

Concentrations of CH₄, CO, CO₂, H₂, H₂O and N₂O in the Upper Stratosphere

D. H. EHHALT, L. E. HEIDT, R. H. LUEB AND E. A. MARTELL

National Center for Atmospheric Research,¹ Boulder, Colo. 80303

(Manuscript received 12 July 1974, in revised form 23 August 1974)

ABSTRACT

On 23 May 1973 a cryogenic air sampler was flown on an Aerobee rocket from White Sands Missile Range. A large air sample was collected between 40 and 50 km altitude and successfully recovered for water vapor and trace gas analysis. The results were as follows: water vapor, $4.0^{+1.3}_{-0.3}$ ppmV; methane, 0.37 ± 0.01 ppmV; molecular hydrogen, 0.47 ± 0.02 ppmV; carbon monoxide, 0.05 ± 0.01 ppmV; carbon dioxide, 316.2 ± 2.8 ppmV; and nitrous oxide, 3 ± 7 ppb.

1. Introduction

On 23 May 1973 a cryogenic air sampler was flown successfully on an Aerobee-150 rocket from White Sands Missile Range, New Mexico (31N). An integrated air sample of 261 ± 2 liter-atmospheres was collected between 40.8 ± 0.2 km and 50.6 ± 0.2 km. The corresponding density-weighted mean altitude is 44.5 km, about 3 km below the average altitude of the stratopause.

Details of design and performance of the cryogenic air sampler have been described previously (Denton *et al.*, 1966; Denton, 1970; Martell, 1970) and here we will briefly review only those points which could lead to modifications of the trace gas concentrations. The cryogenic sampler (see Fig. 1) is essentially a large cryopump cooled with liquid Ne to 28 K. At that temperature all atmospheric gases are condensed as solids at the walls of the sampler with a practically vanishing vapor pressure except for the three noncondensable trace gases, H₂, He and Ne, which will build to a total pressure of ~ 0.01 torr during collection. Air sampling is initiated by ejecting the split nose cone and pulling off the inlet cap at the threshold sampling altitude. (The nose cone is usually filled with dry N₂ prior to launch and vented during ascent to prevent sample contamination by surface air. The cone was filled with He as a contaminant tracer in the May 1973 flight.) The sampler was closed about 10 s later by rotating the closure valve clockwise and compressing the rounded surface onto a Viton O-ring sealed seat.

During the time of collection the rocket is ascending with a velocity of ~ 1200 m s⁻¹. As a consequence a normal shock wave develops above the first condenser

coil but well behind the forward inlet. In this standing shock wave the incoming air is heated to a temperature about four times ambient (i.e., to about 1200 K) and pressurized to about 25 times ambient pressure for a period of less than 10 ms. During this period chemical reaction rates are enhanced and the more reactive gases may experience significant changes in concentration. The intruding (supersonic) air also has the beneficial effect of compressing the noncondensable gases into the rear subsonic region of the sampler chamber. As long as the shock wave remains located between the forward coil and the closure valve, the escape of the noncondensables is prevented and the collected sample is unfractionated, as has been demonstrated previously (Bieri *et al.*, 1970). The position of the shock wave is monitored in flight by measuring the differential pressure between the first coil and a point just below the forward bulkhead (see Fig. 1). In the present flight that pressure difference indicated that the shock wave front moved briefly above the upper reference point, resulting in a fractional loss of the noncondensables (see below). After sampling, the rocket system continues along its trajectory. Payload and rocket engines are separated near apogee. During descent a parachute is deployed at about 6 km altitude, lowering the sampler to the ground at a reduced speed.

2. Sample recovery and transfer

After recovery of the payload (in this instance at about 2 h after launch) the liquid Ne remaining in the heat exchanger coils was flushed out with He, the insulation space was vented, and the sampler was allowed to warm up to room temperature. Prior to sample transfer, the rocket sampler was connected to the transfer line (Fig. 2) and the connecting flexible

¹The National Center for Atmospheric Research is sponsored by the National Science Foundation.

