

ON THE DETERMINATION OF REFRACTIVE INDICES
BY MEANS OF CHANNЕLED SPECTRA.

BY S. R. WILLIAMS.

IF the light reflected from two parallel optical surfaces be examined with a spectroscope of sufficient resolving power, the resulting spectrum will be traversed by dark bands corresponding to those wave-lengths which interfere, the center of a dark band occurring when $2\mu D = 2N\lambda/2$ and the medium between the surfaces is of a less refractive index than that composing the optical surfaces. For the center of a light band $2\mu D = (2N + 1)\lambda/2$, where D is the linear thickness of the space intervening, λ the wave-length and N some integral number. In case μ becomes equal to unity, as occurs when we have a vacuum, the value of N in the above equation may be derived, giving the length of the path D in wave-lengths of light. Using the sun as a source of light there will appear in the spectrum the Fraunhofer lines, in addition to the interference bands, thus furnishing a scale of reference for every interference band.

If two dark bands appear in determinate parts of the spectrum corresponding to wave-lengths λ_1 and λ_2 , then by the above equations $2\mu_1 D = N\lambda_1$ for the longer wave-lengths, and $2\mu_2 D = (N + m)\lambda_2$ for the shorter, whence assuming $\mu = 1$ we obtain

$$N = \frac{m\lambda_2}{\lambda_1 - \lambda_2}.$$

A comparison of the results obtained by various investigators in the determination of refractive indices shows at once that the optical thickness cannot be obtained by the above formulæ for those substances in which μ is such an uncertain quantity.

Dr. D. B. Brace¹ has shown that the difference in path of two

¹ Phil. Mag. (48), 1899, p. 345; (1), 1901, p. 339.

interfering rays, or the optical thickness, may be determined independently of the factor μ . His method is to take a cell, whose thickness can be varied, (usually a wedge-shaped cell) and if, in the variation of the thickness, m bands are shifted past a definite point in the spectrum for which the difference in path N is to be determined, and n is the ratio of the bands between two definite wavelengths, λ_1 and λ_2 , before and after the variation in thickness, then

$$N = \frac{mn}{1 - n}.$$

Being able to determine the difference in path thus, we are furnished with the means for determining the value of μ for any transparent substance. For, if we take as a medium of reference a substance of index μ_r , which is accurately known, $2\mu_r D = N_r \lambda$. In the body whose index is to be determined, $2\mu_e D = N_e \lambda$. D and λ being made the same, we have

$$\mu_e = \frac{N_e}{N_r} \mu_r,$$

that is, the refractive index of any substance is equal to the ratio of the optical lengths of equivalent paths in that substance, and the medium taken as a reference, multiplied by the index of the reference film.

For liquids the path D may be easily made the same by making a thin wedge-shaped cell with its sides parallel, and allowing the light to be reflected from a narrow vertical section of the same. If the upper half of the narrow section reflects from the surfaces of the film taken as a reference, and the lower half from a substance whose index is to be determined, there will occur in the spectrum, simultaneously, two sets of interference bands from which the orders of interference may be calculated, and from these the index.

By the distribution of the two sets of bands thus obtained, the dispersive power of the two substances may be compared, for if μ was larger in one than in the other, the bands would appear more frequent throughout the spectrum as shown by our equation above. In this way the complete record of dispersion of a body may be obtained throughout the spectrum. Furthermore the bands superimposed upon the Fraunhofer lines as a scale may be photographed,

and a permanent record made of the dispersion of the substance examined.

To make this a practical working method was the object of this investigation.

A four-inch Rowland concave grating, 14,438 lines to the inch, with Brashear mounting, and focal length of ten feet was used. Fig. 1 shows the arrangement of the optical system. The slit was illuminated by the direct rays of the sun, and an image of the same was formed on the wedge W by the lens L . In the usual mounting of the Rowland concave grating, the slit or its image should be

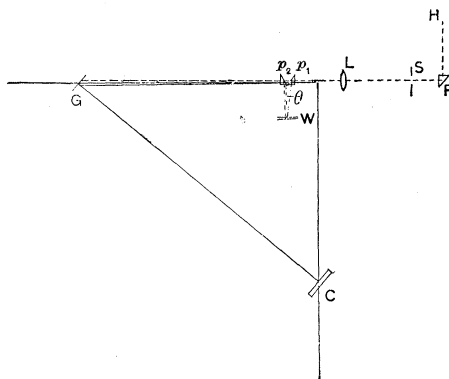


Fig. 1.

placed over the intersection of the ways, in order that the spectrum may be brought to a focus on the proper focal curve. Instead of doing this the light coming from the slit S through the lens L was reflected by means of the prism p_1 upon the wedge W , where the image of the slit was formed. The two surfaces of W returned the light to the prism p_2 , which reflected it upon the grating G . The distance of W from p_1 and p_2 was such, that the image in p_2 was at the intersection of the ways, and thus the conditions for accurate focusing were secured. The image of the slit at W served two purposes, in that it brought the Fraunhofer lines and interference bands into focus at the same time, and also afforded the means of getting a narrow vertical section of the cell.

Plate glass cut in strips, 3 x 13 cm., and 6 mm. thick, formed the sides of the wedge-shaped cell. To keep the plates apart and also

form the bottom and ends of the cell as well as the dividing strip between the films, cork strips about .75 mm. thick were cut out, as shown in Fig. 2. The plates were then held firmly against this strip by means of clamps, those on one end being screwed down more tightly than the other, in order to make the cell wedge-shaped. The mounting of the cell was so arranged by means of a rack and pinion, that it could be raised and lowered in a vertical direction, and also moved in the direction of its length, by means of a micrometer screw. For photographing the two sets of bands simultaneously the cell was so moved that the image of the slit occupied a position as ab in Fig. 2.

$ABCD$ is that part of the cell containing the film of reference, while the rest of the cell holds the liquid whose index is to be determined. The two sets of bands having been photographed together the cell was moved parallel to its length, while the bands

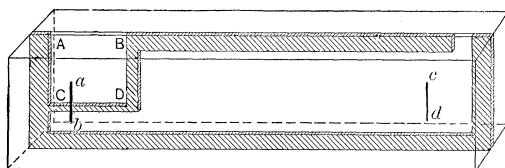


Fig. 2.

from the liquid film were counted as they moved past some fixed point in the spectrum, until the image of the slit occupied a position as cd in Fig. 2. In this position a set of bands throughout the spectrum was photographed, and knowing the index for one wavelength, it could be determined for all others by counting the bands.

Air was used for a reference film. Its index has been very accurately determined, by means of the interferometer, and the presence of a vapor does not effect it, as it has been ascertained that the refractive index of dry air is only about one millionth greater than air saturated with a vapor. The values as found by various investigators, vary by little over one part in a million. Air has also been used as a medium of reference by other investigators, and so is used in this work.

The direction of variation in thickness of the cell is at right angles to the interference bands, since along their length, the thick-

ness must be uniform. They will be parallel to the Fraunhofer lines then, when the refracting edge of the cell is parallel to the image of the slit. This was the means used for getting the plates of the cell, parallel in a vertical direction, for, if the interference bands were brought into coincidence above and below the dividing strip, before the liquid is introduced, the value of D for both films must be the same.

