CHAPTER II

METHODS OF MEASURING OZONE AT DIFFERENT LEVELS IN THE ATMOSPHERE
Methods of measuring ozone at different levels in the atmosphere.

Meteorologists are interested in the problems of the mean meridional, seasonal and day to day variations of atmospheric ozone because they are expected to through light on large scale atmospheric movements in the lower stratosphere and the upper troposphere. The main difficulty in making progress in this respect is due to our poor knowledge of the distribution of ozone with height in the atmosphere and its variations. While it is agreed, that ozone is formed in the stratosphere by ultraviolet radiation from the sun, there are other processes involved in determining its amount and distribution in the atmosphere at any time. Decomposition by light and chemical action, and redistribution by horizontal and vertical movements are very important factors.

Spectroscopists and chemists have assisted in dealing with problems of technique. In this chapter, a brief survey will be made of the methods that have been used for determining the vertical distribution of ozone in the atmosphere.

The methods can be divided broadly into two groups (1) direct methods such as chemical analysis or the use of spectrographs sent up in aeroplanes, balloons or rockets and (2) indirect methods such as by observations on the umbreel effect, on light on the moon during total lunar eclipses and
absorption and emission of infra-red radiation in the 9.6 μm band of ozone.

A. Direct methods

The determination of ozone by the chemical method is direct and reasonably reliable. If the instruments used in this method are properly designed they could be carried in aircraft or sent up in balloons to measure the ozone amount at different levels. Such measurements have been made in Germany by A. Shumert and in England by A.C. Brewer and R.H. Kay. Spectrographs can also be used by being sent up in balloons or aircraft to measure the total amount of ozone above different heights by absorption of solar radiation. L. and V.H. Regener and L.P. Raetzold have worked on this. In Germany, ozone radiosondes using narrow band optical filters in the ultraviolet have been used. All these methods are useful for measuring the ozone distribution in the troposphere and lower stratosphere. For reliable information of ozone quantity in the higher atmosphere use is made of spectrographic observations from rockets. All the optical methods essentially consist in measuring the relative intensities of light in two wavelengths one in the Hartley absorption band in the ultraviolet and another near the long-wavelength edge of the band.

1. Chemical method for the measurement of ozone at different levels.

More than a hundred years ago, C.F. Schönbein (1845)
discovered ozone by its oxidising action on paper soaked in potassium iodide and starch and used the method to find the variation in the ozone content of the air near the ground. As these variations were of great interest, French investigators carried out observations of atmospheric ozone near Paris over a long period of years from 1860 onward. F. A. Paneth and J. I. Edgar made measurements at the new Observatory in 1935. The method used by them was that of oxidising the potassium iodide solution. They gave a mean value of the ozone present at ground level in England as 1.1 x 10^{-6} volume per cent. Although the magnitude of the ozone amount near the ground is very small, the average value being only 2 molecules per 10^3 air molecules, the fluctuations of this concentration are quite large.

V. H. Degener first designed an automatic apparatus for measuring the concentration of atmospheric ozone at ground level. He found that the quantitative production of free iodine by ozone in a neutral aqueous solution of potassium iodide according to the formula

$$\text{O}_3 + 2\text{HI} + \text{I}_2 \rightarrow 2\text{HIO} + \text{O}_2 + \text{I}_2$$

was a very efficient reaction. H. K. Gluekauf and others later introduced electrolytic titration which further simplified the procedure over the earlier starch indicator method. H. K. Gluekauf's method is briefly described below.

A 2% solution of potassium iodide is made in double distilled water with a few microgram of sodium thiosulphate.
a few c.c. of this are taken in a small bottle which is fitted to a bubbling apparatus. A known volume of air is drawn through a sintered glass distributor and the solution. The ozone in the air reacts with the potassium iodide liberating iodine. The presence of $\text{K}_2\text{S}_2\text{O}_3$ removes the free iodine. Excess $\text{K}_2\text{S}_2\text{O}_3$ remains in the solution. Therefore there is no chance of free iodine escaping with air. The sodium thiosulphate in the solution through which air has been passed is determined by an electrochemical method. The difference between the amounts of $\text{K}_2\text{S}_2\text{O}_3$ contained in (1) bubbled solution (2) and the unbubbled (original) solution is the iodine equivalent of the ozone contained in the volume of air which has been passed through the solution.

