SERIES LIMIT ABSORPTION IN SODIUM VAPOR

By George R. Harrison[1]

Abstract

Transmission curves of sodium vapor for wave-lengths near the principal series limit, 2550 to 2150A.—*Reliable ultraviolet photometric measurements* were secured by using a steady rotating disk cadmium spark as source and by taking on a single plate, in addition to three absorption spectra, exposures for eight different intensities varied in steps from 2 to 100 by means of oscillating screens, each exposure being for the same time. (The exposure time was reduced to 16 sec. by using an absorption furnace with a column of vapor only 10 cm long.) Measurements of a single plate thus gave the characteristic curves for that plate which were needed to determine from the absorption spectra the actual transmission as a function of wave-length. As the wave-length decreases, the transmission rises to a maximum at 2465A, then decreases regularly to a sharp minimum at the series limit 2414A, then rises to a value at 2200 about equal to that at 2465. The series limit absorption thus decreases rapidly with decreasing wave-length. The eighteen curves obtained for different vapor densities are very similar, all being convex upward. The maximum discontinuity observed is from 34 per cent transmission at 2465A to 20 per cent at 2414A, for vapor of medium density; for greater or less densities of saturated vapor the discontinuity is smaller. Due to the presence of band absorption even beyond the limit, the precise variation of atomic absorption with wave-length cannot as yet be determined from these results.

Densitometer curves for sodium principal series absorption and for hydrogen diffuse series absorption in stars show great similarity near the limits.

Introduction

A STRIKING correlation made by the Bohr theory between spectroscopic phenomena and atomic behavior is the explanation of the continuous region of absorption or emission frequently found beginning at a series limit and extending towards shorter wave-lengths. The absorption is important because it corresponds to the photo-electric effect in the absorbing vapor, while the emission is due to the fall of free electrons of varying velocities into ionized atoms. Bohr[2] explains the two cases as being due to jumps between a quantized state and a free state incapable of quantization. Taking the principal series of sodium in absorption, for example, we have a large number of lines due to electron jumps from the 1σ level to the various π levels, and finally a continuous region of absorption where electrons have been raised clear of the atom. Thus the original

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[1] National Research Fellow.

[2] Bohr, Phil. Mag. **26**, 16 (1913)

energy $h\nu$ of the light of frequency ν, if more than enough to free the electron completely, is divided into two parts, W, that required to lift the electron above the highest virtual orbit, and a remainder $\frac{1}{2}mv^2$ going into kinetic energy of the freed electron.

In the x-ray region, similarly, we have continuous absorption below the K, L, and M limits. Most investigators find that this absorption decreases as the cube of the wave-length, though the exponent varies for different observers between 2.5 and 3. Kramers[3] has theoretically derived an expression of similar form to that found experimentally, and his work suggests that a λ^3 law might be expected to hold in the optical region as well, although his assumptions apply strictly only to the inner shells of the atom. Milne,[4] attacking the problem from a different angle, expects a λ^2 law to hold in the optical region. The importance of finding the true law connecting series limit absorption with wave-length has been emphasized, but the experimental data are very meager.

In the laboratory the continuous optical absorption has apparently been noted at limits of principal series only, having been found by Wood[5] in sodium, and by Holtsmark in sodium and potassium.[6] It is visible also in the spectra published by Bevan[7] for rubidium and caesium, although not mentioned by him. In hydrogen stars continuous absorption is frequently found at the limit of the Balmer series, but this seems to be the only case so far observed where a subordinate series has been strongly enough absorbed to show the effect.

The ions produced when the vapor absorbs frequencies higher than the convergence frequency of its principal series have been detected by Kunz and Williams[8] and by Williamson.[9] Apparently no measurements have yet been made on the relative efficacy of various wave-lengths shorter than the series limit in producing photo-electrons. This information is desirable as it would afford a second method of attack on the problem considered in the present paper.

