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A modified bubbler sensor for the continuous recording of surface ozone

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ABSTRACT. The surface ozone recorders developed at Poona use a Brewer electrochemical bubbler ozone sensor. Continuous recording with the sensor is possible if a constant level of solution can be maintained in the bubbler. In the Mark I surface ozone recorder this was achieved by incorporating a reservoir of KI solution which automatically siphons the solution into the bubbler. This resulted in changes in the response characteristics of the bubbler. In the Mark II bubbler gradual free mixing between the solution in the bubbler and the reservoir is made possible by enveloping the bubbler with the reservoir. The result is a simple, reliable, surface ozone recording system which requires attention only once in a week. The system is described in detail and sample records are presented.

1. Introduction

The bubbler electrochemical ozone sensor (Brewer and Milford 1960) is extensively used in ozonesondes to measure the vertical distribution of ozone in the atmosphere. The limitation of the bubbler as a continuous surface ozone sensor arises from the fact that the small quantity of KI solution used evaporates after a few hours when air is bubbled through it at the rate of about 200 ml min^{-1}, and when operated continuously, increasing amounts of ozone escape from the solution without reacting with it. The concentration of KI in the solution also increases resulting in changes in the bubbler response. If the concentration of the solution and its level in the bubbler can be maintained nearly constant, the bubbler can be used as a continuous sensor. This can be accomplished if a reservoir of KI solution is incorporated in the system in such a manner that the solution lost from the bubbler is replenished automatically and gradual mixing takes place between the solution in the bubbler and that in the reservoir. Other requirements are the capability of the system for unattended operation over a period of time and the possibility of locating the sensor at a distance from the recorder, constancy of the rate of aspiration of air through the bubbler and minimum destruction of ozone in the intake system and bubbler.

2. Description of the surface ozone sensor Mark I

Fig. 1 shows the Mark I surface ozone sensor assembly developed in the Instruments Research Laboratories of the India Meteorological Department at Poona (Sreedharan and Tiwari 1971). The KI solution contained in the reservoir B is automatically syphoned into the bubbler A, through a syphoning tube T, whenever the level of solution in the latter is reduced due to evaporation. An air-trap S in this tube collects small air bubbles that tend to accumulate and block the syphoning tube. The pressure above the liquid level in both the bubbler and the reservoir is equalised by the polythene tubes F and G. The polythene caps C and D fit airtight over the reservoir and the bubbler respectively. Air from the atmosphere is sucked into the bubbler through a short length of polytetrafluroethylene (teflon) tubing M. The bubbler with its cap is held airtight between the stop K and the holder L and is locked in position by the thumb screw J. The reservoir can be raised or lowered about 3 cm by means of the thumb screw H. This enables minor adjustments to be made in the solution level in the bubbler once in three or four days without fresh solution being added. The sensor is affected by direct sunlight and the entire assembly is therefore protected inside a weather hood which is blackened inside. The teflon air intake tube M is taken out of the hood through one side and extends 15 to 20 cm beyond it. The suction tube N for connection to the pump and two electrical leads are taken out through the base plate I.

The pump is similar to the one used in the Indian electrochemical ozonesonde (Sreedharan 1968) but is driven by an AC motor operating from mains power supply at a fairly constant rate (1330 r.p.m.). The constancy of motor rotation is ensured by supplying a constant voltage through a

