

# Forty Years' Research on Atmospheric Ozone at Oxford: a History

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The development of research on atmospheric ozone at Oxford is traced from the year 1922, when one single instrument was used there to make measurements of the total ozone, to 1966, when some hundred instruments were distributed all over the world. In recent years an important advance has been made by the measurement of the vertical distribution of the ozone in the atmosphere. A digression, covering the war years, describes the measurement of the amount of water vapor in the stratosphere which, however, proved to have a bearing on the effect of the ozone on the temperature of the upper atmosphere.

## I. Introduction

It is now just over forty years since the first daily routine measurements of the ozone in the atmosphere were begun at Oxford, and Beck has just completed ozone instrument No. 100 (Fig. 1). The present, therefore, seems a suitable time to review the progress of this work at Oxford, and it is thought that some of those who are now carrying on the major active research in this subject may be interested in an account of how it all began. This account has been confined to the work connected with Oxford in order to keep it within reasonable limit.

In 1879 Cornu<sup>1</sup> had suggested that the rather sharp limitation of the uv end of the solar spectrum as received at the ground was due to absorption in the atmosphere, and in 1880, Hartley,<sup>2</sup> having roughly measured the absorption of ozone in the uv region (the Hartley band), suggested that it was ozone which was responsible for the absorption. While Meyer<sup>3</sup> in 1903, had measured the absorption coefficients of ozone more accurately, Fabry and Buisson,<sup>4</sup> in 1912, made careful measurements of the absorption coefficients of ozone and compared these with the absorption of sunlight by the atmosphere. From their measurements they concluded that there was about 0.5 cm of ozone in one vertical thickness of the atmosphere. It was suggested that the ozone was formed from oxygen in the upper atmosphere by the action of solar uv radiation.

In 1919 and 1920 Fabry and Buisson<sup>5</sup> returned to this subject and designed a special spectrograph with two dispersions at right angles to each other, thus reducing

the fogging of the photographic plate by light scattered within the instrument (Fig. 2). During May and June 1920 they made measurements of the amount of ozone at Marseilles by taking spectrograms on fourteen days at several times during each day when the sun was at different heights. They found that the amount of ozone was about 0.3 cm (STP) and, owing to rather steady weather conditions at the time, there was little variation in the amount between one day and another. They suggested that it would be of great interest if a sufficiently large institution [sic] could arrange to make daily measurements over a long time. They thought correctly that the ozone was formed by solar uv radiation and suggested that if this were so it would be mainly situated at a height of about 40 km. Rayleigh and Götz had both shown that there was little ozone in the lower atmosphere by taking uv spectra of a mercury lamp through long distances of air near the ground.

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In 1921, F. A. Lindemann (later Lord Cherwell) had shown that it should be possible to obtain some knowledge of the variation of the density of the air with height in the upper atmosphere from observations of the velocity, brightness, and height of meteors. At this time no suitable photographic measurements of meteors were available and, although two automatic cameras were set up, one in Oxford and one on Boars Hill about four miles away, owing to their limited field of view, very few meteors were photographed. However, using the eye observations of Denning and his co-observers (which proved surprisingly accurate), the density of the air was calculated at the height of appearance and of disappearance of a number of meteors. It was generally supposed that the air above the tropopause was cold at all levels and when

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The author has retired from the Clarendon Laboratory, Oxford, U.K.

Received 25 March 1967.

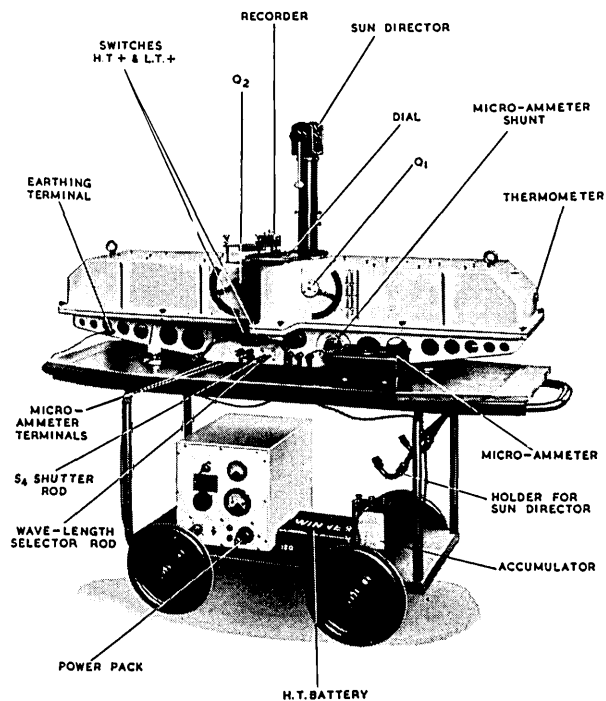


Fig. 1. The ozone spectrophotometer in its present form.

the densities as calculated on this assumption were compared with those obtained from observations of meteors, it was found that, whereas the two agreed fairly well for heights around 30 km, at heights above 50 km, the densities determined from meteors were about 100 to 1000 times greater.

When I first showed the plot of densities obtained from meteors against height, to Lindemann, with its large differences between the calculated and observed values, he immediately suggested (1) that the air above 50 km must be much warmer than was thought and (2) that this high temperature might be caused by the absorption of solar uv radiation by ozone in the upper atmosphere. The paper<sup>6</sup> giving this work on meteors caused considerable discussion at the time and the conclusion that there was a warm region at a height of about 50 km was by no means generally accepted. The subject even got into the daily papers, one of which facetiously suggested that it was unnecessary to go to the Riviera when the temperature was just as warm only 50 km overhead! Confirmation of the existence of the warm region, however, soon came from the work of Whipple<sup>7</sup> on the propagation of sound waves through the upper atmosphere.

At this time it was well known from the work of Dines<sup>8</sup> and others that the stratosphere was warmer in cyclonic conditions and colder in anticyclonic conditions, and Lindemann also suggested that these differences of temperature *might* be due to different amounts of ozone in the stratosphere—cyclonic conditions having much ozone and anticyclonic conditions little ozone. It also seemed just possible that cyclones and anticyclones might be actually caused by different amounts of ozone in the upper atmosphere. We know

now that there is, indeed, more ozone in cyclonic conditions than in anticyclonic conditions but that this is not the cause of the different pressure systems. However, Lindemann's suggestions made it desirable to try to make regular daily routine measurements of the amount of ozone in the atmosphere on the lines of the few measurements then recently made at Marseilles by Fabry and Buisson.

At this time there were no photocells commercially available which were suitable for this work and even valve amplifiers were in an elementary stage of development. A method of photographic photometry similar to that used by Fabry and Buisson was clearly the best method to employ. Fabry and Buisson used a rather elaborate double spectrograph with two dispersions at right angles to each other in order to reduce fogging by light scattered within the instrument. This was not convenient for routine use out-of-doors and, further, there was no money available to buy such an elaborate instrument. A spectrograph therefore had to be designed which could be made in the laboratory.

It was clear that this work would require spectra of sunlight to be taken at all times of the day, and on cloudy days every opportunity would have to be taken to use any brief patch of sunlight. A hut was therefore built in the garden at Boars Hill (Fig. 3), about 6 km from Oxford, half of which was used as a workshop and half as a laboratory with a very small photographic dark room. A serious disadvantage was that for some years there was no main electric supply available and accumulators had to be charged in Oxford and carried up and down on the back of a bicycle!

It was at this time that D. N. Harrison joined in the work while working for a D. Phil. degree and greatly assisted the research for the next three years.

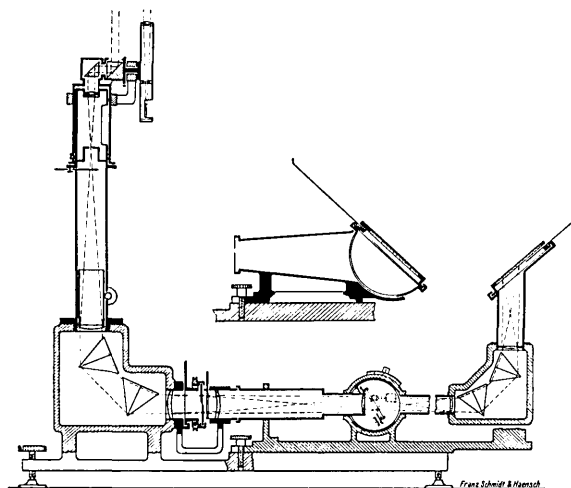


Fig. 2. The Fabry-Buisson ozone spectrograph gives two dispersions at right angles. The right-hand portion is shown rotated through 90°.



Fig. 3. The laboratory and workshop at Robinwood, Boar's Hill, Oxford, in August 1921.

## II. Design of the First Ozone Spectrograph

A little before this time, T. R. Merton of the Clarendon Laboratory had developed a photographic method of measuring the relative intensities of spectral lines. He placed an optical wedge immediately over the slit of the spectrograph, so producing spectra in which the lines were strong at one end and faded to nothing at the other, the length of the line being proportional to the logarithm of its intensity. Merton used a method of development which produced a rather sharp cutoff to the lines so that their length could be measured fairly accurately, but a different method, which is described below, was used in the ozone work. It was anticipated that scattered light within the spectrograph would be likely to cause serious fogging of the weak uv spectra, and Merton suggested that a Féry prism would be a good arrangement, since the light was only scattered by three surfaces, *viz.*, on entering and leaving the front surface and on reflection at the back surface. Another great advantage of the Féry prism was that it was strongly astigmatic and a point of light on the slit produced a nearly uniform line of light on the photographic plate. An optical wedge, consisting of gelatin and carbon black between quartz plates, was mounted immediately in front of the photographic plate so that the image of each line faded off along its length as in Merton's method.

In spite of the small amount of scattering by the Féry prism, the large amount of energy in the visible part of the solar spectrum relative to that in the very short wavelength caused excessive fogging of the uv image. Peskov (1917) had shown that chlorine<sup>9</sup> and bromine vapor would absorb most of the visible light but were transparent to wavelengths around 3000 Å. For our work it was desirable to use a filter which would absorb all the visible light and considerably reduce the intensity of 3300 Å while being almost transparent to 3000 Å. By using photographic plates which were insensitive to the red, the small amount of longwave radiation passed by bromine vapor was rendered unimpor-

tant. The chlorine and bromine vapor were contained in a silica tube about 25 cm long with flat end windows, which was placed in front of the slit of the spectrograph. By putting in the correct amount of chlorine it was possible to obtain spectra in which the intensity of lines around 3250 Å was nearly the same as at 3050 Å and there was very little fogging of even the shortest wavelengths that could be photographed when the sun was high (about 2950 Å). In order to save the expense of two separate quartz vessels—an important consideration at this time—advice was sought from the Chemical Laboratory in Oxford as to whether there might be any chemical reaction between these two gases if they were mixed together. We were assured that, whereas there was a compound of chlorine and iodine, no compound of chlorine and bromine existed, and we could safely mix them together. (At this time we did not know of the uv transmission of  $\text{NiSO}_4$  which is now so useful a filter with observations when the sun is very low.)