The discontinuities occurring at the series limits of sodium and potassium have been roughly measured by Holtsmark[6] and by the writer.[10] In the latter paper it was stated that the continuous absorption in Na and K, beginning near the series limits, does not extend undiminished into the

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[3] Kramers, Phil. Mag. **46**, 836 (1923)

[4] Milne, Phil. Mag. **47**, 209 (1924)

[5] Wood, Astrophys. Jour. **29**, 97 (1909)

[6] Holtsmark, Phys. Zeit. **20**, 88 (1919)

[7] Bevan, Proc. Roy. Soc. **83**, 421 (1910); **85**, 54 (1912)

[8] Kunz and Williams, Phys. Rev. **15**, 550 (1920); **22**, 456 (1923)

[9] Williamson, Proc. Nat. Acad. Sci. **8**, 255 (1922); Phys. Rev. **21**, 107 (1923)

[10] Harrison, Proc. Nat. Acad. Sci. **8**, 260 (1922)

extreme ultraviolet as might be supposed from a casual inspection of the photographs obtained, but decreases quite rapidly with increasing frequency. Rough curves were published showing in a general way the transmission of these vapors to light of wave-length between 2100 and 5000 A.

PURPOSE OF THE INVESTIGATION

The objects of the present work were to develop a satisfactory method of photographic photometry which could reasonably be assumed correct, to find the curve connecting transmission with wave-length for sodium vapor between 2600 and 2100A, to measure the magnitude of the discontinuity occurring at the series limit and to study the cause of any variations that might appear.

Since the convergence limits of the principal series of all elements other than the alkali metals lie below 2100A, we are limited at once in the choice of vapors to be studied. In order to make accurate measurements a fairly large quantity of the vapor must be used, which has so far prevented the study of Rb, Cs, and Li. All samples of potassium studied showed so much sodium as an impurity that the band around line 2853 masked the true form of the potassium absorption curve beginning at 2867. It is hoped that results for other metals than sodium may be obtained shortly, since the interpretation of the results of the present work depends to some extent on the behavior of other elements.

EXPERIMENTAL ARRANGEMENTS

After studying various methods, a general system of photographic photometry was developed which has been briefly described elsewhere,[11] and which has since been somewhat improved in certain details. In Fig. 1 is shown the general arrangement of the sensitometer used. The requirements as to light source were that it should be relatively free from lines over stretches of 20A between 2100 and 2600A, or else that it should contain a large number of lines of approximately equal photographic intensity in this region, regularly distributed. It should also be steady as regards total intensity to within one per cent for a period of ten minutes, and its energy distribution should not vary appreciably during that time. The cadmium spark in air was chosen for work between 2100 and 2600A. It was found that the greatest steadiness could be obtained when the spark was between two disks rotating edge to edge, an arrangement recently described by Bovie.[12] Both disks were driven by rubber bands

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[11] Harrison and Hesthal, J. Opt. Soc. Am. and R. S. I. **8,** 471 (1924)

[12] Bovie, J. Opt. Soc. Am. and R. S. I. **7,** 1026 (1923)

running from a common shaft driving an air blower. This blower was necessary to prevent coating of the lenses by cadmium oxide, which accumulated rapidly. The spark housing was made fairly airtight, and a number of holes were cut in each lens holder. Air was drawn through these by the blower, and the resulting current carried the cadmium oxide and ozone out of the room through a flexible tube.

In order to be able to regulate the spark length readily, the two shafts containing the disks were mounted on vertical ways, and their heights could be separately adjusted by turning screws with insulated handles on top of the housing. In this way the spark length could be varied while running, which was desirable, since this was the finest adjustment for obtaining a "purring" spark, the condition of greatest steadiness. This condition, which existed when a regular number of discharges took place each half-cycle, occurred when the spark voltage, spark length, and capacity in parallel with the spark had the proper values.

