BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3075—3076 (1978)

Gas-chromatographic Measurements of Nitrous Oxide(N_2O) in Air Using a Molecular Sieve Trap

Michio HIROTA

Meteorological Research Institute, Koenji-kita, Suginami-ku, Tokyo 166

(Received February 8, 1978)

Synopsis. The atmospheric mixing ratio of N_2O was measured at the MRI, Koenji (Tokyo), between May and September, 1977, by a gas-chromatographic method. The mean value was 0.32_7 ppm. Judging from the measurements over the last 10 years, the atmospheric N_2O seems to have increased about 20%.

The stratospheric ozone is produced by the photochemical reaction and destroyed by reactions with such tracer components as O, NO, NO_2, HO, HO_2, and halogen atoms. If such species are released in large quantities by man's activity (SST flights or the use of aerosol sprays and nitrogen fertilizer, for instance), the natural balance of the ozone will be damaged. The depletion of the stratospheric ozone will increase the biologically harmful UV radiation on the earth's surface, and will probably lead to the climatic change.[1,2)]

The N_2O which is produced by micro-biological activity in soils and waters is the major source of the stratospheric NO. The N_2O released into the atmosphere is considered stable in the troposphere, at least stable under solar UV radiation,[3)] and is transferred to NO mainly by Reaction 1 in the lower stratosphere.[4)] In order to assess the influence of nitrogen fertilizer on the natural ozone balance, the atmospheric concentration and distribution of N_2O must also be examined.

$$N_2O + O(^1D) \longrightarrow 2NO \qquad (1)$$

The atmospheric N_2O is mainly measured by two methods, *i.e.*, the infrared spectroscopic and gas-chromatographic (GC) methods. In the latter case, N_2O is preconcentrated on a silica-gel trap[5)] or, in many cases, on a molecular sieve trap.

The method of collecting N_2O on the molecular sieve trap was first adopted by Bock and Schütz,[6)] and some improvements have since been made by Schütz *et al.*,[7)] LaHue *et al.*,[8)] and Hahn.[9,10)] In the present paper, the results of some measurements at the MRI, Koenji (Tokyo), will be reported and compared with those of recent studies.

Experimental

Sampling of N_2O. Thirty litre of air was drawn through a series of three U-shaped adsorption tubes (i.d. 8 mm) at a flow rate of 30 l/h. The first tube was filled with drierite to remove the water vapor, the second with sodium asbestos to remove the CO_2, and the third with molecular sieve 5A(1/16 in. pellets, 10 g) to adsorb the N_2O. The third tube was submerged in a Dry Ice–ethanol bath (−72 °C). Impurities were excluded from the molecular sieve by heating the tube to 350 °C and by then passing He gas (99.99%) for 1 or 2 h.

Gas-chromatographic Analysis. GC measurements were performed using a Shimadzu Gas Chromatograph GC-6AM equipped with a thermald conductivity detector (90 °C). He gas was used as the carrier gas at a flow rate of 50 ml/min.

After the sampling, the molecular sieve tube was placed in a gas sampler (Shimadzu, MGS-4). The adsorbed N_2O was transferred from the tube to the GC column by heating the tube to 350 °C. Carrier gas was passed through for 7 min and then for 10 additional min after 8 min's interruption. The N_2O was again adsorbed at 65 °C on the glass column filled with 30/60 mesh molecular sieve 5A (3 mm i.d. × 1.5 m). The GC analysis was started by raising the column temperature to 245 °C at a rate of 15 °C/min. The peak of N_2O appeared 9 min after, and that of CO_2 appeared 1 min after that of N_2O.

The detector response was linear in the range from 3.9 to 30 μl of N_2O.* For the reference measurements, N_2O was injected directly into the column from the gas syringe (Terumo, GAN- 0.25).

Results and Discussion

In 10 reference measurements of 15 μl N_2O over three days, the standard deviation (SD) was 2.4%, while it was 3% in 15 measurements over three months. The error of the calibration curve in the range from 3.9 to 30 μl N_2O was ±4%.

