1. *A Method for the Continuous Measurement of the Local Concentration of Atmospheric Ozone.*

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A semiportable apparatus has been devised for the continuous recording, over periods up to 24 hours, of the local concentration of atmospheric ozone.

The principle of the method is the liberation of iodine from buffered potassium iodide solution, and its electrometric titration at short intervals with very dilute sodium thiosulphate solution. The small current resulting from the depolarisation of a pair of platinum electrodes by the iodine is amplified by a two-stage valve amplifier, and made to actuate the automatic burette, containing the thiosulphate solution, when the iodine concentration reaches a given value.

EDGAR and PANETH (*Nature*, 1938, **142**, 112; J., 1941, 511, 519) described a method for concentrating atmospheric ozone to such an extent as to make its chemical determination possible. The main merit of the process lay in the proof it afforded, by chemical and spectroscopic means, that the oxidising agent of the atmosphere which was measured by its action on potassium iodide actually was ozone; the process was, however, cumbersome and too slow to allow for more than one or two determinations of atmospheric ozone per day.

In the course of routine measurements it is unnecessary to identify the ozone each time by specific tests; it will suffice to check the correctness of the method by comparison with a standard procedure whenever this seems necessary. Having once established such a standard method for the measurement of the local concentration of atmospheric ozone, we set out to develop a simpler one which would enable us to follow up the variations in the ozone content of air as quickly as meteorological interests demand, *i.e.*, every few minutes. Our method is based on the reaction with potassium iodide of the ozone present in the atmosphere, without previous concentration, the iodine liberated being detected by its depolarising effect on a platinum cathode. Since publishing a preliminary note on this electrochemical method for the rapid determination of atmospheric ozone (Gluckauf and Paneth, *Nature*, 1941, **147**, 614) we have succeeded in making the recording of the results automatic. The following is a description of the method at present in use at Durham for this purpose. As, for meteorological reasons, it will be desirable to carry out such recordings at various places, we paid special attention to the necessity of constructing a portable apparatus which can easily be set up, even under primitive conditions. With the apparatus described here, measurements of the local concentration of ozone outside the Durham Science Laboratories have been made at intervals over a period of several months. These experiments have had to be discontinued for the time being.

The meteorological significance of the results obtained so far will be discussed by one of us (E. G.) in the Quarterly Journal of the Royal Meteorological Society.

EXPERIMENTAL.

Method.—The main features of our method are the absorption of the ozone in sprayed buffered potassium iodide solution, and electrometric titration of the liberated iodine with sodium thiosulphate solution. By means of an electrical relay system, the apparatus is made to function automatically, and to give a continuous record of the ozone concentration and its changes over a period of up to 24 hours.

Apart from ozone, the only substances in the atmosphere likely to liberate iodine from potassium iodide are hydrogen peroxide and nitrogen peroxide. There is little evidence for the existence of the former in air, and, in any case, its action upon potassium iodide solution is so slow that it would only become appreciable during a very long run. As regards nitrogen peroxide we have made several concordant experiments in which a known quantity of the pure gas was allowed to flow slowly into the air-stream from a capillary. With the buffered potassium iodide solution used, the quantity of iodine liberated by nitrogen peroxide is not more than 2% of that calculated from the equation $NO_2 + 2H^+ + 2I^- = H_2O + NO + I_2$. This is not surprising, as the hydrogen ions required for this reaction are kept by the buffer at the low concentration of 10^{-7}. If the concentration of nitrogen peroxide is high (approx. 10^{-5} c.c. per c.c. of air), iodine is liberated with much greater efficiency, probably on account of local acidification by the reaction $2NO_2 + H_2O = 2H^+ + NO_2^- + NO_3^-$, which becomes relatively more frequent at higher concentrations of nitrogen peroxide. Since the concentration of this gas in the atmosphere is of the same order as that of ozone (10^{-8}; see J., 1941, 519), its effect may safely be neglected.