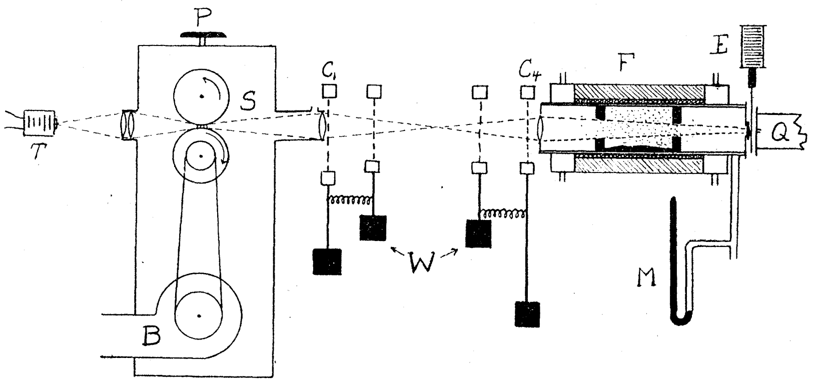


Fig. 1. Detail of part of the sensitometer used. *T*, thermopile; *S*, spark; *C*, screens; *W*, pendulums rocking the screens; *F*, furnace; *E*, magnetic shutter; *Q*, quartz spectrograph slit.

A bismuth-silver thermocouple measured the total radiation from the spark. No provision was made for measuring the energy distribution in the spectrum, conditions being held constant to prevent its variation. Changes in line voltage, which were rare, were quickly compensated by a variable impedance in the primary of the 30 kv, 2 kw transformer feeding the spark.

In order to vary the intensity of each wave-length by the same amount, the screen method was adopted, with several improvements. It was found possible to calibrate the screens and keep them constant in transmission to 0.2 per cent over long periods if certain simple precautions were observed. The screens must not be of too fine or too coarse mesh, they should be carefully oxidized so as to avoid further surface changes, and must be kept in motion laterally while being used or measured, being always put in a beam of fairly large cross-section. Five standard screens were used, which let 51.4, 48.0, 35.1, 35.7, and 31.2 per cent of the light through, respectively. By using combinations of these, from one to four at a time, it was possible to vary the intensity of the light falling on the slit of the quartz spectrograph from 100 to 1.87 by fairly even steps. Each screen was mounted on a pendulum support, and was kept in side to side motion of amplitude covering at least ten small apertures. All four pendulums were kept in irregular oscillation by a heavy master pendulum. Thus errors due to the finite distance between apertures were reduced to a minimum. The screens were also kept in motion while being measured in the thermoelectric densitometer.

The absorption furnace as finally used was a steel tube 30 cm long and 4 cm in diameter, closed with a thin quartz lens at one end, and a quartz plate at the other, both cemented on with sealing wax. Water coolers were placed about 3 cm from each end. A thin layer of mica was wrapped around the central portion of the tube, and on this 20 turns of No. 10 nichrome wire were wound. This was finally covered with asbestos paste, and the whole enclosed in a brass jacket. A 3 kw transformer provided heating current at 40 volts, only about 900 watts being found necessary to keep the furnace at 800°C.

The column of hot sodium vapor was only 10 cm long. Diaphragms were placed in the tube limiting the column to the centermost portion, having apertures just equal to the cross-section of the beam. These were found absolutely necessary for such a short furnace. In Wood's work, and in most of the preceding work on sodium vapor done by the writer, tubes from one to three meters long were used. With these, however, exposures of 20 min. to half an hour were necessary, so the furnaces used were gradually shortened until an exposure of 16 sec. was ample. It was found possible to use such a short column provided the pump was never run while the vapor was hot, and hydrogen at a pressure of several cm was always left in the tube to prevent too rapid distillation. One charge was sufficient to run the tube for an hour at 800°C and at the end of that time the tube could be opened and the sodium which had distilled over into the cold ends could be scraped up and replaced in the center of the furnace.

When fresh sodium was introduced the windows became coated with oxide and hydroxide fairly rapidly. After several heatings, however, the cleaned windows remained clear for some time.

A Hilger quartz spectrograph was used for photographing the spectra. In most cases a wide slit was used to facilitate setting in the center of a line on the densitometer. The plate holder carried two plates; eleven spectra were photographed on each, and they were then fastened back to back with rubber bands and developed and fixed together. Six spectra were absorption pictures, and the remaining 16 were used in two sets of eight each for plotting characteristic curves. The set for the first characteristic curve was taken first, then three absorption pictures; three absorption pictures were then taken on the second plate, and finally the eight points for the second characteristic curve. Thus any coating of the windows occurred after the first curve and before the second, and was corrected for. The time of exposure was controlled by a standard clock operating a magnetic shutter.

