Balloon-borne low temperature air sampler

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(Received 16 December 1974; in final form, 27 February 1975)

Design, construction, and performance of a balloon borne low temperature air sampler are described. The sampler can collect 16 samples of 10 liter STP at different stratospheric altitudes. The collected samples allow measurement of the trace gases H_2, H_2O, CH_4, CO, CO_2, and N_2O. In the future, measurements will include the Freons, CCl_4, SF_6, CH_3OH, and ΣNO_x; also, the altitudes will be extended from the present 35 km to above 45 km.

INTRODUCTION

A number of methods have been devised to study the composition of the stratosphere.[1] In the past we have made a number of balloon flights using a grab sampling system to collect samples of stratospheric air. The samples, 4 liters of air at ambient pressure, were then analyzed by gas chromatography for their H_2, CH_4, and Ne content, later also for their CO content. This method has the advantage that the collection device is rugged and simple and that the most sensitive laboratory instruments can be used to measure concentrations in the ppm range. Grab sampling, however, is disadvantageous because the samples collected become smaller with altitude (23 cm^3 STP at 35 km altitude). Thus outgassing from the sample container walls becomes an increasing problem with altitudes, especially for CO, but also for H_2. For this reason we decided to replace the grab sampler with a low temperature sampling system which allows the collection of large samples (10 liters STP) at any altitude reached by the balloon. This eliminates the contamination problem completely. The larger samples have the additional advantage of allowing the measurement of a larger number of trace gases as well. A first version of the low temperature sampler designed to collect eight samples of 5 liters STP was flown on 9 September 1973. The second sampler capable of collecting 16 samples was flown on 7 May 1974 to a maximum altitude of 35 km. Both flights demonstrated the ability of the system to bring back large contamination- and fractionation-free air samples from the stratosphere. Vertical profiles of H_2, CH_4, CO, CO_2, and N_2O obtained on the first flight have been published.[2] In the meantime we developed a method to measure H_2O in the larger samples, and we are presently setting up to measure Freons. Other low temperature whole air samplers are being developed at the National Bureau of Standards and Air Force Cambridge Research Laboratories.[3] The intent of this paper is to describe construction and performance of the low temperature sampler developed at NCAR in more detail and to demonstrate the integrity of its samples for the trace gases under investigation.

METHOD

Low temperature sampling is based on the fact that at liquid Ne temperature most gases in air are condensed into solids with vapor pressures below 10^{-4} Torr (e.g., at 30 K $p_{N_2} \simeq 3\times10^{-5}$ Torr, and $p_{O_2} \simeq 2\times10^{-7}$ Torr). In this system, the sample containers are partially immersed in liquid Ne and thus act as "cryopumps." The attainable pumping speeds are considerable; even at the lowest inlet pressure of 1 Torr, the cryosystem maintains a volume flow of 23 liters/min (compare Fig. 4). H_2, He, and Ne are not condensed at 30 K and remain gaseous. With the samples described below, 10 liters STP are collected into a volume of 0.8 liter. In that case, the noncondensables build up to a residual pressure of about 0.025 Torr, neglecting cryotrapping of the noncondensables. Thus, provision has to be made to prevent back diffusion of the noncondensables lest fractionation of the sample occur. Another important design criterion is cleanliness of the internal surfaces to prevent contamination from outgassing or desorption of trace gases from the walls.

THE SYSTEM

A. Sample cylinders

The sampling system consists of 16 stainless steel cylinders, 70 cm long and 3.8 cm diam, partially immersed in liquid Ne. Each cylinder is connected to a common manifold by a bellows-sealed stainless steel high vacuum valve which is driven by a 28 V dc motor (Fig. 1). Each motor drives its valve through a clutch which insures proper torque for leak-tight closure. The design of the individual tube is shown in Fig. 2. Tubes used to sample altitudes below 30 km are fitted with a Nupro SS-4H valve with a flow coefficient of 0.24. The four tubes sampling the highest altitudes, and therefore requiring faster flow rates, are equipped with the larger Nupro SS-8TW-SW valve with a flow coefficient of 1.2.

Because of the high sample pressures reached when the sample warms to room temperature, for safety a stainless steel rupture disk is welded into each sample cylinder extension tube just below the motor-driven Nupro valve. The cylinders have been pressure tested to 170 atm without permanent deformation, and the rupture disk burst pressure is set at 102 atm. The sample cylinders are attached to the manifold by compression fittings. Thus, they can be individually removed from the manifold and attached to the gas chromatograph inlet system.