The electrochemical method of determining the sodium thiosulphate in the solution consists of four platinum electrodes in two pairs, inserted in a bottle containing the solution and this is mounted on a stand which can be rotated with uniform speed. Between one pair of electrodes a constant small difference of potential of a few millivolts is applied. The electrodes get polarised, the cathode with hydrogen and the anode with oxygen and there is no current in the circuit. The second pair of electrodes is used to liberate iodine at a constant rate by electrolysis from the solution. When a suitable e.m.f. is applied between these two platinum electrodes the iodine which is liberated is neutralised by $\text{Na}_2\text{S}_2\text{O}_3$ and the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ gradually decreases. As soon as all the $\text{Na}_2\text{S}_2\text{O}_3$ is used up
the iodine begins to depolarise the first pair of electrodes and a current starts in the circuit and steadily increases. The exact time of electrolysis for completing the reaction with $Na_2S_2O_3$ is obtained from the current time graph. $Na_2S_2O_3$ will be used up earlier in the case of the solution through which ozone containing air has been bubbled than in the case of the unbubbled solution. The difference in time for the $Na_2S_2O_3$ to be used up will be the measure of iodine liberated by the action of ozone in the air passed through the solution.

Applying the basic principle of the above method, Bowen and J. H. Segenar developed an apparatus for measuring the ozone concentration at the ground and at flying levels using aircraft. In this method only one pair of platinum electrodes was used. These electrodes are used for detecting the amount of iodine liberated by the reaction of ozone in the air passed through the solution.

The air is allowed to pass through the solution of potassium iodide and $Na_2S_2O_3$ and the iodine is liberated continuously by the reaction of ozone in the air with the potassium iodide. This liberated iodine was neutralised by $Na_2S_2O_3$ and when all the $Na_2S_2O_3$ is used, the free iodine depolarises the cathode and the current begins to flow and steadily increases. This current is amplified and it triggers a relay when the original current reaches a value of $2 \times 10^{-9}$ amp. When the relay is triggered the solution gets discarded automatically and a fresh solution is injected into the reaction chamber and the above process is repeated.
The volume of air which had to pass through the reaction chamber for the current to reach the value of $2 \times 10^{-9}$ amp is obtained by the number of pump strokes knowing the volume of air aspirated by each pump stroke. From this the amount of ozone per unit volume of air is calculated.

J. Cardenay and A. Vassy built another apparatus working with an automatic starter and photographic recording using the same principle as Degener. This device improves somewhat the previous one, particularly by washing out of the reaction bowl after each measurement which eliminates traces of iodine and used products.

It should however, be remembered that in the atmosphere there are in addition to ozone other oxidising agents such as $\text{H}_2\text{O}_2$ and reducing agents such as $\text{HO}_2$. Therefore what we can measure by the above methods is the net equivalent of all the reactions of these substances. (13)

The following is a summary of the results of the measurement of surface ozone.

Although the magnitude of the ozone amount near the ground is very small, the average value being 2 molecules per $10^8$ air molecules, the fluctuations are large. There is evidence that air rich in ozone is brought to the earth's surface by increased eddy diffusion and mixture with the higher levels and subsidence of air under the influence of moving disturbances.
Chemical method for measuring the ozone distribution in the troposphere and the lower stratosphere.

An air borne unit based on the same principles was built by V. H. Megener and Joyen for measuring ozone at different levels. The instrument was also adapted to sounding balloon flights with radio transmissions to the ground. It was arranged that a signal was transmitted every time the instrument cycled and another signal after a fixed number of pump strokes.