Apparatus (Fig. 1).—Air from outside the building (an the west side of the Durham Science Laboratories) is drawn by an electric suction pump into the apparatus at a rate of 30 l./min. All tubes carrying the air before its mixing with the solution are of glass, and where movable connections are necessary these are made with ground joints. Grease on the joints, and rubber connections are avoided because of their destructive effect upon the ozone. The air-stream passes from P to A through a specially designed absorption system, where it atomises the potassium iodide solution into a

B

fine spray at the jet D, and produces a rapid circulation of the solution past the electrodes C.   This arrangement gives extremely thorough mixing, but involves the gradual loss of water by evaporation and of potassium iodide solution as spray.   The diminution of the bulk of solution caused by evaporation is compensated by connecting the absorption vessel to a reservoir, H, of potassium iodide solution, which siphons over and, entering the absorption vessel through a

FIG. 1.
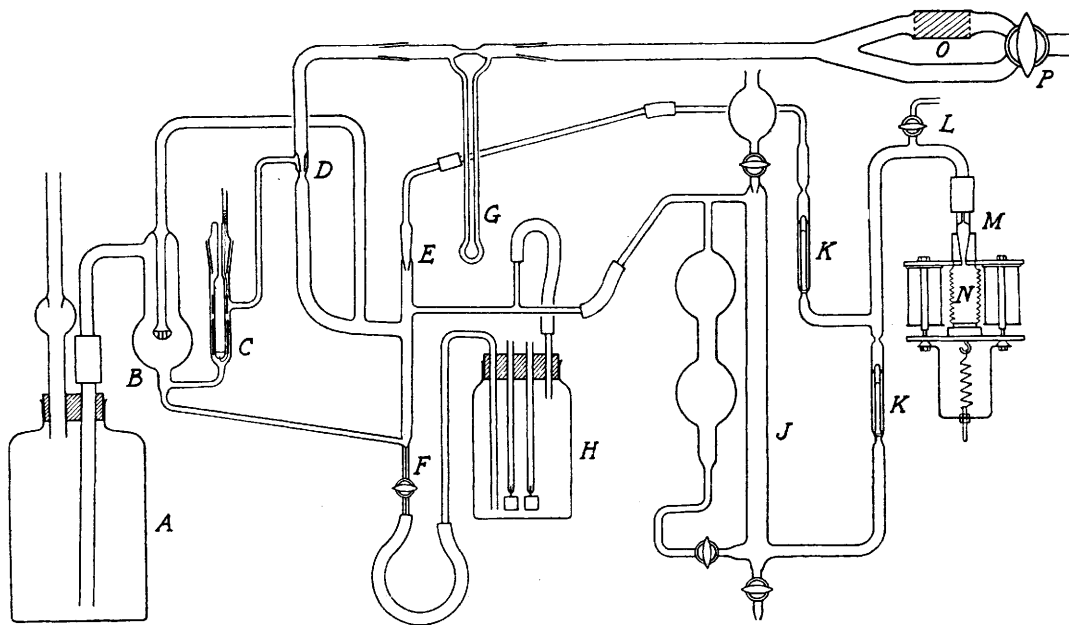
capillary F, maintains a nearly constant level.   The spray is trapped and returned to the main stream of liquid by the spray trap B, in which the air passes through a small glass basket loosely packed with glass-wool.   This trap must not be so low that it always contains a large bulk of solution, for this would give rise to irregularities of mixing with the main stream; nor must it be so high that bubbles of air pass into the liquid stream from it.   The correct height can only be found by trial, but the figure is approximately to scale, and may serve as a guide, if the rate of air-flow is similar to that in our apparatus.

