

THE RATIO OF THE INTENSITIES OF THE D LINES OF SODIUM.

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IT has been known for a long time that the ratio of the intensities of the D lines varies with the intensity of the sodium flame.

Gouy¹ found the ratio D_2/D_1 to vary from 1.3 for a strong flame to 2 for a weak flame.

An investigation by Brotherus² showed that the ratio varied from 1.25 to 1.53.

Some observations made by Wood³ indicated that, for an exceedingly weak flame, the ratio attained a value as high as 3 or 3.5. The estimate was made by comparing photographs made with different times of exposure, and it was assumed that the blackening of the photographic plate was directly proportional to the time of exposure.

This large value of the ratio was questioned in a recent paper by Ladenburg,⁴ and so, at the suggestion of Professor Wood, a more careful investigation was made.

In the present work, three methods have been employed:

- (a) A photographic method, based on the use of a sectorized disc.
- (b) A visual method in which the intensities were made equal by a polarization method.
- (c) A visual method in which screens, having known coefficients of absorption, were used.

We shall consider first the photographic method.—A sectorized disc (Fig. 1) was prepared, for which the ratio of the time of exposure of any element to that of the next adjacent element was 5/4. The disc was backed by a large flame from a Meker burner, and an image of the upper portion of the disc sharply focused on the slit of a large plane-grating spectrograph. The flame was charged with sodium and the slit of the spectrograph opened until the rectangular images representing the two wave-lengths D_2 and D_1 just touched. If, now, the disc was set in rota-

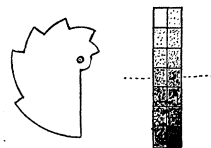


Fig. 1.

¹ G. Gouy, Ann. de Chem. et de Phys., 18, 5, 1879.

² Hj. V. Brotherus, Ann. der Phys., 38, 397, 1912.

³ R. W. Wood, Phys. Zeit., 15, 382, 1914.

⁴ R. Ladenburg, Ber. der Deut. Phys. Ges., 12, 765, 1914.

tion by a small motor, the lines were cut into seven horizontal strips of varying, integrated intensity.

To obtain the maximum value of the ratio, it is necessary to work with a flame of much less intensity than any commonly employed in the laboratory. The easiest method of obtaining such a flame is to charge the air of the room with sodium by operating a rather intense sodium flame for a few minutes. As the work was carried out in a large room, and the doors and windows were kept shut, it was possible to obtain in this way a very feeble flame which remained practically constant for an hour or more. It is important to have the grid of the Meker burner perfectly clean, and the air should be free from dust, for if this is present the particles make bright flashes of sodium light as they pass through the flame. These flashes are many times brighter than the feeble flames with which the large ratios are obtained. By avoiding unnecessary movement in the room after the dust particles had been allowed to settle, the number of flashes could be reduced. With a very intense flame the plate was exposed for three seconds, while forty minutes were required in the case of a very feeble flame. This makes the ratio of the extreme flame intensities somewhat less than 1 : 800. The intensity ratio D_2/D_1 was determined for a given plate by picking out the two exposures (horizontal strips) for one of which D_2 showed the same photographic density as that of D_1 on the other.

The sectorcd disc was rotated at a very slow speed,¹ and it was at first assumed that the density of the image on the photographic plate was directly proportional to the time of exposure. On the above assumption, the ratio D_2/D_1 could be immediately determined as the inverse ratio of the times of exposure which made D_2 and D_1 equally black on the plate.

As no Hartmann photometer was available the comparisons were made by cutting the plate in two at the dotted line, Fig. 1, superposing the two halves, film to film, and matching D_2 on one piece against D_1 on the other, with the aid of a magnifying lens. This method is fairly accurate, as by carefully fitting the plates the dividing line between the two patches under examination can be made to disappear as in a photometer.

Preliminary work showed that an exposure ratio 5 : 4 could be easily detected in this way, and this ratio was accordingly adopted in making the sectorcd disc.

The intensity ratios that could be determined in this way were as follows:

1, 1.25, 1.56, 1.95, 2.44, 3.05, and 3.81.

¹ K. Schwarzschild, *Astrophys. JI.*, XI., 92, 1900.

Care was taken to avoid having any of the horizontal strips either under or over exposed.

