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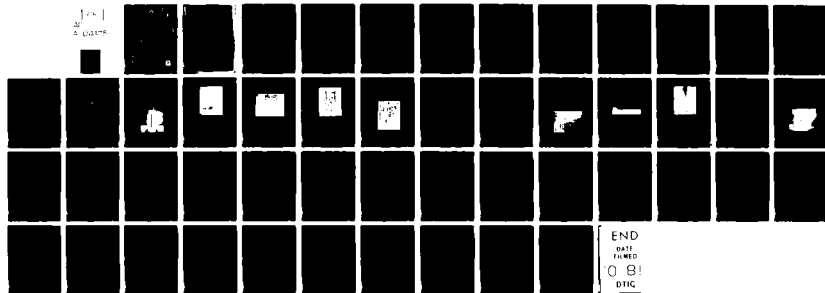   STRATOSPHERIC TRACE GAS COMPOSITION STUDIES UTILIZING IN SITU C--ETC(U)
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Stratospheric Trace Gas Composition Studies Utilizing In Situ Cryogenic, Whole-Air Sampling Methods.

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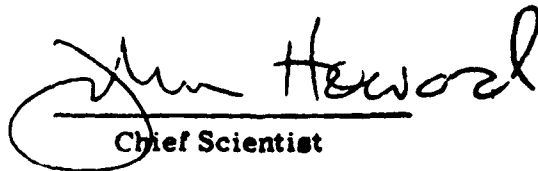
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A balloon borne cryogenic whole air sampler (tri-sampler) is used to obtain one-mole sample quantities at each of three altitudes on a single flight. Samples have been obtained at six altitudes from 12 to 30 km at each of five latitudes from 9°N to 64°N. The samples are maintained frozen until just prior to analysis; chemiluminescence and gas chromatography techniques are used to determine mixing ratios of NO, NO_2, N_2O, $CFCl_3$ and CF_2Cl_2. Variations in mixing ratios with altitude and latitude have been noted, but no variations with time within the stratosphere have been detected over the five-year duration of

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the flights. Gas calibration procedures include two dynamic dilution methods and one permeation tube method, with close agreement among the methods being noted.

Preface

The authors wish to thank Rocco S. Narcisi for initiating the study and for his continued assistance and encouragement; Hans Laping and Alan Bailey for electronics design; M/Sgt. Anthony Coriaty, John Borghetti, and S/Sgt. Richard Ganion for their generous assistance both in the laboratory and field programs; and to the many others within LKD, Det. 1, LC and SU who provided continuing support.

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Contents

Illustrations

Tables

Stratospheric Trace Gas Composition Studies Utilizing In Situ Cryogenic, Whole-Air Sampling Methods

1. INTRODUCTION

The trace gas composition of the stratosphere has received intensive investigation since the early 1970's. The concern that anthropogenic influences might be causing chemical reactions leading to catalytic destruction of the ozone layer is the motivative factor. This tenuous layer, primarily with the lower stratosphere, has effectively filtered the harmful solar ultraviolet radiation that would have impinged on the surface of the earth.

Of particular concern to the Air Force are emissions from Air Force flight operations in the stratosphere, as well as the upward diffusion from ground level of chlorofluoromethanes, widely used in several Department of Defense (DOD) applications. Both sources have been postulated to affect the ozone budget.

In 1974, a program was initiated at the former Air Force Cambridge Research Laboratories for the purpose of obtaining whole air samples cryogenically in the lower stratosphere through use of a balloon platform. The retrieved samples would be analyzed for oxides of nitrogen content, as well as for any other trace species of Air Force interest that might affect the ozone budget. The initial effort involved the obtaining of a single air sample per flight from one mid-latitude launch site.[1]

1. Gallagher, C. C., and Pieri, R. V. (1976) Cryogenic, Whole-Air Sampler and Program for Stratospheric Composition Studies, Tech. Report AFGL-TR-76-0161, AD A032384.

The program was later expanded to include five latitudes and six altitudes. Further, three samples were to be obtained from a single flight, providing several scientific and economic advantages. Compilation of results based on five years of sampling at the several altitudes and latitudes has provided a baseline profile of five trace gas species. This permits potential variations in time for each species to be noted. These are believed to be the only simultaneous measurements, to date, of these five important species. Results are related to the assessment of the environmental impact of the F-15, F-16, KC-10A and any potential advanced manned bomber.

