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VERTICAL DISTRIBUTION OF ATMOSPHERIC OZONE

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PROJECT SKYHOOK

Brian O'Brien
M. Parker Sivens
Leo Krolak
Walter P. Siggsmund
Gordon G. Milne

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The gas ozone, consisting of triatomic oxygen molecules, is so reactive chemically that it is at first surprising to find the substance free in the earth's atmosphere. Little or none of it is found at low altitudes, but more than seventy years ago Hartley (1), observing the abrupt termination in the ultraviolet end of the spectrum of all heavenly bodies, concluded rightly that some invisible component of the earth's atmosphere was responsible. He showed that, qualitatively at least, this atmospheric absorption corresponded to that of ozone. In 1913 Fabry and Buisson (2) made laboratory measurements upon this strong absorption band of ozone in the ultraviolet region of the spectrum, the Hartley band, and found the maximum of absorption to occur at about 2550 Å. In 1920 Fabry and Buisson (3) working at Marseilles, practically at sea level, determined the transmission coefficients of the earth's atmosphere for sunlight at and near the ultraviolet end of the solar spectrum. They showed conclusively that the form of the absorption curve for the atmosphere in the spectral region from 3500 Å to 2992 Å agreed quite exactly with the form of the Hartley band for ozone. Combining their atmospheric absorption measurements with their own earlier laboratory measurements on ozone, they arrived at an amount of the gas in the zenith atmosphere over Marseilles in June of 1920 as approximately 3 millimeters path of pure ozone reduced to standard temperature and pressure.

If one reduces to standard temperature and pressure the total amount of air in a zenith atmosphere, one arrives at an equivalent air path of about 8 kilometers. Thus the total ozone represents somewhat less than one two-millionth part, and would be insignificant but for certain remarkable properties possessed by this gas. Perhaps the most striking property is the absorption coefficient at the peak of the Hartley Band at 2550 Å. At this wavelength in the ultraviolet the optical transmissions through one centimeter path of pure ozone at standard temperature and pressure is approximately $10^{-120}$. Correspondingly the transmission through the
3. millimeters found by Fabry and Buisson in a zenith atmosphere at sea level is of the order of $10^{-4}\text{g}$. Small wonder that the spectrum of all celestial objects ends abruptly, when the measurements are made from at or near the earth's surface.

Much has been written about the effects on plant and animal life of the ultraviolet absorption of ozone in modifying sunlight as received at the earth's surface. It is sufficient at this point to remind the reader that if the amount in the earth's atmosphere were reduced to about one-third, human skin would be destroyed in a matter of minutes exposure to the sun. On the other hand, if the quantity of ozone were doubled compared to the amount normally found, the higher animals and man would die out for lack of the essential vitamin D, unless enough of this vitamin could be produced by synthetic processes to permit survival. Even so, the enormous increase in bacterial growth, normally held in check by solar ultraviolet, might be sufficient to destroy or seriously limit other forms of life upon the earth's surface. All this follows from the fact that both the photoproduction of the antirachitic vitamin D from sterols, and the photochemical destruction of bacteria take place only at wavelengths very near the ultraviolet end of the solar spectrum, and this, as we observe it on the earth, is limited entirely by the amount of ozone in the atmosphere above us.

In addition to these biological effects the study of atmospheric ozone has provided a key to certain processes occurring in the upper atmosphere and so there is much interest in this gas as an atmospheric constituent. Finally, there is an additional possibility which, though remote, may be worth consideration. Ozone in relatively small concentration is toxic to man. It is known that most of the atmospheric ozone lies at high levels in the earth's atmosphere. If it should happen that the bulk is contained in a relatively narrow stratum, then it is important to know the peak concentration in that stratum if that region is to be entered in high altitude flight, and if the air, appropriately compressed, is to be used for respiration.
In all the distribution of ozone in the earth's atmosphere is a matter of both scientific and practical interest, and justifies considerable effort in securing reliable measurements.