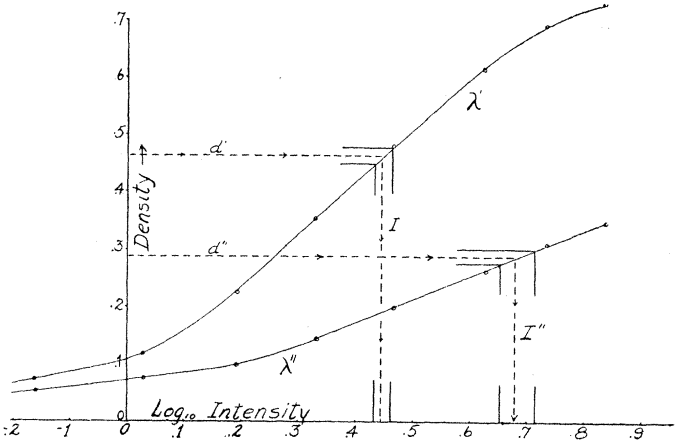


Fig. 2. Typical characteristic curves for two different wave-lengths, as used for determining the intensity which caused a deposit of given density in the negative.

In all of the present work the image densities compared were in each case developed, washed, and fixed at the same time. Since comparatively little is known of the characteristics of photographic emulsions when exposed to ultraviolet light, five standard brands of plate were used.

The densitometer was of the familiar thermo-electric type, improved so that its readings can be trusted to 0.2 per cent. A systematic hunt for the causes of all irregularities, generally less than 1 per cent, has been made, resulting in several simplifications and improvements. Where measurements were to be made at a given wave-length, easily found, the "spotting" densitometer was used, but this would not do for setting on narrow lines or regions in the spectrum where density was changing rapidly with wave-length. For such regions the "running" densitometer was used. A particular wave-length was chosen, and the density of the negative at this wave-length was measured for each spectrum. Each density obtained was then plotted against the logarithm of the transmission of the screen used to produce it. Two typical characteristic curves, for different wave-lengths, are shown in Fig. 2. From such curves the transmissions corresponding to the densities of the absorption pictures were readily obtained. In this way two characteristic curves were plotted for each measured wave-length for each pair of plates, and on each characteristic curve the transmission of the sodium vapor for three separate conditions could be measured. About forty plates were taken in this way, but many being discarded for various reasons, eighteen curves were finally chosen as best representing the data obtained.

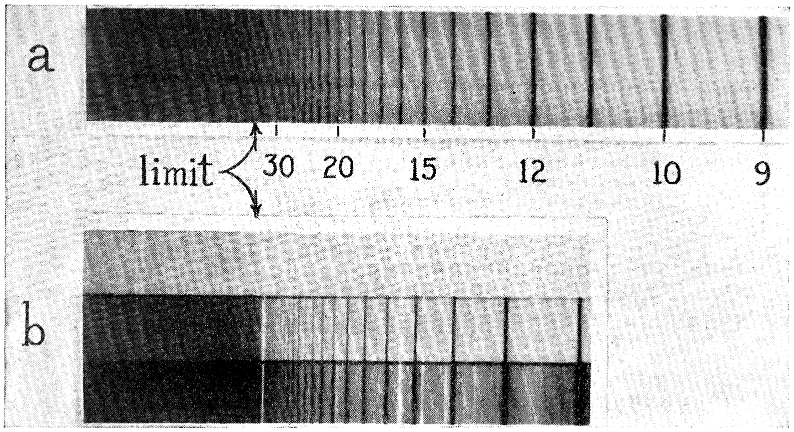


Plate I.

(a) The limit of the Na principal series in absorption, with Al under-water spark background, showing the apparent absence of discontinuity.

(b) The series limit with Cd spark background, showing how the continuous absorption varies with vapor density.