2. BACKGROUND

2.1 Stratospheric Environment

The stratosphere is that region of the earth's atmosphere extending from the tropopause to about 50 km in altitude. Atmospheric pressure is low (for example, 8 mm at 30 km), and a delicate chemical balance exists together with long residence times. There is little transport of gas species across the tropopause. Thus, small rates of injection from various man-made sources can lead to significant buildups, with potentially harmful consequences from various chemical reactions.

Perhaps the greatest fear for alteration of the stratosphere relates to the potential destruction of the ozone layer. Johnston[2] developed a scenario for the growth of supersonic transport operations in the stratosphere and predicted that the accumulated effects of the oxides of nitrogen from the exhausts would lead to catalytic destruction of the ozone layer. The consequent increase in solar ultraviolet radiation reaching the earth's surface was predicted to cause serious biological[3] and crop[4] damage.

Later, Rowland and Molina[5] predicted that the upward diffusion of fluorocarbons widely used in military, industrial and consumer applications would also lead to ozone destruction. These compounds are stable, with few natural sinks,

2. Johnston, H.S. (1971) Reduction of stratospheric ozone by nitrogen oxide catalysts from supersonic transport exhaust, Science 173:517-522.

3. Urbach, F., Berger, D., and Davies, R.E. (1974) Field Measurements of Biologically Effective UV Radiation and Its Relation to Skin Cancer in Man, CIAP Tech. Report DOT-TSC-OST-74-15, pp 525-535.

4. Caldwell, M.M., Campbell, W.F., and Sisson, W.B. (1974) Plant Response to Elevated UV Intensities, CIAP Tech. Report DOT-TSC-OST-74-15, pp 482-497.

5. Molina, M.J., and Rowland, F.S. (1974) Stratospheric sink for chlorofluoromethanes: Chlorine-atom catalyzed destruction of ozone, Nature 249:810-815.

10

and diffuse, though slowly, into the stratosphere. There, solar ultraviolet radiation breaks up the molecules. The chlorine, thus freed, becomes involved in a catalytic cycle postulated to result in ozone destruction.

2.2 Relevance to Air Force Operations

Newer Air Force planes, such as the B-1, F-15, and F-16 can operate in the stratosphere. The respective environmental impact statements require profiles of the oxides of nitrogen as they presently exist and measurements were necessary to help establish these baseline curves for stratospheric altitudes.

Further, Congress has passed legislation that severely restricts the use of chlorofluoromethanes (CFM's). The Department of Defense presently uses CFM's for various specialized cleaning and lubricating applications. They have expressed concern[6] that further CFM restriction would introduce serious consequences for them.

Although some of the early concerns regarding NO_x effects were temporarily lessened,[7] the most recent calculations, as reported at the High Altitude Pollution Program (HAPP) Scientific Advisory Committee meeting in December 1980 show that at the altitudes where supersonic aircraft fly, NO_x injections would certainly result in a decrease in total column ozone.

3. EXPERIMENTAL GOALS

3.1 Oxides of Nitrogen

Nitric oxide (NO) and nitrogen dioxide (NO_2) are reactive species whose stratospheric concentrations are difficult to measure. Optical emission and absorption studies have been conducted from both aircraft[8,9] and balloon platforms.[10,11] In addition, chemiluminescent analyzer measurements have been made in situ from a balloon platform.[12] Diurnal and other natural variations, when combined with experimental errors, have yielded data which, for daytime observations by various laboratories, have varied by better than an order of magnitude at each altitude studied.[9,10,11]

In the present approach, stratospheric air is sampled cryogenically. Molecules are retained on first collision with a near 4° K surface and maintained at this temperature until just prior to analysis. The samples are regenerated and portions studied on chemiluminescent analyzers for nitric oxide and nitrogen dioxide content. Studies have shown that reaction rates are sufficiently low such that the measurements are accurate if performed within 24 hours of sample regeneration to the gaseous state. *

(Due to the large number of references cited above, they will not be listed here. See References, page 49.)

*Private communication, independently by Ronald Pacholec, Capt., USAF and William Swider, both of AFGL.