FIG. 2.
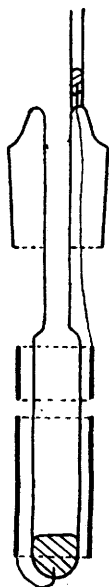
The composition of the potassium iodide solution is as follows : potassium iodide, 100 g.; sodium phosphate, NaH_2PO_4,H_2O, 1·38 g.; sodium hydroxide, 0·20 g.; water, 500 c.c.   The liberated iodine is determined electrochemically by its depolarising action on a pair of polarised platinum electrodes (Foulk and Bawden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045).   The current which it causes to flow is amplified, and works a relay, which results in the addition of a small fixed volume (about 0·3 c.c.) of $N/2000$-sodium thiosulphate solution, from the automatic burette J, through the jet E.

Considerable difficulty was experienced in designing a suitable amplifier.   The well-known instability of simple D.C. amplifiers led us to try supplying the electrodes with low-voltage A.C., but the polarised system then behaved as a high-capacity electrolytic condenser, and passed a large current in the absence of free iodine.   It was therefore necessary to devise some satisfactory method of amplifying the small direct current (~6 microamp., convertible by means of a resistance to a maximum potential difference of ~6 mv.) obtained from the depolarised electrodes.   Two high-magnification stages are needed to bring this up to a value sufficient for operation of the relay.   Battery fluctuations had to be compensated for by the use of a balanced bridge circuit in each stage.   Finally, the problem of biasing the bridge valves automatically, which would be impossible by using a separate bias resistance for each valve, since this arrangement would cause the partial cancellation of the applied E.M.F., was simply solved by using a common bias resistance for each pair of valves.   In this way the influence of the bias resistance in compensating for the applied E.M.F. was balanced out by applying it to both bridge valves at once, and correct biasing was achieved, with additional stability and no loss in sensitivity.

Electrodes (Fig. 2).—The most suitable form for these has been ascertained by trial.   They are maintained at such a small potential difference (0·1 v.) that they are ordinarily completely polarised, and no current flows.   In the presence of free iodine, the hydrogen layer on the cathode is oxidised, causing depolarisation. A current passes, of such a value that the rate of production of hydrogen on the cathode surface is exactly equal to its rate of removal by the iodine.   In order to obtain the maximum current for a given amount of iodine in the solution, and so to minimise the amplification required, it is clearly necessary to bring as much of the iodine as possible into contact with the cathode surface in a given time.   This object is achievable by observing the following requirements : (1) The total bulk of the solution must be kept low, and the iodine concentration correspondingly high (approx. 10^{-6} N).   (2) The cathode surface must be as large as practicable. (3) A rapid flow of solution must be maintained past the cathode.   In practice, (1) and (2) can only be satisfied by a compromise; moreover, we found that large electrodes gave trouble because they prevented rapid mixing of the thiosulphate after each addition, and also because they permitted the passage of a large steady current in the absence of free iodine.   The electrode system illustrated was as sensitive as any examined, responded almost instantaneously to the thiosulphate additions, and gave zero current in the absence of free iodine.   The electrodes are cylinders of platinum foil.   They fit loosely round the glass tube which carries them, so as to allow the solution access to both surfaces.   They are supported only by the connection wires.   Both electrodes were of 37 mm. circumference, and the anode (upper electrode) and cathode were respectively 9 and 24 mm. high.   Connections to the electrodes are made by means of mercury, in the central tube for the cathode, and the side tube for the anode.

