91. *The Determination of Ozone and Nitrogen Dioxide in the Atmosphere.*

By J. L. EDGAR and F. A. PANETH.

By the method described in the preceding paper the ozone present in London air has been concentrated, identified by chemical and spectroscopic tests, and measured. In the same air samples the nitrogen dioxide content has also been determined.

THE claim that ozone is a constant constituent of atmospheric air was made by its discoverer, Schönbein, in 1845 (*Annalen*, **65**, 161); it was based on the observation that potassium iodide was slowly oxidised by fresh air. Schönbein's " ozonometer," consisting of paper soaked in potassium iodide and starch, was used by him and many others for the quantitative determination of atmospheric ozone; the readings of this simple colorimetric device, varying strongly with place and time, were deemed to be of such importance by meteorologists and medical men that regular observations were started in most civilised countries. There are in existence daily records for many decades, and the statement that millions of ozone determinations have been carried out (Schön, *Ber.*, 1880, **13**, 1503) is probably not exaggerated.

Unfortunately, these numerous measurements are open to the criticism that the chemical reaction used is not specific for ozone, other oxidising agents having the same effect on potassium iodide; as the presence in air of at least one of them, nitrogen dioxide, is certain, and can amount to the same order of magnitude (see, *e.g.*, Francis and Parsons, *Analyst*, 1925, **50**, 262; Reynolds, *J. Soc. Chem. Ind.*, 1930, **49**, 168), the value of all these " quantitative " ozone records is extremely doubtful. It is true that it could be shown that part of the oxidising property of air could be destroyed by reagents which decompose ozone; but since all attempts to identify it by specific reagents were unsuccessful some chemists were inclined altogether to deny the presence of ozone in the atmosphere.

The first incontestable statements on ozone in the earth's atmosphere were due to spectroscopists. The characteristic absorption of the ultra-violet light from the sun or stars not only revealed the presence of ozone, but permitted also the determination of its total amount in a column of air extending from the surface of the earth to the limit of the atmosphere (Fowler and Strutt, *Proc. Roy. Soc.*, 1917, **93**, 577; Fabry and Buisson, *J. Physique*, 1921, **2**, 197). It was soon recognised that most of the ozone thus measured was concentrated in higher strata of the atmosphere (Strutt, *Proc. Roy. Soc.*, 1918, **94**, 260), and for a while it remained doubtful whether any could be found at low levels; but by using, instead of star light, an artificial source of light a few kilometres distant, it was possible to evaluate, by the same spectroscopic method, the ozone content of air near the earth (Fabry and Buisson, *Compt. rend.*, 1931, **192**, 457; Goetz and Ladenburg, *Naturwiss.*, 1931, **19**, 373; Chalonge and Vassy, *J. Physique*, 1934, **5**, 309; Dauvillier, *ibid.*, p. 455; *Compt. rend.*, 1935, **201**, 679; Stoll, *Helv. Phys. Acta*, 1935, **8**, 3; Goetz, Schein, and Stoll, *Gerland's Beiträge z.*

Geophysik, 1935, **45**, 237). However, this very elegant method is still more difficult and costly than the spectroscopic measurement of the ozone in the total atmosphere; whereas this is carried out daily by a number of stations all over the world, with standardised apparatus designed by Dobson (*Proc. Physical Soc.*, 1931, **43**, 324; *Quart. J. Met. Soc.*, 1936, Suppl. to Vol. **62**, 11), yet no more than a few dozen spectroscopic determinations of the ozone concentration in the lower atmosphere have been recorded, a number insufficient for meteorological statistics.

The great interest taken by meteorologists in the daily variations of the ozone content of the atmosphere makes a simpler method for the determination of its local concentration very desirable. Several attempts have been made to meet this demand. The old method of allowing atmospheric air to react directly with potassium iodide and titrating the liberated iodine was improved by Hayhurst and Pring (J., 1910, **97**, 868), who passed the air over, instead of through, small quantities of an iodide solution; this idea was further developed by the construction of a microchemical apparatus by Regener (*Meteorol. Z.*, 1938, **55**, 459; Auer, *Gerland's Beiträge z. Geophysik*, 1939, **54**, 137), but if the objections against the use of this method on a larger scale (see preceding paper) are remembered, it is difficult to see how the claimed accuracy of 1—2% can have been obtained. It is still more doubtful whether the complicated chemical reactions used by other workers (Briner and Perrottet, *Helv. Chim. Acta*, 1937, **20**, 293, 458, 1200, 1207, 1523; Konstantinova-Schlesinger, *Acta Physicochim.*, 1935, **3**, 435; *Compt. rend.* (*Doklady*) *U.R.S.S.*, 1937, **14**, 187; 1938, **18**, 337), can form a reliable basis for the measurement of atmospheric ozone. None of the methods mentioned makes any attempt to separate ozone and nitrogen dioxide, and the effects found by Briner (*Helv Chim Acta*, 1938, **21**, 1218) are no doubt erroneously ascribed to ozone.