11

3.2 Fluorocarbons

Fluorocarbons (chlorofluoromethanes, CFM's) are stable and accumulate in the troposphere with few natural sinks. World-wide consumption is down, but most of the fluorocarbons produced still exist in the environment. Transport has distributed them, not only throughout the earth's surface, but also into the stratosphere. One significant mechanism for transport to the stratosphere is believed to be upwelling within tropical regions.[13] Thus, stratospheric concentrations might be expected to be higher over such latitudes. Consequently, a comprehensive profile of CFM concentrations within the stratosphere requires that measurements be made at several latitudes and altitudes.

After the cryogenic samples have been obtained, and later regenerated, and the chemiluminescent analyzer studies completed, aliquots of the remaining sample portions are studied for fluorocarbon content using gas chromatography. Investigation centers on the widely used F11 ($CFCl_3$) and F12 (CF_2Cl_2), but F113 and F114 are monitored both for very low stratospheric concentrations and as possible contaminants. Expected concentrations of F11 and F12 are in the parts per trillion range, and therefore sample handling and instrument calibration procedures require meticulous attention.

4. EXPERIMENTAL APPROACH

4.1 Cryogenic Sampling

Stratospheric whole air samples can be obtained simply by opening an evacuated container at altitude; however, at these low ambient pressures, the small sample quantities limit the opportunities for diagnostics. On the other hand, if the evacuated container is immersed in a dewar of a cryogenic fluid, such as liquid helium at $4^\circ K$, then in the sampling process, as air enters the chamber, it freezes on the inner surface, thereby perpetuating the pressure differential which draws in more air. Thus, substantially greater sample quantities can be gathered. Also, metastable compounds are more likely to remain in their natural concentrations through analysis. The cryogenic approach has been used for most samplings in the present series.

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13. Schmeltekopf, A. L., Albritton, D. L., Crutzen, P. J., Goldan, P. D., Harrop, W. J., Henderson, W. R., McAfee, J. R., McFarland, M., Schiff, H. I., Thompson, T. L., Hofmann, D. J., and Kjome, N. T. (1977) Stratospheric nitrous oxide altitude profiles at various latitudes, J. Atmos. Sciences 34:729-736.

Initially, a single chamber cryogenic sampling unit was used[14] which permitted the obtaining of a one-mole sample quantity at a single altitude. Several flights on separate days are required to obtain altitude profiles for the gas species of interest. Subsequently, a cryogenic sampling unit was designed to contain three chambers (tri-sampler). Thus, samples can be obtained at three altitudes on a single flight. The use of two such units on succeeding flights leads to a more comprehensive picture of the stratosphere within a shorter time frame. Temporal effects become less of a factor on the profiles, and the economy of conducting fewer flights is significant.

The cross section of a tri-sampler is shown in Figure 1. Only one of the three identical sample chambers is shown, immersed in liquid helium. Since liquid helium has a low heat of vaporization, nested chambers enclosing vacuum and liquid nitrogen regions were designed as insulating barriers, in order to provide a 28-hour hold time under static conditions. The air sample tubes were each designed for a specific altitude with the aid of Poiseuille's equation,[15] so that a one-mole sample would be obtained in 50 minutes. This provides a uniform thermodynamic loading and ensures that the molecules are trapped on initial contact with the sample chamber surface, minimizing potential chemical reactions. The mountings for the sample tube come in contact only with the relatively warm tri-sampler top, so as to avoid having the small bore tubes clogged by premature freezing of the air. The helium chamber is supported by stacked, corrugated metal discs that provide low thermal conductivity and good shock mount. The tri-sampler was designed for and periodically tested for 10 g vertical loading. All surfaces which come in contact with the sample are either gold or 316 stainless steel.

Figure 2 shows a completed unit (see Table 1 for specifications). Two right angle, gold seal valves are mounted above each air sample tube as shown in Figure 3. One valve provides for evacuation of the sample cylinder; the other serves as the sampling valve, controlled by a remotely activated motor drive. The sampling valve has been modified by the addition of a second tube opposite to the inlet port so that air may be continually flushed through the valve body, above the seal, prior to the "valve-open" command. An overpressure relief disc is mounted adjacent to each pump-out valve as a safety measure although premature warmup of the desired 1-mole sample would neither damage the chamber nor rupture the disc. In such an eventuality, stable species could still be investigated, although reactive species concentrations would likely be altered.

