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BY SPECTROBOLOMETRIC  
MEASUREMENTS

(WITH THREE PLATES)

BY

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Smithsonian Institution and U. S. Bureau of Chemistry and Soils



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# THE DETERMINATION OF OZONE BY SPECTROBOLOMETRIC MEASUREMENTS

By OLIVER R. WULF

SMITHSONIAN INSTITUTION AND U. S. BUREAU OF CHEMISTRY AND SOILS

(WITH THREE PLATES)

In the fall of 1930, at the suggestion of Dr. C. G. Abbot, measurements of the transmission of visible light by ozone were made on the solar spectrometer of the Smithsonian Institution at Table Mountain, Calif. This determination of the absorption of ozone in the region of its very weak absorption, practical in the laboratory only by the method of photographic photometry, by which it has been done by Colange,<sup>1</sup> can be accomplished by direct energy measurements on the spectrobolometer because of its great sensitiveness and the extreme intensity of the source. At the same time fluctuations in weather conditions are likewise registered with great sensitiveness and constitute a serious source of error in the measurements. But on the other hand it is favorable that observations may be made of the absorption of controlled amounts of ozone placed in the sun's beam with all other conditions of operation identical with those of the regular solar observations. One of the useful results of this work has been the selecting of a large number of points on the solar bologram which may be satisfactorily used for ozone determination. The present paper has to do for the most part with the results of these measurements as forming a basis for the determination of atmospheric ozone from solar bolograms and not with the results of their application.

The essential apparatus used in this work auxiliary to the spectrometer is shown in Plate 1. A cylindrical glass cell, 20.0 cm. long and approximately 13 cm. in diameter, was mounted in the front room of the spectrometer tunnel in such a way that it could be easily moved in or out of the solar beam as it came from the coelostat mirrors on its way to the first slit of the instrument. The circular windows of this cell were made of high-grade plane plate glass. These windows

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<sup>1</sup> Colange, G., *Journ. Phys. et le Rad.*, ser. 6, vol. 8, p. 254, 1927.

of the cell were covered with diaphragms having vertical rectangular openings sufficient to pass a beam that considerably more than covered the first slit of the spectrometer. The absorption cell was sealed with all glass seals in connection on its inlet side with the ozonizers and on its outlet side with an analytical apparatus for ozone. No alterations of any sort were made in the regular observing conditions except for the interposition of the cell. Tank oxygen was supplied to the ozonizers under a small constant pressure through the capillary of a glass flowmeter having nujol as the manometric liquid, this flowmeter being calibrated in a series of independent measurements. The exit ozone was analyzed by the method described by Wulf and Tolman.<sup>1</sup> The samples, whose volumes were known from the time and rate of gas flow, were collected over potassium iodide solution, set aside, and subsequently analyzed. It is evident that, in the filling of such a cell by sweeping at the low rates of gas flow necessary in such a system for producing ozone of relatively high concentration, a considerable amount of time will elapse before the exit gas attains practically the concentration of the entering gas. To study this circumstance a tube was also brought to the analytical apparatus from before the cell as the gas came from the ozonizers allowing a sample of the inlet gas to be taken, and by means of this it was possible to determine the time sufficient for the exit gas to rise nearly to the concentration of the inlet gas. The concentration of the exit gas was taken, in view of the processes of diffusion and mixing going on in the cell, as representative of the ozone concentration in the cell. The ozonizers were of the familiar silent discharge type. For part of the work one alone was used, while for the rest of the work two were used in series and both water-cooled, these giving the largest concentrations employed. Ordinarily over the period of the taking of four ozone bolographs six analytical samples of the ozone were collected.

Knowledge gained from earlier work on ozone permits a description of the character and position of the absorption.<sup>2</sup> A small fraction

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<sup>1</sup> Wulf, Oliver R., and Tolman, Richard C., *Journ. Amer. Chem. Soc.*, vol. 49, p. 1650, 1927.

<sup>2</sup> *a.* Colange, G., *Journ. Phys. et le Rad.*, ser. 6, vol. 8, p. 254, 1927.

*b.* Wulf, Oliver R., *Proc. Nat. Acad. Sci.*, vol. 16, p. 507, 1930.

*c.* Ladenburg, Erich, and Lehmann, Erich, *Ann. Phys.*, ser. 4, vol. 21, p. 305, 1906; *Verh. Deutsch. Phys. Ges.*, vol. 8, p. 125, 1906.