With a very intense flame the ratio $D_2/D_1 = 1.25$ was obtained and with the feeblest flame $D_2/D_1 = 3$. This maximum value 3 was later shown to be too large, owing to a source of error in the photographic method which has not as yet been explained.

The decrease in the ratio with increasing flame intensity is due to the more powerful absorption of the D_2 light. That absorption may fully account for the effect was shown in the following way: The slit of a spectroscope was illuminated by a feeble sodium flame and opened, as before, until the two rectangles corresponding to D_1 and D_2 just touched. A glass bulb, highly exhausted and containing some sodium, was interposed between the flame and the slit, and the sodium was vaporized by playing a flame over the bulb. The large ratio for the weak flame immediately dropped to the smaller value found for a more intense flame. To get the maximum value of the ratio we should abolish absorption completely. We of course approximate this condition in a flame very lightly tinted with sodium, but if we could powerfully excite a very thin layer of the gas, the conditions would be still more favorable. Accordingly, a canal ray tube,¹ Fig. 2, was made. The cathode consisted of an aluminum disc, punched with numerous holes. The copper wire leading to this was insulated by a piece of thin glass tubing. The canal rays issuing from the holes in the cathode struck the lump of rock salt R , and in this way a highly luminous and exceedingly thin layer of sodium vapor was obtained. The ratio D_2/D_1 was no larger than for a very weak flame.

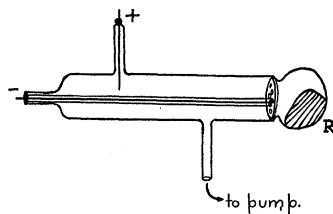


Fig. 2.

The same value of D_2/D_1 as for a feeble flame was also obtained by passing an electrodeless discharge through a vacuum tube containing sodium vapor. An image of the central capillary portion, which was about two millimeters in diameter, was thrown by a lens upon the slit of the spectrograph. The tube was heated to allow the discharge to

¹ If the tube is made of sodium glass, in the absence of the rock salt R a bright sodium fluorescence is obtained on the end of the tube on which the canal rays impinge. It was suspected that the extreme shallowness of the glowing layer might result from the circumstance that a thin layer of glowing sodium vapor is imprisoned by a layer of adsorbed air, and a test of this hypothesis was made by heating a small portion of the bulb, thus driving off the adsorbed air at that point. This region ceased to fluoresce though the rest of the bulb fluoresced brightly. On admitting air into the tube and allowing this to cool, the portion which had been heated gradually recovered its power of fluorescing.

pass, and a photograph of the D lines taken. An exposure of five minutes was necessary. The D_2 line on this plate was matched with a D_2 strip on one of the plates taken with the rotating sector and a weak flame. The D_1 line was found to match with the D_1 strip showing that the ratio was that obtained with a weak sodium flame.

Polarization Method.—The polarization method was next tried. Professor Wood's quartz block,¹ 32 mm. thick and cut parallel to the optic axis, was used.

If a beam of sodium light polarized in a plane making an angle of 45° with the optic axis (which is vertical) is passed through the block, the rays D_1 and D_2 on emergence will be polarized in mutually perpendicular planes. Either D_1 or D_2 can be extinguished by a Nicol prism properly oriented, and with the Nicol in some intermediate position D_1 and D_2 can be made of the same intensity. By observing the position of the Nicol when this condition obtains, the original intensity ratio can be computed.

For a full description of the block and its uses the reader is referred to Professor Wood's original paper. Light from a sodium flame was made parallel by a lens and passed through a Nicol prism, so that on emerging its direction of vibration made an angle of 45° with the vertical. It was then passed through the quartz block, through a second Nicol, and brought to a focus on a slit of the spectrograph by a lens.

The quartz block was first removed and the second Nicol crossed accurately with the first. The reading on the graduated circle of the second Nicol was then taken. The block was now introduced and rotated slightly about a vertical axis until D_1 was cut out. On turning the second Nicol through 90° , D_2 was cut out. Between these two positions there is one position for which the intensities of D_1 and D_2 can be made equal. If θ is the angle between this direction and the direction of vibration of D_2 , then the ratio of the intensity of D_2 to that of D_1 is $\tan^2 \theta$. To obtain large values of the ratio, however, feeble flames must be used, and after passing through the Nicols the light is much reduced in intensity.