14. Gould, P. R. (1974) Cryogenic Whole Air Sampler System, Tech. Report AFCRL-TR-74-0452, AD A003395.

15. Dushman, S., and Lafferty, J. M. (1962) Scientific Formulations of Vacuum Technique, p. 82, J. Wiley and Co.

Two tri-samplers were fabricated and they have operated successfully on every flight on which used.

LHe FILL & VENT PORTS

MOUNTING FLANGE FOR OVERPRESSURE RELIEF DEVICE, RATED 196psia

MOUNTING POINT FOR REMOTE CONTROLLED SAMPLING VALVE

PUMP-OUT PORT FOR GAS SAMPLE CYLINDER

1 OF 3 LN$_2$ FILL & VENT PORTS

1 OF 3 AIR SAMPLE TUBES BUILT FOR USE AT A PARTICULAR ALTITUDE

THERMOCOUPLE TEMPERATURE MONITOR

1 OF 3 SAMPLE CYLINDERS

WALLS OF 316 SST

VOLUME ≈ 2 LITERS

THERMAL SHIELDING VACUUM

LN$_2$

THERMAL SHIELDING VACUUM PRESSURE MONITORING PORT

THERMAL SHIELDING VACUUM PUMP-OUT PORT

Figure 1.   Tri-Sampler Cross Section

Table 1. Tri-Sampler Specifications

Height:		127 cm
Diameter:		43 cm
Materials:		316 stainless steel
Weight:	(empty)	147 kg
	(with cryogens)	172 kg
Liquid nitrogen capacity:		24 liters
Liquid helium capacity:		42 liters
Liquid helium use rate:	(static)	1.5 liters/hour
	(flight)	3.0 liters/hour average
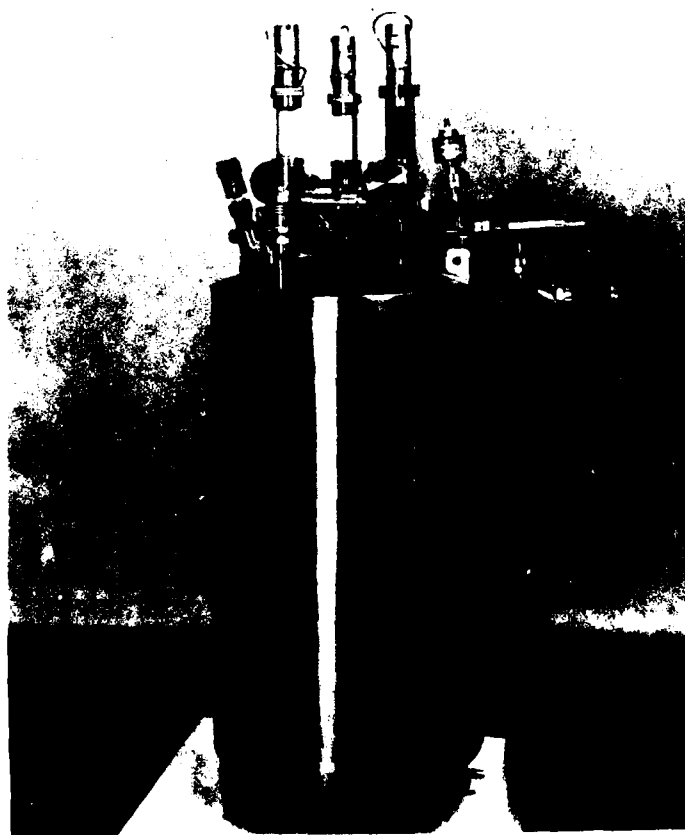
Figure 2. Tri-Sampler
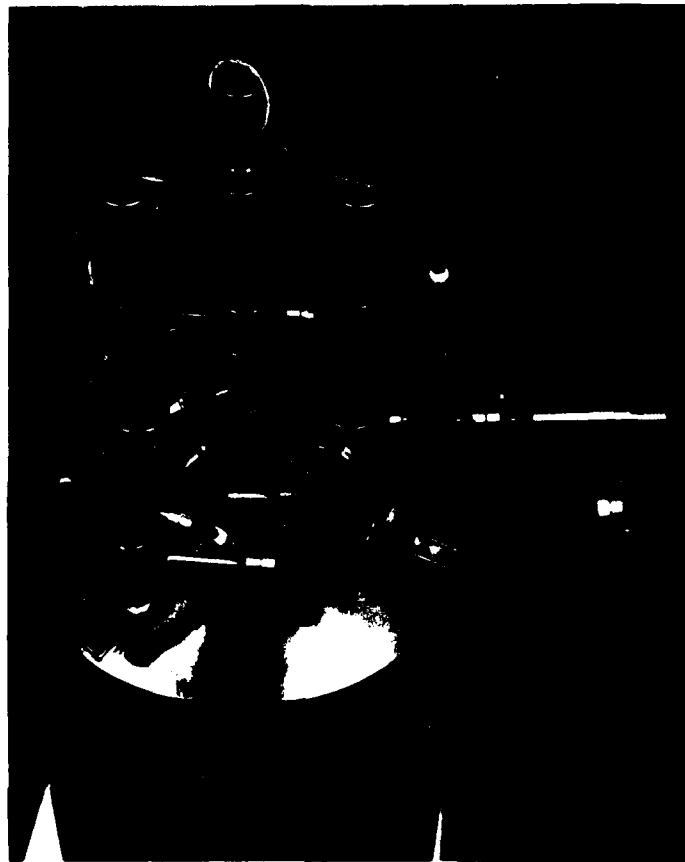
Figure 3. Sampling Control Valves