Since the total amount of ozone in a senith atmosphere as found by Fabry and Buisson (3) was much greater than would be estimated from the very minute traces of this gas observed near the earth's surface, and since a similar result had earlier been observed by Hartley (1) it was concluded that the bulk of the atmospheric ozone must lie at high level. Quantitative estimate of this height was first accomplished by Cabbannes and Dufay (4) in 1926. These investigators used the classical method of determining atmospheric absorption by observing the intensity at a particular wavelength as the zenith angle of the sun changed, the mass of air in the path of the sunlight varying nearly as the secant of this zenith angle. However, Cabbannes and Dufay extended these measurements to zenith angles approaching 90°, near sunrise and sunset. Thus, by taking account of the effect of the curvature of the earth on the zenith angle at successive levels, they were able to determine an approximate height of the ozone layer. This height they reported as between 40 and 60 kilometers above the earth's surface. Subsequent measurements, notably by Götz, Dobson and Meethan (5, 6, 7), using a similar method placed the effective altitudes as between 25 and 40 kilometers. In 1929 Rosseland (5) showed, on theoretical considerations, that these heights represented only a sort of center of gravity of the ozone, and that the method of measurement was incapable of distinguishing between a sharply limited and a diffuse distribution of ozone with height.

Numerous other estimates of the height of the ozone layer were made upon the basis of measurements from the earth's surface, including those by one of the present authors, but since the literature of this subject has been reviewed by O'Brien (9), further discussion of these indirect methods will not be necessary in this report.
The first direct measurements of the distribution of ozone with height were made in June and July, 1944, by the Regener (11). These investigators used a small automatic spectrograph carried by a sounding balloon, and succeeded in obtaining measurements of ozone on two flights above 19 kilometers, on one flight July 31, 1934, to an altitude of 31 kilometers. Unfortunately the measurements were of somewhat limited accuracy because of the small size of the instrument which could be carried. Moreover, the rate of rise of the sounding balloons was so rapid that each spectrographic exposure was made throughout a very considerable spread in balloon altitude. Thus each spectrum represented the average of a stratum of the earth’s atmosphere of considerable thickness, and this led to a loss of vertical “resolving power” which resulted in some dispute and uncertainty.

On July 28, 1934, a few days before the highest flight made by the Regener balloons, spectroscopic determinations of atmospheric ozone were made with much larger spectrographs carried on the first stratosphere flight, jointly sponsored by the National Geographic Society and the U. S. Army Air Corps. A detailed report of these results has been published by O’Brien (9) and the instruments have been described by Passin and Kurtz (12). Unfortunately rupture of the balloon at an altitude 18 kilometers terminated this flight. The spectrograph receiving direct sunlight was parachuted to safety, but the second instrument receiving horizon skylight was destroyed in the crash of the gondola, and only a fraction of its record preserved. The skylight spectrograph permitted the application of a new method for an approximate determination of the ozone distributions some 4 kilometers higher than the ceiling reached by the instrument itself. The theory of this method is described in (9). In 1935 the second stratosphere flight, under the auspices of the National Geographic Society and the U. S. Army Air Corps, reached an altitude of 22 kilometers. This time landing of all equipment was accomplished without mishap, yielding excellent spectrographic
Measurements with the spectrograph receiving direct sunlight gave the ozone distribution to the ceiling of the flight, namely, 22 kilometers. Measurements with the spectrograph receiving light from the horizon sky gave indications of the ozone distribution to about 26 kilometers with considerable accuracy, and some indications of the distribution above that level (10). However, the sky spectrograph method was radical, and there had been some controversy about the theoretical validity of the sky spectrograph method. For this reason the possibility of such uncertainties was carefully pointed out in the conclusions of the report of the 1935 flight (10).

The results found on the 1935 flight (10) showed a far more peaked distribution curve when the quantity of ozone per kilometer of atmosphere was plotted against the height than had been found by any previous workers. Since the previous results depended upon indirect methods of measurement from the ground together with the Wegener measurements discussed above, it is not surprising that any sharply peaked distribution would go unnoticed. With a larger instrument and the slower rate of rise of the man-carrying balloon of 1935, each spectrogram represented a quite narrow stratus, and thus made it possible to detect a sharp gradient of ozone concentration with height wherever this might occur.

From 1935 until 1949 no additional precise measurements of the vertical distribution of atmospheric ozone were attempted. Those reported in (10) were generally accepted as standard, but in spite of the precision possible with the full size spectrographs and slow rates of rise and descent, not everyone was willing to accept the resulting measurements to the exclusion of all previously published work. For this reason, in 1945, we were pleased to accept the invitation to carry out further measurements on the vertical distribution of atmospheric ozone in connection with the large unmanned balloon flights carried out under Project "Skyhook" of the Office of Naval Research.
EXPERIMENTAL METHOD

The spectrograph used to receive direct sunlight on the stratosphere flight of 1935 (9,10) was well adapted to sounding balloon work providing the weight of 130 pounds could be carried to the necessary altitude. Fortunately the large General Mills sounding balloons as developed for Project Skyhook were adequate for this purpose when used in pairs. It did not seem wise to attempt to fly the horizon sky spectrograph, in spite of the successful use of this instrument in 1935. Alone the sky spectrograph is of no service, and to attempt to fly both the direct sun and horizon sky spectrograph together appeared to be beyond the present capabilities of sounding balloon technique.