The silica tube which was used as a filter was filled with air saturated with bromine vapor at  $-5^\circ\text{C}$ , it being important that no bromine should condense in cold weather and so change the absorption of the filter. A small measured amount of chlorine was then added, the required amount being found by trial and error after taking spectra of sunlight. After admitting chlorine to this silica tube it was often found that there was a slight condensation of liquid in the tube which was thought to be due to water vapor and considerable precautions were taken to keep the tube dry, the chlorine being stored over  $\text{H}_2\text{SO}_4$ . Since any condensation might cause a change in the absorption of the gases in the tube, any tube which showed any sign of condensation was refilled. The trouble of condensation continued in spite of all precautions and it was finally decided to use two separate silica tubes, one for each gas. When this was done we were surprised to find quite a different absorption spectrum for the two gases, and it was immediately obvious that we had been using the compound  $\text{ClBr}$  which we had been assured did not exist! Moreover, this mixture of  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{ClBr}$  gave us just the absorption that we wanted for this work while  $\text{Cl}$  and  $\text{Br}$  separately did not. We had, therefore, to continue using one tube containing both  $\text{Cl}$  and  $\text{Br}$ . Tests showed that, very fortunately, the equilibrium proportions of  $\text{Cl}$ ,  $\text{Br}$ , and  $\text{ClBr}$  did not change with temperature so that the absorption of the filter remained constant.

The original spectrograph made in 1924 is now in the Science Museum at South Kensington (Fig. 4).

### A. Development of the Photographic Plates

A few simple tests soon showed that the ordinary method of developing plates in a flat dish gave unsatisfactory results. Thus, if a plate were covered with a mask with holes cut in it and then uniformly exposed to light, the resulting images were found to be denser round their edges than in the center. Clearly, fresh developer was not being brought to the center of the image, or the products of development were not being removed, quickly enough. This effect was known and various

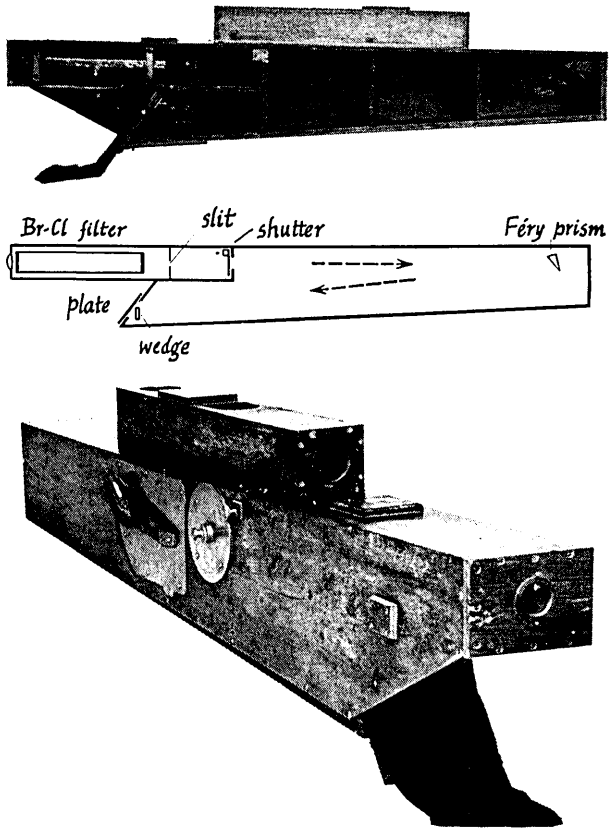


Fig. 4. The Féry spectrophotometer is now at the Science Museum, London; note its extreme simplicity. (Photos British Crown copyright, Science Museum, London.)

methods had been suggested for overcoming it; thus, one suggestion was to brush the plates continuously during development and another to roll them with a felt covered roller. None of these methods seemed ideal and a special developing tank was designed in which excessive stirring of the developer was produced right against the surface of the plate. In this tank, which was deep but narrow, the plates were held in guides flat against the vertical sides, with dummy plates above and below them. A plunger which also ran in guides moved up and down in the tank with only about 1-mm clearance between it and the plates. Thus, as the plunger was moved up and down the whole volume of developer was forced through this small space at a high speed (about 2 m/sec) and would cause excessive stirring right against the surface of the plate. Tests showed that the images given by this method of developing showed no tendency to be denser at their edges than in the center. Four plates could be developed at once, and they were developed, fixed, and washed without removing them from the tank. This proved most useful when large numbers of plates had to be developed.

As a result of this work, a small book, *Photographic Photometry* (Clarendon Press), was published, with I. O. Griffith and D. N. Harrison setting out the principles and methods by which the most accurate results could be obtained.

## B. Microdensitometer

When measuring the spectra it was required to find the distance from the image of the zero line of the wedge to a point on each spectral line where the density was equal to that of a standardizing patch put in the center of each plate by a constant light source. Although the slit of the spectrograph was made fairly wide, so that a single spectral line was about 0.1 mm across, the area to be measured was very small, and a special microdensitometer had to be designed and made in the laboratory for the purpose.

The image of a straight coiled filament lamp was focused on the photographic plate by a microscope objective, the image being about  $0.6 \text{ mm} \times 0.06 \text{ mm}$  in size. (A smaller image gave irregular results because of the graininess of the plate.) The plate was mounted horizontally on a mechanical stage which had scales to measure its movement in two directions at right angles. After passing through the photographic plate, the light passed through a small hole slightly larger than the image of the filament and then fell on a potassium photocell which had been made in the Clarendon Laboratory.

Another part of the light from the lamp traveled by a different path and also fell on the photocell after passing through an optical wedge which was used to adjust its intensity. A shutter, operated by a pedal, cut off one or other beam of light as required. The very small current from the photocell was passed through high resistance of xylene and alcohol (about  $10^9 \Omega$ ), and the voltage across this was measured in a Lindemann-Keeley electrometer which was viewed through a microscope with eyepiece scale.

When measuring a plate, the procedure was first to place the standardizing image under the light and adjust the optical wedge in the reference beam until the electrometer deflection was unchanged whether the pedal was up or down. The plate was then moved until the required spectral line came under the spot of light, the line being parallel to one axis of the mechanical stage. The reading of the mechanical stage was then taken when the image of the zero line of the wedge was under the spot of light and again when the plate was moved to a position where the density of the spectral line was equal to that of the standardizing strip. The readings could be repeated to within 0.1 mm. In general, two long wavelengths and two short wavelengths were measured for each determination of ozone and six spectra could be measured in a little under an hour.

## C. Results Obtained with the First Féry Spectrograph at Oxford

The first Féry spectrograph was built at Boars Hill during the summer of 1924, and a few solar spectra were obtained in September and October. The extraterrestrial constants for the different wavelengths could not be obtained in the winter when the sun was low, but on 17 February 1925 measurements were begun again and solar spectra were obtained on every possible occasion during the year, both for the determination of the extraterrestrial constants and for the daily ozone values.

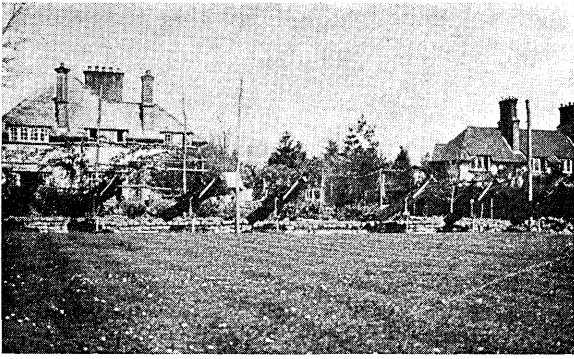


Fig. 5. Comparison of Féry spectrographs at Boar's Hill, Oxford, 1926.

It was at once noticed that there had been a large increase in the ozone values since the measurements made during the previous autumn. At that time nothing was known about the annual variation of the amount of ozone and it was natural to expect that, if there was any annual variation, the maximum would be in summer and the minimum in winter. As the measurements continued it became clear that the high ozone values were a characteristic of spring, especially when the values began to fall during the summer. By the following autumn the maximum in the spring and the minimum in the autumn had become fairly well established, though the reason for this peculiar annual variation was not known.<sup>10</sup>

The Oxford ozone values were plotted daily on a chart as they were obtained and, in addition to the annual variation, it became clear that there were large variations from day to day. When enough ozone measurements had been obtained, they were compared with the surface pressures, and it was of great interest to see a definite negative correlation between them. This was just what would be expected from Lindemann's suggestions. At this time there were no regular upper air measurements which reached up into the stratosphere. Fairly regular airplane ascents were made at Duxford to a height of about 4 km from which it was possible to estimate the pressure at about 9 km. A few and quite irregular ascents were made by balloons carrying Dines' instruments. When the results from the upper air measurements were compared with the simultaneous ozone measurements a much closer connection was found than that with surface pressure. Since at that time it was supposed that the average height of the ozone in the atmosphere would be about 40 km, this close correlation with conditions in the upper troposphere and lower stratosphere was very surprising.

It could be objected that the absorption which we were measuring was not necessarily due to ozone in the atmosphere, but possibly to some other gas. To test this, five pairs of spectral lines were measured for some months on each solar spectrum and the ozone value was calculated from each pair separately. The results showed clearly that the same variations were obtained with every pair of wavelengths was used and as

it was very unlikely that another gas would have just the same absorption spectrum as ozone, this was fairly good evidence that we were really measuring the amount of ozone.

#### D. Ozone Measurements in Europe

The results of the 1925 ozone measurements at Oxford were of such interest that it was decided to try to get measurements at several places scattered over Europe in order to study the *distribution* of ozone in relation to the *distribution* of pressure, etc. The Royal Society gave a grant to buy five Féry prisms and five silica tubes for the chlorine-bromine filters. The winter of 1925-26 was a very busy one, making the spectrographs, filling the chlorine-bromine filters, and, when the sun was high enough in the spring, all the wedges had to be calibrated and all instruments compared with the original instrument (Fig. 5). Finally, all the instruments had to be packed up carefully. This was all done at Boars Hill.