In Fig. 3 is shown an isochronat, connecting wave-length, density, and in a third dimension intensity. The network of points measured on one of the above-mentioned plates forms such a surface. Comparison of the absorption curve with this set of curves gives the true transmission for each wave-length.

Results Obtained

In Fig. 4 are shown three curves plotted by the running densitometer. (a) shows the density distribution in a spectrogram of the region near the limit 1σ in sodium vapor, taken with an aluminum under-water spark as a background. This was run from a negative. (b) shows the same region as measured on a positive (this being reproduced in (a) of Plate I). A comparison of (a) and (b) indicates that practically all of the density range lies on the straight-line portions of the various characteristic curves. (c) is a similar tracing made from a negative of the Balmer limit in Vega, very kindly loaned the writer by Professor Wright of Lick Observatory. Most of the differences between the two kinds of curve can be traced to differences in the backgrounds and in the characteristics of the emulsions used for the different spectral regions.

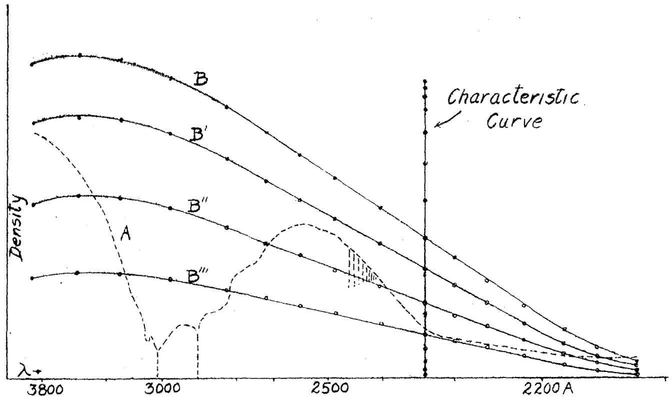


Fig. 3. An isochronat, or surface containing points of equal exposure time. The curves *B*, *B'*, etc. are curves of equal relative intensity, being for points all taken with the same screen covering the light source. Each vertical set of points marks part of a characteristic curve seen edge on. The dotted curve shows the density of the absorption spectrum for various wave-lengths, the relation of dotted to solid curves giving the true transmission for the absorbing medium for each wave-length.

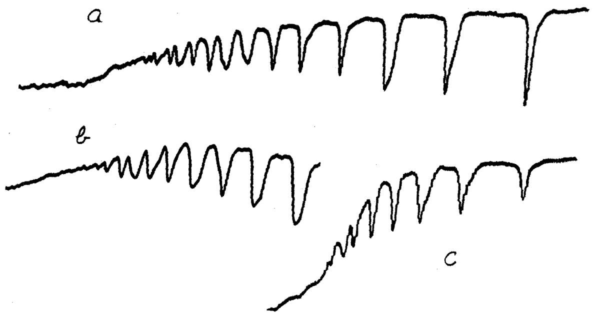


Fig. 4. (a) Densitometer tracing of the principal series limit in sodium vapor, from a negative. (b) Same, from a positive. (c) The Balmer series limit in Vega, showing great similarity to sodium (a) and (b).

In what follows it should be borne in mind that all curves are true transmission curves and not merely density curves as are those in Fig. 4.

In Fig. 5 are given seven typical transmission curves for sodium vapor at various densities. The scale is the same for each, but they have been displaced somewhat along the vertical axis in order to keep the various sets of points apart. The true position of each curve can be found by use of the decimal marked under it, this giving the transmission for the vapor at the series limit, perfect transmission being taken as unity.