Another condition necessary, to give D an equivalent path, in both films, is, that the incidence be normal upon their surfaces, for, owing to refraction at the bounding surfaces the ray will be bent more or less for one than the other depending upon the difference in index, consequently D would vary for the two films. In the system used, normal incidence was not possible, but it was made so small, that it entered no appreciable error. Let AO , Fig. 3, represent the path of normal incidence upon air film xy

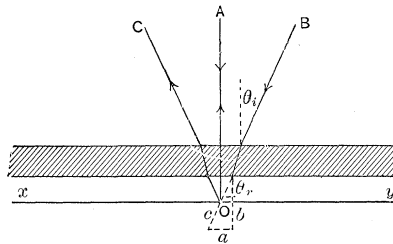


Fig. 3.

contained between two plates. Let BOC be the path of a ray at an incident angle of θ_i . Since the film xy is an air film, the angle of refraction at its surface will be the same as the angle of incidence on the plate ($\theta_i = \theta_r$). θ_r will also be a maximum for air, hence if it can be shown that the angle θ_r does not produce an appreciable error in difference between c and b , which are the lengths of D at normal and oblique incidence, then it can be shown that for a ray incident at an angle θ_i upon two films, as an air and a liquid film, the difference in D for the two is not an appreciable error. For the difference in the angle of refraction at the surfaces of the two films, can never be as large as θ_r , consequently the difference in length can never be as great as $c - b$ in the figure.

$$\begin{aligned}\tan \theta_r &= \frac{a}{b} \\ \sin \theta_r &= \frac{a}{c} \\ c - b &= a \left(\frac{1}{\sin \theta_r} - \frac{1}{\tan \theta_r} \right) \\ \frac{c - b}{b} &= \tan \theta_r \left(\frac{1}{\sin \theta_r} - \frac{1}{\tan \theta_r} \right) = \sec \theta_r - 1.\end{aligned}$$

but $(c - b)/b$ is the per cent. of error introduced. In the apparatus as set up, the light at prism p_1 , Fig. 1, was diaphragmed so that θ_r was about $25'$. Substituting this value in the above equation, shows an error of about three parts in a hundred thousand. With light incident on two films the error due to difference of path D is still less, as shown above.

In the liquid films with oblique incidence, dispersion produces a variation in D for the different wave-lengths, so that if the index of the substance under examination be smaller than that of the containing cells, the path D for the violet ray, will be greater than that of the red, since it will be bent away from the normal more than the less refrangible wave-lengths. We have shown that difference in path, due to refraction, produced a negligible error, and since the angle of deviation is always less than the angle of refraction, no error in difference of D for the various wave frequencies will occur.

Again the length of D , as determined from the bands in the photographs, will be augmented by change of phase, at reflection from the bounding surfaces of the film, if the conditions of reflection for the two beams are not the same. In order to increase the intensity of light in reflection from the surfaces, a full silvered surface was used at the back. After repeated trials, it was found that an approximate half silvered front surface, which gave a brighter image of a flame by reflection, than by transmission, produced the blackest bands in the channeled spectra.

O. Wiener¹ has found that the change of phase by reflection, varies with the thickness of the silvering, increasing as a retardation from 0 to $3/4\lambda$, for all wave-lengths, as the thickness of silver increased from zero to a full silver.

¹Wied. Annal. (31), 1887, p. 647.

The index of silver is about .25, so that in the cell that was used, if the half silvering was placed on the rear surface of the front plate, and the full silvering on the front surface of the rear plate, then for both films, the condition of reflecting from a less refracting substance to a greater, was secured for the two interfering rays.

According to Wiener, the half-silvered surface introduced a retardation of about $\lambda/2$, while at the rear surface it was $3\lambda/4$. This made the difference in phase of the two interfering rays, greater by about $\lambda/4$, since the ray reflected from the back surface has been retarded that much more than the one reflected from the front surface. With the order of interference that was used in this work, this entered an error of less than three parts in one hundred thousand in determining the order.

In making the computation of indices, this change of phase was not regarded, and since in photographing, the bands from the two films were brought into coincidence with the D_1 line, the orders of interference for these were regarded as an odd multiple of $\lambda_D/2$.

$$(2N + 1) \frac{\lambda}{2} = 2\mu D$$

then becomes the formulæ for finding the order of an interference band.

The cell was housed in a pasteboard box, which kept the temperature uniform during the photographing, so that the bands did not shift due to that cause. The temperature was taken at the beginning of the series of photographs, and is indicated on the plates.

At times, a shift of the bands did occur, but this was due to a yielding of the cork strip between the plates, or other mechanical effects. It was found that if the cell was allowed to stand before using, no difficulty was encountered from this source, for an eye piece was attached to the side of the camera box, whose focus was on the focal curve of the grating, and through this the bands were watched to see that they did not shift with respect to the Fraunhofer lines.

Mitchell has shown that the astigmatism of a grating depends upon the length of the illuminated portion of the slit, the length of

the ruled lines, and the angle which the incident light makes with the axis of the grating. On account of this property, comparison work is not possible as in the prismatic spectrum. In photographing the two sets of bands, comparison work was done, but other conditions were introduced that do not occur in ordinary comparison work. The light falling upon a grating was slightly divergent, and the dividing strip in the cell, cut out a narrow section of light across the middle of the ruled portion of the grating. The light above this dark strip came from one film, and that below from the other. The length of ruling that was producing the spectrum for one set of bands, was therefore less than half the actual length of ruling of the grating, and as a result the interference bands, from one film, extended about half the width of the spectrum.

If D is the thickness, μ the index, λ the wave-length, and N is the order of interference, the distribution of the bands throughout the spectrum is represented by the equations :

$$(1) \quad N = \frac{2\mu D}{\lambda}$$

$$(2) \quad N = \frac{2D}{\lambda} \text{ where } \mu = 1, \text{ as for a vacuum.}$$

Differentiating these we have,

$$(3) \quad \frac{dN}{-d\lambda} = \frac{2D}{\lambda^2} \left(\mu + \lambda \frac{d\mu}{-d\lambda} \right),$$

$$(4) \quad \frac{dN}{-d\lambda} = \frac{2D}{\lambda^2}.$$

Equations (1) and (2) are the equations of an equilateral hyperbola, N and λ being the variable parameters. In (3) and (4) the left hand side of the equation, represents the number of bands between wave-lengths λ and $\lambda - \delta\lambda$, and is expressed on the right hand side in terms of D , λ and μ . The variation of the order with wave-lengths in the two equations, (3) and (4), differ by the factor in parenthesis which expresses the difference in variation between the two sets of bands. Since in the two equations $2D/\lambda^2$ appears, which is the expression for the variation of order due to wave-length alone, if we superimpose a set of bands, *e. g.*, those in a vacuum,

¹J. Hopkins, Univ. Circulars, June, 1898.

whose variation is represented by (4), upon a set of bands represented by (3), the differential effect will be that due to the dispersion of the substance whose bands are represented by (3). To do this, the bands from the two films are brought into coincidence, say in the less refrangible portion of the spectrum. If now we go toward the violet, the bands in the spectrum whose variation is represented by (3) will, in general, increase in number more rapidly than those used as a scale. Consequently they will get out of coincidence. If then they should come into coincidence again, due to the bands not increasing so rapidly as those on the scale, the term in parenthesis must diminish, which indicates anomalous dispersion. In a subsequent paper, it will be shown more in detail how this method may be used for the detection of this characteristic.