The British Meteorological Office was helpful in allowing measurements to be made at the meteorological stations at Valentia, Ireland, and Lerwick, Shetland, and also by arranging with other meteorological services for measurements to be made at Abisko, Sweden, and Lindenberg, Germany. Dr. Götz kindly undertook to operate one instrument at Arosa, Switzerland (Fig. 6). Unfortunately, just when all the instruments were ready to be sent off, the General Strike of 1926 started, and it was some weeks before the railways would accept any goods. It was thus not possible to begin observations, other than those at Oxford, until July 1926.

In addition to the six Féry spectrographs made at Boars Hill, the Smithsonian Institution had one made by Hilgers. This instrument, which they sent to Montezuma, Chile, was calibrated with others at Boars Hill and all the photographic plates were returned there for development and measurement as for the other stations.

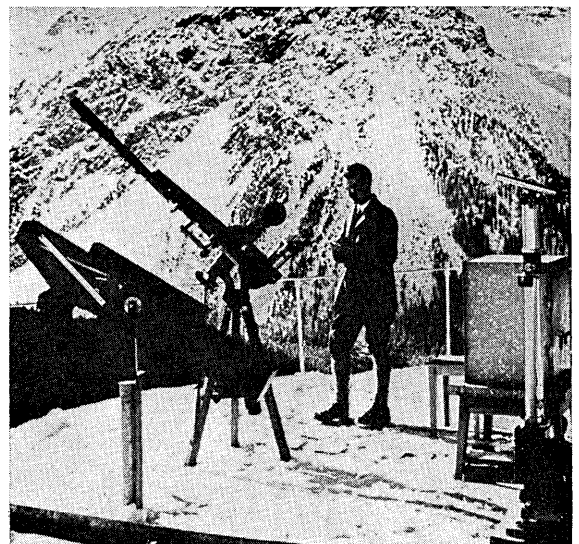


Fig. 6. Early observations at Arosa. From left to right are the Féry ozone spectrograph, Dr. Chalonge with his spectrograph, and part of the Fabry-Buisson spectrograph.

During 1927 Buisson made measurements of the ozone at Marseilles using the Fabry-Buisson spectrograph described earlier. These were a very useful addition to the values obtained with the Féry spectrographs and showed a very interesting relation between the changes of ozone at Marseilles and that at Arosa—some 500 km northeastwards—as small depressions moved eastwards and affected the two stations in turn.

In the work with the photographic spectrophotometers, the observers at all stations were supplied with photographic plates. They were only asked to load the plates into the plateholders, make the exposures, write the date and place on the edge of the plate, and repack the plates in their original packing and return them to Oxford. Special red labels were supplied asking the customs not to open the packages. At Lindenberg they did not consider that it was safe to send the plates through the ordinary post and made special arrangements for them to be sent to the German Embassy in London through the diplomatic bag. The German Embassy agreed to forward them, provided that I would repay the postage of the plates from London to Oxford. In any event we never had any trouble with the plates being opened in the post except some of those sent through the German Foreign Office.

There was much activity when the plates began to arrive from the different stations, as these all had to be developed, measured, and the ozone calculated. Fortunately, the DSIR became interested and gave a grant for a half-time assistant who measured the plates and calculated the ozone values. It was naturally with great interest that the European values were plotted on the weather maps, and the first idea of the distribution of ozone in relation to pressure systems was obtained. Since the 1926 observations began late, it was decided to carry on with the same routine during 1927. The results obtained were reported in two papers to the Royal Society.<sup>11</sup> By the end of the European work, over 5000 spectra had been measured and the ozone values calculated. In order to keep the interest of those taking the photographs at the different stations, the daily ozone values were duplicated each month and sent to all the cooperating stations and any other people interested. On occasions of special interest, the daily weather maps were duplicated with the ozone values entered at each station and these were also circulated.

#### E. Measurements of Ozone Over the World

The European measurements in 1926 and 1927 had allowed us to obtain a rough picture of the distribution of ozone relative to the pressure systems, and gave a limited indication of the variation of mean ozone values with latitude. However, we knew nothing about the variations of ozone in the southern hemisphere since the station at Montezuma was only 22°S and the results were not very reliable. It was therefore decided to redistribute most of the instruments to places widely scattered over the world. Only the instruments at Oxford and Arosa remained at their old stations, the others being sent to Table Mountain, California; Helwan, Egypt; Kodai Kanal, India; and Christchurch, New

Zealand. One instrument was lent to the Italian Polar Airship Expedition. Unfortunately, disaster overtook that expedition, but the spectrograph was not on board and was eventually recovered. Measurements were made on all possible days throughout 1928 and 1929, the photographic plates being returned to Oxford as before, for development and measurement.

J. Lawrence joined us about this time, and while working for a B.Sc. degree studied the relation of ozone to geomagnetic conditions. Chree,<sup>12</sup> using the first year's results at Oxford had shown that there appeared to be a connection between magnetic activity and the amount of ozone, the amount of ozone being greater on magnetically disturbed days. Lawrence used the Oxford ozone values for 1926 and 1927 and in each year found the same relation as Chree had done. However, when he used the average ozone values for Northwest Europe—which should be less affected by local meteorological conditions—he found no relation at all, so it was concluded that both Chree's results and his earlier ones had been accidental. This investigation has never been repeated.

The results of this work<sup>13</sup> gave us a fair idea of the distribution mean of ozone with latitude (except high latitude) and its seasonal variations, though, of course, there were large gaps and little information could be obtained about any possible variations with longitude. The six months difference in phase of the annual variation in the two hemispheres was clearly established, while at Kodai Kanal (10°N) there was very little variation throughout the year. The type of variation of ozone with pressure systems which had been found in Europe was also found at other extratropical stations. Since the ozone is mainly situated within the stratosphere and the Indian monsoon is a relatively low level phenomenon, it was not expected that the change in the monsoon would affect the ozone values; this was found to be the case.

#### F. Design and Construction of the Photoelectric Spectrophotometer

The Féry spectrographs had proved very successful and had provided data which allowed the general relationship between the ozone and the pressure distribution to be found, as well as the general distribution of ozone and its seasonal variation over much of the world. However, experience had shown two serious disadvantages: (1) the time taken in posting the photographic plates back to Oxford, together with their development and measurement, meant that all ozone values were many weeks out of date when first calculated; (2) the light gathering power of the Féry spectrograph is small and measurements could only be taken with sunlight and when the sun was not too low; so it was not possible to work at the higher latitude stations in midwinter. Further, no measurements could be obtained on cloudy days.

By about 1927–28, photoelectric cells were being developed and valve amplifiers were in general use, so much thought was given to the design of a possible



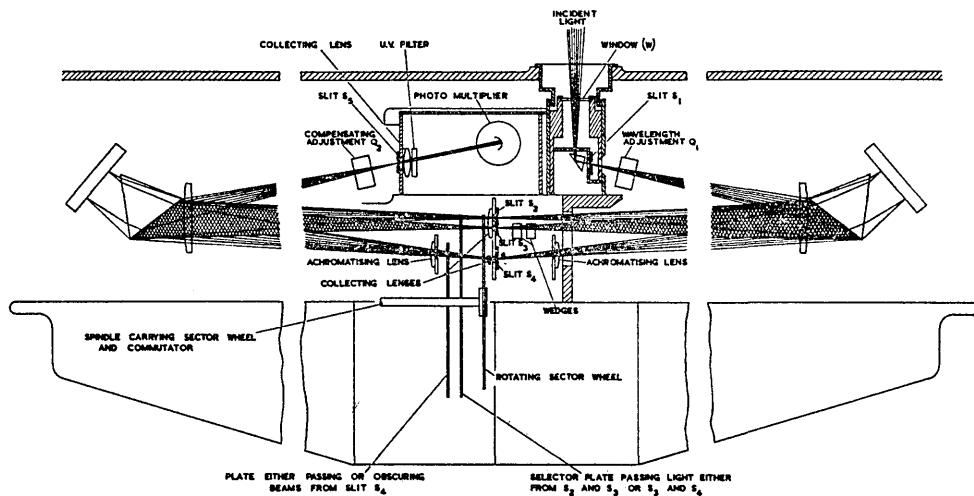


Fig. 7. The optical system of the photoelectric spectrophotometer.

photoelectric instrument in which the ozone values would be obtained without any delay. It was also hoped that a method might be developed by which ozone values could be obtained—even if only approximately—on lightly cloudy days.

Since the design of the instrument will be well known to all readers,<sup>14</sup> it is not proposed to describe it in detail here, but the following notes recall the reasons why the particular design was chosen. It was desired to produce an instrument which should measure the amount of ozone in the atmosphere with an error of less than about 1%. It also had to be an instrument which could be used for routine observations by an assistant, as distinct from one which was used by professional scientific staff only. It was further necessary that the instrument should remain as constant as possible over long periods of time and only require periodic checks in order to see that no important changes had taken place. Thus, for example, changes in the voltage on the amplifier or photocell should make no difference to the values given by the instrument. It was therefore decided to allow the two wavelengths which had to be compared to fall on the same part of the cathode of one photocell, a sector wheel allowing each wavelength to pass in turn, thus in general producing a variable output from the photocell which was easy to amplify by an ac amplifier. The longer (stronger) wavelength was reduced in intensity by passing through an adjustable optical wedge until it produced exactly the same output current as the shorter (weaker) wavelength. When this was the case the output from the photocell was constant, and therefore the ac amplifier gave no output. The output from the amplifier was passed through a commutator and read on a dc galvanometer. The position of the optical wedge, when the galvanometer gave a zero reading, was a measure of the relative intensities of the two wavelengths being measured. The measurement was thus independent of the intensity of the light, the voltage on the photocell, and the amplification of the amplifier, and the only things that were required to remain constant were (1) the wavelength used, (2) the wedge transmission,

and (3) the relative sensitivity of the photocell to two wavelengths 200 Å apart (see Fig. 7).

When the original instrument was made, photo-multipliers were not available, but we were fortunate in being able to use a photocell with sodium hydride cathode made in the Clarendon Laboratory. This was a glass cell with waxed-on silica window, and in spite of the waxed-on window it continued to function excellently for many years until finally replaced by a photomultiplier. The cell contained a small amount of inert gas and considerable gas amplification was used, the normal voltage on the cell being only a few volts below the arcing point. Looking back at the amplifier today, the design seems exceedingly crude but it was passed at the time by the radio experts. The very high grid leak was a small potassium-in-glass photocell illuminated by a small lamp whose brightness could be controlled to give any desired effective resistance (usually about  $10^9 \Omega$ ).