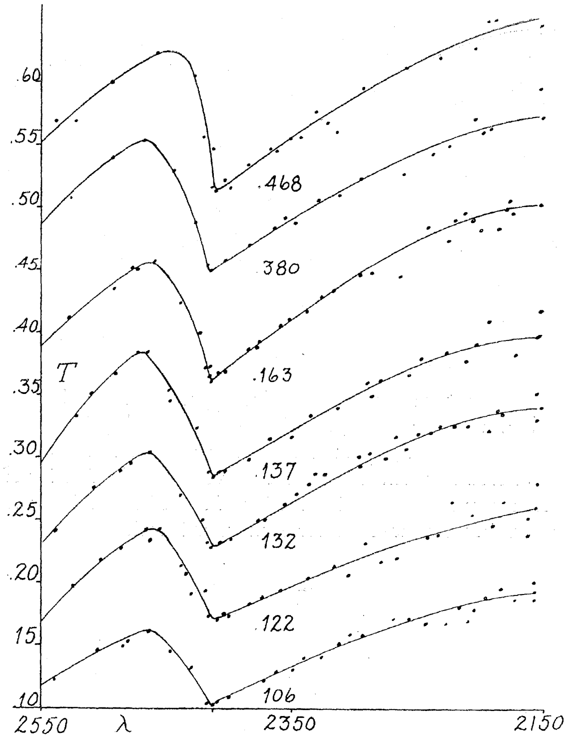


Fig. 5. Transmission wave-length curves for sodium vapor near the principal series limit. The curves for various vapor densities are on the same scale, but are displaced vertically. The decimals under each curve give the true transmission just below the series limit.

A, the angle between the horizontal and the line drawn from *T* at the series limit to maximum *T* above the series limit.

B, the angle between the horizontal and the tangent to the lower part of the curve at the series limit.

C, the angle between the horizontal and the line joining *T* at the limit to *T* at the lower end of the curve, 2144A.

L, the value of *T* at the series limit, 2414A.

M, the maximum value of *T* between series lines below 2600A.

N, the maximum value of *T* below the limit, always at 2144A.

H_1, the difference $M-L$, or amount of discontinuity at limit.

H_2, the difference $N-L$, or increase in transmission between 2414 and 2144A.

To find how the various shapes varied with conditions, each curve had the following quantities measured, shown graphically in Fig. 6.

The values of these quantities are listed in Table I, arranged in the order of increasing vapor density.

Inspection of this table shows the following facts:

(1) Every plate measured gives B greater than C; that is, the transmission curves are always convex upwards.

(2) In every curve H_1 and H_2 are approximately the same, H_2 being generally slightly the greater. That is, the discontinuity at the limit is offset in a space of 270 A below the limit. On an average, H_2 is 5 per cent greater than H_1.

(3) The value of H_1 rises slowly as the vapor density increases, then falls. That is, a certain vapor density gives the maximum discontinuity at the limit. For the conditions of the present work, the maximum discontinuity obtained was about 14 per cent of the light entering the tube; that is, 34 per cent of the original light was transmitted between the lines near the limit, and only 20 per cent just below the limit.

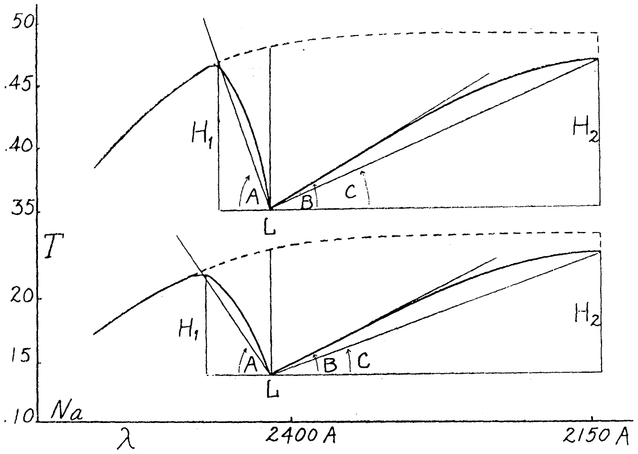


Fig. 6. Two typical average curves drawn from those in Fig. 5 and Table I, showing the shape factors which were measured.

(4) The value of H_2 also slowly rises as the vapor density increases, until a certain density is reached, when it begins to fall.

(5) As the vapor density increases, L, M, and N all decrease.

It is evident that the absorption here measured is due to several causes, and we may expect these to be: (1) The true atomic absorption producing photo-electrons; (2) the band absorption by the molecule Na_2 or NaH, or whatever molecule it may be which produces the well known secondary absorption in Na vapor; and (3) scattering by droplets, molecules, and free electrons.