It was thought safest to make use of the classical reagent, potassium iodide, but after concentration of the atmospheric ozone by condensation, as described in the preceding paper. The more than 10,000-fold enrichment in ozone thus obtained not only increased the accuracy of the iodide method, but also made it possible to identify the ozone by a specific chemical reagent and by spectroscopic observation. This reagent, *pp'*-bisdimethylaminodiphenylmethane ("tetramethyl base"; Arnold and Mentzel, *Ber.*, 1902, **35**, 1324, 2902; Fischer and Marx, *ibid.*, 1906, **39**, 2555), is less sensitive than potassium iodide–starch but permits the recognition of ozone with certainty. The same can be said of the spectroscopic examination of ultra-violet light which has passed through a layer of ozone; the position of the strong absorption bands of ozone is most characteristic. For such a spectroscopic examination the redistilled ozone was collected in a glass tube with quartz windows; thus an ozone thickness equivalent to that of the ozone in more than 30 km. of air could be obtained in a short tube, no complications arose through the absorption of light by dust particles and Rayleigh scattering, and the calibration could be effected by direct chemical analysis. Consequently, the spectroscopy of atmospheric ozone becomes much simpler than if it has to be carried out between two stations several km. apart, and this procedure not only lends itself to the safe identification of ozone, but can probably be developed into a quantitative method, thus providing a check on the chemical determination.

By the procedure described, nitrogen dioxide is sharply separated from ozone; while the latter is distilled off, the nitrogen dioxide remains adsorbed and can later be released and determined; for this purpose the 2 : 4-xylen-1-ol (*m*-4-xylenol) method (McVey, *J. Assoc. Off. Agric. Chem.*, 1935, **18**, 459) was used.

No special attention has been paid so far to the accuracy of the analytical measurements, which could certainly be improved; in the experimental figures given below an accuracy of not more than 10% is all that is claimed for the ozone determinations, whilst the nitrogen dioxide determinations are accurate to not more than 15%.

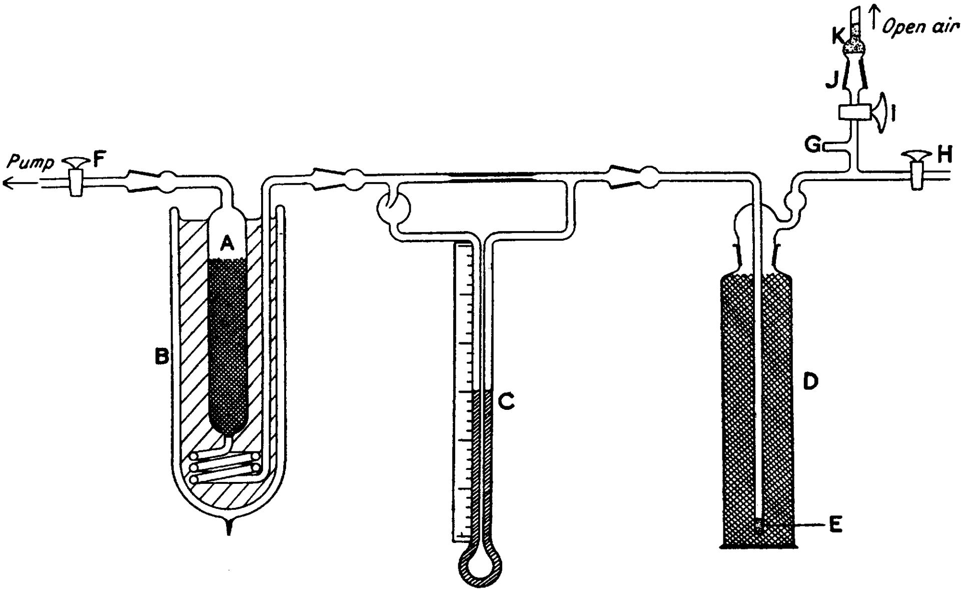
In most of the experiments 1000—1500 l. of air were used; for the qualitative tests with tetramethyl base, ozone from at least 7000 l. of air was necessary. The air was usually taken in South Kensington outside the laboratory in a wide street with little traffic (Imperial Institute Road) between 10 a.m. and 5 p.m. As it was conceivable that both the ozone and nitrogen dioxide values in a town atmosphere are very different from those in country air, a few parallel experiments were carried out at Kew Observatory, which is at least near the open country. Further, ozone in the air of a seaside resort (Southport) was also measured.