*d.* Schoene, E., *Journ. Russ. Phys.-Chem. Soc.*, vol. 16, pt. 9, p. 250, 1884; *Journ. Chem. Soc.*, vol. 48, pt. 2, abstracts, p. 713, 1885; *Chem. News*, vol. 69, p. 289, 1894.

*e.* Chappuis, J., *Ann. l'École Norm. Sup.*, ser. 2, vol. 11, p. 137, 1882; *Compt. Rend.*, vol. 91, p. 985, 1880; *Compt. Rend.*, vol. 94, p. 858, 1882.

of the solar energy will be cut out by the ozone as is illustrated in Figure 1, which represents a normal spectral energy curve roughly similar to that of the sun showing the approximate area removed by the atmospheric ozone in the visible.

However, the actual observing of this reduction of intensity must be made on the complicated solar curve as shown in Plate 2, which is composed of a series of typical bolograms notched by many Fraunhofer absorption lines. The discontinuities in the curves are due to the insertion of rotating sectors in the path of the solar beam to cut down the intensity in the regions of great intensity, to values such that the galvanometer deflections will still fall upon the photographic

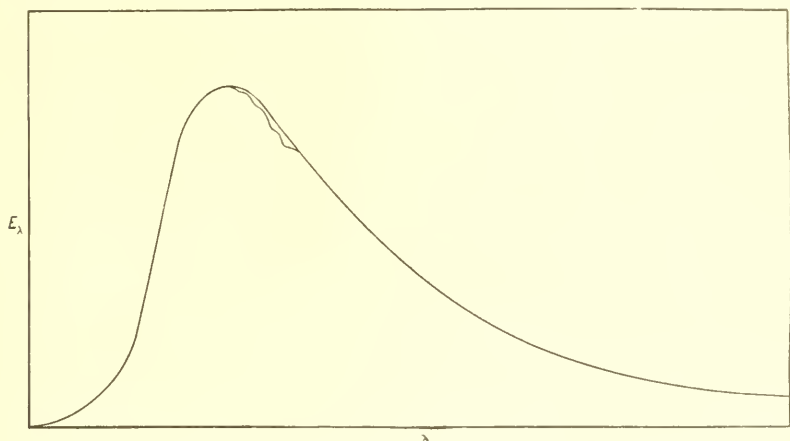


FIG. 1.—Spectral energy curve of black radiator, approximating that of the sun, showing the atmospheric ozone absorption in the visible.

plate on which these deflections are being continuously recorded in the form of these curves. In addition, at two points a shutter is inserted for the purpose of determining the base line, that is, the line of zero deflection. Owing to the scattering of the rays by the earth's atmosphere the apparent maximum of the sun's intensity is shifted to longer wave lengths. The strong atmospheric absorption in the deep red is conspicuous, while over the region of ozone absorption chiefly the Fraunhofer lines are in evidence.

In spite of these complexities, however, comparison of two bolograms, one without ozone in the cell and one with ozone, should show the reduction in intensity caused by the ozone, providing weather conditions remained sufficiently constant between the two. If, for example, we were to take the ratio of ordinates at corresponding points on two such bolograms under ideal conditions this ratio should

be unity in regions not influenced by ozone, and somewhat greater than this where the intensity was reduced by the ozone absorption. In view of the exponential decrease in intensity of light passing through an absorbing medium, it is the logarithm of the ratio of ordinates which is proportional to the amount of ozone in the path. This will be zero evidently for those cases where the ratio is unity, and positive or negative as the ratio is greater or less than unity. This proportionality is based on the assumption that Beer's law may be used here. There appear to be no causes concerned with the apparatus and structure of the spectrum which could bring apparent false deviations from this law, since the spectrum is composed of broad diffuse bands,<sup>1</sup> or perhaps more accurately fluctuations in the absorption coefficient without any apparent discontinuities. The question as to whether the ozone absorption actually obeys Beer's law is an important one and, so far as the author is aware, has not as yet been satisfactorily answered, although attention has been called to it by Ladenburg.<sup>2</sup> However, this assumption is contained in all previous determinations of ozone such as we are employing here and must be similarly contained in the present work. Actually, instead of a single hologram in these measurements, four consecutive holograms were taken with the cell containing no ozone and four more with the cell containing ozone. The average values of the ordinates at corresponding points were compared.