Since a description of the direct sun spectrograph has been published no additional description will be required here. The photographic material used in the present operation was Kodak Linograph Survey film, and the automatic film transport mechanism of the spectrograph was set to take eight pairs of exposures per hour instead of four pairs per hour as had been done in 1935.

A short section of spectrograph film is shown in figure 1. The right-hand edge of these spectra lies at about 3600 A wavelength, while the left-hand edge represents the short wavelength limit at somewhat less than 3000 A as set by the absorption of ozone. As described in our previous work (9,10) the slit of the spectrograph was covered by an evaporated aluminum wedge, the optical density of which had a linear variation with distance along the slit. In figure 2 is shown the plot of the optical density of the wedge against distance in millimeters from an arbitrary zero position. As previously described (9) such wedges are quite neutral over the limited wavelength region in the ultraviolet included in the spectrograms.

At the right-hand margin of the spectrograph film can be seen the photograph of the face of a high grade watch, especially lubricated for operation over
a wide temperature range, and used as a check on the time clock which controlled
the exposure sequence. As in our previous work a small bimetallic thermooher
face can be seen in the center of the watch face, providing a constant record of
the temperature of the interior of the spectrograph camera.

The method used for the determination of ozone from direct solar spectra
is the same as we have previously described (10). This method which involves a
graphical solution, provides for the determination of the ozone above the instru-
ment even when both the altitude of the balloon and the zenith angle of the sun
are continually varying.

Let $\lambda$ be a wavelength which is absorbed by ozone and $\lambda'$ a longer wave-
length for which ozone absorption may be neglected. Let $I_0$ and $I_0'$ be the
intensities at $\lambda$ and $\lambda'$ in the solar spectrum outside of the earth's atmosphere,
and $I_m$ and $I_m'$ the corresponding intensities within the atmosphere at a level and
at a solar zenith angle defining the condition "m".

Let $D_m = \log_{10} \frac{I_m}{I_m}$ and $D_m' = \log_{10} \frac{I_m'}{I_m}$

Then $D_m = D_{m,s} + D_{m,O_3}$
and $D_m' = D_{m,s}'$

where $D_{m,s}$ and $D_{m,O_3}$ refer to optical density due to scatter and ozone
absorption, respectively.

Evidently $D_{m,s} = D_{m,s}' + d_m$

where $d_m > 0$ since $\lambda' > \lambda$

so $D_{m,O_3} = D_m - D_m' - d_m$

$= \log I_m' - \log I_m - (\log I_0' - \log I_0) - d_m$

Let $Q = \log I_m' - \log I_m - d_m$
and $D_{m,O_3} = D_{O_3} \sec z$. 
where \( z \) = zenith angle of sun, and

\[
D_0^3 = \text{optical density of zenith ozone above the observer.}
\]

Then

\[
Q = D_0^3 \sec z + L
\]

Where

\[
L = \log \frac{I_0}{I} = \text{constant for a given } \lambda \text{ and } \lambda'.
\]

If \( D_0^3 \) does not change, as, for example, when observer's depth in the atmosphere is constant, then \( Q \) is a linear function of \( \sec z \). Extending this line back to the fictitious \( \sec z = 0 \), the ordinate at the intercept represents \( L \), the logarithm of the ratio of intensities at \( \lambda \) and \( \lambda' \) outside the atmosphere. The slope of the line is evidently equal to \( D_0^3 \).

If the observer rises through the atmosphere and in so doing passes through ozone so that \( D_0^3 \) diminishes, then the values of \( Q \) will lie below the straight line by an amount \( \Delta Q = \sec z \cdot \Delta D_0^3 \).