The amount of molecular sieve in the tube was the same as that used by LaHue *et al.*[8)] As the sampling time, however, was doubled, the tube was cooled (−72 °C) to ensure the quantitative collection of N_2O. The quantitative collection of N_2O was confirmed by the measurements of 20 μl N_2O which had been diluted with N_2** in a 30 l *aflon* bag and then trapped on the molecular sieve tube. Three measurements showed the value of 19.2±0.4 μl compared with the reference measurements of 20 μl N_2O. The total accuracy of the method was estimated as about ±7% because of 3% error of the flow meter.

Field measurements were performed 14 times between May and September, 1977, at the Meteorological Research Institute (Tokyo). The air was sampled at 1 m above a ground surface covered with weeds through a vinyl tube leading to the inside of the building.

The results were scattered widely between 0.24_8 and 0.45_4 ppm, and the mean was 0.32_7 ppm. The mean values of previous and the present studies are shown in Fig. 1. A wide distribution of the values have also been observed at Mainz, Schauinsland,[7)] and Yokohama.[11)] The values of 0.45_4 and 0.41_5 ppm were unusually high. Such high values have also been observed elsewhere.[11,12)] The values observed over the sea and in the United

---

* Assuming the N_2O mixing ratio of 3×10^{-7}, 30 l of the sampled air contains 9 μl N_2O.

** The N_2 used was 99.9995%, and a molecular sieve tube (−72 °C) was placed before the bag.

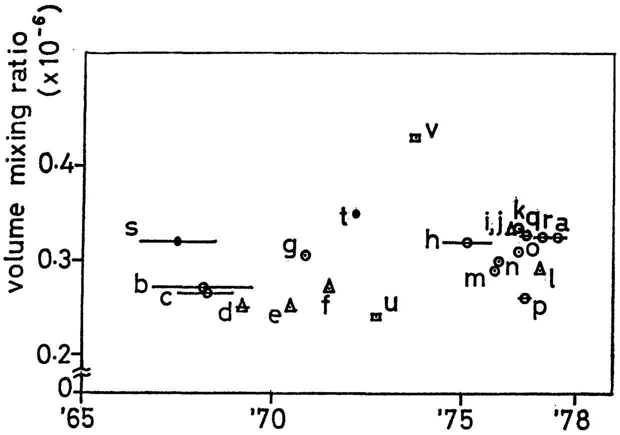

Fig. 1. Atmospheric mixing ratio of N_2O.

○; By GC method above the ground, △; by GC method over the sea, ●; by IR spectroscopic method, □; by mass spectrographic method.

(a) Present study, (b, c) Ref. 7, (d, e, f) Ref. 10, (g) Ref. 8, (h) Ref. 15, (i, j, k) Ref. 16, (l) Ref. 17, (m, n, o) Ref. 18, (p) Ref. 11, (q) Ref. 19, (r) Ref. 20, (s) Ref. 21, (t) Ref. 22, (u, v) Ref. 12.

Table 1. Atmospheric volume mixing ratio of N_2O at the meteorological research institute, Koenji

Date (1977)	Sampling start	Mixing ratio (ppm)	Date (1977)	Sampling start	Mixing ratio (ppm)
23, May	10:40	0.30_9	30, Aug.	13:50	0.30_0
24, May	16:15	0.34_3	31, Aug.	13:40	0.29_4
25, May	14:10	0.45_4	31, Aug.	16:30	0.27_0
26, May	10:00	0.30_5	1, Sep.	9:10	0.25_8
4, July	14:55	0.38_9	1, Sep.	10:10	0.30_4
5, July	11:30	0.32_7	1, Sep.	13:45	0.24_8
6, July	15:05	0.35_9	1, Sep.	17:00	0.41_5

States, on the other hand, have shown a rather small distribution.[13] The distribution must be strongly dependent on the meteorological condition of the observatory and on the sampling platform (ground station, balloon, aircraft, *etc.*). According to Ehhalt *et al.*,[12] a surface station like that of Schütz *et al.* observes both surface air with a high value and free tropospheric air; therefore, the values would be scattered widely.