4.2 Balloon Platform

A balloon platform is used to carry the tri-sampler to the sampling altitudes. Then the sampling process is commanded from the ground station, starting with the highest altitude of interest. After sampling, a termination command destroys the balloon and the experimental package begins its descent on parachute for subsequent recovery.

The standard gondola is shown, empty, in Figure 4. It is constructed from aluminum tubing, bent and welded to form a cage, 6 ft in diameter, except for a flat base. The gondola is rigged to have a low center of gravity. Since flight termination is usually planned for above flat open country, the gondola should roll to an upright position upon impact, thereby avoiding excessive cryogen losses. Principal payload items are mounted on either side of the central support bars so as to keep

16

the center of gravity approximately along the center line of the gondola. One side contains the tri-sampler and air intake system, the other side houses thermal insulation boxes containing command and control electronics, as well as the required batteries.
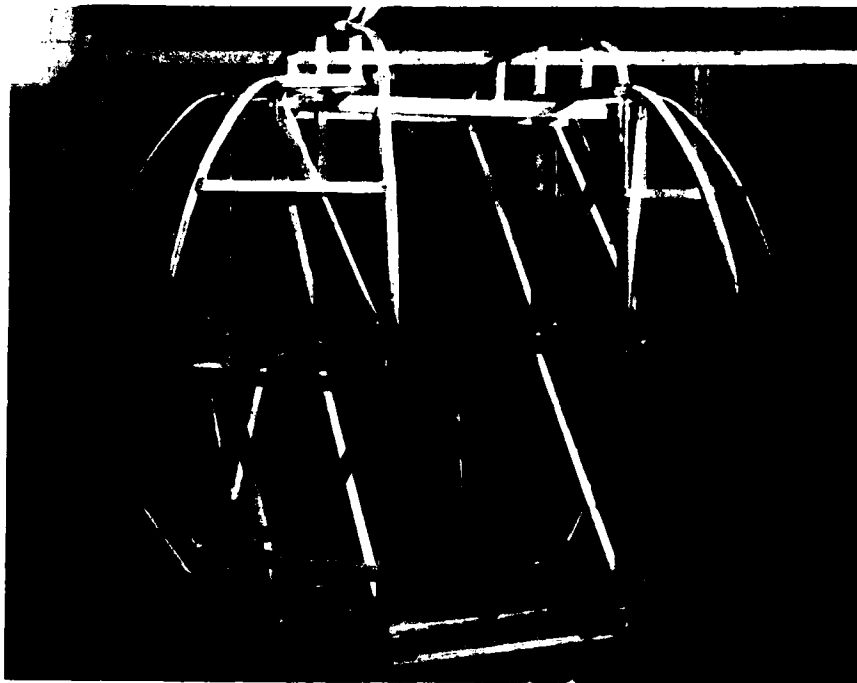
Figure 4. Standard Ground Recovery Gondola