The extension tube extends 10 cm beyond the mounting flange into the sample cylinder. Thus, the airflow has to pass

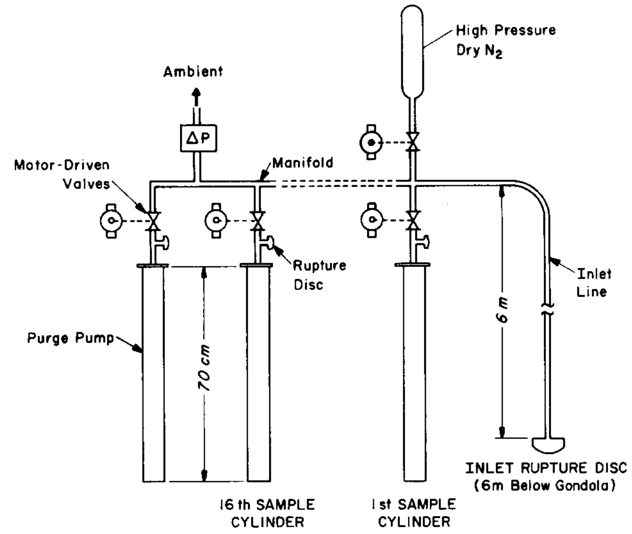

FIG. 1. Schematic of the basic components of the balloon borne low temperature sampler. Sample cylinders are actually arranged in concentric circles of eight cylinders each with the purge pump in the center. The sample cylinders are submerged in liquid neon in a 33 cm i.d., 76-cm deep Dewar.

20 cm of 7.7 mm i.d. tubing between the valve and the cooled sample cylinder. This suffices to prevent diffusion of noncondensed H_2, He, and Ne out of the sample cylinder, because the bulk flow is much larger than and opposite to the diffusive flow. This can be estimated from the following consideration. Even at the lowest sampling altitude where the airflow is highest, the Reynolds number is about 500, indicating laminar flow. Thus diffusion of the noncondensables is governed by molecular diffusion. Assuming the air to move (with the bulk velocity w) uniformly over the cross section of the tube, one obtains for the concentration distribution along the tube $C(z)=C_0\cdot\exp(-w/D^z)$, where C is the concentration and D is the molecular diffusion coefficient. The characteristic length with which the concentration decreases from a value C_0 in the sample cylinder is D/w. Under the measured flows and pressures D/w lies between 0.01 and 0.02 cm for H_2. Therefore, the buildup of H_2 in the sample cylinder is not measurable a few centimeters upstream of the end of the extension tube and certainly does not reach the valve. The lack of fractionation was also confirmed by measuring the Ne content of inflight samples (see below).

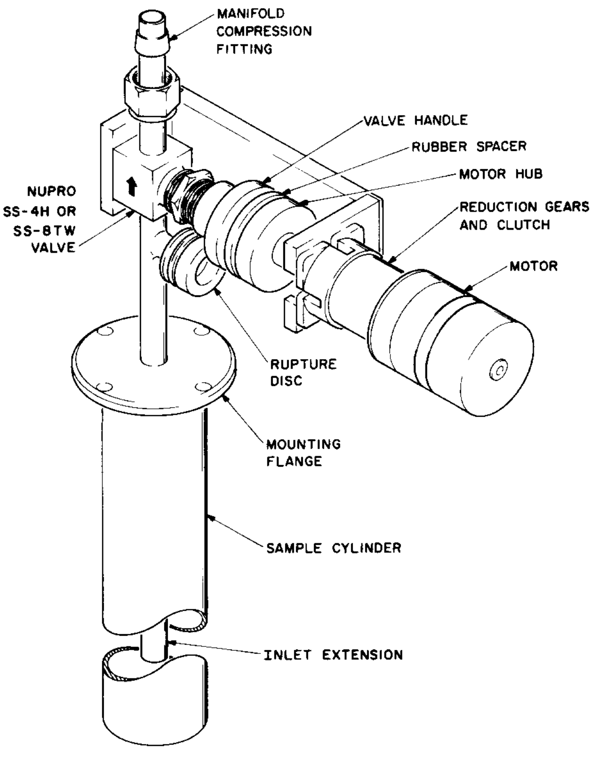

FIG. 2. Sample cylinder with motor-driven valve. Note the rupture disk and inlet extension into the cylinder.