A difficulty enters, however, because of the time which elapses between the taking of the ozone holograms and the uninfluenced ones which we will call the oxygen holograms, since a very appreciable change in air mass, or amount of atmosphere traversed, occurs between the two as well as possible weather changes. This was unavoidable with the apparatus at our disposal at the top of Table Mountain because of the nature of the ozone technique, and is not easy to avoid under any circumstances. Under these conditions, the ratio of ordinates outside of ozone absorption would be far from unity and the logarithm far from zero. Standard correction for air mass was, therefore, applied to the average ozone ordinates to bring them to the air mass of the oxygen observations. It is hardly possible, however, to make correction for all differences between the two sets with accuracy sufficient to bring the logarithm of the ratio of ordinates to zero within a quantity small compared to the small ozone effect, and it is not necessary because it is a difference in the logarithm for different wave lengths that is of interest.

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<sup>1</sup> See footnote 2*b* on page 2.

<sup>2</sup> Ladenburg, R., *Gerlands Beitr. Geophys.*, vol. 24, p. 40, 1929.

The points shown on the holograms were chosen as far as possible with respect to the known position of the ozone bands. These bands are shown in Plate 3 as they were obtained in the work described in footnote 2*b*, on page 2. The attempt was made to find points on

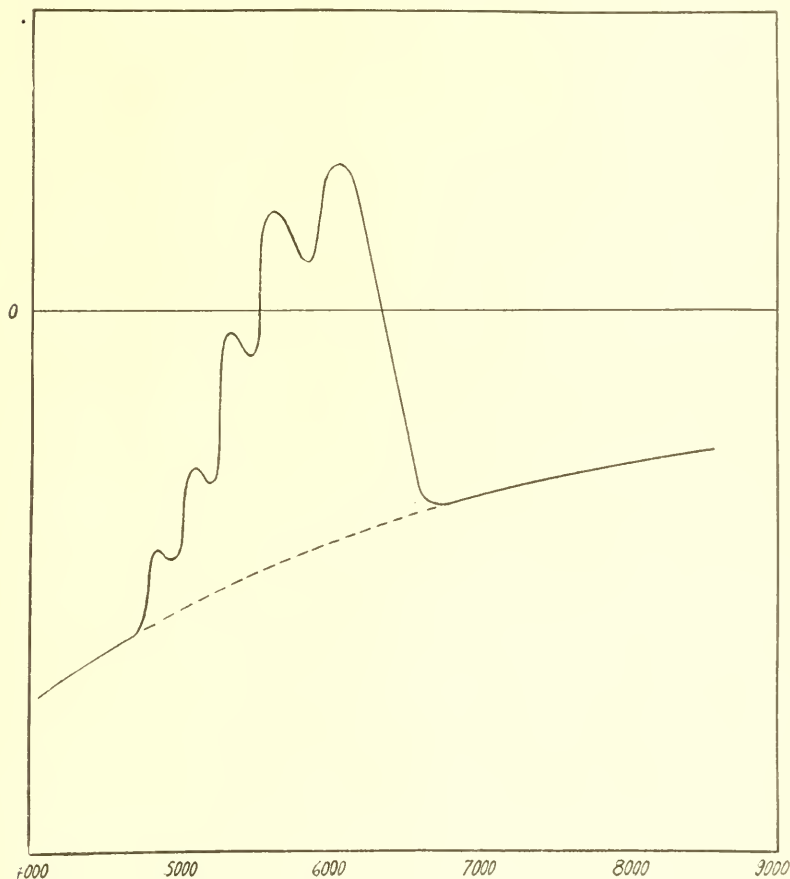


FIG. 2.—Diagrammatic example of ozone area.

the solar hologram suitable for measurement which lay in every ozone absorption maximum and minimum.

From the above considerations, if a plot of the logarithm of the ratio of ordinates is made against wave length, the type of result to be expected is something of the form shown in Figure 2. The failure to make accurate correction for changes in atmospheric transparency or sensitiveness of apparatus will result in the points outside of ozone

absorption being something greater or less than zero, here illustrated as less than zero, but this will not obscure the increased value of the ratio in the region of ozone absorption showing as an increase above

