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ATMOSPHERIC OZONE MEASUREMENTS IN INDIA

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This paper summarises the development of ozone measurements in India since 1928–29 and deals with the present status of the total ozone, vertical distribution of ozone and surface ozone measurement techniques and the ozone network maintained by the India Meteorological Department. The importance of the monitoring of ozone layer and inter-calibration of ozone instruments with the world standard and certain aspects of international co-operation in the field of atmospheric ozone measurements between the India Meteorological Department and U. S. Satellite Ozone Analysis Center, University of California, and NASA have also been discussed in this paper.

INTRODUCTION

THE study of ozone in the atmosphere has assumed great importance in recent years because of the increasing concern regarding the effect of the pollution of the stratosphere due to human activities and the consequent possibility of a reduction in the ozone present at these levels. This concern arises from the danger of increased solar ultraviolet radiation penetrating to the Earth's surface producing biological effects and from the possibility of climatological changes as a result of the decrease in the temperature of the upper stratosphere caused by depletion of ozone. There is, therefore, a pressing need to measure the amount of ozone in the atmosphere at various locations so that any change in its amount can be monitored.

OZONE MEASUREMENTS IN INDIA

In India, the first ozone observations were made in 1928–29 at Kodaikanal as part of Dobson's worldwide total ozone measurements using his photographic photometer. The observations were made by Royds and Narayana. This was followed by measurements at Bombay by Chiplonkar in 1936–38. India Meteorological Department acquired the first Dobson Spectrophotometer in 1940. Preliminary measurements were made at Poona by Ramanathan, Ananthakrishnan and Venkateshwaran but there was a break in the observations during war time and the observations were resumed in 1945 by Karandikar. Daily observations were made at Delhi from 1945 to 1947, and at Poona and Kodaikanal during 1948–49 by Karandikar (1952) and later on by Kulkarni *et al.* (1959) and Ramanathan *et al.* (1965). In the meantime, a network of six stations were established at Srinagar, New Delhi, Varanasi, Calcutta, Ahmedabad and Kodaikanal. These stations were

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equipped with Dobson Spectrophotometer. India took an active part in the ozone measurements during the I.G.Y. and Ramanathan and Dave (1957) developed the well-known method B for numerical evaluation of Umkher data. This method was used all over the world until a method of evaluation using computer was developed by Mateer and Dutsch (1964).

Ramanathan and Dave also made the first measurement of surface ozone at Ahmedabad using the Ehmerts apparatus which showed that substantial amounts of ozone were present at the ground even in tropical areas.

The operation and maintenance of the network of total ozone stations was taken over by the India Meteorological Department from the Physical Research Laboratory, Ahmedabad in 1963. The work on the development of an Indian ozonesonde was undertaken at the Instrument Division of the India Meteorological Department at Poona in 1964 in collaboration with Professor E. L. Simmons, Professor of Physics at Wilson College, Bombay.

At present, the following measurements of ozone are made in India from stations as shown in Fig. 1 :