To reduce outgassing of the sample cylinders, all surfaces exposed to the sample were electropolished and vacuum baked at 400°C, except the valves which were heated only to 200°C. This serves to reduce the outgassing rates of H_2O, H_2, and CO by several orders of magnitude.[4] To reduce the outgassing of H_2 even further, the cylinders were filled with O_2 while at bakeout temperature to provide oxide passivation of the stainless steel.[5] Inlet line and sample manifold were treated the same way. Sample contamination due to outgassing of CO and H_2 was checked experimentally and is reported below.

B. Dewar and inlet line

The sample cylinders are arranged in two concentric circles of eight cylinders each on the cover plate of the liquid Ne Dewar and are held in position leaktight by the O-ring sealed mounting flanges (Fig. 2). The center of the cover plate is occupied by a sample cylinder with somewhat larger volume which serves as a purge pump to flush the inlet line and manifold with ambient air prior to sampling (see Fig. 1). The Dewar is commercially available and has an inner diameter of 33 cm and a depth of 76 cm. It is filled with liquid Ne to 15 cm below the top before flight. This keeps the liquid Ne level below the extension tubes whose temperature therefore remains sufficiently above liquid Ne temperature to prevent the plugging of the extension tubes by solid air. Filling of the Dewar requires 40–50 liters Ne. This amount provides enough cooling capacity to last through a 15-h flight and allows the last samples to be condensed at full rate (see Fig. 4). The Dewar is maintained at a pressure of 0.5 atm above ambient by relief valves to prevent freezing of the cryogen at pressures below the triple point of neon during flight. The cold Ne boil-off gas is warmed to ambient temperatures in a black aluminum "ballast tank" and vented through a hose 20 m above the gondola. Sample analysis shows that this measure prevents the vented Ne from contaminating the air samples (see below). The cover plate of the Dewar is thermally insulated below by a layer of 5 cm of Styrofoam. A layer of Styrofoam balls is spread 5 cm deep on top of the liquid Ne to add to the thermal insulation and to prevent sloshing of the liquid Ne during the abrupt motions of the launch.

The partially flexible inlet line is attached to the manifold by a Swagelok compression fitting and extends 6 m below the gondola to avoid contamination exhaled by the payload. The inlet line intake is capped with a stainless steel rupture disk which is burst after reaching float altitude. This is accomplished by temporarily opening a motor-driven valve

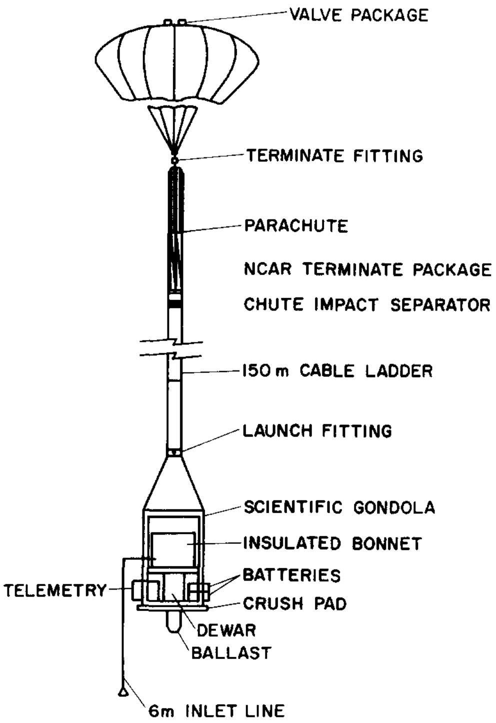

FIG. 3. Balloon flight train. Note the gondola 150 m below the parachute and inlet 6 m below gondola.

connecting the inlet line to a stainless steel cylinder containing high pressure, dry N_2 gas (Fig. 1). This procedure is designed to prevent absorption of water vapor in the baked out inlet line before launch and during the ascent through the moist troposphere. An auxiliary inlet line can be opened by a motor-driven valve if the rupture disk should fail to burst. In that event only the H_2O profile would be lost. Before each launch the assembled sampling system is helium leak checked and again vacuum baked for approximately four days. Bakeout effectiveness for the various gases is monitored with a small mass spectrometer (residual gas analyzer).