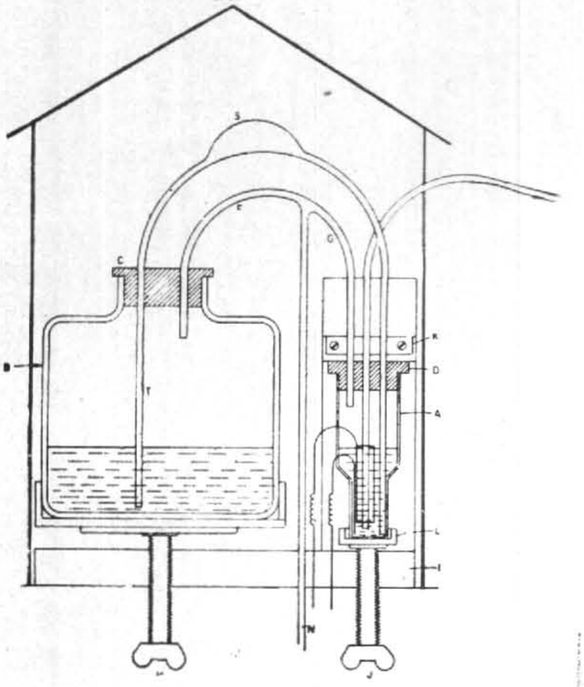

Fig. 1

Ozone sensor Mark I

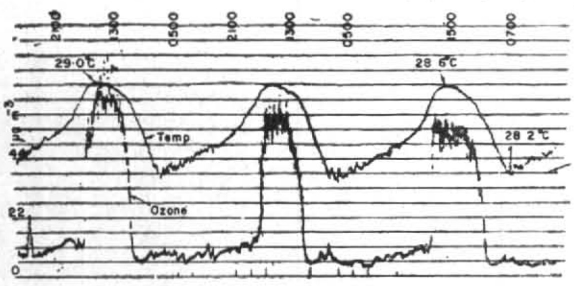

Fig. 2

Ozone and temperature record for 72 hrs from Mark I sensor

voltage stabiliser. A rubber tube connects the suction tube N from the sensor to the pump. The pump is kept well lubricated and its satisfactory performance is ensured by checking the rate of aspiration at the inlet once in about ten days.

The bubbler requires a polarising potential of 0.42 volt which is supplied by a high capacity dry battery (1.5 volts) through a potential divider. The output from the bubbler is connected to the recorder directly through a twin-core shielded cable.

The current output from the sensor is recorded on a multi-channel recorder in which as many as six different parameters can be simultaneously recorded, each for 5 seconds. The current output from the bubbler is fed across a 5 K resistance. The recorder used gives full scale deflection for 2 mV.

3. Some drawbacks of the Mark I bubbler

To check the performance of the bubbler sensor, independent measurements of surface ozone by Ehmert's method were carried out at the level of the continuous sensor. This was generally done between 1300 and 1500 hours local time when the ozone concentration is a maximum and fairly steady. The ozone concentration given by the bubbler sensor was found to agree well with that obtained by Ehmert's method during the humid months when the evaporation of the solution is small. But with the commencement of the dry season it was noticed that the bubbler sensor started to indicate progressively higher values. Fig. 2 represents a continuous record obtained for three days from 31 December 1969 to 2 January 1970. To enable investigations of surface ozone changes, the surface temperature is also recorded on the same chart. The progressive increase in ozone concentration can be clearly observed from the record and is presumably caused by an increase in KI concentration in the bubbler with time. From laboratory investigations, Powell and Simmons (1969) have reported similar changes in bubbler response with changes in KI concentration.

Similar changes in the response of the bubbler with time were also observed in ozone soundings in which the bubbler had been subjected to prolonged pre-conditioning (5 to 6 hours) with low doses of ozone. In these cases the integrated ozone values from the sounding exceeded the total ozone value given by the Dobson ozone spectrophotometer. It may, however, be added that the use of solution of higher concentration initially with only nominal preconditioning does not produce an accelerated response from the bubbler. A convincing explanation of the change in response of the bubbler with prolonged conditioning is still to be found. However, the result has very important practical implications. It is now definitely established that the ozone detection efficiency of a bubbler depends to a large extent on the degree of preconditioning of the bubbler. This may also explain the higher ozone values obtained some times during the descent of an ozonesonde after the balloon bursts.

The Mark I sensor required complete replacement of the solution in the bubbler every day resulting in breaks in the continuity of the records. Also, the ozone values became normal only after about an hour after the fresh solution was added.