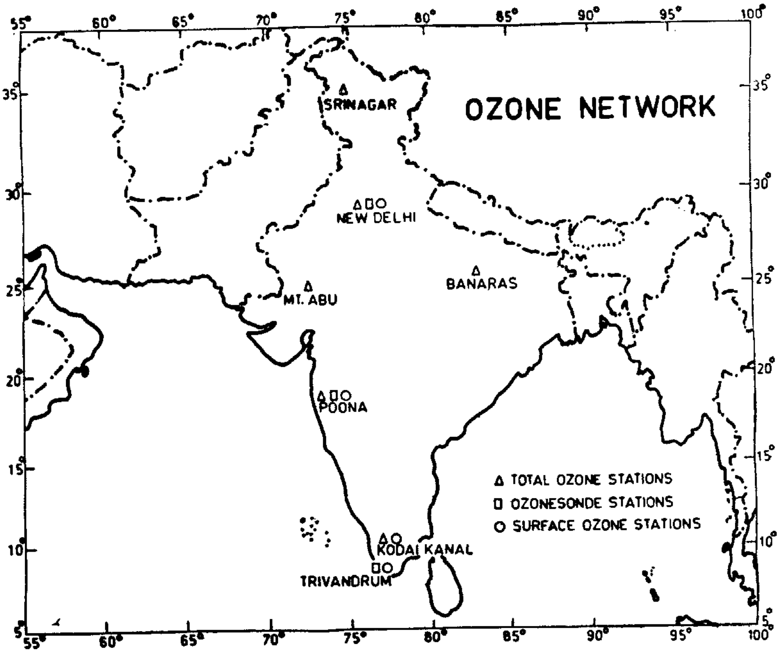

FIG. 1. Map of ozone network.

(*i*) Total ozone amount using Dobson Spectrophotometer; (*ii*) vertical distribution of ozone using the Indian ozonesonde; and (*iii*) ozone at the surface of the earth.

We shall now discuss these measurements in some detail :

Observations of Total Ozone with Dobson Spectrophotometer

Dobson Spectrophotometers are now located at Srinagar, New Delhi, Varanasi, Mount Abu, Poona and Kodaikanal. The Spectrophotometer at Ahmedabad was shifted to Mount Abu in 1969 and the one at Calcutta was shifted to Poona in 1973.

The Dobson Spectrophotometer is the standard instrument for measuring the amount of total ozone in a vertical column of the atmosphere. The principle of the Dobson Spectrophotometer is based on the fact that the absorption coefficient of ozone in the Huggins' band in the near ultraviolet region is a rapidly changing function of the wave length. A pair of wave lengths is chosen such that the absorption coefficient of ozone in one wave length is much greater than that in the other. By measuring the ratio of the intensities of the solar ultraviolet radiation at the ground, received at the two wave lengths it is possible to calculate the total ozone present in the atmosphere in a vertical column above the instrument.

The total amount of ozone X in cm at standard temperature and pressure is given by—

$$X = \frac{L_0 - L}{\mu(\alpha - \alpha')} - Ac,$$

where Ac stands for the atmosphere correction and

$$L_0 = \log (I_0/I_0')$$

and

$$L = \log (I/I').$$

I, I' are the observed intensities of the solar radiation at the two wave lengths λ, λ' at the earth surface and I_0, I_0' are the corresponding undepleted intensities at the top of the atmosphere. α and α' are the decimal absorption coefficient per cm S.T.p of ozone for λ and λ'. μ is the relative path length of the solar beam through the main part of the ozone layer; for a vertically overhead sun $\mu = 1$.

The Dobson Spectrophotometer has special arrangements by which separation of the wavelengths can be made easily and the ratio of the intensities can be measured quickly. A photograph of the Dobson Spectrophotometer is shown in Figs. 2(a) and 2(b). A double monochromator is employed to isolate the two wavelengths sharply and a photomultiplier assembly is used to measure the feeble intensities of the ultra-violet light. Two quartz optical wedges interposed in the path of the ultraviolet beam can be adjusted so that the intensities can be balanced. From previous calibration, the value of log (I/I') can be obtained directly from the settings of the optical wedges (dial readings). The value of L_0 which is known as the extra-terrestrial constant of each instrument is determined once for all by a series of measurements involving different values of μ.

When the sky is clear, observations of only a pair of wavelengths is sufficient. However, when the sky is cloudy or when the atmosphere contains dust reliable measurements of total ozone can be made only by using two pairs of wavelengths. The A(3055 Å, 3254 Å) and D(3176 Å, 3398 Å) pairs of wavelengths, have been internationally accepted for this purpose.