AUXILIARY MEASUREMENTS AND COMMAND SYSTEM

A number of auxiliary measurements are performed during the flight and telemetered to the ground to check proper functioning of the system and to provide additional information about the atmosphere. The measured parameters are converted into a 0–5 V analog signal which is then telemetered to the ground with a standard IRIG FM/FM telemetry system supplied by NCAR's National Scientific Balloon Facility at Palestine, Texas. An important operational parameter monitored is the pressure in the inlet line which, during the bursting of the inlet rupture disk, builds up to about 10 atm and is then suddenly released. A step voltage verifies which sample cylinder is selected. The current of the motors drives the valves; the time variation of this current analog indicates proper opening and closure of the valves. The pressure drop along the inlet line indicates the start and end of sample inhalation and rate of airflow. In addition, thermistor voltages indicating the temperature at battery, ozonesonde, and manifold are also recorded. Atmospheric parameters recorded are ambient temperature, pressure, and ozone concentration. The latter is monitored with a Komhyr-type potassium iodide ozone detector.

The command system, also supplied by the National Scientific Balloon Facility, provides 45 separate pulse code modulation (PCM) commands for the experimenter. All commands actuate 28 V dc, 30 mA latching relays to select, open, and close the motor-driven valves and perform other functions in the sampling sequence.

INFLIGHT OPERATION

The sampling system, together with a battery pack and telemetry system, is housed in a gondola with a total weight of 275 kg. A 1.05×10^5 m^3 balloon is needed to carry the payload to a 35 km altitude. The balloon train is shown in Fig. 3. The gondola is suspended about 150 m below the balloon to minimize contamination from the outgassing of the large balloon surface. About 30 min before balloon inflation and after a thorough final checkout of the telemetry system, the Dewar is filled with liquid Ne. To conserve liquid Ne, the Dewar is precooled with liquid N_2, which is blown out with He after the payload has reached the launch pad. During the ascent to maximum altitude, which takes about 1.5 h, temperature and O_3 are monitored continuously, and the purge pump is opened to remove any residual gas from manifold and inlet line. The temperature and O_3 data are used to determine the location of the tropopause, and if it deviates considerably from the predicted one, the preselected sampling altitudes are rearranged slightly. After reaching maximum altitude the balloon is kept at float for a period of 2 h to allow outgassing of the gondola and balloon. The first sample is also taken during the latter part of the float to serve as a control for contamination coming from balloon and gondola. To do this the purge pump is closed and the rupture disk burst open on command from below. After flushing the inlet line and manifold with ambient air 20 times its volume by reopening the purge pump, the first sample cylinder is opened for 20 min. The only contamination found so far was H_2O, for which the float sample on 7 May 1974 showed a volume mixing ratio of 21 ppm, as compared to 5.4 ppmV for the first sample during descent. All other samples are taken during descent to insure that any contamination from the gondola is swept upward and away from the intake by the relative air motion. The sampling rates attained at each altitude are shown in Fig. 4. The curves were obtained by inhalation experiments in the laboratory simulating inflight conditions and using the

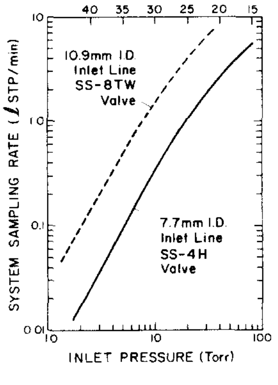

FIG. 4. System sample-rate vs altitude/inlet pressure for the low temperature sampler. Solid line indicates 7.7 mm i.d. inlet line with SS-4H Nupro simple valve, and broken line indicates 10.9 mm i.d. inlet line and SS-8TW-SW Nupro simple valve.