Preliminary work has been done in adapting this method to the determination of refractive indices of solids. The optical system was, in general, the same as used in working with liquids. The difficulty with solid wedges, is to get a reflecting surface for the wedge and an equivalent film of air. If silvered plates be placed on both sides of the solid wedge, as for the liquid film, it is impos-

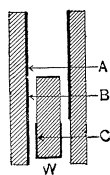


Fig. 4.

possible to get the plates in close enough contact to the wedge, so as not to have thin air films intervening. This difficulty was overcome, by measuring these air films, and thereby obtaining the equivalent film of air for reference. In Fig. 4 is shown a vertical cross section of the cell used in getting the order of interference in the wedge and an equivalent film of air. W is the solid wedge between two glass plates, silvered as they were in the liquid cell described above. The path of the light at A gives the total thickness of air space, B that of the wedge and air films on both sides. By properly silvering the lower part of the wedge, the interference bands due to the wedge itself, may be obtained in C . $B - C$ gives the thickness of the air films on the two sides of the wedge. $A - (B - C)$ gives the thickness of an air film equivalent to the wedge. Consequently $C/[A - (B - C)]$ gives the index as compared with air. It was impossible to get the three sets of bands simultaneously, but A and B were first obtained and photographed, and then by means of rack and pinion, the cell was raised and B and C obtained.

With proper adjustments, there was no shift of the bands in raising the cell vertically, since its sides and that of the wedge are parallel in that direction.

In solids showing double refraction, the optical system was arranged as shown in Fig. 5, with a nicol, *A*, before the slit and another one, *E*, between the prism p_2 and the grating.

If a ray of light, polarized at an angle of 45° to the principal axis of a crystalline wedge, pass normally through and is reflected back again, the emergent light, when resolved by a spectroscope,

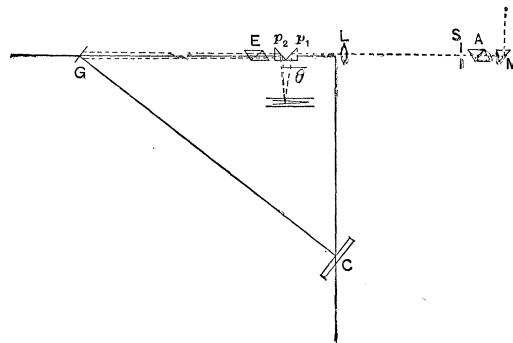


Fig. 5.

will be traversed by interference bands due to double refraction in addition to the ordinary bands arising from the wedge. The superposition of the two sets of these latter bands, give rise to a maximum and a minimum in the intensity, producing the bands from double refraction referred to. The formulæ for these minima, when the nicols are crossed, is $N = 2D[(\mu_e - \mu_o)]/\lambda$. In this way both the bands due to interference between the beams reflected between the front and back surface, and those due to differential double refraction may be photographed.

With double refracting crystals, the system of reflection at p_1 and p_2 had to be changed, and is shown in Fig. 6. In using the prisms p_1 and p_2 only, there would be a change of phase between the component vibrations. By using a double system of reflection, at right angles to each other, as shown in the cut, the two components will have practically the same change of phase introduced. This double reflection will place the image of the slit in a horizontal

position, which necessitates turning the wedge so that its length is at right angles to the image of the slit.

Plate I. is a series of photographs for triple-distilled water. The photographs are arranged with the shorter wave-lengths to the left. In each set of photographs, No. 4 was the first setting made in the spectrum, and is that of the liquid and air bands together, between the Fraunhofer lines, β_2 and D_1 . No. 3 was taken in the same portion of the spectrum, after shifting several hundred bands. The others were taken in the order 5, 6, 2, 1.

In Plate I. the number of air bands between β_2 and D_1 is 276.6 from which the order 1978.5 for the Fraunhofer line D_1 is obtained by the formulæ

$$N = \frac{m\lambda_2}{\lambda_1 - \lambda_2}.$$

In the liquid bands there are 374.7 between these two wave-lengths, and after shifting 338 bands past the D_1 line in the spectrum and photographing again, there are by count 326.7 bands in this same region, substituting these values in our equation

$$N = \frac{mn}{1-n} = \frac{338 \times \frac{326.7}{374.7}}{\frac{48}{374.7}} = 2300.5.$$

The order as found for the liquid is that of the D_1 line in photograph No. 3. For the D_1 line in No. 4 we add 338 to 2300.5 = 2638.5. The ratio between these two orders,

$$\frac{N \text{ liquid}}{N \text{ air}} = \mu = \frac{2638.5}{1978.5} = 1.3336.$$

For the D_1 line in No. 3, the order for air would be the order for liquid at that point, divided by the index,

$$\frac{2300.5}{1.3336} = 1725.0.$$

From these two orders of air and liquid for the D_1 line, the orders for all other points in the spectrum may be calculated and counted from the photographs.

In counting the bands, they were laid on a dividing engine under a micrometer eye piece, and as the photographs were shifted under the cross wires, the bands were counted. The fractional part of a band being estimated only to tenths.

The results from all of the photographs shown, were obtained in the manner described above, and are tabulated below.

PLATE I.

Triple-distilled Water. m = 338. Temp. 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674 $\times 10^{-5}$	1480.9	1971.1	1.3310
6.5630 " "	1549.9	2063.8	1.3316
5.8961 " "	1725.0	2300.5	1.3336
5.6169 " "	1810.7	2416.9	1.3348
5.3283 " "	1908.7	2549.2	1.3356
5.2270 " "	1945.8	2599.4	1.3359
5.1728 " "	1966.2	2627.4	1.3363
4.9577 " "	2051.4	2743.8	1.3375
4.8615 " "	2092.1	2799.4	1.3381
4.6680 " "	2178.7	2917.6	1.3391
4.3837 " "	2320.1	3111.0	1.3409
4.2269 " "	2406.2	3228.5	1.3417
4.1019 " "	2479.5	3330.5	1.3432
3.9686 " "	2562.6	3445.0	1.3443

PLATE II.