In England, A. E. Brewer, E. R. Kay and Johnson have developed a reliable chemical radiosonde which can be carried in air craft for measuring the ozone amount at different levels. (12)

The equipment consists of two parts (1) the new radiosonde transmitter (2) the ozone element with the detector. This equipment, with the ozone element kept inside a Jowar flask, is carried in balloon or air craft.

In a later compact version of the instrument developed by Brewer, the electrodes are parallel wires wound round a roughened insulating tube at the rate of one drop per minute so that a steady supply of KI is obtained. The tube with its electrodes is kept inside an outer enclosure and air is allowed to pass over the wired tube at a steady rate and let out through an outlet. By increasing the length of the electrodes and reducing the gap between them the evaporation of free iodine could be reduced to small proportions.
The electrolysis is carried out by applying a voltage of 0.1 to 0.2 volt between the electrodes. The small current that is developed depends on the free iodine present in the solution and is amplified by transistor amplifier and put on the radio-sonde. With O$_3$ of 0.002 cm/km the current was about 2 - 3 μA and this could be magnified to 100 μA by the use of the amplifier. The accuracy of the instrument was good, the estimated error being about 2%. It can measure a concentration of ozone of one part in 10$^7$ in about 20 seconds. During the IOP the Brewer ozone equipment has been used in England, at Malta and at Halley Bay in the Antarctic to measure ozone up to a height of about 20 km.

In Norway, Vampire air craft of the Norwegian Air Force was used for carrying the equipment. The main results obtained in summer were the following.

1) Fairly uniform concentration of ozone in the troposphere of about 0.003 cm/km was observed.

2) On entering the stratosphere, a large increase of ozone of the value 0.305 to 0.006 cm/km was observed. In England Ray did not observe any such rise at the tropopause. This rise, Brewer interpreted as associated with different airmasses or with the annual variation of ozone. The observations were made in June and July.

Knowledge of the distribution of ozone on either side of the tropopause in different seasons would help in understanding the mechanisms involved in mixing the stratospheric air with the troposphere. This method is well
suited for such measurements.

2. **Measurements with spectrographs sent up in balloons.**

The first attempt to determine the distribution of ozone in the atmosphere with a spectrograph carried in balloons was made by S. and W. H. Segener at Stuttgart in Germany. In June and July 1934 using a small automatic spectrograph and sounding balloons they succeeded in obtaining direct measurements of ozone on two flights. The height reached by the balloon in one of the flights was 31 km. Although the accuracy of the measurement was limited the results were fruitful and experimentally it was a great achievement. The distributions obtained by these two flights were found to agree within reasonable limits with the distributions obtained by the measurements on the Gotz ukehr effect.

As it was found that, for altitudes between 5 and 35 km balloon ascents with ultraviolet spectrographs gave valuable information for the understanding of the ozone distribution and its variations, the ascents were resumed by Segener in 1950 and later by Fastzold in 1953. (20, 21, 22)

In 1950 during February and March four sounding balloon flights were carried out by W. H. Segener over Albuquerque, New Mexico, using a spectrograph and photographic photometry. The method consisted in measuring the steepness of the cut off
which the solar spectrum exhibits at its ultraviolet end near $\lambda 3000 \text{ Å}$. Due to the steep rise in the absorption coefficient of ozone in this region, the slope of the intensity drop is almost entirely due to atmospheric ozone. The instrument with which the four flights were carried out consisted of a small light weight quartz spectrograph. An automatic mechanism provided for successive exposures at regular intervals during the flights while the spectrograph was continuously directed at a white magnesium oxide surface mounted below the vertical collimator tube. From the slope of the intensity of the ultraviolet end of the solar spectrum an independent determination of the thickness of atmospheric ozone layer interposed between the spectrograph and the sun was made at different heights by the known ozone absorption coefficient. By measuring the rate of change of this thickness with altitude, the vertical distribution of ozone was obtained. Maximum height reached by the balloons was between 30 - 32 km on all the flights.