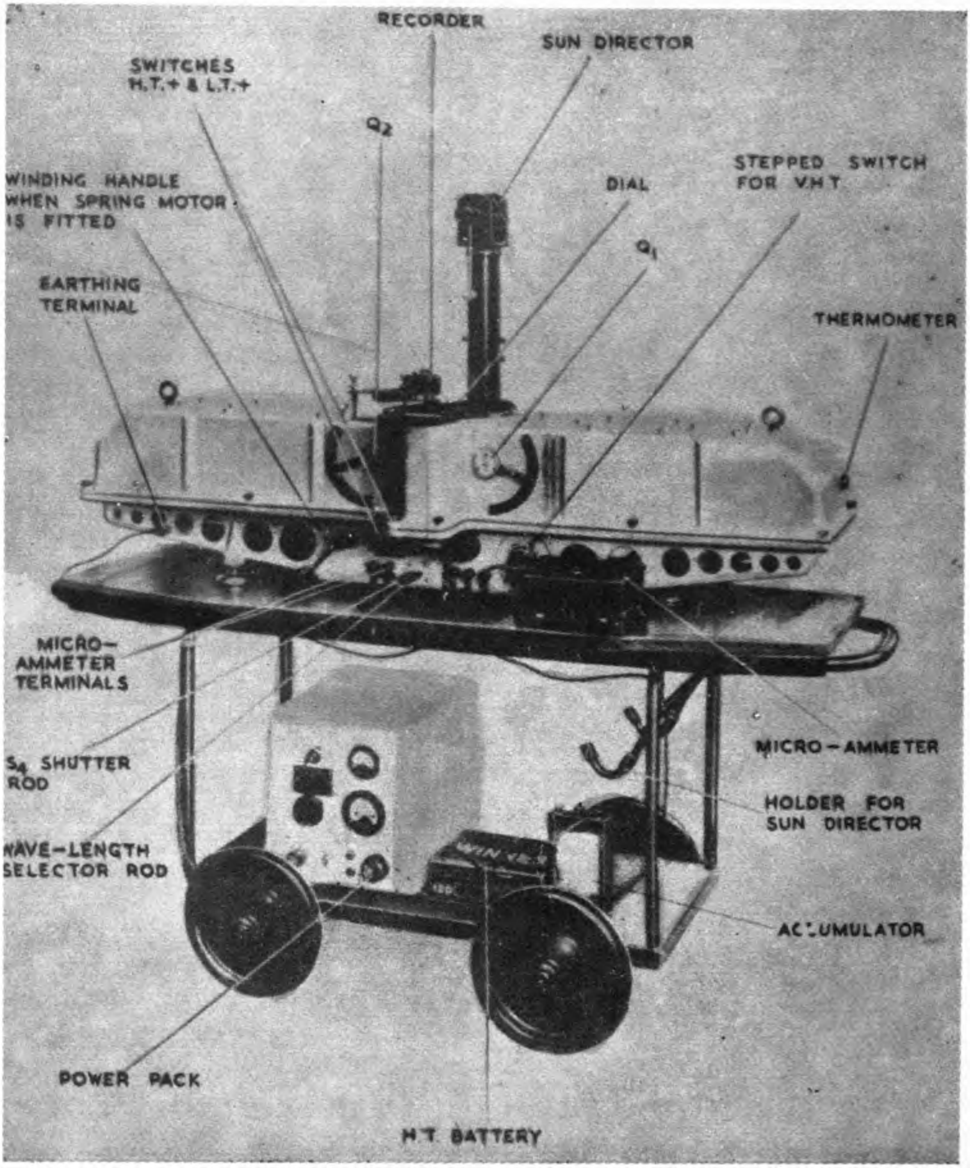

FIG. 2(a). Photograph of Dobson Ozone Spectrophotometer.

Dobson Spectrophotometer observations can also be used to obtain the vertical distribution of ozone. This is known as the Umkher method. In this, a series of observations are made with the spectrophotometer to obtain the ratio of intensities of the Zenith-scattered ultraviolet light from a clear blue sky at one pair of wavelengths as the Zenith angle of the sun increases from 60 to 90 degrees.

