectively.

constant Kettler-Helmholtz dispersion formula as limited to one infrared and one ultraviolet Sellmeier term. The result is

$$n^2 = 7.0537595 - \frac{4091.74975}{797.8925296 - \lambda^2} + \frac{0.00492029}{\lambda^2 - 0.0053160} \quad (2)$$

which is preferable in computations to its equivalent form

$$n^2 = 1 - \frac{5.1281966\lambda^2}{797.8925296 - \lambda^2} + \frac{0.92556295\lambda^2}{\lambda^2 - 0.0053160} \quad (3)$$

The agreement between the indices computed by this dispersion formula and those observed is excellent, as shown by the residuals tabulated in table 2 except for the two instances in which methanol was used. We think that the wavelengths for these two observations are slightly inaccurate and suggest that 2.7088 and 4.870 μ are better values than those listed in table 2 and used in computing the index data.

Figure 3 shows the results of this work on an infrared spectrometer compared with previously reported values of the index of lithium fluoride, the present observed values being represented by circles and the computed values by the line Δn=0. Table 3 expresses these computed values in a form for convenient interpolation at any value of λ from 0.5 to 6.0 μ.

The precise fitting of these data by formula (2) is, we think, the first accurate representation of index of a solid by four constants over a comparable

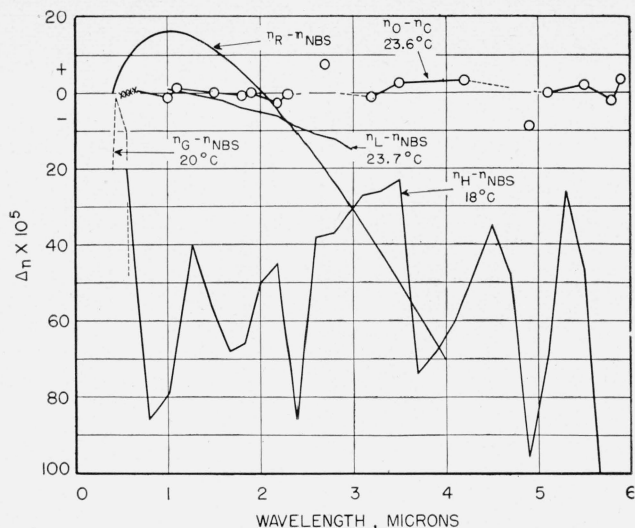


FIGURE 3. Comparison of observed (circles) and computed ( $\Delta n=0$ ) indices of refraction of lithium fluoride with previously reported values.

The indices computed at NBS by formula (2) of this paper have been subtracted from all others. No allowances for effect of temperature have been made, but differences caused by temperature are less than  $10 \times 10^{-5}$ . Recent values of index by Durie (J. Opt. Soc. Am. 40, 879 (1950)) and values that he quotes by Kessler are in good agreement with NBS values.  $n_G$ , Gyulai;  $n_H$ , Hohls;  $n_L$ , Littman;  $n_O$ , observed at NBS;  $n_C$ , computed at NBS;  $n_R$ , Radhakrishnan.

spectral range (the absolute term of formula (2) being 1 plus functions of the four constants). The five-constant form

$$n^2 = b^2 - \frac{M}{L^2 - \lambda^2} + \frac{m}{\lambda^2 - l^2} \quad (4)$$

where  $b^2$  is independent of the other parameters, and also the five-constant form

$$n^2 = a^2 - K\lambda^2 - p\lambda^4 + \frac{m}{\lambda^2 - l^2} \quad (5)$$

(which latter we successfully used for KRS-5 and for Ag Cl) were each tried (in simultaneous solutions) for lithium fluoride, but neither seemed more suitable than the four-constant formula with only the two Sellmeier terms. However, this comparison of formulas is not definite because a least squares adjustment was made only on the one last named.