In order to reduce the amount of scattered light, it was necessary to use a double monochromator. Instead of dispersing the light a second time it appeared better to arrange for the second dispersing system to recombine the two wanted wavelengths onto the slit in front of the photocell. This is just as effective in eliminating stray light and makes it easy to arrange for the two wavelengths to fall on exactly the same part of the cathode of the photocell. The exact wavelengths to be used could not be decided until the instrument was completed and the sensitivity measured, but a separation of about 200 Å, which had been found satisfactory in the Féry spectrograph, was thought to be about right. This gave sufficient difference in the absorption coefficients of ozone, while the scattering coefficients for air were not very different. The dimensions of the instrument were fixed by the minimum separation of the two wavelengths at the central slits (7.45 mm) which was necessary in order to allow the shorter wavelength to pass clear above the wedges while the longer wavelength passed through the wedges without any possible interference by its edges.

The width of the short wavelength slit ( $S_2$ ) was fixed at the maximum which was thought advisable in view of the change of ozone absorption with wavelength. The width of the other slit ( $S_3$ ) had to be such that, with the highest sun and the lowest ozone, the zenith sky measurements came just on the thin end of the wedges. Hence, this slit width could not be fixed until the instrument had been completed and many measurements had been made. No measurements for the determination of the extraterrestrial constant could be begun until this slit width was fixed.

It happened that the separation chosen between the slits  $S_2$  and  $S_3$  was very nearly the same as the separation between the Hg lines 3126–3131 Å and 3342 Å. When this was noticed, it was decided that it would simplify the adjustment of the instruments if the separation were made exactly equal to that between the Hg lines so that when 3126–3131 Å was central on  $S_2$ , the line 3342 Å should also be central on  $S_3$ .

The only optical wedges of evaporated metal which were then available were extremely crude and so far from linear as to be useless for this purpose. It was therefore necessary to use wedges of gelatin containing carbon black between quartz plates. These wedges, made by Ilford, had excellent optical properties but unfortunately, while gelatin will adhere well to glass, it tends to peel off quartz; this gave a good deal of trouble. Moreover, in warm climates mold tended to grow on the gelatin and the wedges became useless. At a much later date Beck developed a method of producing the metalized wedges which are now used.

A great deal of thought was given to the best method of mounting and moving the wedges. It was necessary to be able to move the wedges quickly over a large part of their total travel (e.g., between measurements on the  $A$  and  $D$  wavelengths) and yet to measure their position to within a few hundredths of a millimeter without any backlash. A movement worked by a screw would have been much too slow. The method adopted, using a taut metal band, proved most satisfactory, giving negligible backlash, and, with the magnification produced by the ratio of the radius of the dial to that of the drum around which the metal band was wrapped, ample accuracy of reading was obtained.

In the first instruments, two fixed wavelengths were used, and, to allow for the effect of temperature on the refractive index of quartz, a single thin quartz plate was mounted in front of the central slits and rotated as required to correct for temperature changes. There was no lens at slit  $S_3$ . This was not a very good arrangement since, although the correct wavelengths were kept on the central slits, the patch of light on the photocell moved with change of temperature and in some photocells this caused small differences of dial reading.

The best wavelengths to use could not be decided until the first instrument was made and working so that the sensitivity could be found. If the sensitivity had proved to be very low, it would have been necessary to use relatively long wavelengths where there was more light, while if the sensitivity were very good, shorter wavelengths with larger ozone absorption coefficients,

could have been used. Photographs of the solar spectrum taken at the position of the central slits showed a fairly strong band at about 3115 Å with a rather rapid fall in intensity at shorter wavelengths, so this seemed to be suitable for the shorter wavelength. It was also found that the sensitivity of the instrument was such that good dial readings could be obtained when using this wavelength. (This is, of course, the present  $C$  wavelength.)

In the early days a good deal of exploratory photographing of the solar spectrum was done, and to facilitate this the laboratory was darkened and daylight was led from the hole in the roof down to the window of the instrument through a tube of black cloth. In this way the whole laboratory was dark but the spectrograph received daylight and one could work with the cover off the instrument and place pieces of photographic plate in it as required. When the photographs showed that the short wavelength slit ( $S_2$ ) was fairly close to the strong band in the solar spectrum at 3115 Å, the exact setting and the exact value of the wavelength were determined by the use of the wavelength (temperature) adjusting plate. The central slits, other than slit  $S_2$  were blocked so that the galvanometer deflection was a measure of the intensity of the light passing slit  $S_2$ . Then, using either sunlight or skylight, it was possible to plot out a curve of galvanometer deflections against settings of the wavelength adjusting plate. The setting of the plate which gave the maximum galvanometer deflection was that which was used. (This has been slightly changed in the modern instrument.) Finally, it was necessary to know the wavelength of the light passing slit  $S_2$  as closely as possible, and for this purpose the setting of the wavelength adjusting plate was found at which the Hg lines in the 3126–3131 Å region came centrally on the slit. The difference in the settings of the wavelength adjusting plate naturally allowed the exact wavelength to be calculated.

The working drawings of the photoelectric instrument took about two months to prepare, while the actual construction of the first instrument occupied all available time for nearly a year. While observations with the zenith skylight could be taken through the hole in the roof of the laboratory, it was necessary to wheel the instruments to different parts of the garden at different times of the day to get sunlight. After the instrument (Fig. 8) was completed and before useful ozone measurements could be made, it was necessary to calibrate the wedges and to determine the value of the extraterrestrial constant. The method initially used for calibrating the wedges was to block both slits  $S_2$  and  $S_4$  so that the deflection of the galvanometer was a measure of the light passing that slit  $S_3$  and the wedges. Measurements were taken both with and without a gauze in the solar beam which cut down the sunlight in a known ratio. Owing to variations in the sunlight and variations in the amplifier, the calibration was very poor by present day standards. We did not even have a tungsten filament lamp with quartz window at that time.

On all suitable days, measurements were started early in the morning in the hope of getting a good series of observations with the sun at different heights, from which



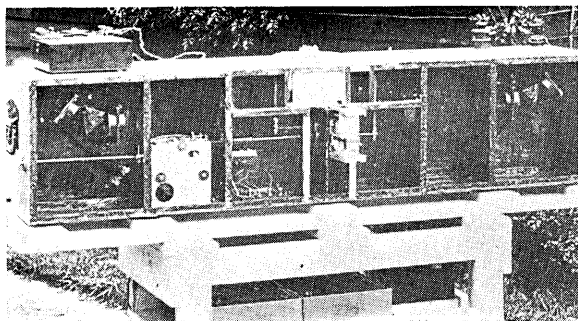


Fig. 8. Photoelectric spectrophotometer No. 1, with front panel removed (about 1927). The clockwork motor driving the sector wheel has now been replaced by an electric motor.

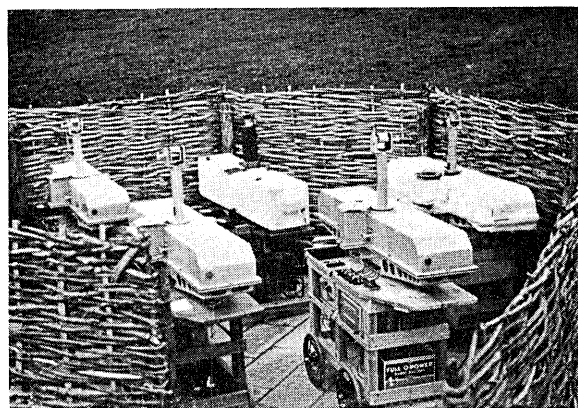


Fig. 9. Comparison of photoelectric spectrophotometers at Shotover, Oxford (about 1948).

it would be possible to find the extraterrestrial constant, but many were the days which were wasted owing to the sky clouding over! After the instrument had been calibrated in a preliminary way, there followed many months during which small improvements were made to the instrument itself or to the methods of calibration. As usual, looking back, one can see that much time would have been saved if more thought had been given to the program of work.

### 1. Measurements on the Clear Blue Zenith Sky

Cabannes and Dufay had calculated the total ozone from measurements on the light from the zenith sky by assuming that all the skylight was scattered below the ozone region, then thought to be at about 40–50 km. This assumption was not justifiable and a long series of measurements were begun in order to find an empirical relation between the results of measurements on the clear zenith sky and the total ozone as given by measurements on direct sunlight. Little help could be obtained from theoretical considerations, since at that time we had no idea of the vertical distribution of the ozone in the atmosphere. Owing to the infrequency of very high or very low ozone values, it was a long time before sufficient measurements were obtained to give a relationship which could be used to convert measurements made on the clear zenith sky to equivalent ozone values as measured by direct sunlight. It might be thought that it was not very important to be able to obtain values of

total ozone from measurements on the zenith sky since, if the zenith sky were clear, it would generally be possible to get observations on direct sunlight. However, the relationship is very important when we try to obtain ozone values from measurements on the cloudy zenith sky as discussed below.

### 2. Observations on Cloudy Days

When the instrument was made it was arranged that a third wavelength could be used if required. This wavelength ( $C'$ ) was in the blue region and was compared with that passing through the wedges in the same way as for the short wavelength, ( $C$ ). Since the  $C'$  wavelengths were little affected by ozone it was hoped to work out a method whereby measurements made on a cloudy sky on the  $C$  wavelengths could be corrected by observations on the  $C'$  wavelengths on the same cloud to give values equal those which would have been obtained if the sky had been clear. A great deal of time was spent in trying to get pairs of observations on the  $C$  and  $C'$  wavelengths as the zenith sky changed from clear blue to uniformly cloudy.

After some years of experience with the first photoelectric instrument, it was clear that reasonably accurate measurements of the total ozone could be obtained with the instrument when using sunlight, the light from the clear blue zenith sky, or that from the cloudy zenith sky. It was, therefore, very desirable that it should be possible to obtain a number of these instruments in order to make a more thorough survey of the distribution of ozone than had been possible with the Féry spectrographs (Fig. 9). There was no question of building a number of instruments in the laboratory in the same way as the Féry spectrographs had been built since the time and labor would have been too great. Beck\* was therefore approached to see if they would be interested in making the instrument, and they agreed that, if the money could be found, they would produce one prototype instrument for £500. Fortunately, the Royal Society agreed to provide this sum and in due course instrument No. 2 was delivered to Boars Hill, where all the adjustments of the instrument and its calibration had to be done. The instrument made by Beck was optically exactly similar to instrument No. 1, but the mechanical construction was entirely different in order to suit their methods of machining, etc.