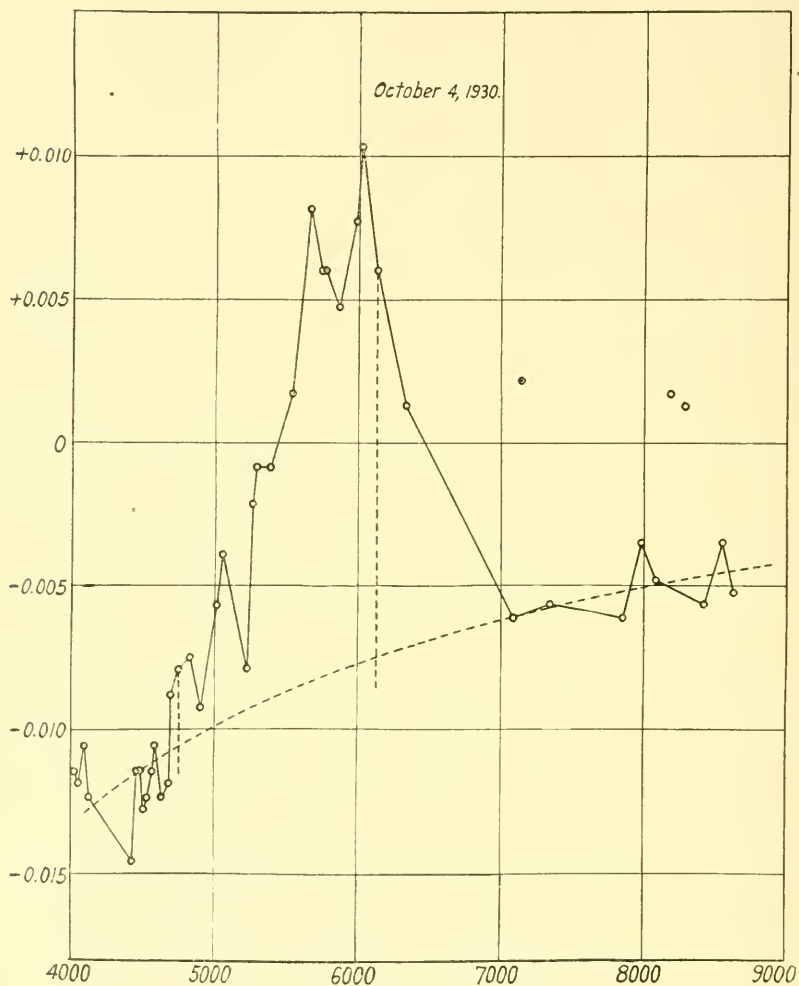


FIG. 3.—Typical ozone area.

the smooth curve passing through the values of the points on both sides of the absorption. It is the area under this curve above the smooth curve which is closely proportional to the amount of ozone in the path.

Figure 3 shows the results of one typical day's observations. For clearness of illustration Figure 2 was made similar to this. In this case



an amount of ozone approximately equal to the average atmospheric quantity was present in the cell. Failure to correct exactly for all differences between the two sets of bolograms led to the smooth curve of the points in the absence of ozone absorption being below zero, but the area due to ozone appears clearly and can be measured with sufficient accuracy to be of much use. Several days' determinations were made with larger quantities of ozone in the path, giving areas which can be measured with greater percentage accuracy. On other days smaller amounts were used in order to observe how well such areas could be determined. Included in figure 3 are also three points lying far off the curve which are illustrative of unsuitable points. They lie in weak atmospheric water absorption in the red, which absorption may vary considerably over short intervals of time, rendering the points evidently unsuitable for aiding in ozone determination.

The area under the observed curve should evidently be limited between ordinates whose values are still large compared with the uncertainty in placing the base line. In the blue this has been taken as the value at  $4750 \text{ \AA}$ , while in the red it was necessary to terminate the area at  $6135 \text{ \AA}$  because of the uncertainty in the point at  $6335 \text{ \AA}$ . This limitation was caused by instrumental circumstances which can be altered in the future to include a greater area.

These areas were determined for 10 independent sets of observations, the amount of ozone in the cell being known in each case from the analytical work carried on at the time of the measurements. From these results, shown graphically in Figure 4, a value sufficiently accurate to be useful can be had for the amount of area per unit path length of pure ozone at  $0^\circ\text{C}$  and one atmosphere pressure, the common meteorological form of expressing atmospheric ozone. The least-squares solution, assuming the ozone concentration values essentially free from error compared to values for the areas, which method automatically weights the individual values in proportion to the area, leads to the result  $21.5 \text{ sq. cm. of area per mm. of ozone at standard conditions of temperature and pressure when a plot is made to the scale ordinates } 0.001 \text{ per cm., abscissa } 200 \text{ \AA per cm.}$  This area can thus be stated as  $4.30 \text{ \AA}$  independent of the scale to which it is plotted. Plotting the data and planimentering the area is a procedure which has the decided advantage of giving a visual record of the amount of ozone which can be judged approximately at a glance. From the results of Colange's data on the absorption coefficient of ozone one can compute this same area, and it may be estimated directly from his published curve of the absorption coefficient. One finds thereby that the value obtained in the present work is about 4 per cent higher than

that given by Colange's results, a difference which lies within the limits of error of the present work. With a larger number of sets of observations than the 10 of the present work, and particularly at high ozone values, the accuracy of the determination could, of course, be greatly increased.