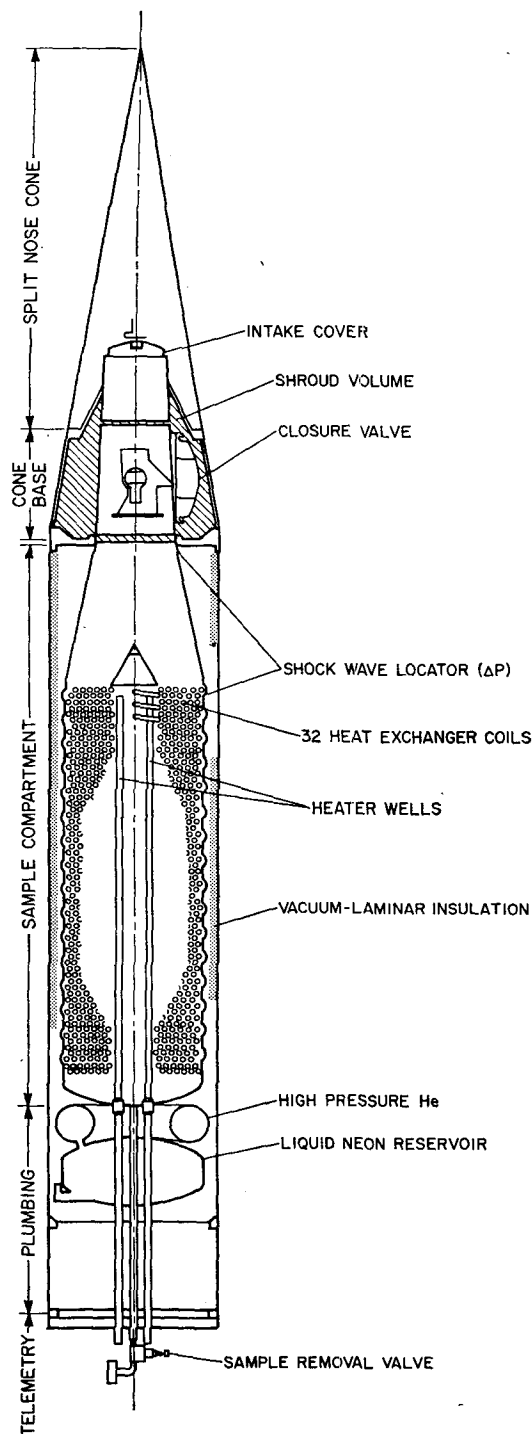


FIG. 1. Schematic diagram of the rocketborne cryogenic air sampler used on the 23 May 1973 flight.

tubing was pumped and baked to remove water adsorbed on its walls.

After warmup, which took about 7 h, the sample pressure, measured with a precision Heise pressure gauge (see Fig. 2), was determined to be 3337.5 ± 0.5

torr. At that time the sample chamber walls had not attained a uniform temperature. The rear of the compartment, close to the heavy Ne reservoir, was still $\sim 8^\circ\text{C}$ below the ambient temperature of 20°C . However, the temperature of the sampler was monitored at five points which allowed estimation of the average sample temperature ($14.5 \pm 1.0^\circ\text{C}$) fairly accurately. Based on the above pressure and temperature and the measured total volume of sampler and connecting lines ($62.3 \pm 0.4 \text{ l}$), the total amount of air collected was determined to be $11.64 \pm 0.09 \text{ mol}$ or $260.7 \pm 2.0 \text{ l STP}$.

A small portion of the air sample was transferred into four stainless steel cans of 4 l volume. Thereafter, the bulk of the sample, 238.7 l STP , was condensed into a 3 l stainless cylinder cooled with liquid Ne. During transfer the air was passed through an orifice and a liquid N_2 (LN_2) cooled cold trap which condenses H_2O , CO_2 and N_2O . The orifice of 1.1 mm diameter limited the flow rate to about 12 l min^{-1} which prevented overload of the heat exchange capacity of the condensation cylinder, and maintained the air pressure in the cold trap below 400, thereby preventing condensation of N_2 and O_2 . The cold trap was designed to freeze out H_2O , N_2O and CO_2 quantitatively at high flow rates. About 25 torr of the air sample was left behind in the sampler to serve as carrier gas during the subsequent final 400°C bakeout for recovery of the main fraction of the collected H_2O from the sampler.