Some modifications were made by Haetzold and the flights were resumed in 1953 in Germany. A spectrograph which is very light and which would need no readjustment even after rough landings, was developed. To get homogenous observations it was necessary to have spectrographs of standard type which remained optically constant throughout the flight. The optics, the barograph and the thermograph were fitted in a closed metal case and sent up in the balloon. An HgO plate irradiated by the sun served as a source of light in the same way as in the earlier flights. A ring diaphragm was used for reducing the
scattered light of the sky to 40°. The height of the balloon equipment was determined by the barometer and additionally by means of a theodolite.

The highest altitude reached in these flights was 44 km, the average height being 35 km.

The results of these flights can be summed up as follows.

1) The distributions measured up to the altitude of about 30 km show considerable individual differences. It was observed that the distributions were sometimes different between the ascent and descent of the balloon.

2) Sometimes very high ozone amounts were found even above 30 km.

3) In spring, a second maximum always appeared more or less clearly at about 15 km on days on which the air between 11 - 16 km originated from higher latitudes than 60°N.

4) Some of the distribution curve at Weissenau, Germany showed a distinct third tropospheric ozone maximum at about 6 km altitude.

3. Ozone 'radio sonde' methods.

Recently an ozone radio sonde has been developed in Weissenau for routine measurements of ozone distribution by Dr. Kulcke and Paetzold. The method is similar to that of the radio sondes used for measuring pressure and temperature. The ozone radio sonde works with filters transmitting in the
ultraviolet region ($\lambda \leq 3250$ Å) with maximum transmission at $\lambda 3100$ Å and a selenium photoelement. The photo currents are amplified by a three stage amplifier and the intensities telemetered to the receiving station through a morse cylinder. This radio sonde takes measurements by an automatic cycle of 40 seconds of (1) the intensity of the ultraviolet light of wavelengths not absorbed by ozone (2) the intensity of u.v. light in a narrow band of wavelengths which are absorbed (3) pressure (4) control voltage for checking the work of the amplifier and (5) temperature.

Development of these radio sondes was said to be still in progress but detailed description is not yet available.

4. Determination of ozone concentration at higher levels.

The first attempt to measure the concentration of ozone at higher levels was made in 1934 by J'Uršič et al by use of V2 rockets. In this flight of 'Explorer I' along with many other instruments to measure other parameters of the atmosphere two quartz spectrographs with identical optical systems were also sent up. One of these spectrographs was arranged to receive direct sun light and was used for the measurements of atmospheric ozone in the conventional manner. The second spectrograph was arranged to receive only light from the horizon sky for the purpose of determining the ozone content independently, checking the observations of the direct
sun light. Due to the fogging of the sky the spectrograph could not give the necessary accuracy needed for the purpose. The conclusion they drew from their 'Explorer I' flight was that the distribution of ozone agreed well with that obtained by the theunkehr method having a maximum at about 25 km. They did not find any secondary maximum at 15 or 16 km as reported earlier.

Next year in 1935, a second attempt to explore the atmosphere was made (Explorer II) using a V2 rocket. In this exploration as in the previous one, the same equipment was carried. The ozone distribution obtained upto 22 km was based on a direct method of measurement and had only a small probable error. The estimates of ozone above 22 km were, however, somewhat uncertain. In this flight the distribution of ozone obtained show a second maximum at 30 km besides the one at 22 km.

The first reliable direct measurement of the amount of ozone at different heights upto an altitude of 70 km came from F.S. Johnson et al from the series of solar ultraviolet spectra photographed near sun-set from two spectrographs in rockets fired at White Sands.