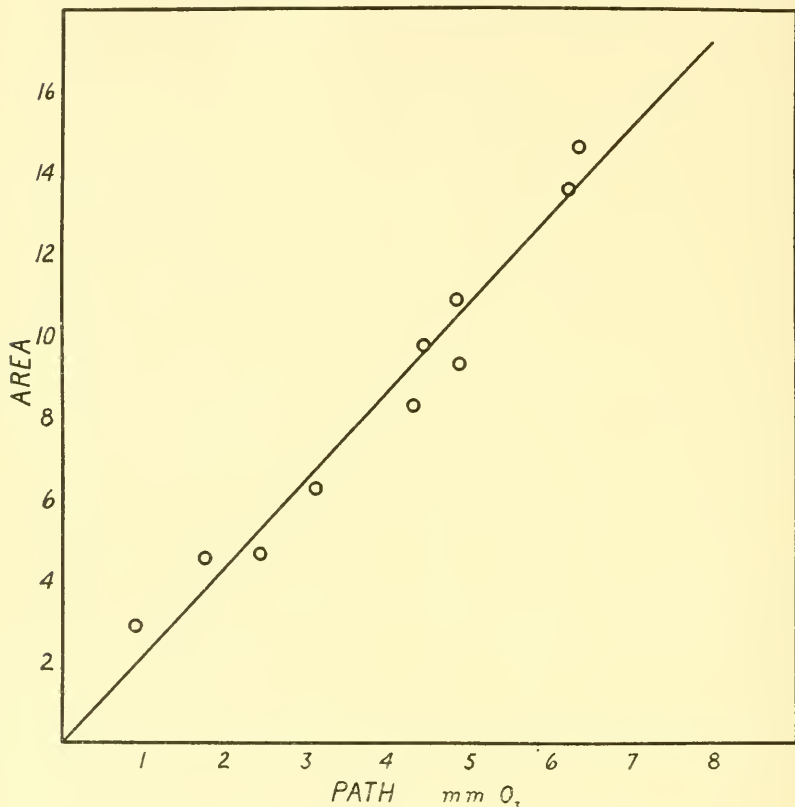


FIG. 4.—Character of the results of the absorption of ozone.

An area such as that illustrated in Figure 3, and pertaining to atmospheric ozone only, can be obtained from atmospheric transmission coefficients, if combined with the knowledge that there is no important atmospheric absorption except ozone across this spectral region. That atmospheric transmission coefficients show unmistakably the ozone absorption has been pointed out and used by Fowle and others.<sup>1</sup>

<sup>1</sup> Fowle, F. E., Smithsonian Misc. Coll., vol. 81, no. 11, pp. 1-27, 1929. Cabannes, J., and Dufay, J., Journ. Phys. et le Rad., ser. 6, vol. 7, p. 257, 1926.

Figure 5 shows an area analogous to the one shown earlier, determined from the transmission coefficients for March 24, 1929, as a typical day used simply as an illustration. The logarithms of the