The complete air sample transfer procedure had previously been rehearsed and checked to insure fractionation-free transfer of air and quantitative recovery of H_2O and CO_2 , using lab air contained in a pressurized cylinder. The results of the rehearsal demonstrated that the noncondensable gases are not fractionated during transfer, and that H_2O and CO_2 are quantitatively retained in the cold trap.

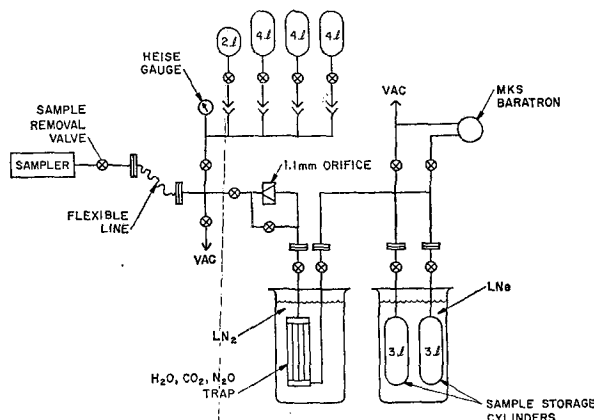


FIG. 2. Schematic diagram of the vacuum system used to transfer the air sample from the payload sample chamber into various storage containers and to separate H_2O , CO_2 and N_2O from the bulk air sample.

3. Results for Ne and He

To determine if the collected high-altitude air had experienced any fractionation, the relative concentrations of N_2 , O_2 and the rare gases were measured by mass spectrometry and compared to those measured in surface air. The concentration ratios for the rare gases were obtained after the reactive gases had been removed by circulating a 4 ℓ air sample fraction over hot calcium. Concentration ratios for the stratospheric and surface air samples were calculated by normalizing the peak heights in the mass spectra for O_2 , ^{40}Ar , 4He , ^{20}Ne , ^{84}Kr and ^{136}Xe relative to N_2 , and by assigning a value of 1.00 to the N_2 ratio between surface air and stratospheric air. The data are summarized in Table 1. They show that the condensable gases, N_2 , O_2 , Ar , Kr and Xe , in the rocket sample have the same ratio as in surface air. However, of the noncondensables, He is enriched by 40% and Ne is depleted by 14%. The depletion of Ne appears to represent a fractional loss of noncondensables due to the fact that the shock front moved forward during collection beyond the gap formed between closure valve and bulkhead (see above). This allowed $\sim 14\%$ of the noncondensable gases to pass forward into the shroud and this fraction is lost when the valve is closed. (The volume within the shroud forward of the closure valve amounts to about 15 ℓ , about one-fourth of the sampler volume of 62 ℓ .) We can expect the loss to be about the same for each of the collected noncondensables, H_2 , Ne and He .

The excess of He in the recovered sample resulted from filling the nose cone with dry He prior to launch as a tracer. From the total increase in the He (39.4% over its normal concentration in air, plus 14.2% correction for loss, or 63% above normal) we can estimate the contamination we might expect for other trace gases from the region inside the split nose cone. At the height of 40 km, where the sampler is opened, the residual partial pressure of He in the nose cone was approximately that of the ambient atmospheric pressure, 2.4 torr. This contributed an increase of about 3 ppm in He and involved only 1.8% of the gas in the nose cone space at the moment of cone deployment. All other minor gases should have very much lower partial pressures in the nose cone—even H_2O should be at least a factor of 100 lower. Thus contamination by H_2O from this source should be less than 0.03 ppm.

4. Molecular hydrogen

The concentration of molecular H_2 in each of the 4 ℓ containers was measured with a gas chromatograph as soon as the air samples were brought back to the laboratory. The technique has been described in detail elsewhere (Heidt and Ehhalt, 1972; Ehhalt and Heidt, 1973). The H_2 concentration measured in the air sam-

TABLE 1. Concentration of N_2 , O_2 and the rare gases in the rocket sample relative to those in surface air. Isotopes selected for analysis are indicated by superscript. Errors are less than ± 0.01 .

| $^4He^*$ | $^{20}Ne^*$ | $^{28}N_2$ | $^{32}O_2$ | ^{40}Ar | ^{84}Kr | ^{136}Xe |
|----------|-------------|------------|------------|-----------|-----------|------------|
| 1.394 | 0.858 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |

* He and Ne measurements were carried out by G. M. Wood, Jr., and B. T. Upchurch of the NASA Langley Research Center and D. B. Hughes of E. I. DuPont.

ples averaged 0.40 ± 0.01 ppmV. This value must be divided by a factor of 0.86 to compensate for its 14% fractional loss along with the other noncondensable gases. Thus we obtain 0.47 ± 0.02 as the H_2 concentration for the unmodified upper stratospheric air. (In calculating the error we assumed a 30% relative error in the 14% correction for the H_2 fraction lost.)