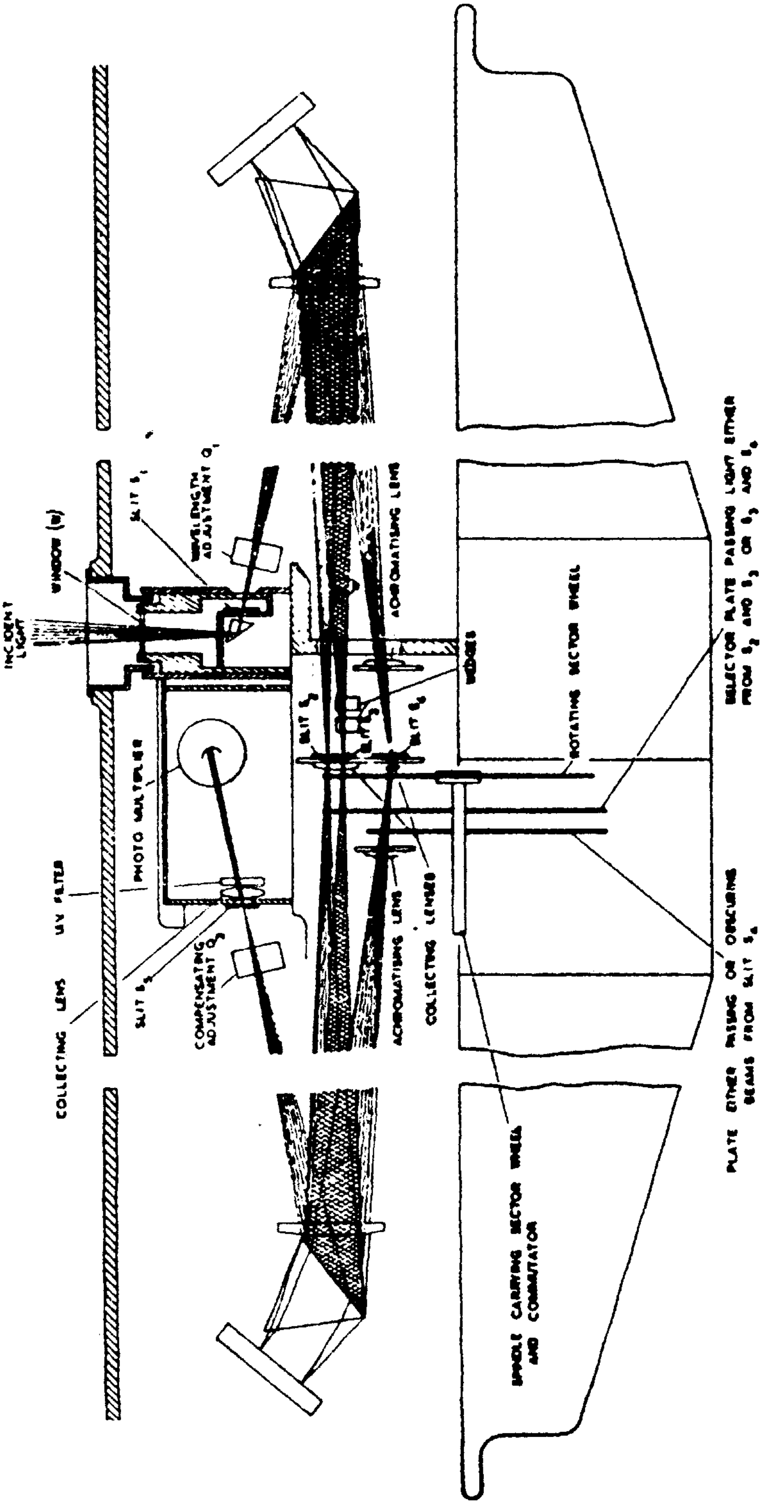

FIG. 2(b). Optical system of ozone spectrophotometer.