Since the spring of 1946, rockets have been employed at White Sands, New Mexico for measuring pressure and temperatures in the upper atmosphere. Initially the German V-2 was used, but at present V-2 and the U.S.A. navy's Aerobee and Viking are also being used.
As the rocket ascends, the amount of ozone above it decreases and the spectra extends to shorter and shorter wavelengths. The amount of ozone above the spectrograph was determined by comparing each spectrum with a spectrum obtained when the rocket was above all detectable ozone.

The comparison of the spectra were made by photographic photometry. The data were obtained with a very low sun so as to increase the optical path through ozone and thus increase the amount of ozone that could be detected.

The ozone distribution curves obtained by these rocket firings supported and agreed in general with the curves obtained by Gotz, Meetham and Dobson for Arosa, by Tonberg for Tromso and by Karandikar and Ramanathan in India by the mukehr method for the same amount of ozone. However, the distributions obtained on the same day by the mukehr method and by the rocket borne spectrographs often disagreed in the height of maximum concentration. This is probably due to the error introduced by the neglect of secondary scattering in the calculation of ozone distribution from mukehr observations.

The observed curves were compared with the curves calculated photochemically by Bates and Nicolet (1950), by Craig (1950) and by Johnson. In general, there was satisfactory agreement above about 30 km.
B. **Indirect methods.**

Although the determination of ozone concentration at any height by reaching to that height and measuring the concentration directly, is more direct, the derivation of ozone distribution from ground observations is more convenient and easier of operation.

There are three methods that have been used for the determination of ozone distribution from ground measurements (1) observations on umkehr effect (2) lunar eclipse method (3) observations on infra-red $9.6 \mu$ ozone band.

1. **The Umkehr method.**

In 1929, F. von Paul Götz working in Spitzbergen at latitude $73^\circ 35'N$. observed that the light scattered from the zenith sky was relatively richer in the shortest wavelength when the sun was setting or rising than when it was a little higher. He called this effect the umkehr effect and explained it as being due to the fact that the principal path of the zenith sky light at very low altitudes of the sun came from the atmosphere above the ozone layer.

This experimental result has been used to determine the distribution of ozone in the scattering atmosphere. The shape of the umkehr curve determines the distribution. Due to the simplicity of its operation from the ground, this method remains the most convenient for obtaining the ozone distributions on many days whenever the sky is clear.
Iota, Meetham and Jobson developed two methods, \( \text{Method } \) and \( \text{Method } B \) for calculating the vertical distribution of ozone from the umkehr observations. These two methods differ only in matters of detail.

\textbf{Method } \textit{a} \:-\quad \text{In this method the atmosphere is divided into five sections namely 0-5, 5-20, 20-25, 35-50 and above 50 km. A known amount of ozone (which is estimated from spectroscopic or chemical measurements) is measured to exist in the ground layer. Ozone amount above 50 km is assumed to be zero. Knowing the total ozone amount (\( x \)) from the sun observations, the remaining two unknown amounts in two layers are determined by taking two suitable values of \( \log \frac{I}{I'} \) corresponding to two values of the zenith distance \( Z \) from an umkehr curve and writing down two numerical equations.}

\textbf{Method } \textit{B} \:-\quad \text{The whole atmosphere is divided into eight sections and arbitrary amounts of ozone are assumed to be present in each, the sum of the amounts in all the sections together being equal to the total ozone amount obtained by observations on direct sun. By calculating the scattering and absorption of light at all heights under these conditions, a theoretical umkehr curve is calculated. Agreement is obtained between this theoretical curve and the observed umkehr curve by adjusting the ozone amounts in various sections by trial and error.}

The detailed description of the method and the results obtained in India and at other places in the world will be
given in another chapter.

2. Lunar eclipse method.

Barbier, Chalonge and Vigroux\textsuperscript{23} in 1942 suggested utilising measurements of the earth's shadow on the moon for studying absorption in the earth's high atmosphere. In 1950, N.M. Paetzold in Weissenau used the method for determining the ozone distribution in the atmosphere.

This method has the advantage that the ozone distributions at high and low geographical latitudes can be obtained simultaneously from measurements at one place.