There is another possibility of H_2 loss—oxidation during passage through the shock wave. It can be shown, however, that such loss must be negligibly small. H_2 can be consumed by reaction with ground state and excited atomic oxygen, $O(^3P)$ and $O(^1D)$, as well as with the radicals OH and HO_2 . Over the altitude range of sampling the ambient number density of $O(^3P)$ is about 5×10^9 cm^{-3} , that of $O(^1D)$ 5×10^2 cm^{-3} , and that of OH and HO_2 combined about 2×10^7 cm^{-3} [values from Crutzen's (1974) one-dimensional chemical model]. Since the number density for H_2 averages about 2×10^{10} cm^{-3} , reactions of H_2 with $O(^1D)$, OH and HO_2 are negligible. The H_2 reaction rate with $O(^3P)$ at 1200 K, extrapolated from the values given by Baulch *et al.* (1972), is 8.6×10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$. This rate and the $O(^3P)$ number density in the shock wave of 1.25×10^{11} cm^{-3} give a destruction time of 9 s. This time so far exceeds the time spent by the air in the shock wave that reaction of H_2 with $O(^3P)$ can also be neglected. At 44 km altitude, the number density of O_3 is 4×10^{11} , about 10 times greater than that of $O(^3P)$. Reaction of O_3 with H_2 is too slow to influence the H_2 concentration. However, it is expected that O_3 is partly dissociated in the shock wave to form $O(^3P)$ and O_2 . Assuming complete dissociation, the destruction time of H_2 would be 0.9 s. On this basis $\sim 1\%$ of the H_2 , a conservative upper limit, is oxidized in the shock wave.

5. Methane and carbon monoxide

Previously we measured CH_4 with the same gas chromatograph used for molecular H_2 using an RF detector (Heidt and Ehhalt, 1972). We now measure CH_4 and CO with a Becker 407 instrument which uses a hydrogen flame ionization detector. After separation of CO from CH_4 on a 5 \AA molecular sieve column, the CO is converted to CH_4 by passing it over a Ni catalyst and using the H_2 which feeds the detector flame for conversion (see Porter and Volman, 1962).

N_2 is used as carrier gas and the injection system is the same as that in the system previously reported (Heidt and Ehhalt, 1972). Again air in each of the 4 l sample containers was analyzed for CH_4 and CO. The resulting mean concentrations are 0.37 ± 0.01 ppmV for CH_4 and 0.05 ± 0.01 ppmV for CO. Incidentally, it was determined that for CO, contamination from the stainless steel container walls becomes significant during prolonged air sample storage. Such contamination adds about 0.02 ppmV CO to the sample in a 4 l container during one month.

It was shown previously that shock wave heating may oxidize at most 1.5% of the CH_4 present in the collected stratospheric air (Ehhalt *et al.*, 1972). Similar considerations apply for CO. It also should be mentioned that none of these trace gases are formed in significant amounts during shock heating. Thus the measured values should closely represent the actual concentrations in the sampled stratospheric air averaged over the altitude interval of collection.