The commonly used wavelengths pair is the C viz., 3114 Å and 3324 Å. If the values of log (I/I') are plotted against the zenith angle of the sun, the curve descends with increasing Zenith angle until a minimum point occurs near 86°–88° and then the curve ascends. Because of the occurrence of this inversion, the method has been called the Umkher or reversal method. For a given Zenith angle of the sun, the intensity ratio of the zenith scattered ultraviolet light reaching the instruments for the two wavelengths can be calculated. For this, the atmosphere is divided into several layers and each layer is assigned one ozone content according to an assumed distribution. The calculations of the intensities involves evaluation of the depletion of the solar beam due to ozone absorption as well as due to Rayleigh Scattering through each one of these layers. The vertical distribution of ozone is then derived by finding out by trial and error which pattern of assumed distribution makes the observed and calculated intensity ratios equal for different Zenith angles. Mateer and Dutsch (1964) developed computer methods for rapid and objective evaluation of the vertical distribution of ozone from the Umkher data. Mean ozone density is obtained for 10 layers of atmosphere (Surface to 5.8, 5.8–10.6, 10.6–14.6, 14.6–19.2, 19.2–23.7, 23.7–28.0, 28.0–32.8, 32.8–37.8, 37.8–43.2 and 43.2–49.8 km). With this it has now become possible to process rapidly the Umkher data from all the stations in the world ozone network.

The Umkher method is used widely for obtaining the general distribution of ozone in the vertical. Its advantage is that the ozone distribution above 30km can be obtained while other existing methods may not give good estimates in this region. The main defect of the Umkher method is that the ozone distribution within the troposphere cannot be obtained with sufficient accuracy.

Measurement of Surface Ozone

Continuous recording of surface ozone is made by an adaptation of the Brewer 'Bubbler', Sreedharan and Tiwari (1971) at four stations in India—Trivandrum, Kodaikanal, Poona and Delhi. The bubbler ozone sensor is based on the electro-chemical reaction of ozone with potassium iodide in solution. A glass bubbler containing about 3 ml of buffered KI solution is surrounded by a reservoir of the same solution. A small hole at the bottom of the bubbler allows the solution from the reservoir to enter the chamber. Air is aspirated through the bubbler using a suction pump. The output from the bubbler is recorded on a chart after necessary amplification. The surface ozone sensor is shown in Figs. 3(a) and 3(b). The ozone recording system consists of a modified bubbler sensor, a suitable miniature pump, a network for supplying a polarising potential to the bubbler and a recorder capable of full scale deflection for a current of 2μA. The recorder is calibrated by a micro amp current source. From the record, the ozone current in μA is determined and the partial pressure P of ozone is calculated from the formula