The spectral intensity of light is measured at the edge of the umbra on the moon perpendicular to the boundary of the shadow. The easiest way of doing this is to take photographs of the darkened moon using interference filters at 6000 $\AA$ in the Chappius ozone absorption band and at 4000 $\AA$ and 5000 $\AA$ in various phases of the eclipse.

From measurements taken at 4000 $\AA$ and 5000 $\AA$ one can determine the atmospheric extinction outside the ozone absorption band in the form $a \lambda^B$ and from additional measurements taken in the Chappius band the ozone distribution can be calculated. Vigroux in one case has given the plot of relative spectral intensity distribution of the shadowed portion on the moon's surface for various shadow points and for wavelengths from 4500 $\AA$ to 6500 $\AA$. One can calculate how the intensity Chappius band would vary for different ozone...
distributions.

**Evaluation:** Let \( \gamma \) be a point on the darkened noon near the boundary of the earth's shadow, where \( \gamma \) is the angle between the line joining \( P \) with the centre of the earth and the line joining the centres of the sun and the earth. Let \( O_3(\gamma) \) be the mean ozone mass in the earth's atmosphere traversed by a beam of light arriving at \( P \). \( O_3(\gamma) \) is determined from the spectral observations made at the shadow point \( P \). Let us consider a ray of light from the sun at a height \( h_0 \) from the surface of the earth and let \( O_3(h_0) \) be the mean ozone mass traversed by that ray in the earth's atmosphere. Now, assuming the sun as a point source, the height \( h_0 \) can be calculated when \( O_3(h_0) \) equals \( O_3(\gamma) \) using the data of atmospheric refraction given by Hink. By knowing \( O_3(h_0) \) for different shadow points on the moon, the distribution of ozone in the vertical can be calculated.

The results obtained of the ozone distributions by this method were comparable with the distribution obtained by other methods. The method is however of limited use being available only when there is a lunar eclipse and the sky is clear at that time.

3. **Infra-red method.**

Strong in 1941 suggested a method of determining the ozone distribution from simultaneous measurements of the solar intensity in the ultraviolet and in the infra-red 9.6 \( \mu \) ozone band. Absorption in the ultraviolet depends only on the total
amount of ozone in the path while in the infra-red it
depends also on the pressure at the levels in which ozone is
distributed. Thus simultaneous observations in two spectral
regions can be combined to yield a mean pressure for the
level of atmospheric ozone.

Watanabe (1955) carried out Strong's suggested
method but was not able to obtain any useful new results. He
used the 'resstrahlung' method for the infra-red observations
and obtained for the mean effective height of ozone a level of
23 km. Watanabe realised that more accurate measurements
would be possible if the complete contour of 9.6 µ band
could be recorded and the absorption due to ozone found by
evaluating the background intensity across the band.

The manner in which the intensity of the 9.6 µ
absorption band depends on the amount of ozone and the total
pressure of air with which it is mixed has been determined by
laboratory experiments by Summerfield and by Walshaw and Goody.
We shall briefly describe Goody and Walshaw's method. 33,34

Experimental procedure:—The spectrometer used was
a double monochromator having two 30° rocksalt prisms in
Biotrow counting so arranged that the dispersion reinforced
one another. The detector was a delay pneumatic cell. The
radiation was chopped at 12 cycles per second and the output
signal from the detector operated a pen recorder after
amplification and detection by a selenium system. Care was
taken to prevent stray radiation reaching the detector. Prism
compartments and the detector compartments were optically

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enclosed. The spectrometer was sealed in a vacuum tight chamber and dried with silica gel. Radiation was allowed to enter through a window and the scanning mechanism and the slit width control were operated electrically from outside.