6. Nitrous oxide and carbon dioxide

During air sample transfer, the N_2O and CO_2 were recovered quantitatively together with H_2O in a LN_2 cooled cold trap (see above). Subsequently in the laboratory the cold trap was cooled to LN_2 temperature and pumped to 10^{-6} torr. The liquid N_2 coolant was then replaced by a sealed dewar containing a dry ice-butyl ether slush. The slush was pumped down to lower its temperature from about $-80^\circ C$ at atmospheric pressure to $-100^\circ C$ at 100 torr. This insured that the H_2O was quantitatively retained in the trap while CO_2 and N_2O were transferred by a Toepler pump into a special volume calibrated McLeod gauge in which the gas volume was determined to be 75.5 ± 0.3 ml STP. The N_2O - CO_2 gas mixture was divided into two fractions: one for ^{14}C analyses and the other for mass spectrometric analyses of sample purity, its ^{13}C and ^{18}O isotopic content, and the N_2O to CO_2 ratio. Except for the presence of less than 10^{-4} parts N_2O (see below), the sample consisted of pure CO_2 . Thus from the amount of gas (75.5 ml) and the amount of stratospheric air sample passed through the cold trap (238.7 ± 2 l STP) we calculate a CO_2 mixing ratio of 316.2 ± 2.8 ppmV. The isotopic data will be reported elsewhere.

The most abundant isotopic species of N_2O and CO_2 , $^{14}N^{14}N^{16}O$ and $^{12}C^{16}O^{16}O$, both have a molecular mass of 44 and could not be resolved in our Atlas M-86 mass spectrometer. However, both molecules are dissociated by the impact of the ionizing electrons in the ion source and form ions of $^{14}N^{16}O$ and $^{12}C^{16}O$ which have the masses of 30 and 28, respectively, which are easily resolved. The ratio of CO^+ to CO_2^+ ions is about 1:6, that of NO^+ to N_2O^+ about 1:2, and both ratios seem constant under constant-ion-source working conditions. In addition to $^{14}N^{16}O^+$, ions

of $^{12}C^{18}O^+$ contribute to the peak at mass 30. Since the O^{18}/O^{16} ratio in CO_2 is only about 2×10^{-3} , the contribution from CO_2 to the mass 30 peak is much less than that to the 44 peak. For a N_2O/CO_2 standard mixture, corresponding to mixing ratios in air of 0.25 and 320 ppmV, respectively, the contribution of $^{12}C^{18}O$ to the mass 30 peak is about 60%, the remainder being due to $^{14}N^{16}O$. The N_2O/CO_2 ratio in the sample mixture is measured by comparing the ratio of the peak heights at mass 30 and 44, to those for a set of standard N_2O/CO_2 mixtures covering the concentration range of interest, including pure CO_2 . The peak height ratios of mass 30 to mass 44 are directly proportional to the N_2O mixing ratio in CO_2 which allows for accurate measurement. A small correction for the difference in the ^{18}O content of CO_2 in the sample and standard mixture must be applied. Details of the method will be described elsewhere. Analyses of the stratospheric sample gave a N_2O/CO_2 ratio of $(9.5 \pm 22) \times 10^{-6}$ which corresponds to a N_2O volume mixing ratio of 3 ± 7 ppb in the upper stratosphere based on the CO_2 mixing ratio of 316 ppmV.

It can be shown that thermal decomposition or other reactions of N_2O in the shock wave are too slow to influence the N_2O concentration (cf. Johnston, 1951). Thus the measured value should reliably represent the N_2O concentration in the upper stratosphere.

7. Water vapor

The measurement of the stratospheric H_2O concentration presented a number of experimental difficulties. These were due to numerous sources of H_2O contamination inherent in the design of the cryogenic sampler. In order to provide an adequately rapid heat exchange, the sample chamber walls have a large internal surface area, about $10 m^2$, from which adsorbed water has to be removed. This requires that the sampler be baked out and evacuated thoroughly prior to launch. For purposes of bakeout, two heating rods are inserted into guide tubes leading from the rear into the interior of the sampler. Unfortunately, the desired bakeout temperature of $400^\circ C$ cannot be maintained uniformly throughout the sampler because Viton O-rings, which are used as seals around the bulkhead, cannot be subjected to temperatures exceeding $200^\circ C$. A prolonged bakeout time of about four weeks is required to reduce the residual wall water to an acceptable degree.

Another problem is presented by the inlet opening and valve closure procedure of the sampler, dictated by the short sampling time and high rocket flight velocity. As a result, the inlet valve remains open prior to launch and allows diffusion of water vapor from the forward section back into the sample chamber. This forward section contains a lubricated valve mechanism which can only be baked to $100^\circ C$ and

continues to outgas H₂O at a rate of 1-2 mg of H₂O per day even after weeks of degassing under vacuum.