FIG. 3.
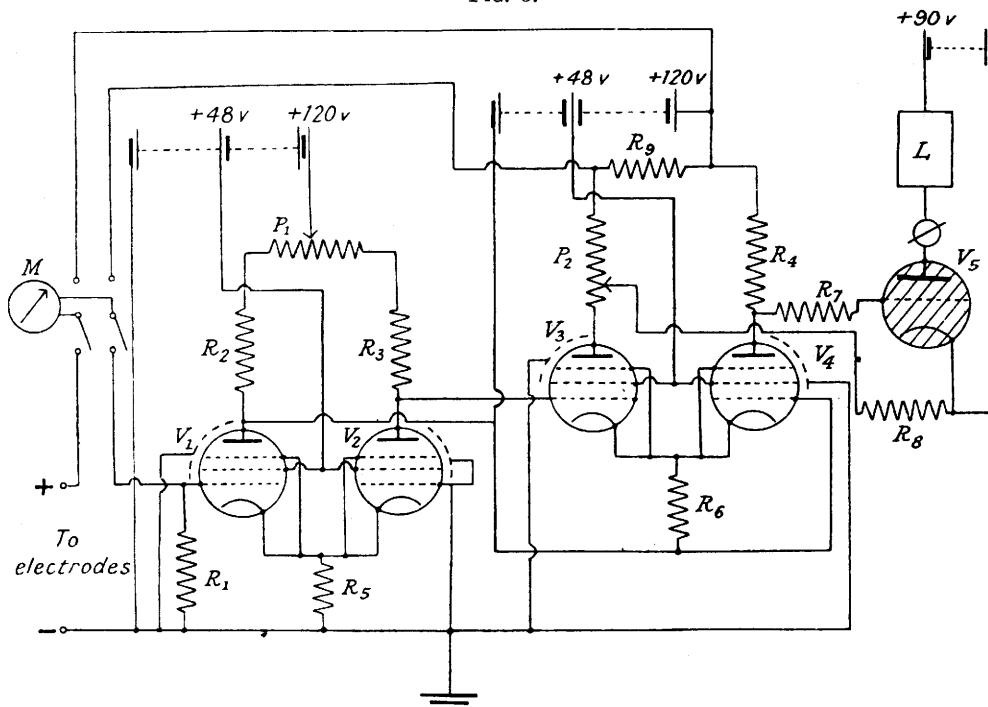
Key to Fig. 3. (Resistances in ohms.) R_1, 1000; R_2, R_3, R_4, 30,000; R_5, R_6, 200; R_7, R_8, 100,000; P_1, 5,000; P_2, 30,000; R_9, shunt for meter; V_1, V_2, V_3, V_4, Cossor MS 4 PEN; V_5, Osram GT1B; M, microammeter reading 0—50 microamps.; L, magnetic relay.

It is advisable to clean the surface of the electrodes before use, by heating them to whiteness in a hydrogen flame.

The suction pump used in our apparatus is an Edwards "Type 4, Compressor and Vacuum Pump." In order to prevent fouling of the mechanism with potassium iodide spray from the absorption apparatus, the air is bubbled through a small depth of water in wash-bottle A before entering the pump.

Automatic Burette (Fig. 1, *JKLMN*).—This is constructed of Pyrex glass, except the bellows N, which are of copper, and the short metal capillary tube M, serving to prevent too violent ejection of the thiosulphate solution, which would result in the rubber joints being loosened. The connection between M and the glass portion of the burette is made with pressure-tubing. Direct connection with vacuum wax is satisfactory if the magnets are run from direct current, but the wax is soon cracked by the vibration set up when alternating current is used. In a semiportable apparatus it is a great convenience to use mains A.C. wherever possible, and we have therefore used a rubber joint in our apparatus. The valves K are ordinary ground-in glass valves weighted with mercury. These need to be of a somewhat better fit than the usual mercury float-valves, but if they are symmetrical and carefully ground, the leakage through them is negligible. The tap L facilitates filling of the burette.

The N/2000-sodium thiosulphate solution is obtained by two dilutions of N/10-solution. It is not very stable, and must be made up afresh for every run. It can be standardised by titration in a separate vessel against the iodine liberated by very dilute potassium dichromate solution. The end-point is best determined electrometrically, the liquid being stirred by an air-stream.

A simpler method is to pass a known electric current through the potassium iodide solution in the apparatus, by means of two small separate platinum electrodes, while destroying the ozone of the air on a charcoal filter. The iodine liberated at the anode is then titrated continuously and automatically; at the iodine concentrations attained, no measurable reduction of it takes place at the cathode. In this manner the calibration values are obtained on the same record, at the expense of a few minutes of ozone measurement.