actual inlet line manifold and liquid Ne cooled sample cylinder. The dashed curve gives the sampling rate for the bigger SS-8TW Nupro valve and the presently used 10.9 mm i.d. inlet line. The full curve represents the sampling rate for the SS-4H Nupro valve with the 7.7 mm i.d. inlet line used in the first version of the sampler. The curves were well confirmed by the inflight sampling rates calculated from the amount of stratospheric air collected and the sampling time. The sampling rates for the combination of SS-4H Nupro valve and 10.9 mm i.d. inlet line which is presently used at altitudes below 30 km lie about a factor of 1.5 above the full curve. For inlet pressures above 10 Torr, i.e., below 30 km altitude, most of the pressure drop occurs across the SS-4H Nupro valve. At inlet pressures higher than 30 Torr, i.e., at flow rates 21 liter STP/min, the internal resistance of the sample cylinder starts to become significant. From Fig. 4 we readily obtain the sampling times required for a 10 liter STP sample at each altitude (for example about 20 min at 35 km altitude). After float, the balloon is brought to a slow descent of about 50 m/min and leveled off to slower descent rates around the higher sampling altitudes to prevent the balloon from falling too much during sampling. At the upper altitudes the height interval over which the sampling is done is about 0.5 km. At altitudes below 25 km the sampling rate is fast enough that the balloon is allowed to fall with a constant descent rate of 50 m/min. Ozone, temperature, and pressure are monitored continuously during the flight. After completion of the sampling series, the balloon is allowed to descend at a faster rate to around 12 km. The balloon is eventually cut off, and the payload returns to the ground on a parachute. We attempt to have a recovery crew as close as possible to the landing site and a member of our group present to inspect possible damage to the payload and to take the necessary precautions for safe surface transport of the samples.

EXPERIMENTAL CHECK OF SAMPLE CONTAMINATION AND FRACTIONATION

Contamination from the outgassing of the stainless steel[1] walls is expected for some of the trace gases, especially H_2O, H_2, and CO. Bakeout of the system to 400°C removes H_2O adsorbed at the stainless steel walls sufficiently well to eliminate that contamination problem. Details of the precautions taken, together with the method used for analyzing the water vapor content in the low temperature samples, will be published elsewhere. To test sample integrity with respect to the CO and H_2 concentrations several experiments were performed. To test for outgassing, the entire sampling system was filled to 1000 Torr with ultra-pure grade nitrogen containing no H_2, CO, or CH_4. A sample of the nitrogen gas was analyzed during the filling process, and each sample cylinder was monitored after a period of about two weeks. No H_2, CO, or CH_4 could be detected in any of the samples by our gas chromatographs, which have a detection limit of 0.003 ppmv for these gases. Therefore, at sample pressures above 1000 Torr, contamination of CO, H_2, and CH_4 from the walls is negligible.

TABLE I. Comparison of trace gas concentrations in air samples with and without O_3. Concentrations in ppmv.

	Ne	H_2	CH_4	CO
Tube No. 1				
(without O_3)				
after 10 min	20.0±0.5	0.96±0.03	2.47±0.03	1.20±0.03
after 5 days	20.4±0.5	0.99±0.03	2.48±0.03	1.31±0.03
Tube No. 2				
(5 ppmv O_3)				
after 10 min	20.0±0.5	0.97±0.03	2.51±0.03	1.28±0.03
after 5 days	60.0±0.5	0.96±0.03	2.48±0.03	1.26±0.03

TABLE II. Test of sample fractionation during condensation of air. Concentration of trace gases in ppmv.

	Ne	H_2	CH_4	CO
Air in tank before run	18.4±0.5	1.01±0.03	1.47±0.03	1.24±0.03
Air in tank after run	17.9±0.5	0.98±0.03	1.50±0.03	1.24±0.03
Condensed sample	17.4±0.5	1.01±0.03	5.47±0.03	1.27±0.03

Another experiment was conducted to insure that none of these trace gases were removed from the sample by adsorption from the wall or by reaction with O_3 on the surfaces. Compressed air was filled into two tubes simultaneously; directly into tube no. 1, and through a Welsbach ozone generator into tube no. 2. The ozone generator added about 5 ppmv O_3 to the compressed air. Both samples were analyzed on the gas chromatograph within 10 min after filling and again 5 days later. The concentration data are shown in Table I. Neither sample shows any reduction in the concentration of H_2, CH_4, and CO, indicating that adsorption or reaction with O_3 on the cylinder walls can also be neglected.

Finally, fractionation was checked by simulating inflight sample collection in the laboratory. Air from a large pressure tank, which had been previously analyzed for its trace gas concentration, was reduced to 80 Torr, passed through the inlet line and manifold, and condensed into a liquid neon cooled sample cylinder. The results of the analyses are shown in Table II. No fractionation could be detected. This is also confirmed by the sample collected in flight which, within the error of the measurement, shows a neon concentration of 18.2 ppmv, the concentration in air.

ACKNOWLEDGMENTS

The authors would like to thank the NCAR machine shop and Russell White in particular for skillful and conscientious fabrication and assembly of the gondola and sampler parts; Walt Pollock for his valuable help in launch preparations and payload recovery; and the National Scientific Balloon Facility for excellent cooperation and efficient support.

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

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