Some difficulty was experienced at first in making settings for the position of equality, but after much practice settings could be made which differed by less than two degrees. The mean of many readings was taken. The chief source of error lay in the setting of the first Nicol so that the light incident on the block was polarized in a plane making an angle of 45° with the optic axis. If this angle was less than 45° , on emerging from the block D_2 made an angle less than 90° with D_1 as can be seen from Fig. 3.

¹ R. W. Wood, Phil. Mag- 27, 524, 1914.

OD_1 represents the condition of vibration of incident light. It is analyzed by the block into OX and OY . On emergence the direction of vibration of D_1 is parallel to its original direction, but in the case of D_2 , OX is rotated through 180° to OX' , and the resultant direction of vibration is now parallel to OD_2 , also making an angle ϕ with the optic axis. If ϕ is less than 45° the angle between OD_1 and OD_2 is less than 90° , and similarly if ϕ is greater than 45° , the angle is greater than 90° .

Now the ratio of the intensities D_2/D_1 is given by $\tan^2 \theta$, where θ is the angle between the position of equality of the second Nicol and the direction of vibration of D_2 .

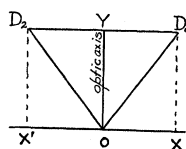


Fig. 3.

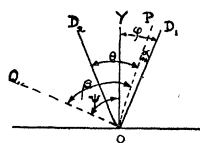


Fig. 4.

In Fig. 4, OD_1 and OD_2 represent the directions of vibration of D_1 and D_2 respectively. OP represents that position of the second Nicol for which D_1 and D_2 on emergence are of equal intensity. OQ is perpendicular to OD_1 .

If $< 2\phi$ (Fig. 3) is less than or greater than 90° , $< 2\psi$ (Fig. 4) is greater than or less than 90° .

If, as in Fig. 4, $< 2\psi$ is greater than 90° the true value of the ratio D_2/D_1 is $\cos^2 \alpha / \cos^2 \theta$, while the measured ratio is

$$\tan^2 \beta = \frac{\sin^2 \beta}{\cos^2 \beta} = \frac{\cos^2 \alpha}{\cos^2 \beta},$$

and is larger than the true ratio. Similarly, if $< 2\psi$ is less than 90° the measured ratio is too small. After the first Nicol had been set approximately, and the quartz block put in position, the second Nicol was turned until D_2 was cut out. It was found difficult to make this setting accurately owing to the small intensity of the light. The observed values of D_2/D_1 increased rapidly as 2ψ became greater than 90° and diminished rapidly for values of 2ψ less than 90° .

Values in the neighborhood of 2 were obtained for the ratio, with a flame colored only by the sodium in the air when the air was heavily charged with sodium vapor. Such a flame is fairly bright, though considerably less bright than a flame colored by an asbestos wick dipped in brine. As will be shown later, the value 2 was also obtained for such a flame by the third (most accurate) method employed.

For the feeble flames, burning in air only lightly charged with sodium, it was extremely difficult to make accurate settings. From one set of readings a value 2.3 was obtained for the ratio, while another set, under apparently identical conditions, gave a value 2.6. The readings of this latter set are given below:

Second Nicol Crossed with First.	D_2 Extinguished by Second Nicol.	Position of Equality of D_1 and D_2 .
— 21°	70°	$37^\circ.3$
— 22	67	36.2
— 21	68	36.8
— 21.5	70	37.6
— 21	66	37
— 21.8	71	37.5
Means — $21^\circ.4$	$68^\circ.7$	$37^\circ.1$

From these, $2\psi = 90^\circ.1$ and $\theta = 58^\circ.5$

$$\frac{D_2}{D_1} = \tan^2 \theta = 2.6.$$

This method can be used therefore for flames varying from very bright to fairly weak, but is unsuitable for the feeble flames.

The largest accurate value given by this method is 2 and is obtained for a flame burning in air strongly charged with sodium.

Visual Method.—The third method will now be discussed. Some gray gelatin films, whose coefficients of transmission had been determined to a tenth of one per cent., were supplied through the courtesy of Dr. Mees, of the Eastman Kodak Co. Narrow strips of these were cut and put across the plateholder of the large plane-grating spectrograph (Fig. 5). The strip *a* let through $33\frac{1}{3}$ per cent. of the incident light, *b*, 40 per cent. and *c*, 50 per cent.

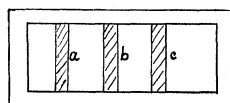


Fig. 5.