Densitometry of the spectrograms was accomplished with a Sinclair Smith recording microdensitometer. A sample of a typical trace of a spectrum, made at a constant height above the bottom edge of the spectrum (Figure 1) is shown in Figure 3. Included on this trace are the wavelengths of certain landmarks in the Fraunhofer spectrum. These are the same selected wavelengths used in our previous determinations of ozone (10), and were chosen because they fall between solar absorption peaks and so represent wavelength regions in which the solar emission is high. Actually only a single wavelength, substantially outside the Hartley absorption band, together with a single wavelength well within the band, are necessary for determination of quantity of ozone. However, we have found advantage in using at least two different spectral regions within the absorption band together with the third region outside, and this has been the practice followed in the present determination. Thus two complete independent sets of ozone determinations were obtained eight times per hour throughout the flight.
The procedure used to reduce the microdensitometer traces to relative spectral intensity was the same as we have reported previously (10). Six or more microdensitometer traces were made at different heights above the bottom edge of the spectrum, each trace running along the direction of dispersion. Since the linear aluminum wedge mounted in front of a spectrograph slit produced a linear scale of logarithms of intensity along any given spectrum line, it is evident that the observed densities of the photograph determined from the microdensitometer trace can be converted directly to form a characteristic or EMD curve for the particular type of film used. Since the microdensitometer read directly the transmission rather than density, it was convenient to plot transmission against position on the spectrum corresponding to the position on the aluminum wedge or "wedge step" as here labelled. A set of typical curves are shown in figure 4.

Since the spectral range involved in this work is so small, and since the region is one over which both the sensitivity and gamma of the film are nearly constant, it is possible to combine the results of a large number of curves such as shown in figure 4 into a single curve typical of the characteristic curve of the photographic emulsion over the range involved. This is shown in figure 5, the actual points of observation being indicated by small dots. A template cut from this mean curve was used to draw the actual curves shown in figure 4, the small circles in figure 4 representing experimental points for the particular spectrum selected as an example.

At the request of the Office of Naval Research the equipment was made ready in the late summer of 1948 and transported to Camp Ripley, Minnesota from which point the General Mills Company was launching balloons. Since we had developed a refined technique for continuous triangulation upon a sounding balloon some years previously (13) our theodolites and plotting instruments were also transported to Camp Ripley in order to provide balloon altitude determinations.
of a higher order of accuracy than possible with a radio meteorograph.

Unfortunately, difficulties were encountered by the General Mills Group, and a number of trial flights carrying instruments other than our spectrograph failed at very moderate altitudes due to balloon rupture. After several weeks in the field we were informed that it was unlikely that any successful flights could be obtained that year, and the equipment was returned to the University of Rochester.

The following year, 1949, we were informed by the Office of Naval Research that the General Mills Company had so perfected their own theodolite triangulation technique as well as triangulation by radio direction finding, that it would be unnecessary for the University of Rochester group to do its own triangulation upon the balloon. The spectrograph was again prepared and transported to Camp Ripley, but altitude determinations were left entirely to the General Mills group. Unfortunately, their theodolite triangulation failed completely as did triangulation with radio direction finders. The only determination of altitude, therefore, came from the radio meteorograph. Fortunately this instrument appears to have behaved well.

In addition to knowing the altitude of the spectrographic instrument above sealevel as a function of time, it is necessary that the zenith angle of the sun be likewise known. Since this is a function of local apparent time and latitude, it is necessary that, in addition to standard time, the approximate latitude and longitude of the instrument be known for each spectrogram of the series. Although the triangulation upon the balloon had failed, small slow speed airplanes were able to follow along, keeping the balloon in sight, and were thus able to record the time at which several map positions were passed. Values for latitude and longitude at four times along the four hour flight are shown in figure 7, the points being connected by straight lines since the exact path of the balloon between these points was unknown. Fortunately the changes in both
latitude and longitude are sufficiently small so that the straight line approximation is entirely adequate.

When the spectrographic instrument is a substantial distance below the center of gravity of the ozone layer, and when the zenith angle of the sun is large as was the case in the early morning portion of the flight, it is necessary to correct the zenith angle of the sun for the curvature of the earth in the manner described on page 80 or reference (10). This has been carried through giving the corrected angle \( \theta \) the secant of which is plotted against central standard time in figure 7. Also, plotted in figure 7, is the altitude above sea level.

Because of the failure of the triangulation it is not possible to state the accuracy with which the altitude determinations were made. However, the radio meteorograph had been especially modified for sensitive response to the very low barometric pressures encountered at 30 kilometers. In laboratory tests before flight it had behaved well and consistently, and during the flight its indications, as telemetered at the radio receiving station, showed every evidence of consistent and proper instrument functioning. It seems likely, therefore, that the altitudes are correct to within perhaps one-half kilometer, and may, in fact, be somewhat better than this.