The results obtained show that it is possible to determine the local concentration of ozone and nitrogen dioxide in the atmosphere by reliable chemical methods.

EXPERIMENTAL.

(1) *The Condensation and Chemical Determination of Atmospheric Ozone.*—The apparatus for condensing atmospheric ozone was based on the results of the experiments described in the preceding paper. It was very simple (see Fig. 1). *A* is the trap packed with pure silica gel (see preceding paper, p. 515), and this is immersed in the Dewar vessel *B* filled with liquid oxygen. It is connected to a high-velocity flow-gauge *C* and a large calcium chloride drying tower *D*; this had been carbonated, and the bottom of the exit tube had a small plug of cotton wool *E* in it to prevent calcium chloride particles being carried over in the air stream. A tap *H* was provided so that the apparatus could be swept out as required.

FIG. 1.

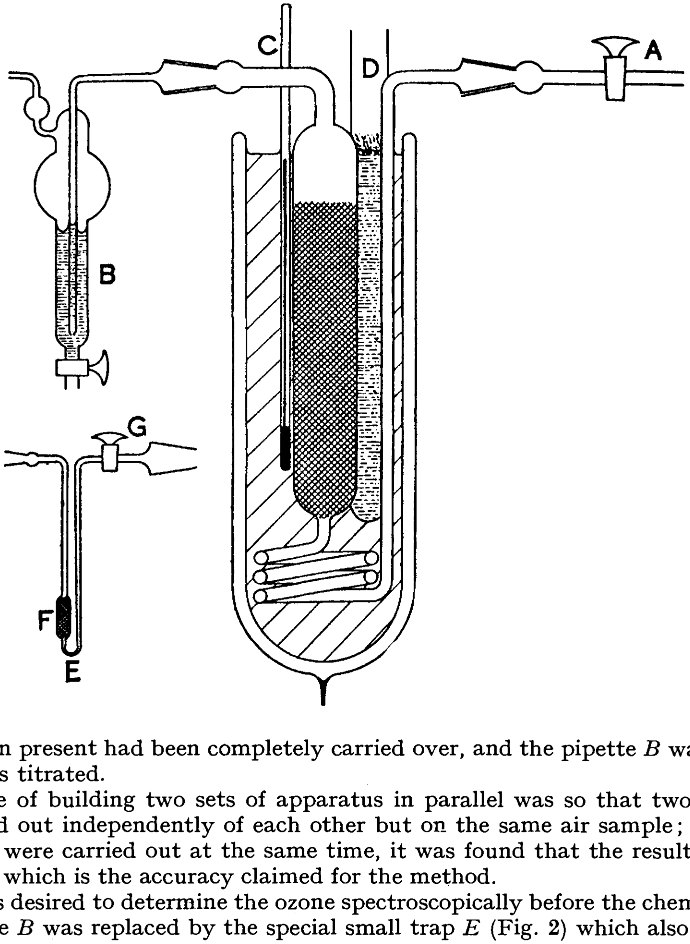


Two sets of this apparatus were built in parallel, the second being attached by the T-piece *G*. Air was drawn through the apparatus by means of a pump connected to a large bottle, this being used for buoyancy. The tap *F* was used to regulate the amount of air passing through; two other taps were provided, one for the second apparatus, and the other to act as a " throttle " so that the apparatus on the pump side of the trap should not be under any great vacuum. The air was led in from an open window through the tube *J*, in which there was a thick cotton-wool filter *K*, a fresh filter being used for every experiment, and then through the main control tap *I*. The gauge readings, which usually kept fairly constant, were taken every half hour, when the Dewar vessel was refilled with liquid oxygen, and at the end of the experiment the average of the readings was taken; the velocity of flow was then read off from the calibration curves—this velocity was usually kept at about 3—4 l./min.—and thus the total volume of air drawn through the apparatus was measured. The gauges were calibrated by displacement of water, and they were finally checked against each other by placing one in the position shown and another at the entrance to the apparatus at *K*; they were accurate to within 5%.