$$P(\mu \text{ mb}) = 4.31 \times 10^{-3}\, iTt,$$

where i is the ozone sensor current in μA, T is the temperature of the air in

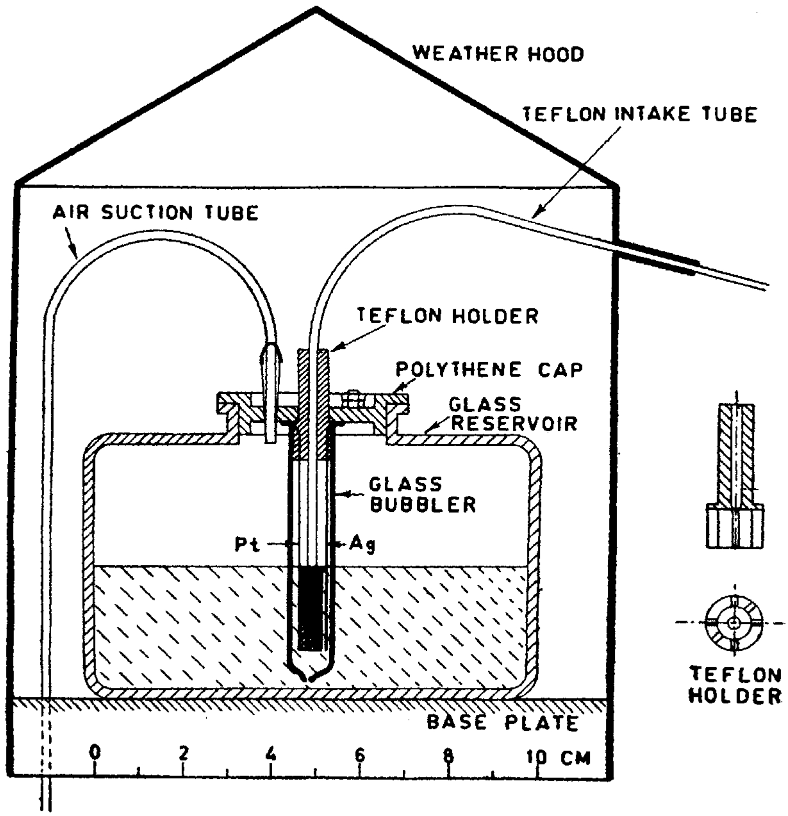

FIG. 3(a). Surface ozone sensor.

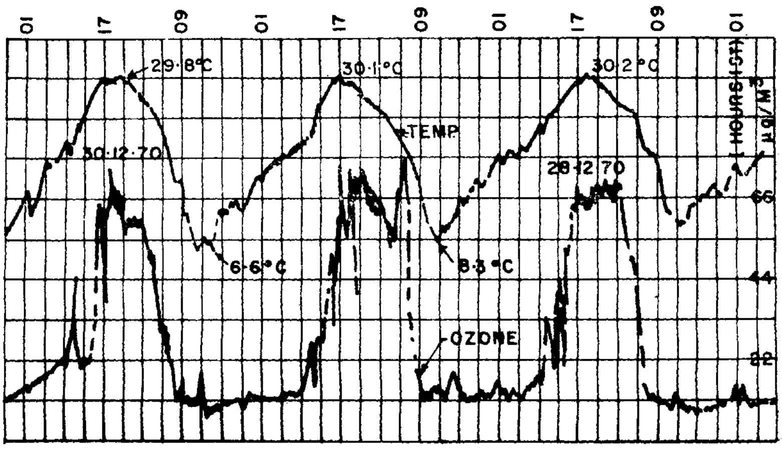

FIG. 3(b). Record of surface ozone.

degrees Kelvin and t the time in seconds for pumping 100 ml of air. The ozone density in μ gm^{-3} is calculated from the relation

$$P(\mu\,\text{mb}) = 1.732 \times 10^{-3}\, T\rho$$

The system has a response time of a few seconds and has a resolution capability of 0.1 part of ozone per 100 million parts of air. The overall accuracy is about 5 per cent. The system is capable of unattended operation for 10 days.

Measurement of Vertical Distribution of Ozone by Ozonesonde

Observations of the vertical distribution of ozone are being made at Trivandrum, Poona, New Delhi once every fortnight using the Indian electrochemical ozonesonde. A photograph of the ozonesonde is given in Fig. 4.