Spectral intensity measurements reduced as described above were used for the quantitative determination of ozone in the same manner as described in reference (10). The absorption coefficients for ozone used in our earlier work were those reported by Fabry and Buisson in 1931 (14). These values are modified very slightly by the work of Hy Tei-Za and Choong Sain-Piau in 1933 (15). The difference between the results of these authors and Fabry and Buisson are very slight, but the newer measurements have been used in the reduction of the present work. The optical density of ozone per centimeter of the gas at standard temperature and pressure has been tabulated against wavelength and shown in table I.
In the same manner as described in reference (10) the quantity $Q$ derived above has been plotted against the secant of $\theta$ for wavelength 3100A and 3050A and is shown in figure 7. As described in reference (10) a plot of $Q$ against the secant of $\theta$ will be a straight line so long as the spectrographic instrument remains beneath the atmospheric ozone, no matter what the zenith angle of the sun may be. As the instrument rises through the ozone, however, the actual values of $Q$ will fall below the straight line, the amount indicating the quantity of ozone through which the instrument has risen.

**TABLE I**

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>cm</th>
<th>D₀, T.P.</th>
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<tr>
<td>3300</td>
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<tr>
<td>3270</td>
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<tr>
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</tr>
<tr>
<td>2992</td>
<td>5.25</td>
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</tr>
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</table>
RESULTS

The findings for the various spectra at different altitudes are shown in Table II. \( \Delta Q \) is the amount by which a point is above or below the straight line portion of the curve. The total ozone concentration above 3 kilometers was found from the straight line portion of the curve to be \( 0.296 \) cm. at standard temperature and pressure. The values of \( \Delta Q \) when negative indicate that this value should be added to \( 0.296 \) cm. Positive values of \( \Delta Q \) indicate that this quantity should be subtracted from \( 0.296 \) cm. to give the total zenith ozone above the spectrographic instrument.

In Figure 9 are plotted the quantity of ozone in centimeters path at standard temperature and pressure in the zenith atmosphere above the spectrographic instrument at altitudes from 3 kilometers to the top of the flight of 30.5 kilometers. The circles containing crosses represent the determinations made by comparing wavelength 3110 \( \AA \) with 3300 \( \AA \). In the same figure the results of our 1935 determinations are shown in a dotted curve labeled Explorer II, while the results of the sounding balloon observations of the Ragenars in 1934 are shown by the dashed curve. It must be remembered that the flight of the balloon Explorer II took place in November, when, in the northern hemisphere, the absolute quantity of ozone in the earth's atmosphere is low. The curve labelled Operations Skynook, on the other hand, represents a flight made on June 16, 1949, a time of the year when the quantity of atmospheric ozone in the northern hemisphere is high.

In spite of the difference in the absolute quantity of ozone encountered in 1949 as compared to 1935, a difference typical of the difference in time of year, the relative amounts of ozone as a function of altitude are surprisingly similar. This is shown in Figure 10 where the amounts are plotted as percent of ozone remaining above the instrument as function of height of instrument. The total amount above 15 kilometers has been taken arbitrarily as 100 percent, although
shown by figure 9 there is a very small amount of ozone lying below this level. Perhaps the most striking feature of figure 10 is the fact that the determination of ozone from direct sunlight on Operation Skyhook agrees not only with the determination from the direct sunlight up to 22 kilometers in the flight of Explorer II, but that this agreement should continue up to an altitude beyond 27 kilometers. This confirmation of the sky spectrograph method is very reassuring. It must be remembered that each flight was made in a polar air mass, the meteorological conditions being chosen rather carefully to provide both clear weather and the minimum of wind velocity in the early morning hour during balloon inflation. Thus one might expect a very similar vertical distribution of atmospheric ozone even though fourteen years elapsed between the measurements.

In figure 11 the ozone per kilometer of height is plotted against the altitude of the instrument. The curves of figure 11 are the derivatives of the curves of figure 10, and thus sensitive to small errors in slope determinations. Nevertheless, even in figure 11 the agreement between the Skyhook and Explorer II curve remained quite good. The fact that the determination by the Regener does not agree with our results is not surprising. As discussed above, the rapid rate of rise and relatively long exposures of each spectrum prevented detection of the sharp maximum actually present.

It is of interest to note that the maximum path of ozone per kilometer of height was found to be 0.025 cm at standard temperatures and pressure, and that this maximum concentration was found at an altitude of about 14 kilometers. At this altitude a mean barometric pressure is approximately 0.044 atmospheres and, at the mean temperature of -55°C the density of the air is 0.055 that of air at sea level at 0°C. Air taken in at this altitude and compressed in a supercharger without decomposition of the ozone would, of course, retain the same.
relative concentration. This value is within the rather wide spread limits which have been published for onset toxicity, so this aspect of the results should be considered.
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Figure 2

Figure 3
Figure 6

Figure 7
Figure 2

Table II
Figure 9

Figure 10