The slit of the spectrograph illuminated with sodium light was opened until the two rectangles corresponding to D_2 and D_1 just touched. By sliding the plateholder along, D_2 could be covered successively by *a*, *b*, or *c*, and values 3, $2\frac{1}{2}$ and 2 distinguished for the ratio D_2/D_1 . When the air of the room was charged with sodium vapor, and the flame of a Meker burner put before the slit, D_2 and D_1 appeared of exactly the same intensity when D_2 was covered by *c*, the 50 per cent. screen. This was true for the fairly bright flames obtained in this way (and even these are considerably weaker than the flames colored by an asbestos wick dipped in brine), and also for the weaker, down to the very feeble flames. In every case the match was perfect.

Since it was easily possible to distinguish the difference in ratio when D_2 was covered by the 40 per cent. and by the 50 per cent. screens, it was estimated that the value 2 for the ratio D_2/D_1 was correct to within 10 per cent. This direct method is certainly the most reliable of the three.

Investigation of Apparent Inconsistency of Results of the First and Third Methods.—It was now necessary to investigate the inconsistency in the value 2 given in this method for the ratio in the weaker flames and the value 3 given by the first (photographic) method.

An oblong slit, 24×6 mm., was cut in a sheet of cardboard and covered with a yellow screen which cut off everything below the D lines. Half of this slit was covered with a strip of the 50 per cent. gelatin screen. This was backed first by a sodium flame and between the flame and the slit was placed a piece of uniformly diffusing ground glass. Photographs of the slit were now taken with varying times of exposure by means of an ordinary box camera. The photographs were all taken on the same plate by sliding the plate along in the plateholder between exposures. One set of times of exposure were as follows: 4, 8, 12, 16, 24, 36, and 4 seconds. The last exposure of 4 seconds was taken to determine whether the intensity of the flame had changed during the experiment. A constant flame was obtained by putting a small piece of sodium glass tubing on the grid of a Meker burner. The times of exposure were determined by the swings of a seconds pendulum. The plate was cut lengthwise, the two parts placed film to film, and the darker half of one strip was matched against the light half of another. In every case it was found that the ratio of the times of exposure of two half-images that matched was 3 : 1, exactly as had been obtained in the photographs with weak flames for D_1 and D_2 in the first method.

Great care was taken to have the density of the image uniform throughout the length of the strip, as otherwise an error would be made in matching the strips unless the match was made exactly at the dividing line.

The slit was now backed by a tungsten lamp placed behind a diffusing screen made of two sheets of ground glass and a set of exposures again made. The ratio of the times of exposure of the strips that now matched was 2 : 1. The difference in the effects obtained with a sodium flame and with a tungsten lamp cannot be due to a difference in the coefficient of transmission of the gelatin film for sodium light, for the yellow film placed over the artificial slit cut off everything below the D lines, and the sensitivity of the Cramer isochromatic plates used falls off rapidly above the D lines. This was further verified by illuminating the slit

with a very sharp continuous spectrum in the region of the D lines, obtained from a monochromator. In this case also the ratio of the times of exposure was 2 : 1.

It is also impossible to explain the difference by a variation with the wave-length, in the quantity k in Schwarzschild's equation for the blackening of the photographic plates, $S = It^k$ (S is the density of the image, I the intensity of the light, t the time of exposure, and k a quantity varying slightly with the plate used and the wave-length of light), owing to the very narrow range of wave-lengths used.

These results made it appear as if a curious difference existed between the behavior of the photographic plate towards white light and monochromatic light. This would bring the results obtained by the first method into perfect agreement with those obtained by the other two methods. For a ratio 3 for the times of exposure obtained with the sector disc means a ratio of $D_2/D_1 = 2$.

A large number of experiments were made, all of which gave very nearly the same results. Dr. Mees has however failed to confirm them in the research laboratory of the Eastman Co. and the source of the discrepancy has not been located at the present time.

SUMMARY.

By three independent methods it has been shown that the maximum value for the ratio of the intensities of the D lines of sodium is $D_2/D_1 = 2$, correct to within 10 per cent.

In conclusion the author wishes to express his hearty thanks to Professor R. W. Wood for suggesting the problem to me and for the many suggestions made throughout the course of the investigation.

JOHNS HOPKINS UNIVERSITY,
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