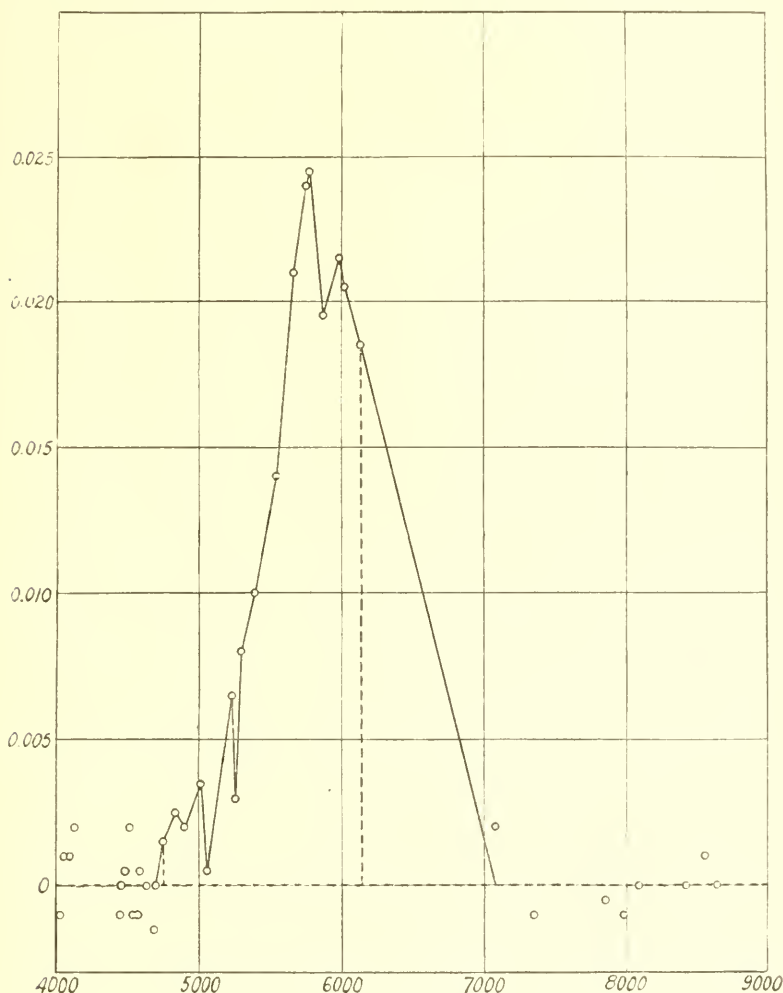


FIG. 5.—Ozone area for March 24, 1929.

transmission coefficients for this day, read for all the wave lengths selected in this work, were plotted against wave length and a smooth curve passed through the values lying to both sides of the ozone absorption, and the differences of the points lying in the ozone region from the smooth curve were read. These differences were then plotted against wave length to the scale used above, yielding the area

shown in Figure 5. Thus the ordinates are the logarithms of the ratio of the intensities before and after passing through the atmospheric ozone. Referring this area so obtained to the results of these present measurements pictured in Figure 4 affords a method of determining the atmospheric ozone based on direct intensity measurements, and yields for this day over Table Mountain, Calif., an ozone value of 3.8 mm., while the value given by Dobson for Table Mountain on this same day was 3.42 mm. A somewhat more satisfactory extension of this method of determining the ozone transmission may be employed, whereby the curved base is reduced to a straight line. Instead of plotting the logarithm of the atmospheric transmission coefficients against wave length and determining the difference of the observed points from the smooth curve in the ozone region, the logarithm of the logarithm of the transmission coefficients may be plotted against the logarithm of the wave length, yielding very closely a straight line, except for points in the ozone region. This fortunate circumstance is due to the approximate inverse  $\lambda^n$  dependence of the logarithm of the transmission coefficients on the wave length. The ozone transmission can be determined from this plot in a similar way from the difference of observed points from the straight line. The transmission coefficients for March 24 were treated independently in this second way. The area resulting was very closely the same as that shown in Figure 5, yielding 3.9 mm. ozone path. It is believed that the application of this method to data of days which give good transmission coefficients affords a satisfactory method for determining atmospheric ozone from direct intensity measurements.

In order to make a somewhat more extensive comparison of ozone values determined by this method with those previously known from observations made with the Dobson apparatus, a series of eight days in 1928 and 1929, for which values by the Dobson method have been obtained at Table Mountain, was treated according to a somewhat abbreviated form of the above method. For these days there were available the atmospheric transmission coefficients as regularly read and already computed from the "long method" observations at Table Mountain. These values are not given at all points used in the determination of the area defined in this present work, but at the regular spectrum points ordinarily determined in the solar-constant work. These relatively few points are scattered over the spectrum in such a way as to outline, somewhat less accurately to be sure, essentially the same area as that defined in the present work. In particular there were but four ordinates lying in the ozone region, but if these values were sufficiently accurate the area of ozone absorption outlined by them, and lying between the wave lengths specified above, would be suf-

ficiently close to the area defined in the above work to yield a satisfactory determination of the ozone.