Method of calculating the mean height of ozone:

The principle of the method is that the area of the 5.6 μ band depends both upon the total ozone amount and on its mean pressure. If we knew the law of variation of absorption in the whole band with ozone amount and with pressure we can find the effective mean pressure at which the whole ozone in the atmosphere may be supposed to be concentrated. Curtis has shown that an approximate solution to the problem of absorption along a pressure gradient is given by regarding all the absorbing gas to be concentrated at a mean pressure given by the formula

\[ \bar{p} = \frac{\int_0^b p \cdot f \, dh}{\int_0^b p \, dh} \]

where \( f \) is the density of ozone between \( h \) and \( h + \Delta h \).

The total ozone amount can be obtained by the ultraviolet absorption method with a Dobson's spectrophotometer.

The area of the band is determined by planimetering the area enclosed below the curve of background intensity and the width of the band and then by multiplying the area by a constant determined from the frequency calibration of the spectrometer. The complete description of the band apart from
the ozone effects is, however, very complicated due to such problems as the combined effect of Doppler and collision broadening, etc. Analytical approach to this problem has been made.

Thus, by knowing the band area and the total ozone amount, the mean pressure at which the ozone is situated is known. The effective pressures were then converted into heights in the I.S.T.A. standard atmosphere (i.e., a pressure of 175 m of Hg at 11 km and a constant temperature of 216.5° C above).

This method has an advantage in that the molecular scattering is unimportant. It has the disadvantage that conditions in the lower atmosphere including dust and haze have a significant influence on the total radiation even within the 9.6 μ band.

Salahau and Goddy found from their observations in
Cambridge in 1952-53 that the ozone height was a minimum in the summer with a seasonal range of height 3.4 km between March and October. They suggested that during the winter months in England there is little ozone in the troposphere and lower stratosphere and that in spring, the latitudinal gradient brings in polar air and increases the ozone amount in 10-16 km. They attribute the low value of ozone height in summer to increased convective activity, mixing of tropospheric and stratospheric air. They found in March-April a maximum ozone in 10-16 km with a minimum in 0-10 km and in July-August a maximum in 0-10 km and minimum in 10-16 km.

In later papers Epstein, Osterberg and Adol (1955) and B.M. Good and T.P. Roach have given a method using both absorption measurements on the 9.6 μm band and emission measurements of the same band.

The emission measurements were made by comparing the intensities of radiation in 9.6 μm band received from the sky at a number of zenith angles, from liquid air and from a black cavity at constant temperature near the temperature of the room.

The following expression for the emission area of the 9.6 μm band was derived from the usual theory of radiation.

\[
\frac{A}{\tau(d)} = \int B \cdot dx
\]

where \( A \) is the Planck black body radiation in the 9.6 μm band and \( \tau(d) \) in the mean background radiation transmitted to the
ground and $A/T(b)$ is the emission area of the 9.6 m band
just above the emitting layer responsible for the background
and which can be calculated from the R.H.S. of the equation.
Ozone distribution is then determined by adjusting ozone
in different layers by trial and error to give the best fit
to this ozone emission area.

Goody and Rach divided the atmosphere into three
layers and assumed the following distribution of ozone in
each layer.

1. Ground to tropopause
   \[ a \frac{p_1}{p} \]

2. Tropopause to 30 mb
   \[ b \left( \frac{p_1}{p} \right)^2 \]

3. $> 30$ mb
   \[ c \left( \frac{p_1}{p} \right)^{-1} \]

where $p_1$ and $p$ are the pressures at the bottom and top of
each layer and $a$, $b$, $c$, are the constants to be adjusted to
give the best fit for the ozone emission area.