The apparatus was so constructed that it could easily be built into a case. The gauge readings were then taken through a panel in the front of the case, this panel opening like a door; the liquid oxygen was fed in through an opening in the top of the case which was normally closed by a brass disc. Thus, the whole apparatus was portable, and the only additional equipment needed at the locality of the experiment was a pump and a supply of liquid air. For the final part of the determination it was brought back to the laboratory, the Dewar vessel being kept full of liquid air. With such a portable apparatus results have been obtained at Kew and at Southport.

After the condensation of sufficient ozone from the air, the trap, still in liquid oxygen, was detached from the apparatus, and a female joint carrying a tap *A* (Fig. 2) was placed in the entrance; a pipette *B* containing standard potassium iodide solution was placed on the other end as shown in the figure. An alcohol–solid carbon dioxide bath cooled by means of liquid air to about — 110° was then prepared, the tap *A* was closed, and the liquid oxygen bath removed and replaced, as quickly as possible, by this bath; a long test-tube *D* and a pentane thermometer *C* were then placed in the bath by the side of the trap, and liquid air was poured into *D* until the temperature had fallen to about — 120°; as the temperature of the trap rose from — 180° to — 120° there was, of course, an expansion in volume, and gas bubbled through the solution in *B*. After about 10 mins., the tap *A* was opened, and oxygen at a velocity of about 50 ml./min. was passed through the apparatus for about an hour; at the end of this time any ozone that might have been present had been completely carried over, and the pipette *B* was then removed and its contents titrated.

FIG. 2.



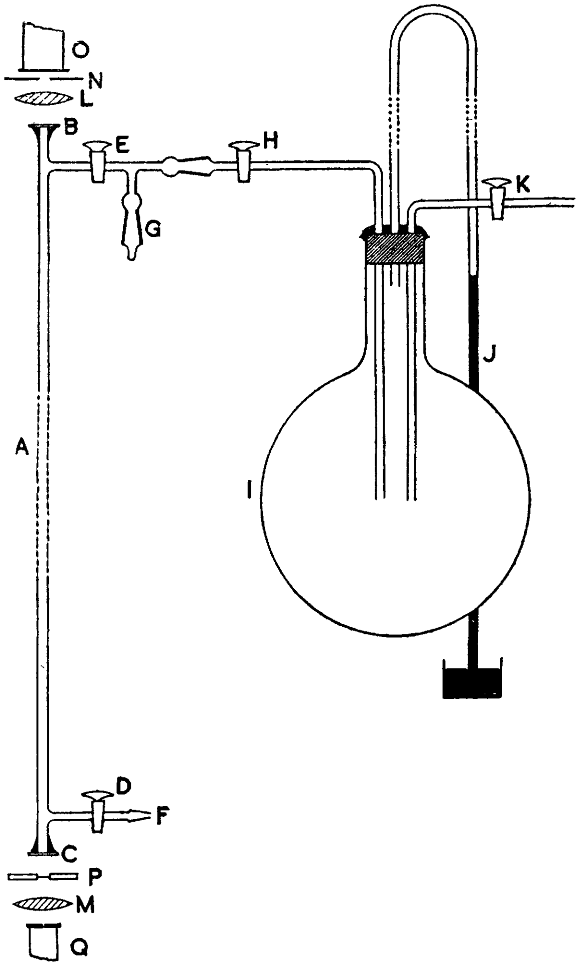
The purpose of building two sets of apparatus in parallel was so that two determinations could be carried out independently of each other but on the same air sample; when two such determinations were carried out at the same time, it was found that the results always agreed to within 10%, which is the accuracy claimed for the method.

When it was desired to determine the ozone spectroscopically before the chemical absorption, then the pipette *B* was replaced by the special small trap *E* (Fig. 2) which also contained silica gel in the bulb *F*. This was cooled in liquid oxygen, and the ozone as it distilled off from the large trap was again condensed in this small one. At the end of the distillation the trap was placed on the end *F* of the optical tube (Fig. 3), which had been previously evacuated; the tap *G* on the trap was closed, the tap *D* on the optical tube opened, and the liquid oxygen then removed; the contents of the trap were thus transferred to the optical tube; when the trap had reached room temperature, *G* was slowly opened and thus more air was sucked through into the tube, thereby washing out the trap. After the photograph of the spectrum had been taken, the contents of the tube were blown out with oxygen into potassium iodide solution, where the ozone was absorbed and titrated in the usual way. Further details of the apparatus used for taking the spectrograms are given in Section (2).