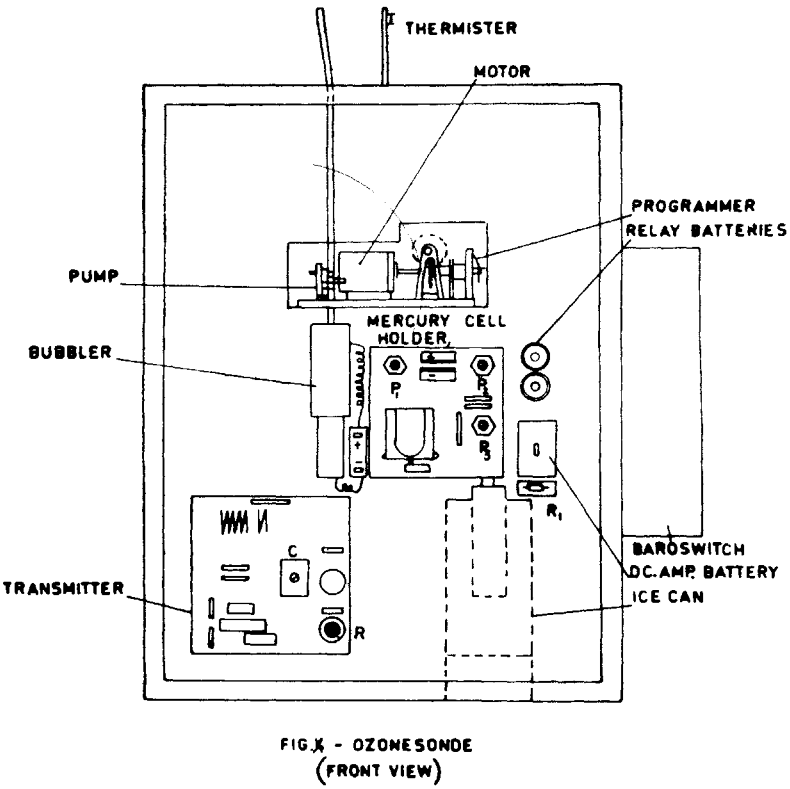

FIG. 4. Ozonesonde schematic diagram.

The ozonesonde designed at the Instruments Division of the Meteorological Department at Poona (Sreedharan, 1968) consists of the electrolytic reaction cell, a miniature air pump operated by a small motor, a d.c. amplifier for the ozone current, a modulator coupled to a VHF transmitter, a motor-driven programmer which switches on the various elements in sequence and batteries. All the components are embedded in a thermocole block for physical and thermal protection during transport, preparation, launch, flight and recovery.

The sensor of the Indian ozonesonde is the Brewer wet chemical cell or bubbler in which the reaction of ozone with KI solution is made use of for the detection of ozone.

$$O_3 + 2\,KI + H_2O \rightarrow 2\,KOH + O_2 + I_2$$

The iodine liberated is detected by immersing in the solution a platinum and silver electrode with a potential of 0.42 volts applied between them. When free iodine appears in the solution, a current flows across the electrode. Every molecule of ozone that reacts with the solution liberates two iodine atoms which in turn result a flow of two electrons in the circuit. From this, it can be derived that the partial pressure of ozone

$$p \text{ (micromillibar)} = 4.31 \times 10^{-3}\, iTt$$

where i is the ozone sensor current in μ A, T is the temperature of the air in degree Kelvin and t the time in seconds for pumping 100 ml of air.

A motorised switch consisting of a 8-segment commutator over which slides a moving cam switches ozone, air temperature, pump temperature and modulator reference for ten seconds each in sequence. The modulator and transmitter used are similar to those used in the audiomodulated radiosondes.

Laboratory and flight tests indicated that a 5cm thickness of foamed polystyrene around the bubbler is sufficient to prevent the KI solution from boiling at reduced pressures or freezing during a 2hr flight.

The ozonesonde without batteries weighs 900gm and with batteries 2200gm. Records of ozonesonde and the ozonagram in New Delhi are given in Figs. 4(a) and 4(b).

In the international inter-comparison of ozonesondes which was conducted in 1970 in the Meteorological Observatory at Hohoenpiessenberg in the Federal Republic of West Germany, the Indian ozonesonde was inter-compared with five other ozonesondes. The main comparison of the sondes was done by taking the differences against daily mean values. From the observations taken, it was found that in the stratosphere the deviation from the mean is less than 5 per cent for each instrument but in the troposphere the relative errors are larger (upto 25%).

Comparison of Dobson Spectrophotometer

India took part in the international inter-comparison of Dobson Spectrophotometer conducted at Boulder, Colorado under the auspices of the WMO in August, 1977. During this inter-comparison, the Indian National Standard was compared with the world standard. This Indian National Standard Dobson Spectrophotometer No. 112 is now located in Delhi and all the other Indian instruments on the network are being calibrated with reference to this standard.

FIG. 4(a). Record of sounding.