Absolute Alcohol. m = 393. Temp. 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674 $\times 10^{-5}$	1268.0	1721.0	1.3572
6.5630 " "	1326.4	1802.1	1.3586
5.8961 " "	1476.2	2009.5	1.3612
5.6169 " "	1549.5	2111.5	1.3627
5.3283 " "	1633.4	2227.5	1.3637
5.2270 " "	1665.1	2271.5	1.3642
5.1728 " "	1682.5	2296.0	1.3646
4.9577 " "	1755.5	2397.7	1.3655
4.8615 " "	1790.3	2446.3	1.3664
4.6680 " "	1864.4	2550.4	1.3679
4.3837 " "	1985.5	2721.3	1.3705
4.2269 " "	2059.1	2825.1	1.3720
4.1019 " "	2121.9	2913.5	1.3731
3.9686 " "	2193.0	3014.5	1.3746

PLATE III.

a-Monobromonaphthalin. $m = 475$. Temp. 24°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1440.1	2374.0	1.6485
6.5630 " "	1507.2	2489.2	1.6515
5.8961 " "	1677.5	2787.5	1.6617
5.6169 " "	1760.9	2934.6	1.6665
5.3283 " "	1856.2	3103.6	1.6720
5.2270 " "	1892.2	3168.2	1.6743
5.1728 " "	1911.0	3204.1	1.6767
4.9577 " "	1994.9	3354.9	1.6817
4.8615 " "	2034.5	3427.5	1.6847
4.6680 " "	2118.7	3584.6	1.6918
4.3837 " "	2256.2	3844.7	1.7034
4.2269 " "	2339.5	4007.6	1.7130
4.1019 " "	2411.2	4149.7	1.7210
3.9686 " "	2492.1	4322.5	1.7345

One of the difficulties met with in this method, is the shifting of the bands during the photographing as occurs in all interference work. This was mechanical, and was overcome by shifting the cell, for all the shift of the bands, with respect to the Fraunhofer lines, originated in the cell itself. That the Fraunhofer lines and

PLATE IV.

Oil of Cinnamon (Cassia). $m = 273$. Temp. 25.5°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1229.0	1919.1	1.5615
6.5630 " "	1286.3	2014.2	1.5659
5.8961 " "	1431.6	2257.5	1.5769
5.6169 " "	1502.7	2379.3	1.5833
5.3283 " "	1584.0	2519.0	1.5903
5.2270 " "	1614.8	2572.5	1.5937
5.1728 " "	1631.7	2602.4	1.5949
4.9577 " "	1702.4	2728.0	1.6024
4.8615 " "	1736.2	2788.5	1.6061
4.6680 " "	1808.1	2920.0	1.6149
4.3837 " "	1925.5	3141.0	1.6312
4.2269 " "	1997.0	3283.5	1.6437
4.1019 " "	Absorption, no bands visible.		
3.9686 " "	" " " "		

PLATE V.

Benzole. m = 235. Temp. 22°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1298.7	1924.9	1.4822
6.5630 " "	1359.2	2017.7	1.4844
5.8961 " "	1512.8	2254.4	1.4902
5.6169 " "	1588.0	2371.6	1.4934
5.3283 " "	1673.9	2505.4	1.4967
5.2270 " "	1706.4	2556.4	1.4981
5.1728 " "	1724.3	2584.4	1.4988
4.9577 " "	1799.0	2702.5	1.5022
4.8615 " "	1834.7	2758.9	1.5037
4.6680 " "	1910.6	2880.4	1.5076
4.3837 " "	2034.7	3079.4	1.5134
4.2269 " "	2110.2	3202.8	1.5177
4.1019 " "	2174.5	3308.4	1.5214
3.9686 " "	2247.4	3429.4	1.5259

interference bands appear simultaneously, is one of the important features of this method. No matter what apparatus is used, the scale of the Fraunhofer lines will always be the same, from which the measurements are made, and no mechanical errors can enter. The shift of bands which might arise due to changes of temperature, must be guarded against in all methods.

PLATE VI.

Olive Oil. m = 267. Temp. 26°.

λ cm.	N, Air.	N, Liquid.	Index.
6.8674×10^{-5}	1190.3	1721.0	1.4458
6.5630 " "	1245.7	1802.1	1.4474
5.8961 " "	1386.5	2012.5	1.4514
5.6169 " "	1455.4	2116.5	1.4542
5.3283 " "	1534.2	2234.5	1.4565
5.2270 " "	1564.0	2279.5	1.4567
5.1728 " "	1580.3	2304.2	1.4581
4.9577 " "	1648.8	2407.6	1.4602
4.8615 " "	1681.5	2457.5	1.4615
4.6680 " "	1751.1	2563.5	1.4639
4.3837 " "	1864.9	2733.0	1.4655
4.2269 " "	1934.0	2839.5	1.4682
4.1019 " "	1992.9	2930.6	1.4705
3.9686 " "	2059.8	3034.5	1.4732

It is also possible with the normal spectrum, to determine directly the index for any wave-length. In the prism method, we are dependent upon the more prominent Fraunhofer lines, for points of reference.

In conclusion, the author desires to express his thanks to Professor Brace for valuable assistance rendered him, whereby he was enabled to carry out this research.

PHYSICAL LABORATORY,
UNIVERSITY OF NEBRASKA, June, 1903.