After Beck's instrument had been shown to be satisfactory, a few other instruments were ordered, the first being for Egypt and China. A letter arriving one day at Boars Hill from China said "I enclose cheque £100, please arrange to send me one ozone spectrograph. If you want more money I will send it." In accordance with the principle of having nothing to do with the financial side of the question, this letter was sent on to Beck who agreed to make the instrument. These two instruments and some half a dozen other instruments made before the war were all adjusted and calibrated at Boars Hill.

\* R. and J. Beck Ltd.

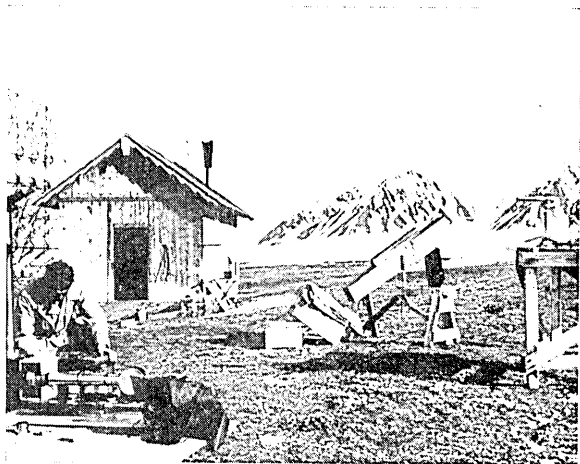


Fig. 10. Dr. Götzt is shown adjusting the Fabry-Buisson spectrograph (on the left) during the expedition to Spitzbergen in 1929. The Féry spectrograph is in the center.

### G. Measurements of the Vertical Distribution of Ozone 1927-34

During 1927-29, an attempt was made to measure the average height of the ozone in the atmosphere by taking solar spectra with the Féry spectrograph over the maximum possible range of the height of the sun. Owing to the curvature of the earth and the height of the ozone above the surface, an apparent daily variation in the amount of ozone will be found if a wrong height is assumed. Although the method was the only one possible at the time, the results are inaccurate and depend on using the true value of the extraterrestrial constant, which itself has to be found from similar measurements, both when the sun is high and not too low for the effect of the curvature of the earth to be important. Many spectra suitable for these measurements were taken at Arosa with the Féry spectrograph and sent back to Oxford for development and measurement but the heights deduced were much too high, as were those of other workers using the same method.

In 1929 Götzt took a Fabry-Buisson type of spectrograph, as well as the Féry spectrograph, to Spitzbergen to make measurements in a very high latitude (Fig. 10). His measurements,<sup>15</sup> made in July and August, confirmed the general increase in mean ozone value with increasing latitude and also showed the fall in ozone during the summer months owing to the annual variation.

While in Spitzbergen, Götzt took spectra of the zenith skylight while the sun was rising or setting and found that, when the sun was fairly high, the shorter wavelengths decreased in intensity more rapidly than longer wavelengths with increasing zenith distance of the sun. This was to be expected, owing to the greater absorption of the shorter wavelengths. He found, however, that when the sun was very low, the reverse occurred and the shorter wavelengths decreased in intensity more slowly than the longer ones. He rightly interpreted this as being due to the fact that, when the sun is high, most of the short wavelength zenith skylight is scattered from

the direct solar beam below the ozone region, but when the sun is very low the absorption of direct sunlight by the ozone is so great that the amount of light scattered above the ozone region and which passes down to the instrument by the short vertical path becomes predominant. Near the end of 1930 he wrote to me telling me of the effect and suggested that it might be used as a means of estimating the vertical distribution of the ozone in the atmosphere. He also suggested that the ratio of two wavelengths, as measured by the photoelectric ozone instrument, should show a similar effect. Not really believing in Götzt's suggestion, I made measurements on the zenith skylight on the first clear day early in January 1931, starting before sunrise, and was surprised to find that the dial readings really did increase at first as the sun rose, then became constant, and finally showed the normal decrease with the increasing height of the sun. This was the first umkehr curve\* to be obtained. I immediately wrote to Götzt telling him of the success of his suggestion. Then followed a lot of work, both making measurements on the zenith skylight and also trying to work out a theory by which we might calculate the vertical distribution of the ozone. It was at this time that A. R. Meetham joined us and contributed greatly to the work both in making the observations and in developing methods for calculating the vertical distribution.

As usual at Oxford there was great difficulty in getting days with clear zenith skies on which we could obtain good umkehr curves and Götzt kindly invited us to go to Arosa and placed living accommodations at our disposal. Meetham and I therefore spent six weeks at Arosa in 1932 taking both instrument No. 1 and instrument No. 2, the latter recently made by Beck (Fig. 11). The plan was to take more or less continuous observations from before sunrise until after sunset on all good days. One instrument made measurements on direct sunlight while the other used the zenith skylight. The routine was for one of us to get up just as it was getting light, decide whether the weather might make observations possible and if so wake the other two and put the coffee on. In bad weather we were kept fairly well occupied in evaluating the measurements obtained on fine days. At that time the instruments used photocells and the sensitivity was only just sufficient when the sun was low, so that it was necessary to average several observations to get smooth curves. After we returned to England one instrument was left at Arosa, and Götzt continued to take measurements which were sent back to Oxford to be calculated.

The chief result of these measurements at Arosa<sup>16</sup> was to show with certainty that the average height of the ozone in the atmosphere was about 22 km and not about 40-50 km as had been thought before. They also gave a fair idea of the vertical distribution, showing that the main changes took place at heights between 10 km and 25 km. This made it much easier

\* The term "umkehr curve" was suggested by G. Götzt for the "turning back" of the curves when the sun is low.

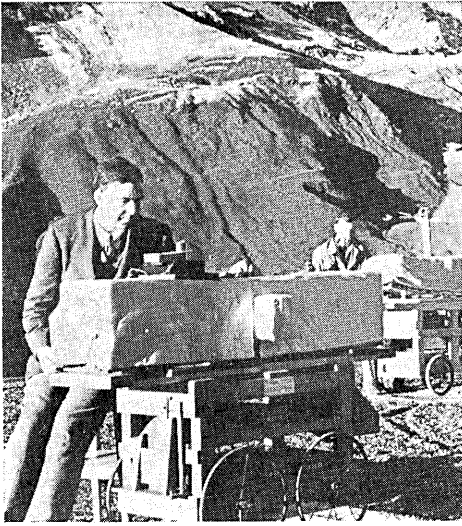


Fig. 11. The first umkehr observations at Arosa in 1932. The instrument on the right (No. 2) operated by A. R. Meetham, is being used for sun observations, while No. 1 is being used for simultaneous observations on the zenith sky.

to understand why changes in the total amount of ozone should be so closely correlated with conditions in the upper troposphere and lower stratosphere.

Having obtained a fair idea of the vertical distribution of the ozone in middle latitudes, we wanted to know what it would be in high latitudes, so we took an instrument to Tromsø where we made measurements during May and June 1934. Though the weather was poor, these measurements indicated that the average height of the ozone was slightly lower than at Arosa and that the ozone was confined to a rather narrower belt.

Since World War II, when photomultipliers were fitted to the ozone instruments, the measurements have become much more accurate and many results have been obtained at places all over the world. The theory of the umkehr effect has been greatly improved while the use of electronic computers has made methods of calculation possible which were impossible before. The Arosa observations, continued under Dr. Dütsch after the death of Dr. Götz, are still an outstanding contribution.

## H. The Pole Star Camera

It was very desirable to obtain some evidence as to whether or not there was any appreciable diurnal variation in the amount of ozone in the atmosphere. This cannot be obtained from solar observations since, in obtaining the extraterrestrial constant, it is necessary to assume that there is no such variation. It would be at least some evidence about a possible diurnal variation if any changes through the night could be detected. At this time the photoelectric instrument used a photocell and was too insensitive to make useful measurements on moonlight. Spectra of the brighter stars could probably be used to make ozone measurements at night but, as in the case of the

sun, it was necessary to determine the extraterrestrial constant for each star. However, the Pole Star, which changes little in altitude, could be used to *detect* changes, though it would be impossible to *measure* their amount. Although the Pole Star is a cool star with weak uv radiation, it was thought worth while to try to take spectra of this star, and an automatic prismatic camera was built which started and stopped at the required times and changed the photographic plate each hour. Owing to the very small movement of the Pole Star, it was possible to mount the prismatic camera on a rather simple mounting which kept it pointing accurately at the star through the night. As in the case of the photoelectric instrument, it was impossible to know whether there would be enough light to make useful measurements until the whole apparatus was built. Unfortunately, it was found in this case that there was just too little light to make observations of any value.

In 1934, R.A. Hamilton took a Féry type spectrograph and the Pole Star prismatic camera to Spitzbergen. It was hoped that with the clear atmosphere and the high altitude of the Pole Star, useful spectra of the star would be obtained. Unfortunately, even here, there was not enough light for accurate measurements to be made. Owing to an accident in landing the stores, the Féry spectrograph was broken and so never used.

During the late 1930's most of the time was taken up with adjusting and calibrating the new Beck instruments. In addition, about this time an attempt was made to make photon counters with sodium cathodes—following the work of Schein and Stoll—as it was thought that these would be more sensitive than the photocells which were used until then. However, while exceedingly sensitive counters could be made with platinum cathodes, they were, of course, only sensitive to very short wavelengths and were of no use for the ozone work; no success was obtained in making counters with sodium cathodes. About this period, a great deal of time was also spent on atmospheric pollution research in connection with the Atmospheric Pollution Research Committee of the DSIR.



Fig. 12. The laboratory and workshop at Watch Hill, Shotover, Oxford. (Photo Oxford Mail and Times 1957.)

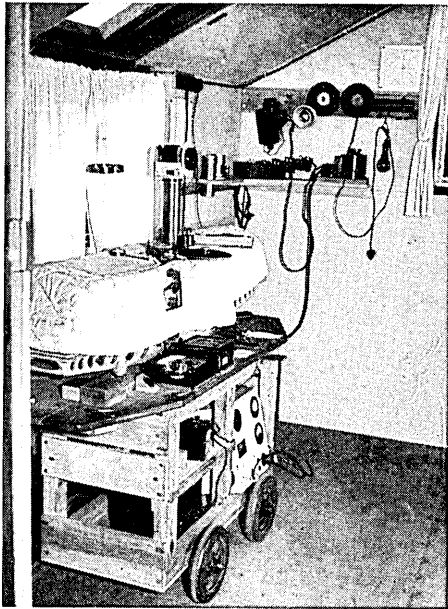


Fig. 13. The observing hut, Watch Hill, Shotover, Oxford. (Photo Oxford Mail and Times.)