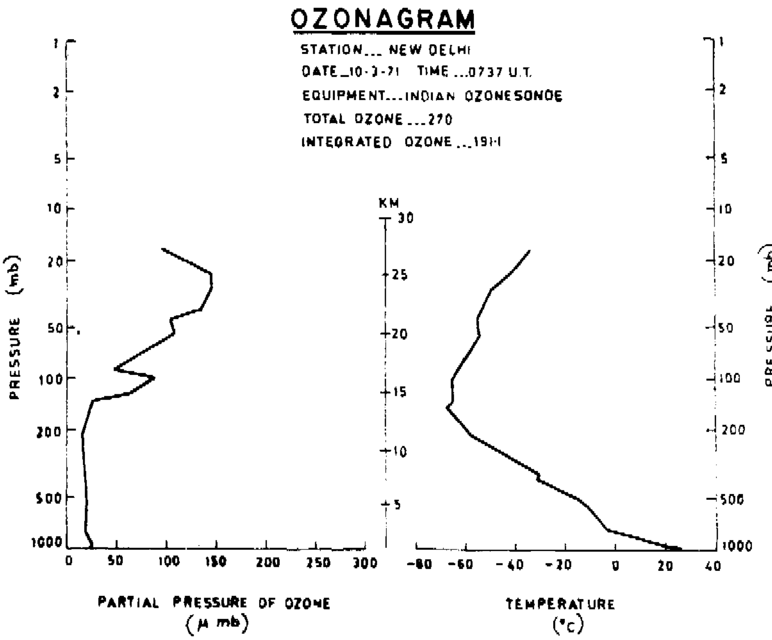

FIG. 4(b). Ozonagram.

COLLABORATIVE PROJECTS WITH SATELLITE GLOBAL MEASUREMENT MONITORING OF TOTAL OZONE PROGRAMMES

India Meteorological Department is collaborating with the U.S. Satellite Ozone Analysis Centre (SOAC) at the Lawrence Livermore Laboratory of the University of California by providing total ozone measurements over Delhi at the time of overpass of their satellites to provide a ground truth for the satellite measurement of total ozone. This will also provide the most intensive space/earth ozone sensor calibration. The F_1 and F_2 Spacecraft of SOAC use Multifilter Radiometer (MFR) ozone sensor. Each spacecraft theoretically transmits 68,400 total ozone observations each day or a total of 1,36,800 ozone measurements for the dual system.

In reality due to data drops for various seasons, observations less than 68,400 are actually available.

India Meteorological Department is also collaborating with the total ozone measurement by the Nimbus-7 Satellite by providing total ozone measurements coincident with the Satellite overpass time over Delhi.

REFERENCES

Karandikar, R. V. (1952) Measurements of atmospheric ozone and its vertical distribution at Kodaikanal (Lat. 10°N). *Proc. Indian Acad. Sci.*, **35A**, 290–302.

Kulkarni, R. N., Angreji, P. D., and Ramanathan, K. R. (1959) Comparison of ozone amounts at Delhi, Srinagar and Tateno in 1957–58. *Pap. Met. and Geophys. Met. Res. Inst., Tokyo.*, 85–92.

Mateer, C. L., and Dutsch, H. U. (1964) Uniform evaluation of the Umkher Observations from the world ozone network. Part I, Proposed standard evaluation technique. *Rep. natn. Center Atmos. Res., Boulder*, 105.

Ramanathan, K. R., Angreji, P. D., and Shah, G. M. (1965) Note on ozone observations made with moonlight. *Indian J. Met. Geophys.*, **16**, 675–676.

Ramanathan, K. R., and Dave, J. V. (1957) The calculation of the vertical distribution of ozone by Gotz-Umkher effect, method B. *Ann. I.G.Y.*, **5**, 23–45.

Sreedharan, C. R. (1968) An Indian electrochemical ozonesonde. *J. Phys. E. Sci. Inst-Sr.*, **2**(1), 995–997.

Sreedharan, C. R., and Tiwari, V. S. (1971) The use of a Brewer 'bubbler' as a continuous surface ozone sensor. *Appendix II (iii) J. Phys. E. Scientific Instruments*, **4**.