In some of the experiments the re-evaporated ozone was not passed through potassium iodide solution but through a saturated solution of " tetramethyl base." This reagent shows the following characteristic colorations with ozone and nitrogen dioxide: Ozone, deep reddish-violet; nitrogen dioxide (small amounts) yellow, (large amounts) green. Hydrogen peroxide does not produce any colour.

With the help of a simple optical comparator it was possible to detect, by the violet coloration of the tetramethyl base, the presence of as little as 0·02—0·03 mg. of ozone. This method was used, in addition to the others, for the safe identification of ozone; since it is, however, about four times less sensitive than the iodine–starch colorimetric titration, no attempt was made to make quantitative determinations of atmospheric ozone with tetramethyl base.

FIG. 3.



(2) *The Spectroscopy of Atmospheric Ozone.*—The apparatus used for the photography of the absorption spectra of ozone is shown in Fig. 3. *A* is a straight glass tube, 111 cm. long and with a total volume of 60 ml., the ends of which are ground flat; to each end is fixed, by means of red wax on the outside of the tube, quartz windows *B* and *C*. About 2 cm. from each window there are T-pieces which are closed by the taps *D* and *E*; on to *D* there is attached a small ground joint *F*; *E* has attached to it two standard joints at right angles to each other, as shown. One of these is closed by the plug *G*, and to the other is attached the apparatus used for calibrating the tube.

The calibration part of the apparatus consists of a 3-l. flask *I*, closed by a cork through which three tubes pass; one of these, *H*, is closed by a tap and terminates in a ground glass joint by means of which the apparatus is attached to the optical tube; the second, *K*, also closed by a tap, goes to the pump; and the third leads to a mercury manometer, *J*, the top surface of which is protected from the action of the ozone by a layer of sulphuric acid. The flask is rendered air-tight by sealing in the cork and the tubes with a thick layer of picene wax.

The optical system consists of a hydrogen-discharge tube *O* with a quartz window, which serves as a source of ultra-violet light, a pierced card *N*, two quartz lenses *L* and *M* which are used for focusing on to the slit of the quartz spectroscope *Q*, and a shutter *P*.

Calibration is effected as follows: The hydrogen tube is switched on, and when, after about 20—30 mins., its light has become steady, the whole arrangement is accurately focused, special care being taken to clamp the tube *A* firmly in position. The flask with its tubes is then removed from the rest of the apparatus, and evacuated through the tap *K*, which is then closed; an ozoniser with a slow stream of oxygen passing through it is attached to the ground joint at *H*, the tap of which is then slightly opened, and the flask is allowed to fill slowly with ozonised oxygen up to atmospheric pressure. The amount of ozone produced by the ozoniser and passing into the flask may be controlled either by increasing or decreasing the velocity with which the gas enters the flask, or by regulating a spark gap across the induction coil which activates the ozoniser. When full, the apparatus is once again attached to the optical tube, which is then ready for calibration.

The taps *E* and *D* are opened, *H* is closed, and the tube is evacuated through *F*; *D* is then closed and *H* opened, thus allowing the ozonised oxygen to enter the tube. An exposure is then taken with the spectroscope, special plates (Ilford Q 2), which are sensitive to ultra-violet light of short wave-length, being used. *H* is closed, and the plug *G* is removed and replaced by an absorption pipette containing standard potassium iodide solution. Oxygen is then passed through the tube from *F* into the potassium iodide solution at *G* until it is certain that all the ozone has been blown out; the amount of ozone present may then be determined by titrating the solution as usual.

D, *E*, *G*, and *H* are then closed, *K* is opened, and the flask is evacuated to about 0·5 atm. pressure, as indicated on the manometer *J*; the flask is then filled with oxygen through *K*, which is then closed, the oxygen being blown in very rapidly in order to ensure complete mixing of the gas; *E* and *D* are then opened, the plug *G* is replaced, the tube is evacuated through *F*, and the whole process is repeated, as before.

This process of decreasing the concentration continuously by about one half is repeated until a negligible amount of ozone is left. It was found that quantities of ozone which were not detectable by a visible coloration of the starch were clearly indicated by the spectrograms if analysed in a microphotometer.