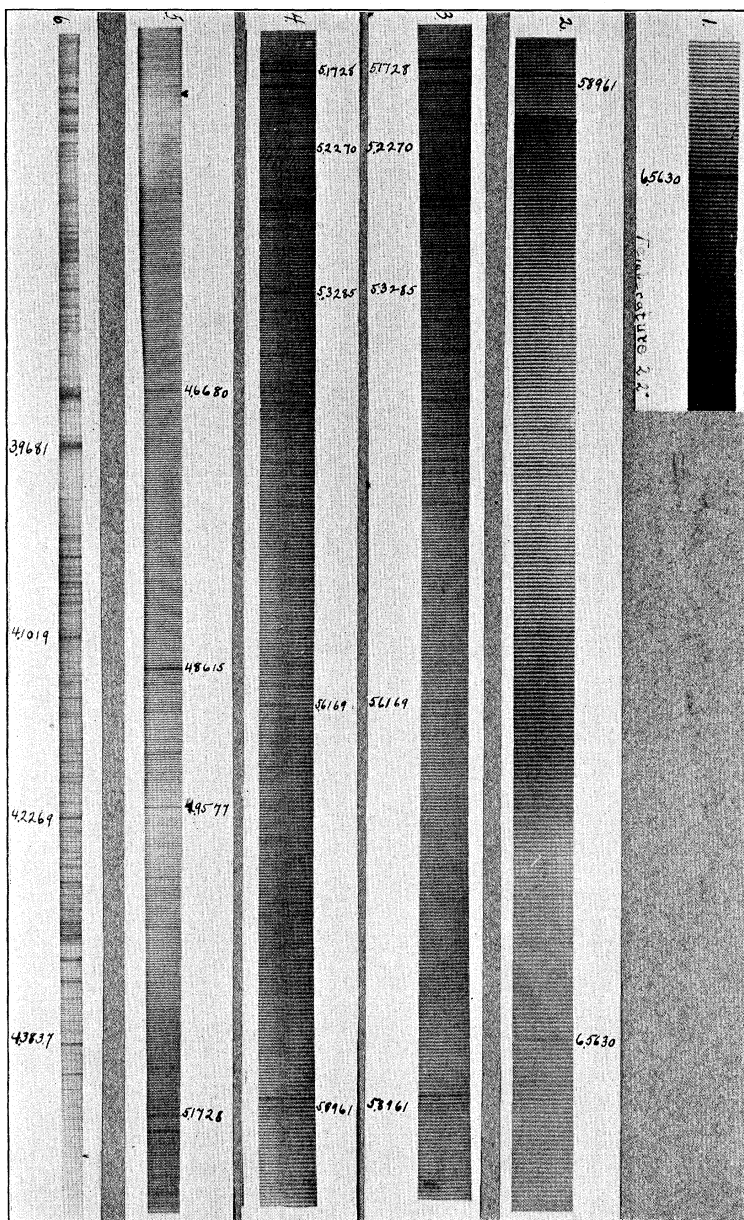


PLATE I.
S. R. WILLIAMS

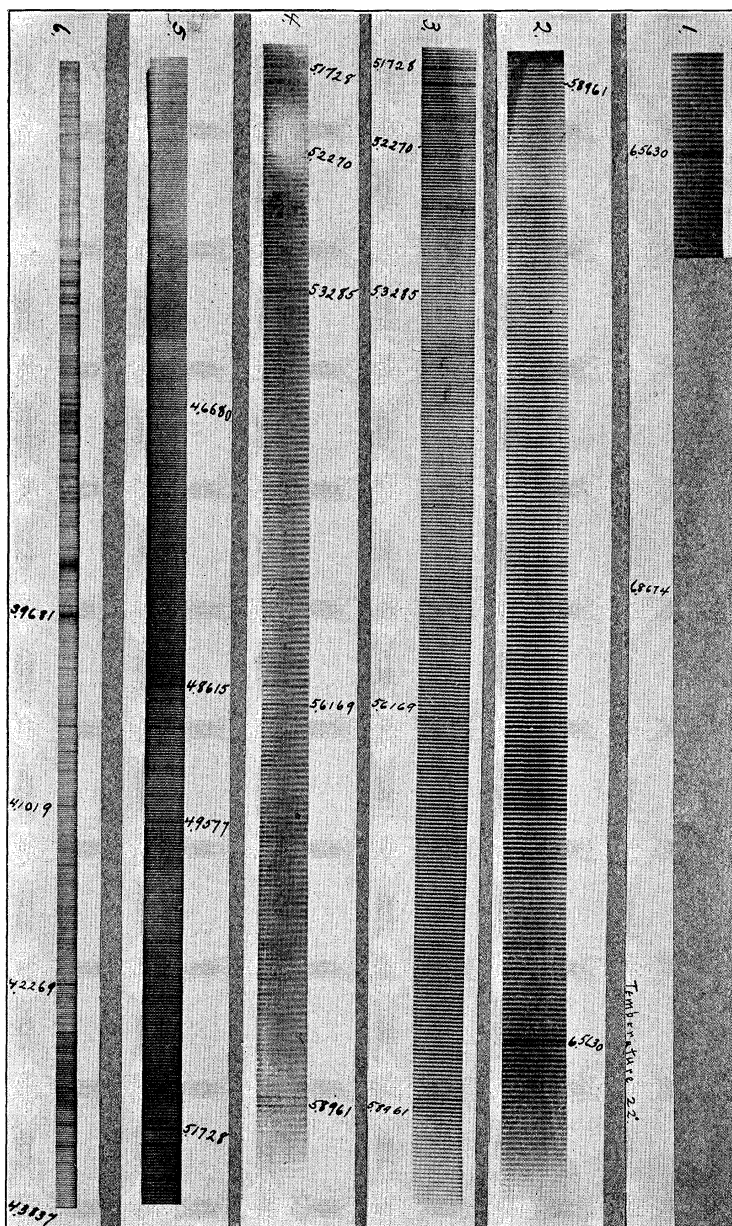


PLATE II.
S. R. WILLIAMS.

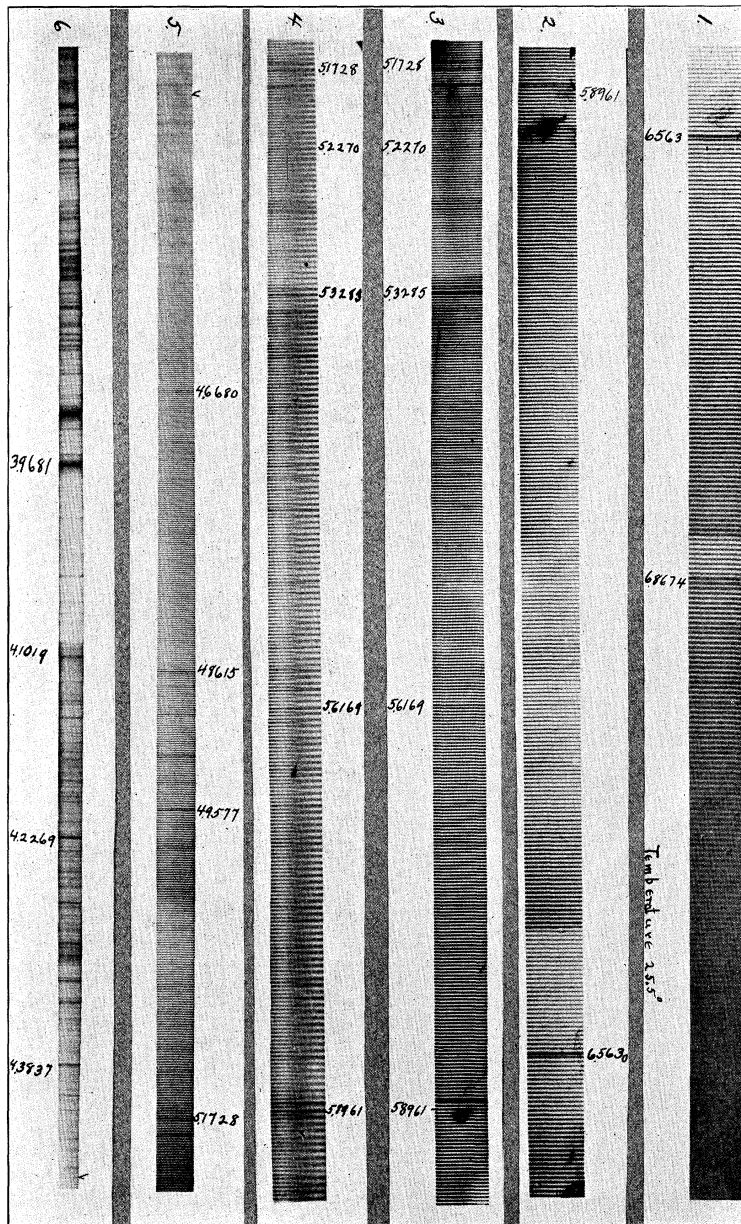


PLATE IV.
S. R. WILLIAMS.