In 1937, the move was made from Boars Hill to Shotover, a hill on the opposite side of Oxford. Here a laboratory was built on a site where there was an open horizon (Fig. 12), together with an adjacent observing platform from which the instruments could see the sun throughout the day without having to be wheeled about to different places (Fig. 13) as at Boars Hill. Here the adjustment and calibration of new instruments was continued until the beginning of World War II.

### I. War Years. Measurement of the Humidity of the Stratosphere

Since it was thought that the measurements of the amount of ozone might be of some use in forecasting weather, particularly when many European observations were cut off, the ozone observations were continued at Oxford, Valentia, Eskdalemuir, Aberdeen, and Lerwick, and the Meteorological Office lent assistance for this work. However, the problem of condensation trails formed by aircraft became of great importance to long range, high flying reconnaissance aircraft since they immediately made the plane's presence known. The Meteorological Office therefore asked for help in investigating the conditions in which such trails were formed so that it might be possible to issue warning to the RAF when trails might be made. It might be thought that this work had nothing in common with the work on atmospheric ozone, but it is seen later that it became linked with the work on ozone in a very interesting way.

It was clear that the temperature and the humidity of the air at great heights were both important factors governing whether trails would or would not be formed. While the temperature could be satisfactorily measured by radiosondes, the gold beater skin hygrometers

then in use were far too sluggish at these low temperatures to give useful values of humidity. It thus became necessary to devise a means of measuring the humidity at very low temperatures. Although other instruments have since been designed for this purpose—notably the  $P_2O_5$  coulometric method of Goldsmith—only the frost point (dew point) method seemed at that time to hold out much hope of being developed into a satisfactory instrument. The chief difficulty was the tiny amount of water vapor even in saturated air at these very low temperatures, so that the amount of deposit on the test plate was minute; at the lowest temperatures this was less than the equivalent of a layer one molecule thick. Fortunately, the hoar frost tended to be deposited as minute crystals of the order of a few wavelengths of light in diameter. Thus, it appeared as a very faint blue deposit; and by arranging for the deposit to form as a light streak on an otherwise dark test plate, even this small amount of ice could be seen and it could be judged whether, with the test plate at any given temperature, the deposit was growing or evaporating. The method of illuminating of the test plate was most important—a nearly tangential illumination being the best, so that the deposit appeared bright against a dark background. The test plate was cooled either by a jet of liquid air or a jet of petrol which had been cooled by solid  $CO_2$ . The temperature of the test plate was measured by a resistance thermometer (Fig. 14).

Another type of instrument was also designed in which the deposit on the test plate was measured by a photocell. This instrument was somewhat more sensitive than the eye observation instrument, but in general observers preferred to be able to see the deposit and the photoelectric instrument was liable to accumulate dust slowly which, of course, scattered light in the same way as hoar frost. In all this work A. W. Brewer and B. Cwilong contributed much to the successful final result.<sup>17</sup>

After the instrument was designed and the first model made in the laboratory at Shotover, a great deal of time was occupied in testing it, to make sure that it measured the true frost point. Air saturated at the temperature of solid  $CO_2$  was produced by passing air roughly dried over silica gel, through a cotton wool filter cooled in solid  $CO_2$ . Two interesting points

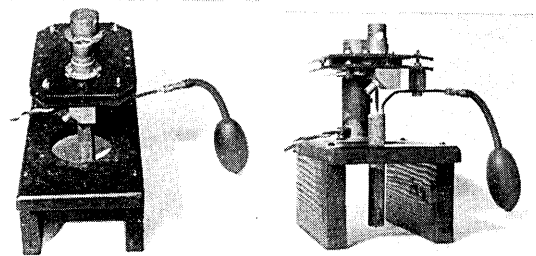


Fig. 14. The frost point hygrometer is on view at the Science Museum, London. (Photos British Crown copyright, Science Museum, London.)

arose as side issues out of this work. (1) It was found that when the test plate was cooled to very low temperatures, no visible deposit was formed when a stream of relatively moist air was passed over it, but as the test plate warmed up a deposit gradually appeared. It was shown that at the very low temperatures the water was deposited as a uniform layer, the molecules moving over the surface too slowly to grow into crystals. (2) Secondly, it was found that the test plate had, in general, to be cooled to the *dew point* before any deposit occurred initially, no deposit being formed at the frost point unless some ice were already on the test plate. At that time it was thought that water vapor would be deposited at low temperatures directly as ice on what were called sublimation nuclei. This work showed that the supposed sublimation nuclei were rare or nonexistent in natural air. There was sometimes a difficulty in knowing whether the deposit was of dew or hoar frost, but it was found that if the test plate were cooled to about  $-40^{\circ}\text{C}$ , a deposit of dew always froze and once any ice was present further deposits were always of ice.

While two earlier flights by Brewer had just penetrated into the stratosphere, it was on 22 December 1943 that he made measurements in a Fortress aircraft (not pressurized) at Boscombe Down to a height of 11 km. On that day the tropopause was at a height of 9.0 km so that he had penetrated well into the stratosphere and made the first measurements of humidity there. It was of great interest when he found that while the temperature increased somewhat above the tropopause, the frost point continued to fall rapidly up to the greatest height reached and that at the top of the ascent the air contained only a very small percentage of the water vapor which would have been required to saturate it. The next flights were made on 5 May 1944 and 30 May 1945. Both these flights showed that the air was nearly saturated near the top of the troposphere but was very dry in the stratosphere. Other flights made later by Brewer confirmed the dryness of stratosphere.<sup>18</sup> Since then the well known pioneering work of the Meteorological Research Flight of the Meteorological Office, using the same frost point hygrometer, has shown that the stratosphere up to heights reached by aircraft is dry in nearly all conditions and over a large range of geographical latitudes.<sup>19</sup>

The wartime measurements of the humidity of the upper atmosphere, showing that the stratosphere is very dry, were of interest in relation to the question of the equilibrium temperature of the stratosphere. The temperature of the stratosphere was generally regarded as being controlled by the absorption and emission of longwave radiation, the chief absorbing gases being water vapor, carbon dioxide, and ozone. If the air in the stratosphere were nearly saturated with water vapor, then water vapor would far outweigh the others in importance. When it was found that the stratosphere only contained a few percent of the water vapor required to saturate it, the picture appeared quite different and the three gases appeared to be of

equal importance in determining the temperature of the stratosphere. Another interesting result to come out of the measurements with the frost point hygrometer was that there were often layers of very dry air quite low down in the troposphere, which must have descended from high in the troposphere if not from the stratosphere. The results of this wartime work were presented in the Bakerian Lecture of the Royal Society for 1945.<sup>18</sup>

## J. The Post-War Period

During the years immediately after the War most of the time was taken up with adjusting and calibrating further ozone instruments made by Beck. However, in early 1947 Sir Charles Normand joined in the ozone research, and the output of work was greatly increased. A little later R. H. Kay also joined us. The second important thing that happened was that photomultipliers, sensitive to the uv region, became commercially available. One of these tubes (an RCA 1P28) was obtained as early as possible and fitted in instrument No. 2. As expected, the sensitivity of the instrument was found to be greatly improved, though the relative increase in sensitivity to visible light caused errors due to scattering, in spite of the double dispersion, until a glass filter, transparent to the uv but nearly opaque to the visible region, was used. (Even this is not enough when the sun is very low, and a  $\text{NiSO}_4$  filter had also to be added.)

Owing to the increased sensitivity which resulted from the use of a multiplier, it became possible to use shorter wavelengths with their larger ozone absorption coefficients, and the present *A* and *B* wavelengths were selected. In addition, it seemed desirable to have a rather longer wavelength, and the present *D* wavelengths were selected. In order to be able to use this wider range of wavelengths, it was necessary to replace the thin temperature compensating quartz plate by a thicker plate placed near slit  $S_1$ , and, in order to keep the two halves of the instrument symmetrical, a second plate ( $Q_2$ ) was placed close to slit  $S_5$ . A good deal of work was necessary to fix exactly the best settings for these wavelengths and to determine their wavelength in angstrom units. In addition, the wedges had to be calibrated for each wavelength and the values of the extraterrestrial constants found. The increased sensitivity given by the multipliers was a great advantage in the wedge calibrations.

It was about this time that Normand<sup>21</sup> suggested that if we used the *difference* between the values of the *A* and the *D* measurements, the effects of scattering by the atmosphere would be almost completely eliminated, while the difference between the absorption coefficients of ozone would still be large enough to give accurate ozone values. This method proved successful and is, of course, the standard method used today. Once, when calculating the ozone value from an *AD* zenith blue sky observation I made a mistake and calculated it as if it had been a direct sun observation. When the mistake was corrected it was found that the resulting



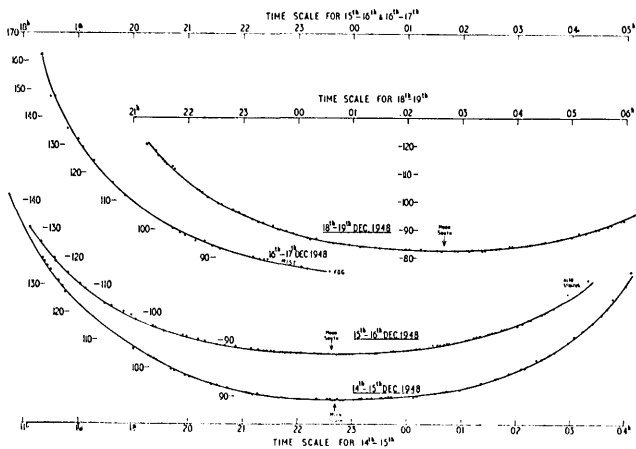


Fig. 15. The first (Oxford 1948) trial observations using moonlight after photocells had been replaced by photomultipliers. Ordinates are dial readings.

ozone value was almost the same as before. This led to an examination of several near simultaneous measurements on sunlight and on the blue sky, when it was found that the *difference* of the *AD* values was almost the same for both cases although, of course, the individual values were quite different. This immediately led to the suggestion that, if the sunlight and skylight which illuminate the upper side of a cloud both have the same *AD* value, it does not matter in what proportion the light from the two sources is mixed within the cloud but (provided there is no absorption in the cloud) the *AD* value of the light emerging from the lower surface of the cloud will be the same as if the zenith had been clear blue. Many pairs of measurements were then made on uniform cloud and on patches of adjacent blue sky as they drifted overhead. These measurements showed that, provided the sun was not too low, *AD* measurements made on a cloudy sky could be treated as if they had been made on the blue sky (provided, of course, that the clouds were not of the cumulus type).