By using this apparatus, and the method for the concentration of ozone described in the preceding paper, it is possible to get the ozone content of a large quantity of air into the optical tube. For instance, in an experiment carried out on July 1st, 1938, 1700 l. of air were treated and its ozone content collected in the 60 ml. of the tube; since the ozone concentration was thus increased 28,000 fold, the intensity of the ultra-violet light absorption by the ozone in the tube of 111 cm. length was equal to that of a column of the original air 31 km. long. The greatest distances used in the experiments mentioned on p. 519 for the direct spectroscopy of atmospheric ozone near the surface of the earth were about 5 km.

The absorption spectrum obtained in this experiment is shown in Fig. 4 (No. 2); No. 1 is a blank, taken while the optical tube was filled with pure oxygen, and No. 3—10 are the absorption spectra of ozone prepared artifically and progressively diluted by the method just described; noted against each spectrum is the quantity of ozone found iodometrically.

The spectral region photographed begins (on the right) with 5000 A. and extends, in the case of oxygen and the most dilute ozone, to about 2100 A. It can be seen that the length of the absorption band increases markedly with increasing ozone concentration, and that the amount of absorption in the spectrum of the atmospheric ozone (No. 2) lies between those of spectra 4 and 5; this agrees very well with the quantities of ozone determined afterwards by titration (8·4, 14·5, and 6·3 $\times$ 10^{-3} ml. respectively). However, since it is not possible to evaluate the spectra exactly by simple comparison of the photographs they were analysed with a microphotometer; the results fully confirmed the visual impression, the trace for spectrum 2 being bracketed between those for 4 and 5 when the microphotometer curves were superimposed.*

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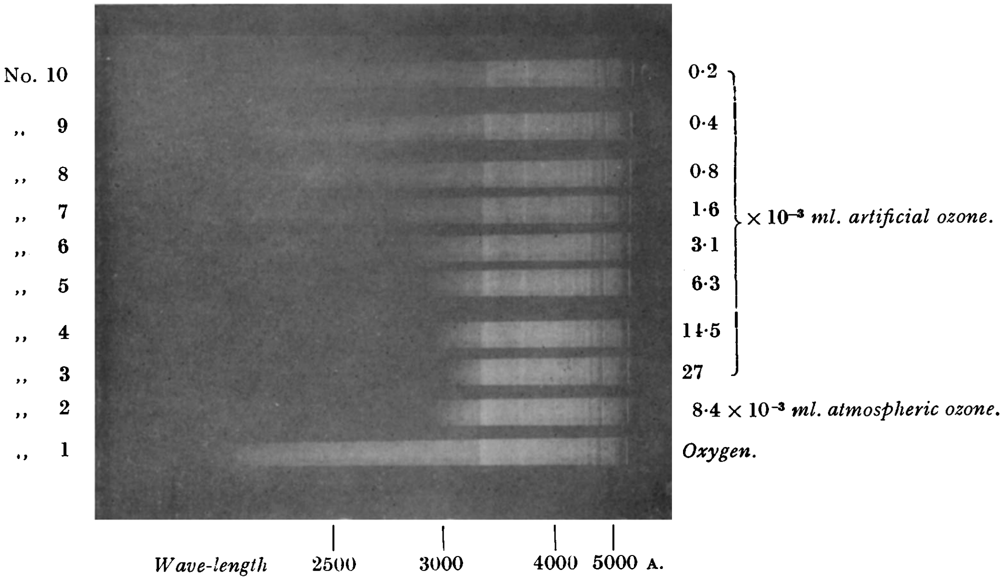
* See J. L. Edgar, Ph.D. Thesis, London University, 1938. This Thesis also contains photographs of the spectra obtained in the experiment of June 20th, 1938.

FIG. 4.


No. 10
,, 9
,, 8
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,, 1
0·2
0·4
0·8
1·6
3·1
6·3
14·5
27
× 10⁻³ ml. artificial ozone.
8·4 × 10⁻³ ml. atmospheric ozone.
Oxygen.
Wave-length
2500
3000
4000
5000 A.

The main result of this spectroscopic investigation is the independent proof that the atmospheric oxidising agent separated from air by the adsorption method is identical with the substance measured as ozone by spectroscopists.

(3) *The Chemical Determination of Atmospheric Nitrogen Dioxide.*—As described in the preceding paper, a trap filled with silica gel and kept at a temperature not exceeding – 120° can be relied upon to hold back all the nitrogen dioxide condensed from air; consequently, in the course of the present procedure, after the ozone had been distilled off, the nitrogen dioxide in the cooled trap was available for a quantitative determination. In its preliminary stage, the method used was identical with that employed by Francis and Parsons (*loc. cit.*) and consisted of fixing the nitrogen dioxide by converting it into potassium nitrate; for the measurement of the nitrate, however, McVey's method (*loc. cit.*) was used.