To reduce the H₂O contamination problems to the extent practicable, the following bakeout procedure was developed and tested. The sampler with the closure valve open is baked at ~400°C and evacuated through a valve in the inlet diffuser wall for 14 days for "rapid" removal of most of the adsorbed water. Thereafter, a flow of dry N₂ is maintained forward through the sampler during continued baking to prevent backstreaming of H₂O from the closure valve section. The N₂, dried by passing it through a pair of LN₂ cooled cold traps of special design, enters at the rear of the sample compartment, passes forward through the sample removing valve, and is pumped out at the forward end. The outgassed H₂O is collected in a second pair of cold traps. This procedure requires about 14 days or longer, depending on the rocket launch date. About four days prior to launch when the payload is moved into the launch tower, baking is discontinued and the sampler is kept full of dry N₂. After tower installation of the payload, N₂ flow is resumed and continued until 12 h prior to launch. Thereafter, the sample chamber is evacuated continuously prior to precooling the heat exchanger coils with He at LN₂ temperature and filling the cooling coils and reservoir with LNe.

Our laboratory bakeout rehearsals showed that even with these precautions, the amount of contaminant wall water left in the sample chamber prior to sampling would be about 5 mg, mainly due to backstreaming from degassing in the forward section. This is about ten times the amount of H₂O we expected to collect in the stratosphere. Thus to obtain useful information on the stratospheric H₂O concentration, we must rely on isotopic measurements to assess the contribution of contaminant wall water. The substantial contamination from wall water was confirmed by the size and isotopic composition of the H₂O fractions recovered after the actual rocket sampling flight, shown in Table 2. Fraction #1 is the H₂O recovered during air sample transfer at White Sands Missile Range. Most of the H₂O in the air sample was recovered as fraction #2 during laboratory bakeout at 400°C for one week. During H₂O recovery, the same transfer line and an identical LN₂ cooled trap were used. Before recovering fraction #3, 2 mg of water with a deuterium (D) content² of 0‰ and a negligible tritium (T) content were injected into the sampler and allowed to adsorb on the walls for one day prior to H₂O recovery. This was done to assess whether most of the T had been recovered and to estimate

TABLE 2. The deuterium (D) and tritium (T) content of the water vapor fractions. The first fraction was obtained during transfer at WSMR, the second during a bakeout at 400°C for one week. The third was recovered after adding 2 mg of H₂O with a D content of 0‰ and a T content of 0 T.U. into the sampler and baking it for one week.

| Fraction | Amount of H ₂ O (mg) | T content (T.U.)* | D content (‰)** |
|----------|---------------------------------|---------------------------|-----------------|
| #1 | 0.10 | (3.0±0.1)×10 ⁶ | -171±1 |
| #2 | 5.7 | (2.2±0.1)×10 ⁶ | -150±1 |
| #3 | 2.6 | (2.7±0.2)×10 ⁶ | -54±1 |

* 1 T.U. corresponds to the isotopic ratio, T/H=10⁻¹⁸.

** The D content is given in ‰ relative to SMOW (Standard Mean Ocean Water).

how much H₂O was left in the sampler. The isotopic composition of the contaminant wall water also was measured. Its D content was δ_w(SMOW) = -134±1‰, determined for the last water fraction collected during preflight bakeout. The T content of the wall water was about 200 T.U., completely negligible compared to that of the high-altitude water (Table 2) and corresponds to the T content of the water used to rinse the sampler prior to final preflight bakeout.

The isotopic data (Table 2) indicate that of the total T, 93% was contained in H₂O fraction #2. Since the wall water was essentially free of T, this means that 93% of the collected stratospheric water is contained in fraction #2. Unfortunately, the T content of water vapor in the upper stratosphere is not known. However, its D content can be estimated. Thus we make use of an isotopic balance equation [(2)] in addition to the mass balance equation [(1)] and can calculate the amount of stratospheric water in fraction #2:

$$\text{Mass balance: } [H_2O]_w + [H_2O]_s = [H_2O]_2, \quad (1)$$

$$\text{D balance: } [H_2]_w \delta_w + [H_2O]_s \delta_s = [H_2O]_2 \delta_2. \quad (2)$$