To allow for the small quantity of iodine entering the vessel continuously with the fresh potassium iodide solution, it is useful to make a blank run, by destroying the ozone with a filter containing about 5 oz. of active charcoal (Fig. 1, *O*). The large tap P (Fig. 1) allows air to be drawn into the apparatus either directly or through the filter.

Amplifier, Relay System, and Recording Apparatus.—The electrode voltage, 0·1 v., is provided by a single dry cell with a potential divider. The current is amplified by means of a two-stage direct-current amplifier, stabilised by using a bridge circuit in each stage (Fig. 3). The voltage available for amplification is up to 10 mv. (10 microamps. electrode current, with a resistance of 1000 ohms in the circuit). The amplification is approximately 3,000, and the voltage output up to 30 v. This is used to trigger a gas-filled relay valve, the anode current from which operates a delayed-action magnetic relay, causing

FIG. 4.
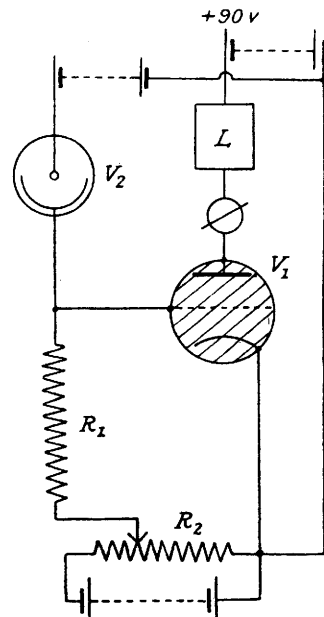
Key to Fig. 4. (Resistances in ohms.) R_1, 250,000; R_2, 200,000; V_1, Osram GT1B; V_2, Osram CMG8; L, magnetic relay.

an injection to be made by the automatic burette. Every such injection is recorded upon a rotating drum, operated by a geared-down electric clock motor. The total volume of thiosulphate used during a run is found by reading the burette, and the volume per injection is given by dividing this by the total number of injections. Hence the average ozone concentration over any given period, short or long, can be calculated from the intervals between injections on the record.

The amplifier requires some time to attain equilibrium, and must be switched on at least $1\frac{1}{2}$ hours before use. It is necessary to earth it as indicated, and if this precaution is observed it is electrically and mechanically very stable. Potentiometer P_1 is set to balance the first bridge; this is done by adjustment until the current through V_3, as measured by the meter M, is about 1·5 milliamps., approximately equal to that through V_4. This adjustment need not be made exactly. P_2 is then set so that the gas-filled relay " strikes " when the electrode current, measured by the same meter on a different switch setting, reaches the desired value; 6—7 microamps. is a suitable value, but, again, exact adjustment is not necessary. Once made, the amplifier adjustments need not be altered for days. The magnetic relay remains on for 5 secs. when actuated, then breaks the anode circuit of the gas-filled valve. This delay is necessary in order to allow time for the thiosulphate injection to mix with the solution.

Galvanometer–Photocell System (Fig. 4).—This is an alternative arrangement for operating the relay system, which was used in an earlier form of our apparatus, before we had succeeded in amplifying the electrode current sufficiently to work a relay. It has the advantage of being simpler in construction, and operates well when carefully set up, but it is less compact and more troublesome to adjust than the valve amplifier; nor is it conveniently transportable. The simple principle of its operation is that the light-spot from a sensitive mirror galvanometer in the electrode circuit falls upon the photocell when the electrode current reaches the desired value, and so triggers the gas-filled relay.

Electric Current Supplies —The only external source of supply needed is A.C. mains. From this are supplied the burette magnets, recorder motor, and recorder stylus direct, and the valve heaters through a transformer giving 4 v. The four amplifier valves are heated from one filament winding, the centre of which is earthed, and the gas-filled relay from a separate winding, with its centre connected to the negative side of the relay high-tension battery. This is done to avoid a large potential difference between the heater and the cathode of the relay.