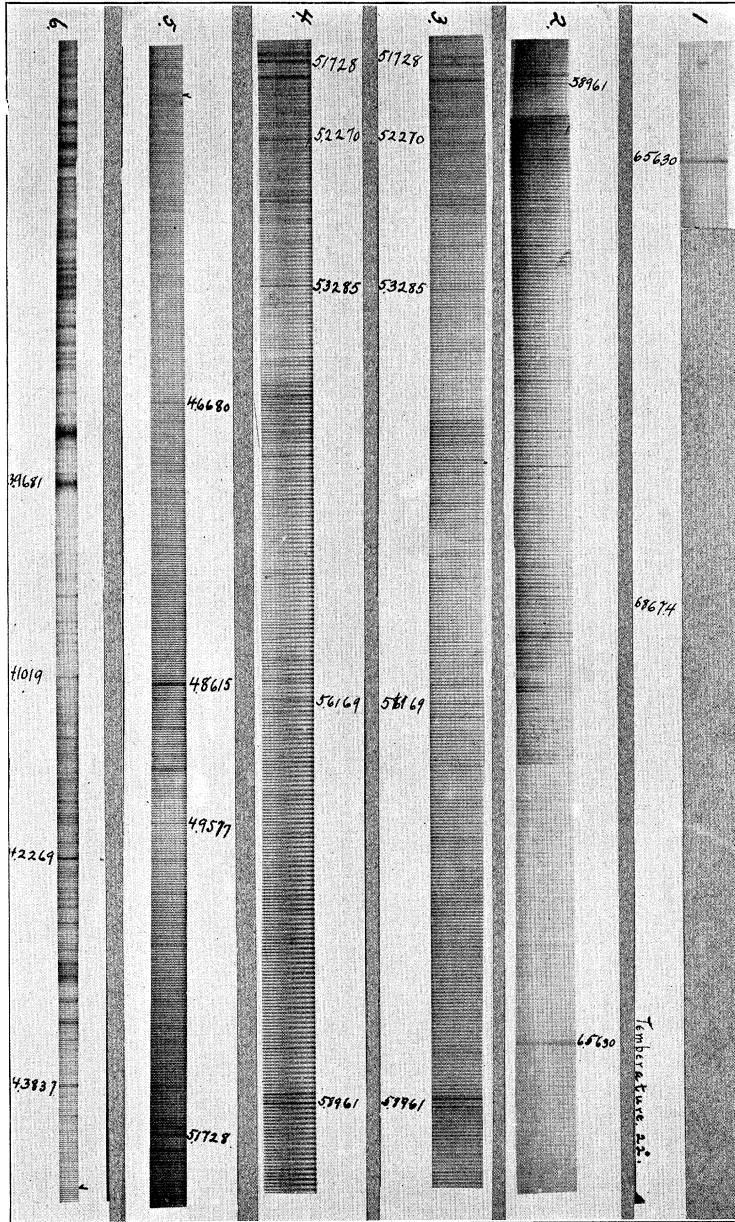


PLATE V.
S. R. WILLIAMS.

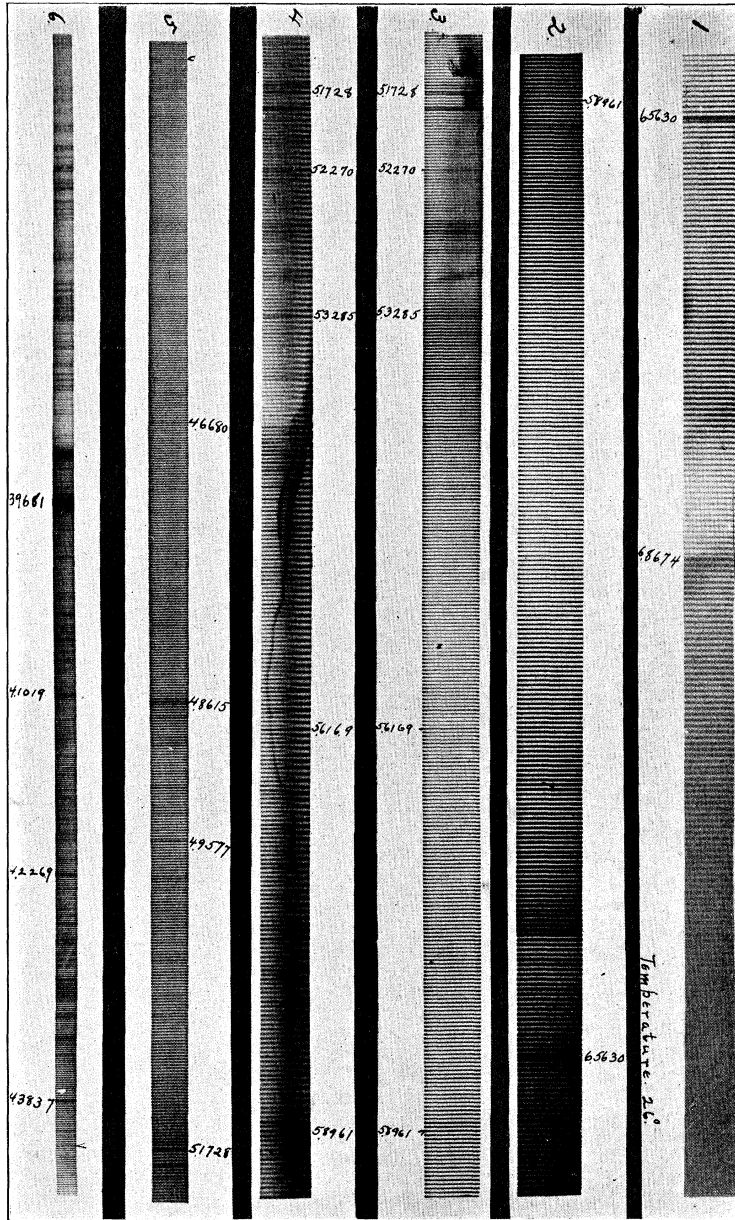


PLATE VI.
S. R. WILLIAMS.