The integral in the equation (1) is evaluated by
summing the contributions from these three layers treating
each layer as though it had a unique average value of $A(T)$.
For an optically thin layer $\bar{B}$ is given by

\[
\bar{B} = \frac{\int_{p_1}^{p} B \cdot \delta \cdot dp}{\int_{p_1}^{p} \delta \cdot dp}
\]

and for an optically thick layer $\bar{B}$ corresponds to a level
near to the bottom of the layer and this expression is used
to evaluate $\bar{B}$ for all the three layers.
For each day of observation $\beta$ is determined. A value of 'a' is selected and 'b', 'c' are then calculated from the known $m(o)$ and $f(o)$ where $m(o)$ is the mean ozone amount obtained from Dobson's spectrophotometer and $f(o)$ is the mean pressure of ozone determined by the absorption of ozone in 9.5 $\mu$ band. The integral in the equation (1) is then determined for a range of zenith angles. The calculation is repeated for different values of 'a' until the best fit to the corrected ozone emission is found.

In this method the number of layers is too small and the accuracy is also small.

Epstein, Osterberg and Adel, in their computation of vertical distribution of ozone from the infra-red and ultraviolet observations, have divided the atmosphere into 13 layers 1.75 to 5 km thick, between 2 km to 47.5 km. They assumed that ozone was distributed uniformly in each layer and that each layer was isothermal and isobaric. In the computation of the ozone distributions they have made use of (1) $T_{90}$, effective radiation temperature of ozone region (2) $b_o$, the fractional absorption by atmospheric ozone over the 9.5 $\mu$ band in the direction of observation (3) $w$, the precipitable water vapor in a vertical column of the atmosphere and (4) $u$, the total amount of ozone in a vertical column.

The radiation from the ozone was compared with that of a black body radiator corrected for the observed grayness of ozone. This corrected radiation intensity was converted to
a temperature, 300K, by the Planck black body relationship. \( \lambda_c \) for the entire band was determined from the area of the band \( \delta \), obtained by planimetering after allowing for the absorption by water vapour \( w \). The total ozone amount was determined by Dobson's spectrophotometer.

From \( \lambda_c \), the fractional absorption over the central 0.14 \( \mu \) of the band (\( \epsilon_c \)) was determined. Sumerfield has given a relation from laboratory experiments, between transmissivity, \( u_p \) - the effective thickness of ozone, \( u \) - the actual ozone amount and the pressure. The relationship between transmissivity and \( u_p \) was determined to fix the data where \( u_p \) was equal to \( u_p/p_0/0.295 \).

Thus from \( \lambda_c \), the transmissivity (1 - \( \epsilon_c \)) was obtained and substituting this in Sumerfield's relationship between \( u_p \) and transmissivity, \( u_p \) was calculated in the direction of observation. To determine the effective thickness of the ozone in the vertical column, \( u_p \) is divided by \( \mu \) (the cosine of the zenith angle).

The infra-red radiation temperature, \( T_{IR} \), is maximum from the lowest layers of the atmosphere (troposphere). So, the method would be insensitive to changes of ozone in the stratosphere. Still, Epstein, Osterberg and Adel have obtained some interesting results. They have observed marked seasonal variation in the vertical distribution of ozone and an indication of annual variation of ozone in phase with season above 30 km.
Dust and haze particles can contribute substantially to 9.6 μm radiation. Hence use of this method in a place subject to fog and haze is likely to lead to confusing results.

Conclusion.

Each of the methods of measuring the vertical distribution of ozone in the atmosphere has advantages and disadvantages. A spectrograph carried in a rocket is the only satisfactory method available for determining the ozone in the highest parts of the atmosphere. The balloon methods are useful for levels from 5 to 35 km. The chemical method allows the measurements of the detailed distribution in the first 15 km fairly accurately and has a very promising future. The lunar eclipse method is interesting but non-useful as a meteorological tool. The infra-red method appears promising but needs further work. Most of the existing knowledge of the distribution of ozone at different latitudes has come from the Götz maker method and the use of spectrographs in balloons and rockets. Götz's method is simple and inexpensive and many measurements can easily be obtained provided the atmosphere is clear. There is some slight uncertainty in the calculation of the distribution from the observations and the method is rather insensitive to changes in ozone concentration in the lower atmosphere.
References

2. Ebert, A. 1951 Cat. Rundschau, 4, 64.