For KRS-5 it seems that the inferiority of the four-constant formula may be said to occur because one fictitious infrared band cannot represent the band near  $117\mu$  and also the other near  $152\mu$  as well as can be done by three terms in the expansion of each of their respective Sellmeier terms. On the other hand, for lithium fluoride, the band near  $16\mu$  is so comparatively unimportant that its effect and also that of the band near  $23\mu$  can be effectively represented as one. That the effective location ( $28\mu$ ) of this one infrared band is not in this case intermediate between the actual locations mentioned is of no particular import. These dispersion equa-

TABLE 3. *Refractive indices of lithium fluoride at 23.6° C*

(Computed by formula 2)

Wavelength	Tenths of microns									
	0	1	2	3	4	5	6	7	8	9
$\mu$						1.39430	1.39181	1.39017	1.38896	1.38797
0					1.38400	1.38320	1.38238	1.38153	1.38064	1.37971
1	1.38711	1.38631	1.38554	1.38477	1.37446	1.37327	1.37203	1.37075	1.36942	1.36804
2	1.37875	1.37774	1.37669	1.37560	1.36037	1.35868	1.35693	1.35514	1.35329	1.35138
3	1.36660	1.36512	1.36359	1.36201	1.34100	1.33875	1.33645	1.33408	1.33165	1.32916
4	1.34942	1.34740	1.34533	1.34319	1.31575	1.31287	1.30993	1.30692	1.30384	1.30068
5	1.32661	1.32399	1.32131	1.31856						
6	1.29745									

tions have an approximately theoretical basis, but caution is necessary in quantitative reasoning based on their use. Whenever parameters are determined by purely statistical methods their values must to some extent perform functions other than those attributable to their particular simple interpretations unless the formula is in every way theoretically adequate.

The advantages of using an equation rather than a graphical method in the calibration of an infrared spectrometer are pointed out by McKinney and Friedel [11], but such procedure cannot be relied on for accuracy [12] unless the equation used is theoretically applicable or is thoroughly tested throughout the range of use.

In special cases, particularly for short intervals of wavelength, sufficiently remote from the resonance regions, one may find comparatively simple relationships between drum readings,  $D$ , and the wavelength,  $\lambda$ , but in general with any spectrometer and prism the safe procedure is (1) to express  $D$  in terms of the emergent angle,  $E$ , and (2) to find the proper relation between  $E_\lambda$  and the corresponding refractive index,  $n_\lambda$ .

For the spectrometer used in this investigation, the drum readings are nearly proportional to changes in emergent angle, and one may write

$$D = (E - e)/s, \quad (6)$$

where  $e$  is the particular value of  $E$  corresponding to  $D=0$ , and  $s$  is an average angular equivalent of the screw.

The values of  $E$  for use in computing  $D$  for any prism of known refracting angle  $A$  are obtainable from eq 1, which may be written

$$\sin E = \sin A (n^2 - \sin^2 i)^{1/2} - \cos A \sin i, \quad (7)$$

where  $i$ , the angle of incidence, will be known by the manner of installation ( $\sin i = n \sin A/2$  if set for minimum deviation) and values of the index,  $n$ , must be obtained from a table or computed from an appropriate equation expressing  $n$  as a function of  $\lambda$ .

For this spectrometer and our installation of this prism, after writing equations

$$sD_\lambda + e = E_\lambda \quad (8)$$

for all our observations and adjusting by the method of averages, we find  $s = 0.444259^\circ$  and  $e = 45.1802^\circ$  if the unit of  $D$  is 0.01 turn. For our prism,

$$\sin E = 0.9512720 (n^2 - 0.6686737)^{1/2} - 0.2521473, \quad (9)$$

and we have by these means obtained the computed values of  $D$  as listed in table 2.

In figure 4, where the observed and computed values of  $D$  are compared, it will be noticed that the observed values of  $D$  are systematically low by about 0.01 turn of the drum, between  $D$  readings of 440 and 1980 (turns  $\times 100$ ) and of opposite sign elsewhere. These slight differences are a result of two causes. First, the angular equivalent of the screw is only an average value. A calibration of the screw was used in the precise reduction of the observed data but is ignored in this subsequent proposal for computation of drum readings. Second, the small angular subtense of the entrant and emergent slits is also ignored in this computation of drum readings from the adjusted observed data.