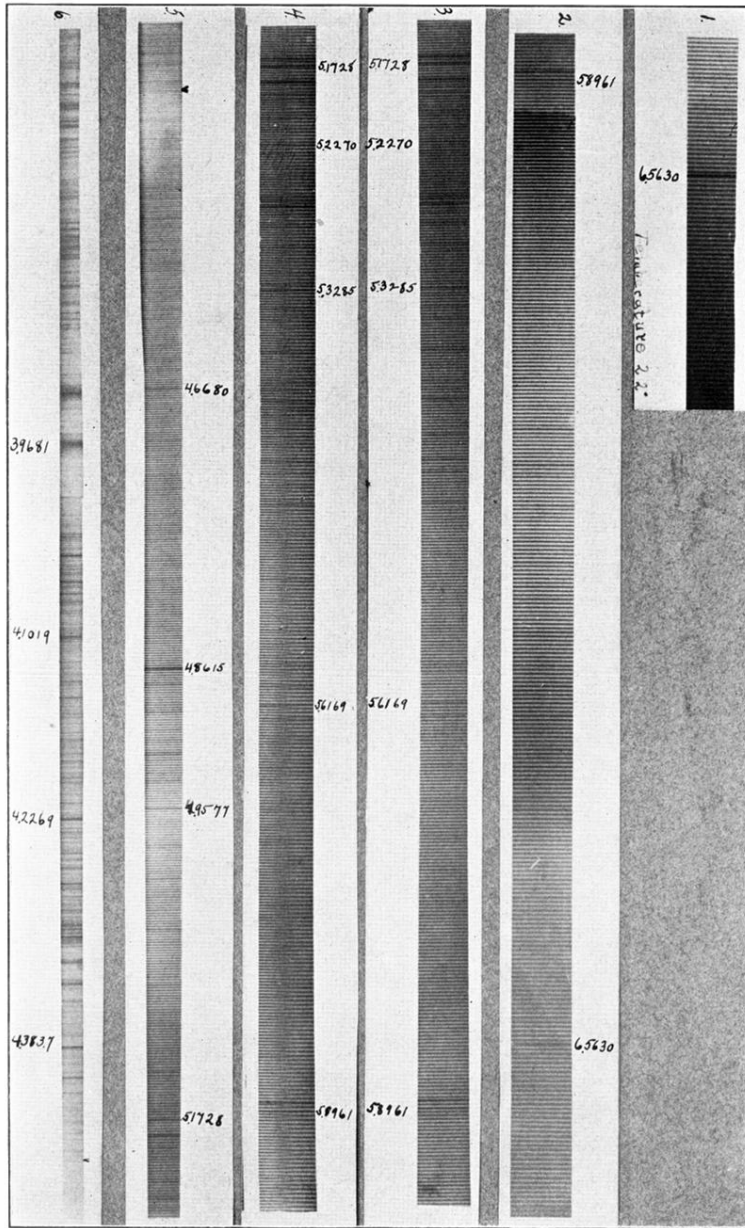


PLATE I.

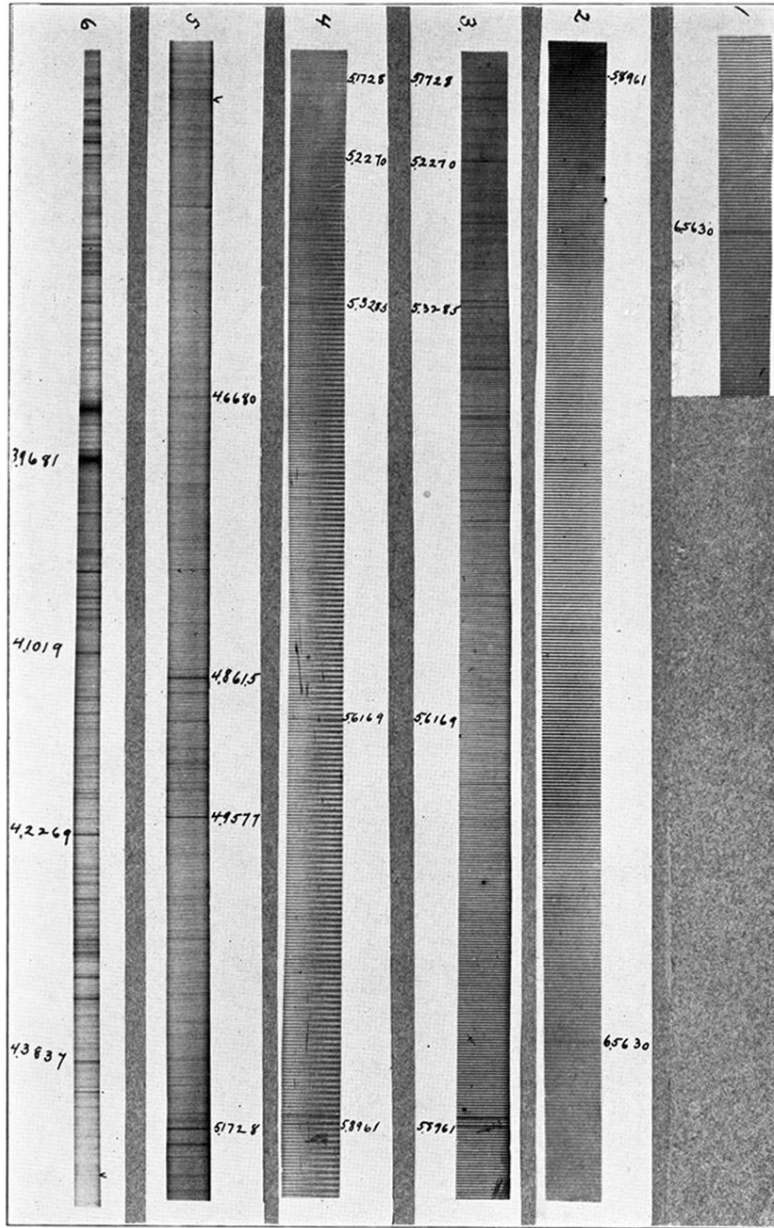


PLATE III.

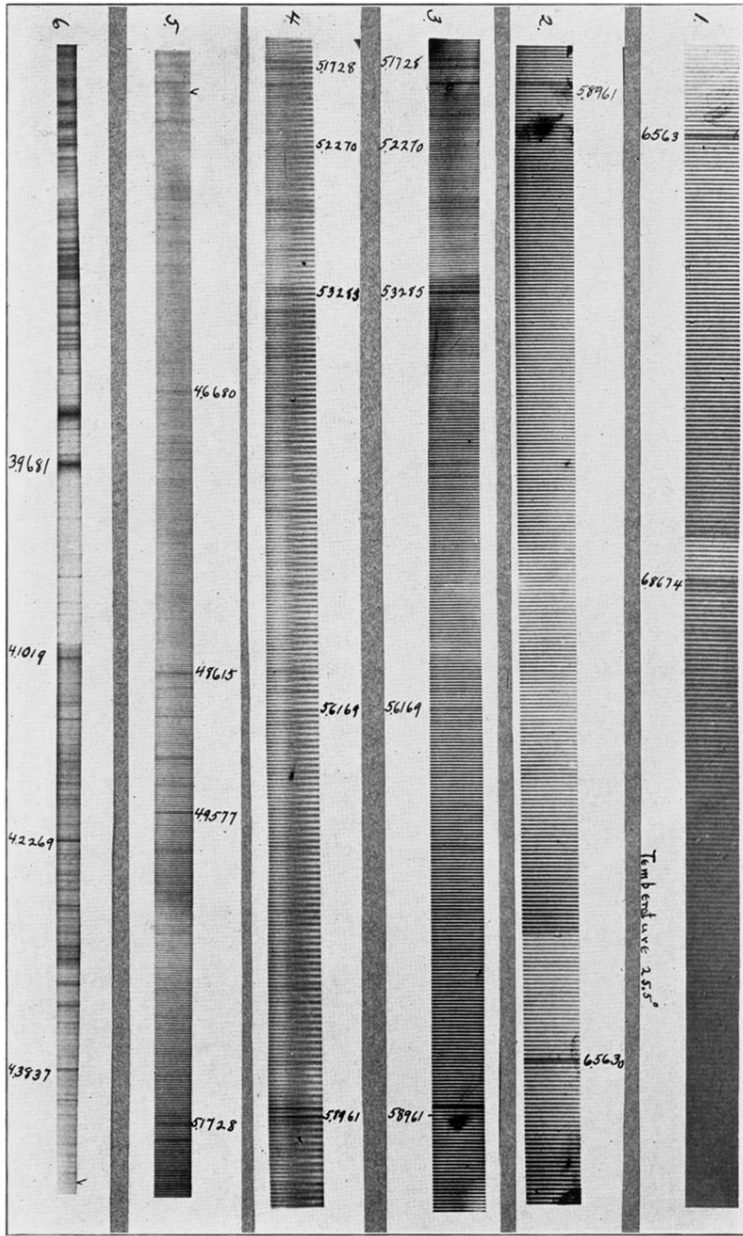


PLATE IV.