The values of 4 measurements on September 1 were scattered. A similar feature was also observed by Katou *et al.*[11] Brice *et al.* reported a regular diurnal variation of N_2O on the basis of measurements over 10 days.[14]

In comparison with the mean values, especially in Refs. 7, 19, and 20, it is evident that the atmospheric N_2O has increased over the last 10 years (about 20%), at least as shown by the GC data. The value was, however, exceptionally low in Ref. 11. This variation was considered significant because the SD was 10% in the measurements of Schütz *et al.*,[7] while those of the others were all less than 3.1%, though they were not shown in Ref. 10 and 15, and the values of Katou *et al.* and the present study were very scattered.

In the calculation of the mean, unusually high values which, according to Ehhalt *et al.*,[12] did not represent the tropospheric value were also used. This is because the ground surface is considered not only as the source of N_2O but also as its sink;[14] therefore, the lower value does not neccessarily represent the tropospheric value.

References

1) CIAP Monograph, DOT-TST-75-51 (1975).
2) "Fluorocarbons and the Environment, Report of Federal Task Force on Inadvertent Modification of the Stratosphere," (1975).
3) D. H. Stedman, R. J. Cicerone, W. L. Chameides, and R. B. Harvey, *J. Geophys. Res.*, **81**, 2003 (1976).
4) M. B. McElroy and J. C. McConnell, *J. Atmos. Sci.*, **28**, 1095 (1971).
5) H. Craig and L. I. Gordon, *Geochim. Cosmochim. Acta*, **27** 949 (1963).
6) R. Bock and K. Schütz, *Z. Anal. Chem.*, **237**, 321 (1968).
7) K. Schütz, C. Junge, R. Beek, and B. Albrecht, *J. Geophys. Res.*, **75**, 2230 (1970).
8) M. D. LaHue, H. D. Axelrod, and J. P. Lodge, Jr., *Anal. Chem.*, **43**, 1113 (1971).
9) J. Hahn, *Anal. Chem.*, **44**, 1889 (1972).
10) J. Hahn, *Tellus*, **26**, 160 (1974).
11) T. Katou, Y. Hanai, and M. Mimura, *Bull. Inst. Environ. Sci. Tech., Yokohama National Univ.*, **3**, 5 (1977).
12) D. H. Ehhalt, N. Roper, and H. E. Moore, *J. Geophys. Res.*, **80**, 1653 (1975).
13) P. J. Crutzen and D. H. Ehhalt, *AMBIO*, **6**, 112 (1977).
14) K. A. Brice, A. E. J. Eggleton, and S. A. Penkett, *Nature*, **268**, 127 (1977).
15) A. L. Schmeltekopf, D. L. Albritton, P. J. Crutzen, P. D. Goldan, W. J. Harrop, W. R. Henderson, J. R. McAfee, M. McFarland, H. I. Schiff, T. L. Thompson, D. J. Hofmann, and N. T. Kjome, *J. Atmos. Sci.*, **34**, 729 (1977).
16) R. A. Rasmussen, J. Kransec, and D. Pierotti, *Geophys. Res. Lett.*, **3**, 615 (1976).
17) Y. Cohen, *Anal. Chem.*, **49**, 1238 (1977).
18) H. B. Singh, L. Salas, H. Shigeishi, and A. Crawford, *Atmos. Environ.*, **11**, 819 (1977).
19) D. Pierotti and R. A. Rasmussen, *J. Geophys. Res.*, **82**, 5823 (1977).
20) P. D. Goldan, Y. A. Bush, F. C. Fehsenfeld, D. L. Albritton, P. J. Crutzen, A. L. Schmeltekopf, and E. E. Ferguson, *J. Geophys. Res.*, **83**, 935 (1978).
21) R. Goody, *Planet. Space Sci.*, **17**, 1319 (1969).
22) A. Goldman, D. G. Murcray, F. H. Murcray, and W. J. Williams, *J. Opt. Soc. Am.*, **63**, 843 (1973).