Consequently, if the slits are in near angular coincidence, and if the screw advance (reasonably free from periodic error) is nearly proportional to

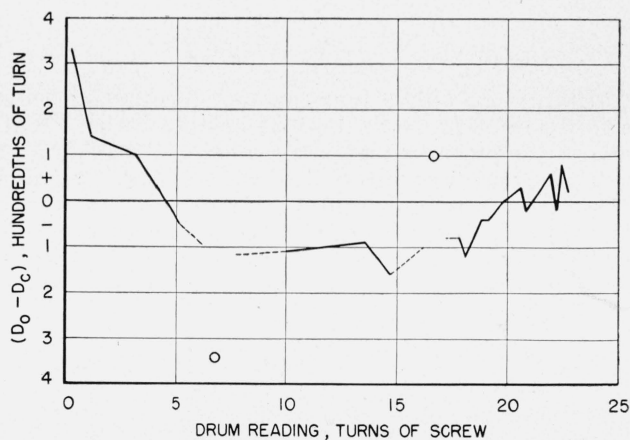


FIGURE 4. *Computed drum readings,  $D_c$ , compared with observed drum readings,  $D_o$ .*

The systematic difference occurs chiefly because the relation between drum reading and angular orientation of the mirror is not strictly linear. An error of one hundredth turn is approximately equivalent to an error of  $4 \times 10^{-3}$  in refractive index. (The two circles represent data based on the absorption bands of methanol for which there may be small errors in the reported values of wavelength.)

angle of orientation of the mirror, then a satisfactory calibration of the drum readings in terms of wavelength can be made, provided the drum readings are known for some 10 or 15 wavelengths for which the indices are reliably known or obtainable. In fact, if the drum readings can be observed with sufficient accuracy (higher than that needed in subsequent use of the spectrometer) then four or five wavelengths will in most cases be sufficient for the calibration (but with no remaining data to confirm the correctness of procedures).

For precision and reliability in expressing refractive index as a function of wavelength the Sellmeier dispersion equation

$$n^2 = 1 + \frac{C\lambda^2}{\lambda^2 - \lambda_c^2} + \frac{K\lambda^2}{\lambda^2 - \lambda_k^2} \quad (10)$$

and its variants are unexcelled. It is best known in its slightly expanded form in which it is exactly equivalent to the Ketteler-Helmholtz equation having only four disposable parameters. For use in the most frequently encountered conditions, where the ultraviolet critical frequencies are proximate or more important than those in the infrared, one further expands the infrared term and writes

$$n^2 = a^2 - k\lambda^2 - p\lambda^4 + \frac{m}{\lambda^2 - l^2}, \quad (11)$$

in which the term in  $\lambda^4$  can often be omitted. Similarly, for the opposite case, where the infrared bands are near and predominant, one uses

$$n^2 = a^2 + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} - \frac{M}{L^2 - \lambda^2}, \quad (12)$$

but sometimes when both the ultraviolet and infrared effects are important it is advantageous, from the standpoint of high precision and accuracy, to keep the fractional remainders of both Sellmeier terms

$$n^2 = a^2 - \frac{M}{L^2 - \lambda^2} + \frac{m}{\lambda^2 - l^2}, \quad (13)$$

which may be only a four-constant formula ( $a^2$  being a function of  $L^2$ ,  $l^2$ ,  $M$ , and  $m$ ) or may be used with  $a^2$  as an independent parameter.

The shorter the interval of wavelength, the more remote the critical frequencies, and the less precise the data, the greater are the chances for successfully using the fully expanded forms and those simpler forms written with the first power of  $n$ , such as

$$n = a + b\lambda^2 + \frac{c}{\lambda^2} + \dots \quad (14)$$

and the numerous empirical variants that are now and then proposed, tested, and found satisfactory under one or more of the three limitations just stated.

In selecting the best variant of these dispersion equations for use in any given instance, and in deciding how many constants should be used, it is usually advantageous to make simple simultaneous solutions before resorting to least squares. In such solutions it is advantageous to solve by systematic elimination and arrange the work so that the solution for  $c-1$  constants can be made with very little additional work after a solution for  $c$  constants.<sup>3</sup> Likewise, in arranging the work for least squares solutions, one can so manage that most of the sums of the squares and cross products for the  $c-1$  adjustment are obtained from among those computed for the  $c$ -constant adjustment, and then the normal equations can be so written and solved that little work will thereafter be necessary in obtaining the adjusted solution for  $c-1$  constants.

Much of the effort made to substitute simplified dispersion equations for those of the Sellmeier type stems from the nonlinearity of the constants when Sellmeier terms are present. An objection is that direct least squares solutions are not possible, and the differential process of betterment of some approximate solution must be used. Much of this objection vanishes whenever it is advisable to make preliminary simultaneous solutions in the process of selection of a proper equation.

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<sup>3</sup> For example, the observational equation that is not to be used in the second solution should be written either first or last, but not among the other  $c-1$  observational equations, and one eliminates last, or solves first, for the constant not to be used later.