TABLE 3. Concentrations of trace gases in high-altitude air samples collected on rocket flights on 23 May 1973 and 4 September 1968. Both flights were made over White Sands Missile Range, (31N).

| Trace gas | Flight of 23 May 1973 (40.8-50.6 km altitude) | Flight of 24 September 1968 (43.6-62.3 km altitude) |
|------------------|---|--|
| H ₂ O | 4.0 ^{+1.3} _{-0.9} ppmV | 3-10 ppmV ¹ |
| CH ₄ | 0.37±0.01 ppmV | 0.25±0.02 ppmV ² |
| H ₂ | 0.47±0.02 ppmV | 0.40 ^{+0.50} _{-0.10} ppmV ¹ |
| CO | 0.05±0.01 ppmV | not measured |
| CO ₂ | 316.2±2.8 ppmV | 308±3 ppmV ³ |
| N ₂ O | 3±7 ppb | 0.3±7.0 ppb ⁴ |

¹ Scholz *et al.* (1970).

² Ehhalt *et al.* (1972).

³ Martell (1973).

⁴ Unpublished.

² The D content is given as a δ value (unit: per mil), defined as the relative deviation of the D/H ratio of the sample from that of standard mean ocean water, SMOW:

$$\delta = 1000[(D/H)_{sa} - (D/H)_{SMOW}] / (D/H)_{SMOW}.$$

It follows that

$$[\text{H}_2\text{O}]_S = [\text{H}_2\text{O}]_2 \frac{\delta_2 - \delta_W}{\delta_S - \delta_W}, \quad (3)$$

where the subscripts S, W, 2 refer to stratosphere, wall and fraction #2. All quantities on the right-hand side of (3) have been measured except δ_S which can be estimated as follows: 23 measurements of the D content of water vapor in the lower stratosphere at around 13 km altitude show an average $\delta(\text{SMOW}) = -373 \pm 22\%$ (Ehhalt, 1974). Water vapor in the upper stratosphere has an additional contribution from the oxidation of CH_4 which has to be considered. The few measurements of the D content in tropospheric CH_4 (Ehhalt, 1973) show an average $\delta(\text{SMOW}) = -102 \pm 9\%$. The errors quoted are the standard deviations of the means. It is assumed that the contribution of water vapor from CH_4 oxidation has the same D content as tropospheric CH_4 . This should be approximately true. It also is assumed that 3/5 of the water vapor in the upper stratosphere is derived from the lower stratosphere and 2/5 from CH_4 oxidation. These contributions appear to be reasonable on the basis of the generally accepted assumption that the total elemental hydrogen mixing ratio in the stratosphere remains constant with altitude. We assume that the error in the above fractional contributions is unlikely to exceed 1/10. With these assumptions we estimate a D content of $\delta_S = -265 \pm 35\%$ for water vapor in the upper stratosphere.

Inserting δ_S into the above equation, we obtain 0.7 mg H_2O for the stratospheric water content of fraction #2. To include the stratospheric water vapor contained in fractions #1 and #3 we have to multiply this value by 1.08. Thus the total amount of stratospheric water vapor recovered was $0.76^{+0.25}_{-0.18}$ mg, which corresponds to a volume mixing ratio of $4.0^{+1.3}_{-0.9}$ ppmV.

8. Summary and conclusions

The trace gas results are summarized in Table 3 and compared to the data obtained for a previous rocket sampling flight on 4 September 1968. The two sets of data agree rather well. The water vapor measurement has been improved considerably, mainly due to the fact that the wall water contamination was decreased by about a factor of 5 and that more reliable data on the D content of water vapor in the lower stratosphere became available. The difference in CH_4 results reflects the decrease in CH_4 concentration with altitude. These two results establish the fact that CH_4 is present in significant concentration near the stratopause. The two H_2 measurements show good agreement. Our present CO measurement is the only result for CO at rocket altitudes. No other experimental data are available. There is an apparent discrepancy in the two CO_2 concentrations. However, the tropospheric CO_2 concentration increased by about 4 ppmV

between 1968 and 1973. Assuming a corresponding increase with time near the stratopause, the two CO_2 measurements agree within their error limits. However, both CO_2 results are significantly lower than the CO_2 concentration in the troposphere. Along with N_2O measurement of the 1973 rocket sample we also determined the N_2O content of the 1968 sample. The 1973 sample result indicates a somewhat higher N_2O concentration than that of the 1968 sample. The sampling altitude interval also was somewhat lower. However, within error limits the difference is not significant, both measurements indicating a N_2O concentration of essentially zero.