For these eight days, then, the logarithms of the logarithms of the transmission coefficients were plotted against the logarithm of the wave length and a straight line passed through the values lying to both sides of the ozone absorption. The differences of the anti-logarithms of those points lying in the ozone region from the anti-logarithms of the corresponding points on the straight line were read. These differences were then plotted against wave length to the same scale as that described above and the areas planimetered and divided by the area corresponding to 1 mm. of ozone path, determined as the result of the work described in this paper. Thus an approximate determination of the ozone on these days was afforded, utilizing an area practically the same as that described above, defined by the

TABLE I.—*Atmospheric Ozone for Eight Days*

Date	Path mm. o <sub>3</sub>	
	Present work	Dobson
Aug. 1, 1928.....	2.1.....	2.24
Oct. 3, 1928.....	2.9.....	2.28
Nov. 4, 1928.....	2.5.....	1.97
Dec. 8, 1928.....	1.9.....	1.98
Dec. 18, 1928.....	1.8.....	2.53
Dec. 19, 1928.....	2.4.....	2.43
Mar. 24, 1929.....	2.8.....	3.42
Apr. 23, 1929.....	2.4.....	3.08
Mean .....	2.35	2.40

positions in which these points lay. The results are shown in Table 1. For these eight days the values of the ozone over Table Mountain as determined by the Dobson method were also available and they are given in this table for comparison. From these results it appears that the average amount of ozone given by the two methods is essentially the same. The independent values, however, are not in good accord, which may be entirely due to the uncertainties in the present determinations. It must be emphasized that this is due to the insufficiency of the data used to make such a determination, which had been collected from solar-constant work, and not to the method employed. It is to be noted especially that differences in the *relative* values for the eight days obtained by the two methods of Dobson and of Wulf cannot be due to the *method* of the ozone absorption measurements described in this paper, but must be contained in the roughness of the data. For quite independent of the evaluation of the areas in terms of ozone, these areas should be closely proportional to the ozone values on these days. That they are not is actually due largely to the uncertainties in

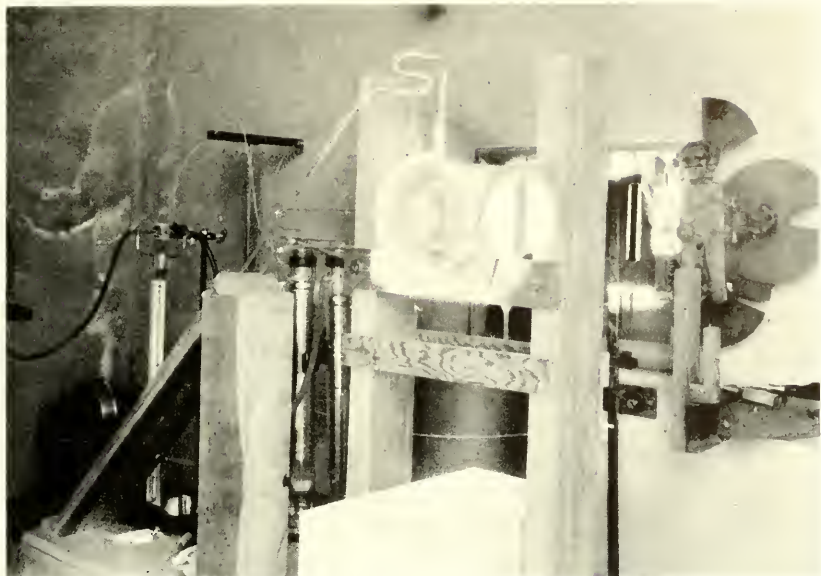
the transmission coefficients, which in this case define the ozone area. This is shown by a comparison of the March 24 value in this set of eight with the value for this same day as given above, which was determined from the transmission coefficients at all the points chosen in the above work. The former value is 2.8 mm., while the latter 3.9 mm., and the latter is, as stated above, believed to be a satisfactory determination. The cause of this discrepancy appears to lie chiefly in the fluctuations in the few observed transmission coefficients. To summarize: The use of the few single values of the transmission coefficients as regularly determined in the solar-constant work only suffices to define an area which gives the approximate amount of ozone and is not ordinarily competent to show the fluctuations from day to day within an error small compared to the fluctuations.