A great deal of time was taken up in making observations from which to construct zenith sky ozone charts for the *A*, *C*, *D*, and *AD* wavelengths, as well as testing the *AD* zenith cloud method just described, as suitable conditions of sky occurred only seldom. Since the *AD* cloud method gives too small a value for the ozone when the sun is low, a lot of work was done to try to devise a method of correcting these values by the use of other wavelengths, as is done in the *CC'* method. However, little success was obtained, largely because it would have meant taking nearly simultaneous measurements on three different pairs of wavelengths instead of two, which was rather impracticable.

The first instrument fitted with a photomultiplier had been sufficiently well adjusted and calibrated for daily routine measurements of the ozone to be restarted in November 1947 and they have been continued ever since then. It was also arranged that the ozone values from all the observing stations should be sent in to Shotover where they were duplicated and sent

out to all ozone observers and any others who were interested. It thus became necessary to get assistance with the paper work, and Miss Trollope, Miss Robinson (Mrs. Cole), Miss Luck, and finally Miss Trollope again (now Mrs. Sykes) helped successively in the work.

### K. Observations Using Moonlight

The increase in sensitivity of the ozone instruments when fitted with photomultipliers made it possible to take measurements with moonlight provided that the moon was nearly full and fairly high, the image of the moon being focused on the slit. Many observations, extending right through the night in winter, were made to test the method (Fig. 15). The importance of being able to get observations when using moonlight was partly to see what regular changes there might be through the night, and, secondly, to be able to get measurements in high latitudes in winter. Observations of this type have given valuable information in the Arctic and Antarctic.<sup>21</sup> It was difficult to determine the extraterrestrial constant for moonlight since the range of  $\mu$  at which observations could be taken was small and the accuracy of an observation was much less than that with sunlight. It was found that, when using the *AD* wavelengths, nearly the same ozone values were obtained from moonlight as from sunlight on adjacent days, if the same extraterrestrial constant was used as for sunlight, but if only a single pair of wavelengths was used the value was appreciably different.

### L. The International Ozone Commission

An event of major importance occurred in 1948 when the International Ozone Commission was appointed at the Oslo meeting of the UGGI. At first it was a sub-commission under the Radiation Commission but later came directly under the IAMAP. This gave the ozone work official recognition and more money became available. As Normand was Secretary of the IOC, its headquarters were at Oxford, and the collection and distribution of ozone data from all stations became part of its official functions. It also undertook the general coordination of all the work in order to keep the results of different stations as far as possible comparable with each other.

### M. Post-War Work on the Vertical Distribution of Ozone

It became clear that the most important thing which was now required was a better knowledge of the vertical distribution of the ozone in the atmosphere. The Götze umkehr method gave an accurate value for the average height of the ozone but only a general indication of its vertical distribution and could never be expected to show detailed changes with height. Ehmert had developed his well known chemical method of measuring the concentration of ozone in air, and in 1952 Kay, working at the Clarendon Laboratory, adapted the method for use on aircraft. The apparatus could take about eighteen samples at different levels and in cooperation with the Meteorological Research Flight of



the Meteorological Office, a number of flights were made with the apparatus to a height of about 12 km and three to about 15 km. These showed that the ozone content of the troposphere, though everywhere small, increased slightly with height up to the tropopause and there seemed to be a larger increase as soon as the stratosphere was entered. In 1956, Brewer took the same apparatus to northern Norway, and, in co-operation with the Norwegian Air Force made a number of flights there. While there was some trouble due to destruction of ozone in the pipes leading the air into the apparatus, a large increase of ozone content of the air in the stratosphere was found.

In 1956, S. Larsen, who had previously taken ozone measurements at Spitzbergen and Tromsø, came to Oxford to work on the scattering properties of the atmosphere, since lack of knowledge had been causing difficulties in calculating the vertical distribution of ozone from umkehr measurements.

Chemical methods of estimating the amount of ozone in the air, which require titration and only take spot samples, are not at all suitable for a balloon-borne apparatus such as is necessary if measurements at great heights are to be obtained. In 1957, Brewer, working with Milford<sup>22</sup> and later with Griggs,<sup>23</sup> showed that if ozone is passed into KI solution, the amount of iodine released can be measured coulometrically, provided that the iodine formed at the anode is not allowed to recirculate to the cathode. In the first type of instrument the iodine was washed away as it was formed by a current of KI solution while in the second type of apparatus a silver or mercury anode was used so that the insoluble AgI or HgI was formed. The current passed by the solution under average conditions was only about 5  $\mu$ A but this was enough to control the audiofrequency of a small radio transmitter and so telemeter the concentration of ozone to a ground station. Many very valuable ascents were made in the British Isles in conjunction with the Meteorological Office, while other flights were made at Tromsø, Malta, Nairobi, and Halley Bay.<sup>24</sup> Just after Brewer's work at Oxford, Regener produced his well known chemiluminescent method.<sup>25</sup> Both these chemical types of ozone sondes require measurements with the spectrophotometer to check the absolute values.

## N. Preparations for the IGY

It was clear that the IGY would bring a large increase in the number of ozone instruments required, and several new Beck instruments were ordered by different countries. It was too much work to do all the adjustment and preliminary testing at Shotover and a member of Beck's staff came to Shotover for several weeks to learn the technique. New instruments still, however, had to come for final calibration and comparison with instrument No 1 (Fig. 9). In order to keep the methods as uniform as possible at the different stations and to help observers to keep their instruments in good order, the *Observers Handbook*, which was first written when the instruments used photocells, was rewritten and a new section added on adjustment and

calibration of the instruments. These booklets, together with that written later, *Determination of Constants*, were published in the *Annals of the IGY*.<sup>20</sup>

An important step was taken at this time when it became possible for the IOC to appoint a Travelling Physicist (C. D. Walshaw) who, having become familiar with the adjustments and calibration of the instruments, toured all the stations measuring ozone in Europe to ensure that they were all in good order before the start of the IGY, so that the measurements from different stations should as far as possible be comparable with one another.

In addition to testing new instruments and checking existing ones, many observers came to Shotover to learn the best methods of using the instruments and maintaining them in good order. This alone took up a lot of time.

In March 1957, an intensive series of observations was begun with the object of checking the extraterrestrial constants and the accuracy of the zenith ozone charts for the different wavelengths. Whenever conditions were suitable, measurements on all four wavelengths, on both the sun and the zenith sky, were made six times a day from early morning to late evening—a very exhausting program in fine weather. Although the weather for the first few months was better than usual, the results for the extraterrestrial constant were very disappointing, giving large differences from day to day. This was shown to be due to changes in the amount of ozone during a set of observations, and no further attempt has been made at Oxford to measure the extraterrestrial constant since it can be done so much better at other stations in better climates.

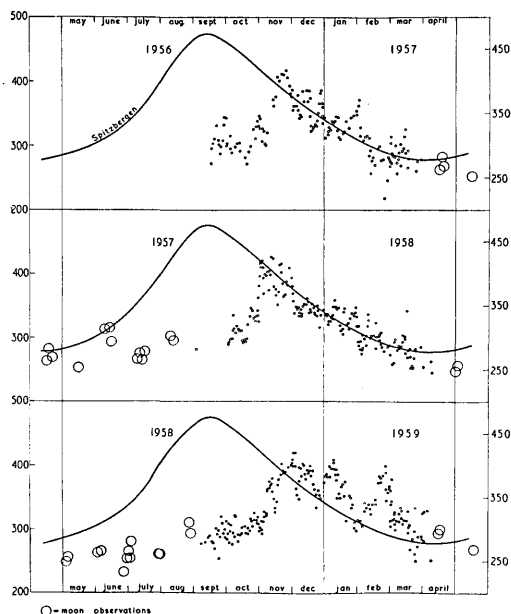


Fig. 16. The first three years' observations at Halley Bay, Antarctica. The full curve is for Spitzbergen, shifted by six months. Note the lower values of ozone in the southern spring and the sudden increase in November at the time of the final stratospheric warming.



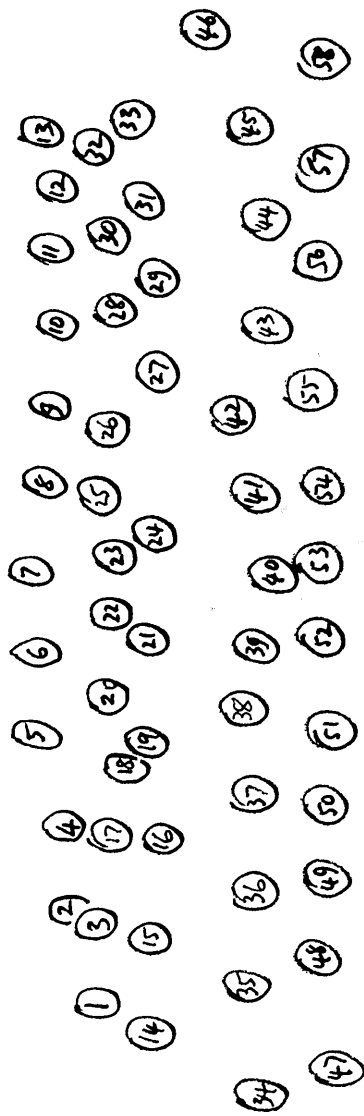


Fig. 17. The participants in the Conference on Atmospheric Ozone, Oxford, 9-11 September 1936. 1 G. M. B. Dobson; 2 Capt. Heck; 3 J. Bjerknes; 4 M. Hessaby; 5 Prof. Cario; 6 T. W. Wornell; 7 Dr. White; 8 D. Barbier; 9 F. J. Scrase; 10 F. J. W. Whipple; 11 E. H. Gowran; 12 M. Prettre; 13 R. Penndorf; 14 H. G. Kuhn; 15 W. Mörikofer; 16 A. Ångström; 17 E. Vassy; 18 B. Lyot; 19 O. R. Wolf; 20 J. A. Ratcliffe; 21 R. H. Weightman; 22 R. Ladenburg; 23 Fr. L. Dumas; 24 F. W. P. Götz; 25 E. Stenz; 26 H. D. Harradon; 27 M. Dedebant; 28 J. Bartels; 29 C. L. Pekeris; 30 S. Chapman; 31 C. H. Collie; 32 F. A. Paneth; 33 A. R. Meetham; 34 Fr. P. Lejay, S.J.; 35 D. Chalonge; 36 J. A. Fleming; 37 R. Ayres; 38 D. F. Martyn; 39 S. K. Mitra; 40 B. Gutenberg; 41 E. V. Appleton; 42 Dr. Hoelper; 43 Prof. Schmidt; 44 J. Cabannes; 45 J. Gauzit; 46 C. L. Godske; 47 V. Conrad; 48 Mile. Michel; 49 Mme. Gauzit; 50 Mme. Vassy; 51 Mme. Prettre; 52 Mme. Lyot; 53 Mme. Chalonge; 54 Mme. Cabannes; 55 W. Gorczyński; 56 E. van Everdingen; 57 P. Wehrli; 58 L. Weickmann.