The cooled trap was first attached to an evacuated Winchester-quart vessel of about 3 l. capacity which had been provided with suitable air-tight joints and taps; it contained 20 ml. of an acid hydrogen peroxide solution (62·5 ml. of 20-vol. "AnalaR" hydrogen peroxide plus 1 ml. of 2N-sulphuric acid made up to 100 ml. with distilled water). A tap connecting the trap to the evacuated vessel was opened, the trap being closed at its exit by a second tap, and the cooling bath was then removed and replaced by boiling water; most of the evaporating nitrogen dioxide passed over at once into the evacuated vessel, and the gradual admission of air through the trap until atmospheric pressure was reached ensured that the small residue in the trap was likewise collected in the large vessel. This vessel was then closed, and the nitrogen dioxide left for several hours in contact with the hydrogen peroxide solution, the process of absorption being accelerated by frequent shaking. After this period the solution was rinsed into a porcelain dish, made slightly alkaline to litmus with 1 ml. of a N-solution of "AnalaR" potassium hydroxide, and evaporated to dryness on a steam-bath. As Francis and Parsons have shown (*loc. cit.*), the whole of the nitrogen dioxide is thus fixed in the form of potassium nitrate.

For the determination of small quantities of nitrate it was found that the 2 : 4-xylen-1-ol method was very suitable, and preferable to the use of phenoldisulphonic acid. It depends on the fact that the nitro-compound of 2 : 4-xylenol is highly coloured (brown) in alkaline solution, and that it is very easily volatile in steam; the reaction was first recommended by Blom and Treschow (*Z. Pflanz. Düng.*, 1929, **13**, *a*, 159) and applied to the determination of nitrates in meat by McVey (*loc. cit.*). A 1% solution of the xylenol in glacial acetic acid was used; this was supplied as a standard solution by the British Drug Houses, as also was a standard nitrate disc for use with the Lovibond Nessleriser. The procedure is as follows.

The nitrate residue to be measured is dissolved in 3 ml. of distilled water and washed into a boiling-tube with a further 4 ml. of water; 15—20 ml. of 85% nitrogen-free sulphuric acid are added and the tube is placed in a water-bath at 35°; 1 ml. of the xylenol reagent is then added, the whole is well stirred, and the tube carefully stoppered. After ½ hour the mixture is allowed to cool and is diluted with 100 ml. of distilled water, the temperature being kept down by immersing the tube in a bath of cold water. The nitro-compound is then steam-distilled off in a special apparatus, consisting of a flask with a splash head and a condenser. 40 Ml. of the distillate are collected in a Nessler glass containing 10 ml. of a 2N-solution of "AnalaR" sodium hydroxide, this being cooled in a beaker of water; the whole is then stirred, the temperature adjusted to 20°, and the coloration produced compared with the standard disc in the Nessleriser.

At the same time a complete blank is run; 20 ml. of the hydrogen peroxide solution are neutralised, diluted, and evaporated, and any nitrate present is determined in exactly the same way as in the actual experiment. This blank seemed to remain constant at about 3 or 4γ of nitrate nitrogen. According to these experiments, the average value of the nitrogen dioxide content of London air is $1{\cdot}5 \times 10^{-8}$ mg./ml. or $7{\cdot}5 \times 10^{-7}\%$ by volume, which is equivalent to 5×10^{-9} mg. of nitrogen per ml. of air. The 1000 or 1500 l. of air used for the condensation of ozone contained, therefore, sufficient nitrogen dioxide at least to double the intensity of the nitrate coloration produced by the reagents.

Before use, the disc was tested with a standard nitrate solution and found to be accurate to within 10%, which is inside the experimental errors.

Results.—The results of the ozone and the nitrogen dioxide determinations are collected in the following table. The nitrogen dioxide was in all cases determined by the xylenol method; the ozone was usually determined by the potassium iodide method, but on April 11th and 25th, 1938, it was absorbed in an alcoholic solution of tetramethyl base. In these two experiments as much as 10,000 and 7000 l. of air were used, respectively, because it had been found that the ozone from the usual 1000—1500 l. was not sufficient to produce a clear coloration with the tetramethyl base; with the larger quantities the violet colour characteristic of ozone was very distinct.