The present rocket results (Table 3), together with recently published balloon flight data (Ehhalt *et al.*, 1974), make it possible to construct stratospheric profiles for some of these trace gases up to 50 km.

Acknowledgments. We are pleased to acknowledge the excellent support of E. H. Denton and R. B. Jacobs with cryogenic sampler payload preparations and of George Kraft and L. C. Briggs for Aerobee launch and payload recovery at White Sands Missile Range. We also thank G. M. Wood, Jr., B. T. Upchurch and D. B. Hughes who carried out the helium and neon measurements.

This research was jointly supported by the National Aeronautics and Space Administration under Contract NASr-224 and by the National Center for Atmospheric Research.

REFERENCES

- Baulch, D. L., D. D. Drysdale, D. G. Horne and A. C. Lloyd, 1972: *Evaluated Kinetic Data for High Temperature Reactions*, Vol. 1, *Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-O}_2$ System*. Butterworths, London, 433 pp.
- Bieri, R. H., M. Koide, E. A. Martell and T. G. Scholz, 1970: Noble gases in the atmosphere between 43 and 63 kilometers altitude. *J. Geophys. Res.*, **75**, 6731-6735.
- Crutzen, P., 1974: A review of upper atmosphere photochemistry. *Can. J. Chem.*, **52**, 1569-1581.
- Denton, E. H., 1970: Rocketborne cryogenic air samplers. *Sci. Prog.*, **58**, 539-561.
- , J. Hord, R. B. Jacobs and E. A. Martell, 1966: Preliminary design, ENCAR-1 rocketborne cryogenic air sampler. National Center for Atmospheric Research, Tech. Note NCAR-TN-8, 136 pp.
- Ehhalt, D. H., 1973: Methane in the atmosphere. *Carbon and the Biosphere*, G. M. Woodwell and E. V. Pecan, Eds. *Proc 24th Brookhaven Symposium in Biology*, Upton, N. Y., 16-18 May 1972, 144-158.
- , 1974: Vertical profiles of HTO, HDO and H_2O in the troposphere. National Center for Atmospheric Research, Tech. Note TN/STR 100, 131 pp.
- , and L. E. Heidt, 1973: The concentration of molecular H_2 and CH_4 in the stratosphere. *Pure Appl. Geophys.*, **106-108**, 1352-1360.
- , —, and E. A. Martell, 1972: The concentration of atmospheric methane between 44 and 62 km altitude. *J. Geophys. Res.*, **77**, 2193-2196.
- , —, R. H. Lueb and N. Roper, 1974: Vertical profiles of CH_4 , H_2 , CO, N_2O and CO_2 in the stratosphere. *Proc. III*

- CIAP Conference*, February, 1974, Boston, Mass., U. S. Department of Transportation.
- Heidt, L. E., and D. H. Ehhalt, 1972: Gas chromatographic measurement of hydrogen, methane and neon in air. *J. Chromatogr.*, **69**, 103-113.
- Johnston, H. S., 1951: Interpretation of the data on the thermal decomposition of nitrous oxide. *J. Chem. Phys.*, **19**, 663-667.
- Martell, E. A., 1970: High altitude air sampling with a rocketborne cryocondenser. *J. Appl. Meteor.*, **9**, 170-177.
- , 1973: The distribution of minor constituents in the stratosphere and lower mesosphere. *Physics and Chemistry of Upper Atmosphere*, M. B. McCormac, Ed., Reidel, Dordrecht-Holland, 24-33.
- Porter, K., and D. H. Volman, 1962: Flame ionization detection of carbon monoxide for gas chromatographic analysis. *Anal. Chem.*, **34**, 748-749.
- Scholz, T. G., L. E. Heidt, E. A. Martell and D. H. Ehhalt, 1970: Water vapor, molecular hydrogen, methane and tritium concentrations near the stratopause. *J. Geophys. Res.*, **75**, 3049-3054.