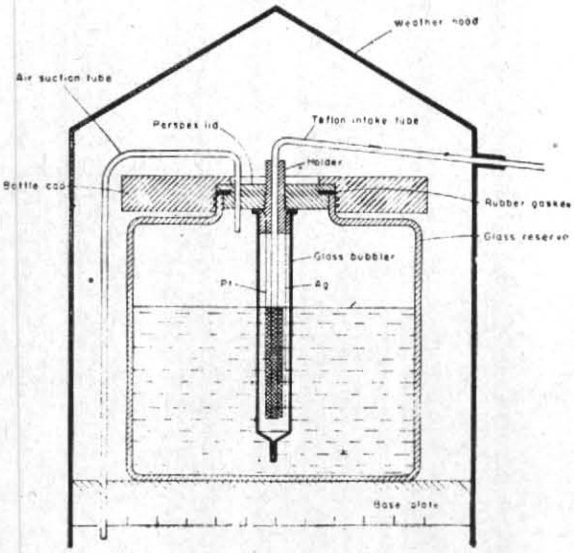

Fig. 3

Surface ozone sensor Mark II

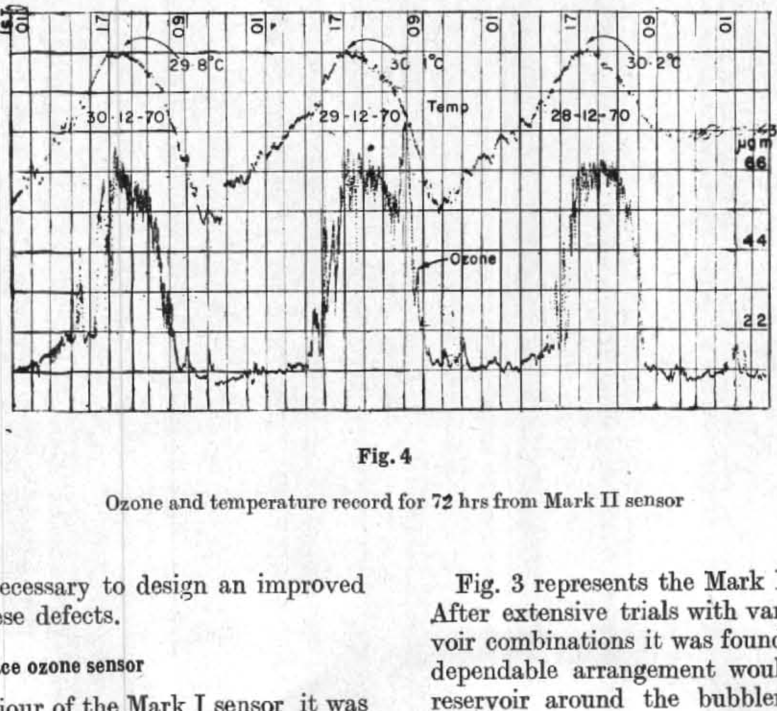

Fig. 4

Ozone and temperature record for 72 hrs from Mark II sensor

It was therefore necessary to design an improved sensor without these defects.

4. An improved surface ozone sensor

From the behaviour of the Mark I sensor it was apparent that both the material of the bubbler(acrylic plastic) and the concentration of the solution contributed towards the changes in sensitivity and a glass bubbler would give more consistent results. It also seemed desirable to allow a very gradual mixing between the solutions in the bubbler and the reservoir both ways. To achieve this, a new sensor was developed. In the Mark II sensor a glass bubbler is *kept inside a reservoir* with a communicating hole at the bottom of the bubbler.

Fig. 3 represents the Mark II sensor assembly. After extensive trials with various bubbler-reservoir combinations it was found that a simple and dependable arrangement would be to provide a reservoir around the bubbler. The bubbler is made of pyrex glass and has a hole 0.5 mm diameter and about 5 mm long at the bottom. The reservoir is a glass bottle having a diameter of about 10 cm with an airtight perspex cap. A split teflon holder fixed to the centre of the perspex cap supports both the bubbler and the platinum and silver electrodes. The teflon air intake tube passes through the centre of the teflon holder. A suction hole is provided in the perspex cap. The solution is added to the reservoir whenever necessary through the suction hole after removing the suction tube. The KI solution is buffered and consists of 1 gm of KI, 2.522 gm of $Na_2HPO_4.12H_2O$ and 1.15 gm of $NaH_2PO_4.H_2O$ dissolved in one litre of double distilled water. The sensor takes about 12 to 24 hours to stabilize. Thereafter the agreement between Ehmert's method and bubbler sensor is within ± 10 per cent.

The level of solution in the reservoir comes down by about 5 mm in 10 days during the dry season for air flow rates of 200 ml min^{-1}. With a reservoir capacity of 375 ml this results in a change of concentration from 0.10 to 0.11 per cent. Since these changes in the depth of solution and KI concentration do not adversely affect the performance of the bubbler, replenishment of the solution in the reservoir once in 10 days is found to be adequate. A typical record for a period of 72 hours from 28 to 30 December 1970, from the Mark II sensor is shown in Fig. 4.

5. Summary

The consistency in the performance of the system over long periods and its simple design make this form of sensor suitable for continuous monitoring and recording of surface oxidants from a network of stations. There are no serious limitations on the exposure of the sensor as the distance of the sensor from the recorder and pump unit can be in practice as large as 500 m. For use in a polluted atmosphere it will, however, be necessary to use suitable filters at the inlet of the instrument to absorb any reducing agents present in the atmosphere (Desjardins 1967). The basic system has also the potential for being adapted for monitoring other constituent gases present in the air.

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