As can be seen from the table, in most experiments both gases were measured. Sometimes, however, one of them was used for special experiments, or its analysis was omitted for simplicity, so that both values do not always appear in the table. Usually the air was drawn from street level in South Kensington (see p. 520); on some days, however, the portable apparatus was used for taking air samples on the roof of the Royal College of Science (June 6th to 9th, 1939), at the Meteorological Observatory at Kew (May 6th and 10th, 1938, and June 13th, 1939), and at the Fernley Observatory on Hesketh Park Hill, not far from the beach, at Southport (July 5th, 6th, and 7th, 1939). Concurrently with two of the Kew experiments the usual determinations were carried out at South Kensington.

TABLE.

Date. 1938.	Weather conditions.	O_3 content, % by vol. × 10^6.	NO_2 content, % by vol. × 10^6.	Location.
Feb. 1	Fine and bright; no clouds	0·9	0·8	S. Ken.
7	Rather dull; heavy morning frost; overcast but no rain	0·8	0·4	,,
8	Dull but warm; overcast	0·5	0·6	,,
10	Very dull and overcast; slight rain at first, heavy later	0·8	0·1	,,
14	Extremely cold; heavy snow previously and snow storms during day	0·8	$<$0·05	,,
18	Fine; clear sky, cold and sunny	—	0·5	,,
22	Dull and overcast; warmer, no rain	1·1	1·2	,,
Mar. 3	Very fine; clear sky, warm and sunny	0·9	1·3	,,
7	Fine and warm; thick haze but no fog	1·9	$<$0·05	,,
10	Fairly fine; clear with some dull spells	0·6	$<$0·05	,,
14	Very fine; warm, clear and sunny	0·9	$<$0·05	,,
17	Very dull and overcast; break of fine spell	1·1	0·5	,,
21	Fairly fine but some clouds	0·8	0·4	,,
28	Fine early, but later very dull and overcast	0·6	1·8	,,
31	Very fine; clear, warm and sunny	1·7	2·0	,,
Apr. 5	Very dull and overcast	—	1·5	,,
11	Fairly fine; mainly clear but some cloud	T.M.B. + ve	1·3	,,
25	Very dull and overcast; some rain in the evening	,,	0·8	,,
May 3	Very wet, dull and overcast; raining	2·6	0·7	,,
6	Rather dull and cloudy; bright and clear p.m.	2·3	0·2	,,
	,, ,, ,, ,, ,,	2·3	$<$0·05	Kew
10	Warm and sunny a.m., cloudy p.m.	1·3	0·5	S. Ken.
	,, ,, ,, ,,	2·2	0·3	Kew
26	Very dull and overcast	—	0·7	S. Ken.
June 1	Very dull and a little rain	—	1·7	,,
20	Bright, warm, and sunny	0·8	—	,,
July 1	Bright and sunny early; overcast later	0·5	—	,,
1939.				
June 6	Fair; light E. wind	2·1	—	Roof, S. Ken.
7	Fair; light S.E. wind	0·4	—	,, ,,
8	Fair; light E.N.E. wind	1·5	—	,, ,,
9	Fair; light S.E. wind	4·5	—	,, ,,
13	Fair	2·8	—	Kew
July 5	Wind mainly from S.E.	1·7	—	Southport
6	Wind S.S.W. to S.S.E.	2·9	—	,,
7	Wind S.W.	2·2	—	,,

In the table are given a few indications as to the weather conditions prevailing during the experiments; no attempt is made, however, to discuss their possible bearing on the ozone or nitrogen dioxide content of the air, since the authors hope soon to be in a position to report on an improved method permitting the determination of ozone in smaller quantities of air and within a much shorter time, thus making the exact study of the influence of meteorological conditions possible. Experiments on these lines are in progress.*

As to the nitrogen dioxide content, it seems to be proved by these experiments that in London air its quantity is usually comparable with that of the ozone present; but once, after a heavy snow fall (Feb. 14th, 1938), and during a period of very fine, warm and sunny weather (March 7th to 14th, 1938), no nitrogen dioxide could be detected, which means that its quantity was less than 5 × 10^{-8}% by volume. On the very day this spell of good weather had broken up (March 17th) a measurable quantity appeared again. Although Kew Observatory is situated

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* (Added in proof.) See Paneth and Glückauf, *Nature*, 1941, **147**, 614.

in open country and is more or less clear of London, on one day not much less nitrogen dioxide was found than in London.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON.
UNIVERSITY OF DURHAM, DURHAM.

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