#### SUMMARY

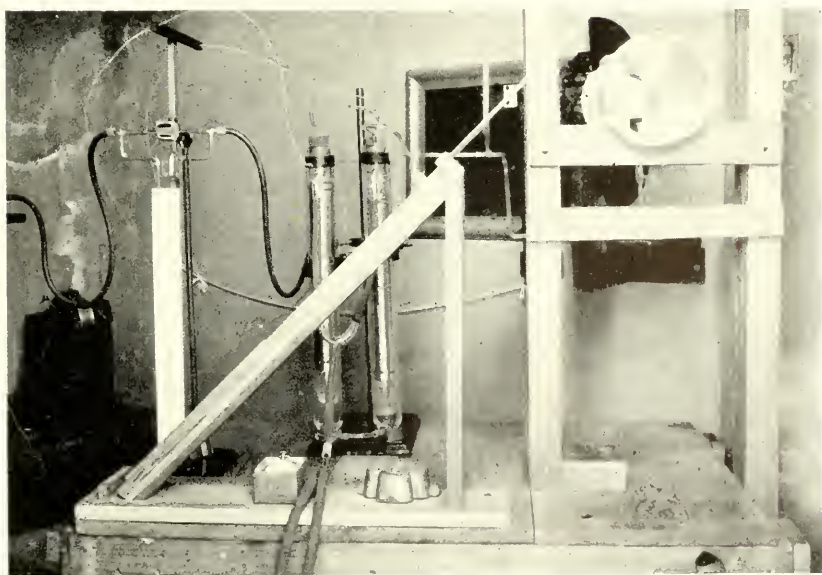
The transmission of ozone for visible light has been determined from spectrophotometric data using the solar spectrometer of the Smithsonian Institution at Table Mountain, Calif., with the sun as the source and introducing chemically determined quantities of ozone in the path of its rays. The results are in close accord with the laboratory results of Colange. Using the results of this study the amount of ozone over Table Mountain for one typical day as an illustration has been determined. By an abbreviated method, using only the transmission coefficients normally measured in the regular solar work, the value for the ozone over Table Mountain has been determined for a series of eight days. The mean of these eight days presumably gives a good value for the mean amount of ozone, but this abbreviated method is not ordinarily sufficient to show the fluctuations in the ozone, since the possible error in a single determination is of the order of the fluctuations. The mean value for the eight days differs but about 6 per cent from the mean value for the same days determined by the method of Dobson. It is very interesting that the bolographic method depends on ozone absorption in the yellow, while Dobson's photographic method employs the ultraviolet ozone absorption.

The author wishes to express his sincere thanks to Dr. C. G. Abbot for suggesting the problem and for his continued interest and help throughout the work, and to Mr. J. A. Roebeling for a financial grant which made the work possible. The efforts of a number of people have contributed directly to the completion of this work, especially Mr. Alfred F. Moore, Mrs. Beatrice J. Wulf, Mr. Fred Greeley, and Mr. George Cox. The author is grateful to the members of the Smithsonian Astrophysical Observatory for their frequent kind assistance.





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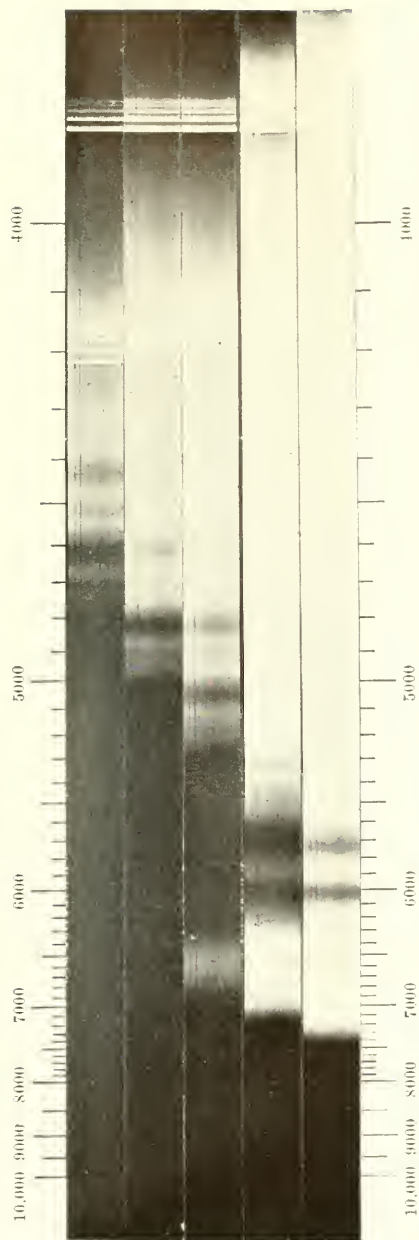


2

Two views of absorption cell and auxiliary apparatus.







Absorption spectrum of ozone in the visible.