No photographs show bands in the region below the limit. At the vapor densities used in this work, all light for some distance around the D-lines has been wiped out, as well as around the 3303 doublet. Around the third member bands are still strongly visible, and to some extent near the fourth. Beyond these the bands are very faint, but densitometer measurements indicate that they still exist, since the decrease in transmission on the long wave side of the limit in the curves of Fig. 5 is due to them. By raising the furnace temperature 100° above the temperatures commonly used, it is possible to wipe out completely all light except in the very transparent region between the lower D bands and the 3303 bands, and in the short wave-length region around 2200. It is evident, then, that a semi-continuous but variable band absorption must be considered even below the series limit. We can roughly extrapolate the curve beyond the series limit, assuming the atomic absorption to be absent, but this will not give a definite form for the absorption function of which we can be certain. It will not serve, for instance, to differentiate between Kramers' λ^3 law and Milne's λ^2 law.

TABLE I

Shape factors for sodium series limit absorption curves

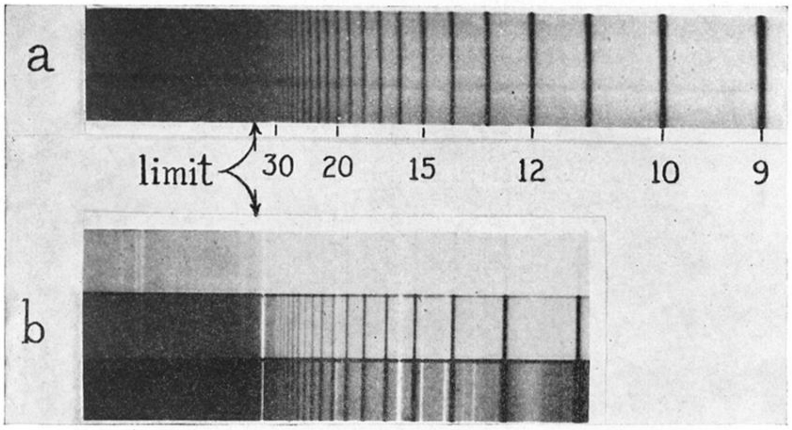
The data are arranged in order of increasing vapor density. Decimals denote fraction of light passing through vapor, perfect transmission being 1.00

Plate	A	B	C	L	M	N	H_1	H_2
18a1	73	37	28	.468	.578	.610	.110	.142
18a2	73	32	21	.437	.546	.546	.109	.109
18a3	74	30	20	.398	.520	.502	.122	.104
18b4	67	29	20	.380	.480	.477	.100	.097
18b5	64	30	21	.354	.450	.456	.096	.102
18b6	58	34	25	.350	.455	.475	.105	.125
19a1	70	38	33	.285	.417	.458	.132	.173
19a2	70	40	31	.230	.370	.390	.140	.160
19a3	71	40	31	.205	.350	.370	.145	.165
15a1	53	23	18	.181	.237	.259	.056	.078
15b4	64	38	28	.163	.262	.305	.099	.142
15a3	60	31	20	.147	.224	.245	.077	.098
15a2	60	27	16	.142	.206	.224	.064	.082
16b4	59	26	18	.137	.230	.230	.093	.093
15b5	54	33	23	.132	.208	.245	.076	.113
16b6	61	34	18	.126	.220	.215	.094	.089
16b5	56	24	19	.122	.200	.214	.078	.092
15b6	49	27	20	.106	.163	.197	.057	.091

For this reason it does not seem possible in the present paper to determine rigorously the exact relation between atomic absorption and wave-length. Where other elements are used, as potassium, this function should be similar, whereas the band absorption will probably be found different. Therefore a detailed discussion of this relation will be reserved until results for one or more other metals have been obtained. A determination of the relative intensities of the absorption series lines in sodium is now in progress, this being independent of bands.

The writer wishes to express his gratitude to Professor D. L. Webster for his interest and advice in the early part of the work, which was done at Stanford University, and to Professors Theodore Lyman and F. A. Saunders for similar favors during its completion.

Jefferson Physical Laboratory,
Harvard University.
June 15, 1924.



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