One of the more interesting results on atmospheric ozone which came out of the IGY was the discovery of the peculiar annual variation of ozone at Halley Bay (Fig. 16). This particular ozone instrument had been to Shotover to be checked up immediately before leaving England. Moreover, Evans, who took the original observations at Halley Bay, had also been to Shotover to become familiar with the working of the instrument and its maintainence. The annual variation of ozone at Spitzbergen was fairly well known at that time, so, assuming a six months difference, we knew what to expect. However, when the monthly telegrams from Halley Bay began to arrive and were plotted alongside the Spitzbergen curve, the values for September and October 1956 were about 150 units lower than was expected. We naturally thought that Evans had made some large mistake or that, in spite of checking just before leaving England, the instrument had developed some fault. In November the ozone values suddenly jumped up to those expected from the Spitzbergen results. It was not until a year later, when the same type of annual variation was repeated, that we realized that the early results were indeed correct and that Halley Bay showed most interesting difference from other parts of the world. It was clear that the winter vortex over the South Pole was maintained late into the spring and that this kept the ozone values low. When it suddenly broke up in November both the ozone values and the stratosphere temperatures suddenly rose.

### O. Transfer of the IOC Work from Shotover

In 1959 Normand resigned as Secretary of the IOC and the work at Shotover was much reduced but new Beck instruments still continued to go there for their final comparison and checking.

The appointment of the IOC in 1948, together with an annual grant of money, had been a great help to the research on atmospheric ozone, and four international conferences on the subject had been held under the aegis of the IOC with great success. With the beginning of the IGY, the WMO became interested in the work and undertook the publication of all the IGY ozone results. Later, after WMO had appointed a Working Group to consider the whole matter, the Canadian Meteorological Department undertook—on behalf of WMO—to collect and publish the daily ozone values from all stations after the end of the IGY. This was clearly a much more satisfactory arrangement, since the work at Shotover, being on a private basis, could not be permanent, nor did it lend itself to the expansion which could be envisaged in future years. At the beginning of the work, an informal organization was necessary, but as more and more people became interested in atmospheric ozone a much more permanent organization became necessary. The arrangements for the general control of the work now seem very satisfactory.

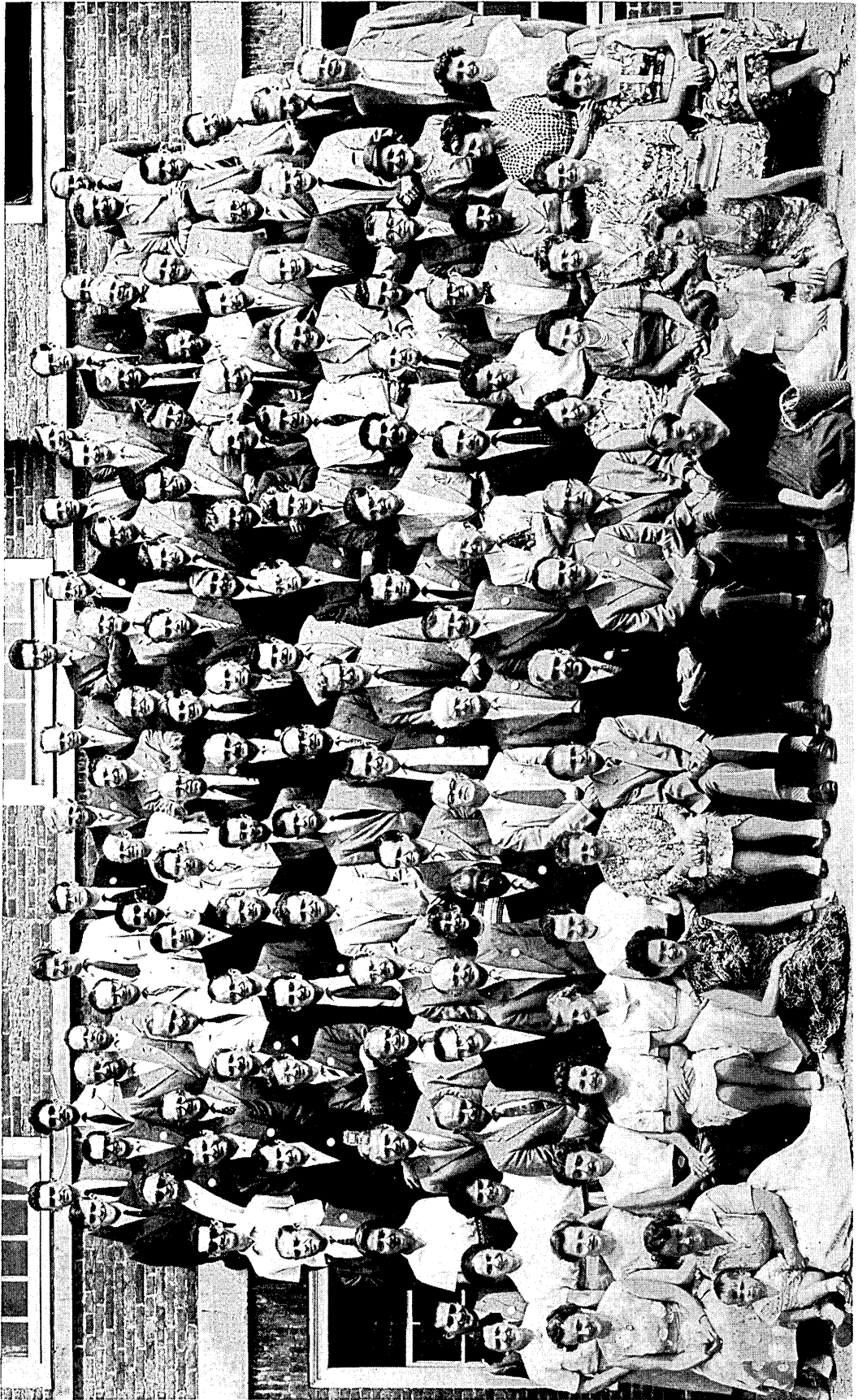


Fig. 19. The participants in the ICO/WMO Symposium on Ozone and Radiation, Oxford 1959. (Photo B. J. Harris, Oxford.)

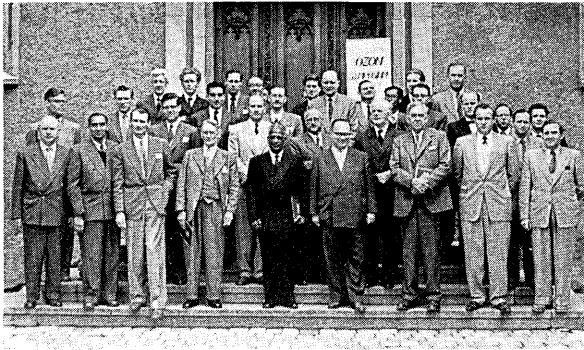


Fig. 18. ICO Ozone Symposium participants, Ravensburg 1956.

Since the transfer of much of the work from Shotover, a number of minor researches have been carried on, *viz.*:

On methods of measuring the ozone when the sun is very low using the  $\text{NiSO}_4$  filter;  
 Measurements of the absorption coefficients of ozone using the ozone instrument itself;  
 Method of calibrating wedges using the two-lamp method and the quartz-iodine lamps;  
 The suitability of the quartz-iodine lamps as standard lamps;  
 A critical examination of the accuracy of the ozone instrument.

I would conclude by quoting from the paper by Fabry and Buisson published in 1921<sup>5</sup>:

Le tableau suivant donne pour quelques jours de mai et juin 1920 les valeurs de  $x$  (épaisseur en centimètres d'ozone pur, comptée suivant la verticale.)

21 Mai	0.304	4 Juin	0.293
25 Mai	0.310	5 Juin	0.297
27 Mai	0.298	7 Juin	0.325
28 Mai	0.290	9 Juin	0.321
29 Mai	0.285	10 Juin	0.335
31 Mai	0.306	11 Juin	0.314
		21 Juin	0.286
		23 Juin	0.289

Les variations sont indubitables. D'autres déterminations faites dans l'été de 1919 ont conduit au même résultat avec des variations du même ordre de grandeur.

Ces changements paraissent irréguliers et à courte période. Dans l'intervalle assez court où nous avons pu les suivre, nous n'avons pas pu remarquer de relations entre eux et les conditions atmosphériques. *Il serait intéressant de les observer d'une manière continue; ce travail ne présenterait aucune difficulté, mais il ne pourrait être entrepris que par un établissement ayant un personnel suffisant.*

I feel sure that Fabry and Buisson would have been very pleased to see the way that their work in 1920 has grown into a worldwide network of stations making daily measurements of atmospheric ozone. Perhaps even more important for the understanding of the meteorology of the troposphere and stratosphere are the large number of measurements of the vertical distribution of the ozone made both by the Götzt umkehr

method and by the ozone sondes developed by Brewer and by Regener, particularly the magnificent series of ascents extending from Panama to Thule and Alaska in North America.

I am much indebted to Sir Charles Normand, to Dr. Houghton, and to Dr. Walshaw for their help in producing this article.

The following international conferences on atmospheric ozone have been held:

Informal		Under the IOC		Under the IOC and WMO	
Paris	1929	Brussels	1951	Oxford	1959
Oxford	1936	Oxford	1952	(see Fig. 19)	
(see Fig. 17)		Rome	1954	Arosa	1961
		Ravensburg	1956	Albuquerque	1964
		(see Fig. 18)			

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