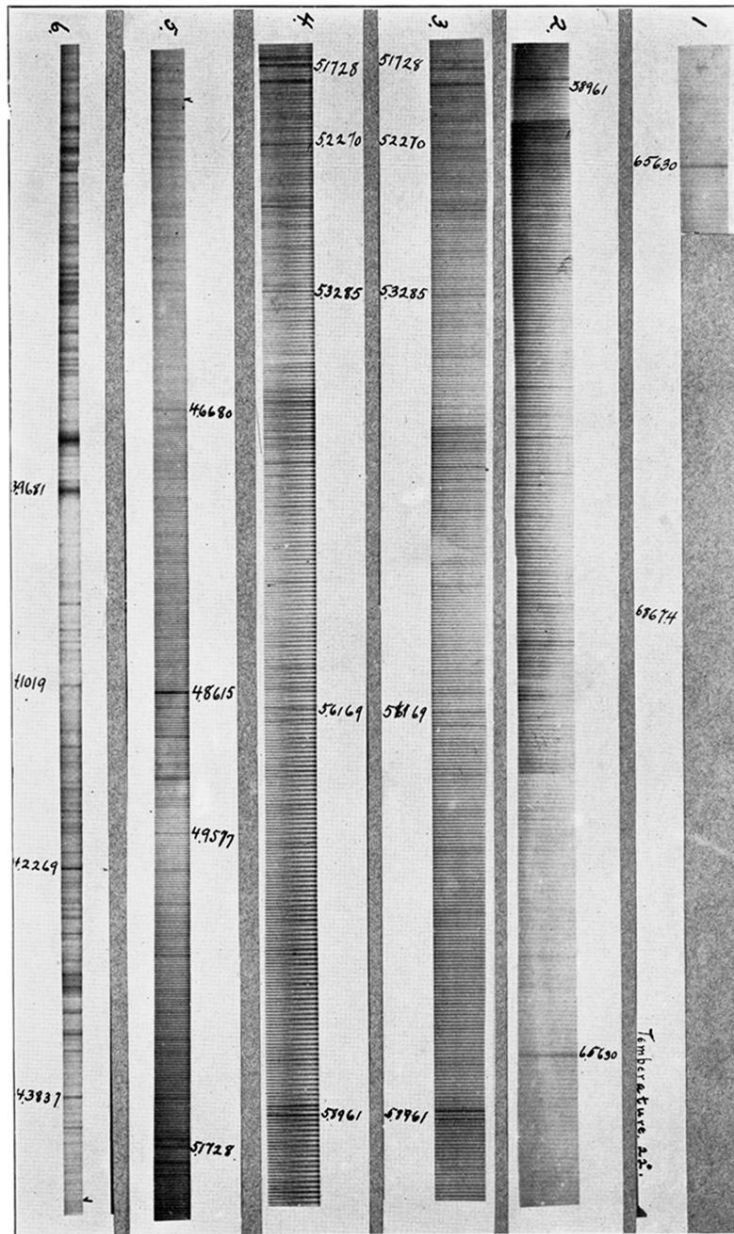


PLATE V.

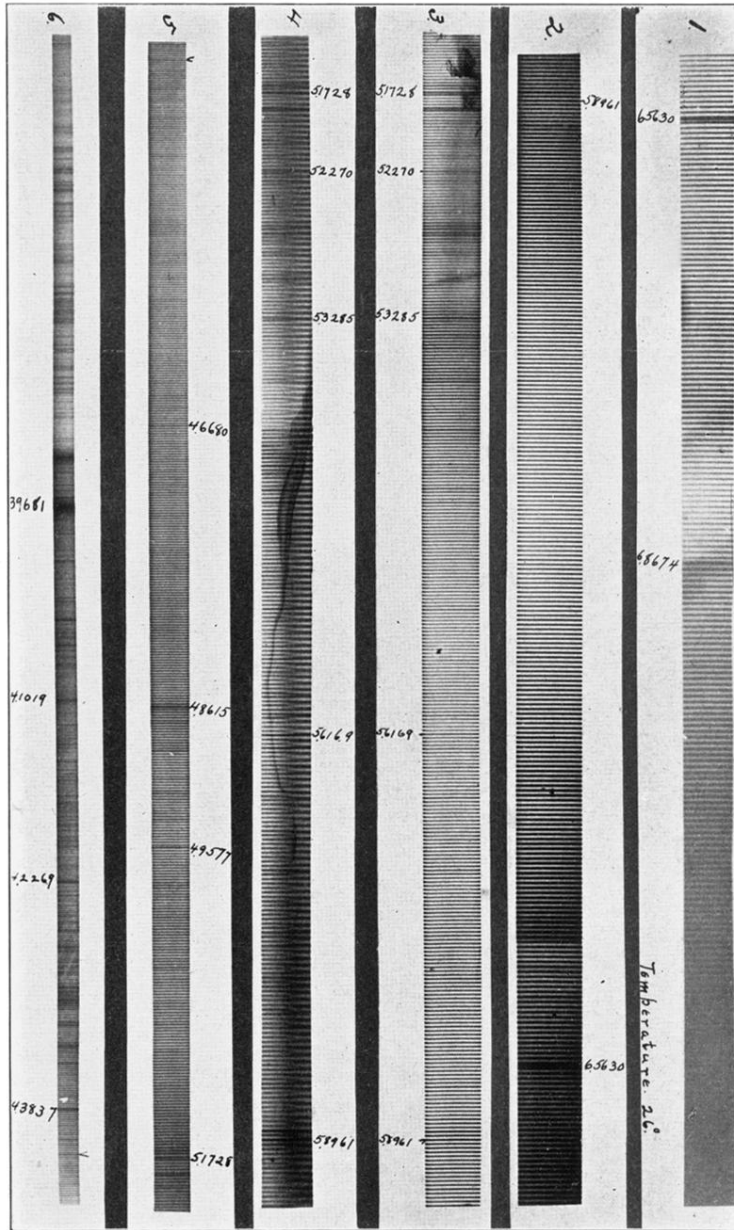


PLATE VI.