An air snatch gondola (no roll bars), rigged for flight, is shown in Figure 5. The tri-sampler rests on a shock mount which employs fluorocarbon-free foam. In Figure 6, the air intake system is shown close-up, attached to the tri-sampler. A single blower, downstream of the sampling valves, draws air up from below the gondola through a 3-inch diameter flexible, stainless steel intake tube and then through all three sampling valve bodies. Air enters the valve bodies through the rigid tubing and flows out through the flexible tubing. An exhaust tube diverts outflowing air through the top of the gondola. Two ballast hoppers with a total capacity of 400 lb of glass beads are mounted symmetrically about the center line. Typical pour rate capability is 37 lb per minute.

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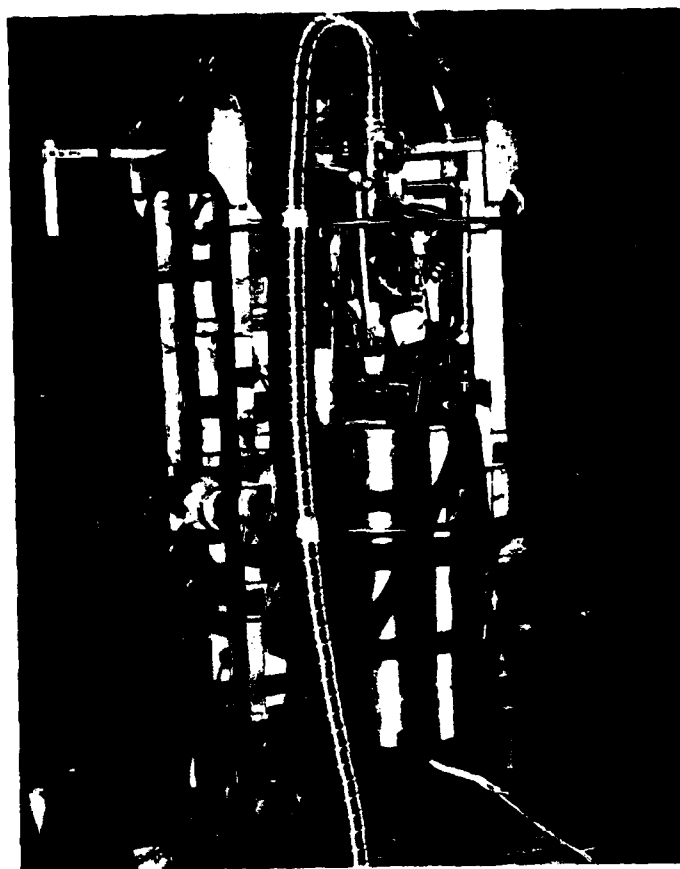
Figure 5. Air Snatch Gondola Rigged for Flight

4.3 Electronics

All power, command, control and data gathering capabilities were maintained
in the electronics system supplied by the Aerospace Instrumentation Laboratory
at AFGL. The system was specially designed for this mission. It will only
be functionally described here. The unit basically contains: battery supplies,
command receiver, command decoder, data transmitter, data encoder, flight
safety timing, logic control unit, impact switch control unit, pressure and
temperature sensors. There is also a separate backup package which provides
command redundancy for the more important control functions. The command
receiver works in conjunction with the decoder, and finally with the logic control
unit which energizes all control functions and sequences. Upon channel acquisition,
the decoder provides a voltage output which is encoded and transmitted to ground

18

control for command verification. This guarantees proper command channel
execution. Eighteen coded channels are available in the main package and
six in the backup package. The encoder converts a 0 to 5.1-V d-c input signal into
a 9-bit octal code which is transmitted to the ground station where it is decoded and
recorded. An example of the accuracy of the encoder is ± 5 mV which corresponds
in altitude to ± 60 ft in the sampling region of the balloon flights. A combination
of three pressure sensors is used for each flight in order to maintain a good
pressure versus altitude resolution. All pressure sensors are carefully calibrated
and cross referenced to a standard altitude-pressure profile.

Figure 6. Air Intake System

19

4.4 Command and Monitoring

Several aspects of the flight were monitored primarily for post-flight analysis in the event that a problem developed. The interface and tri-sampler control electronics, as well as various on-board sensor systems directly related to the experiment, were designed and fabricated within the Composition Branch. The electronic co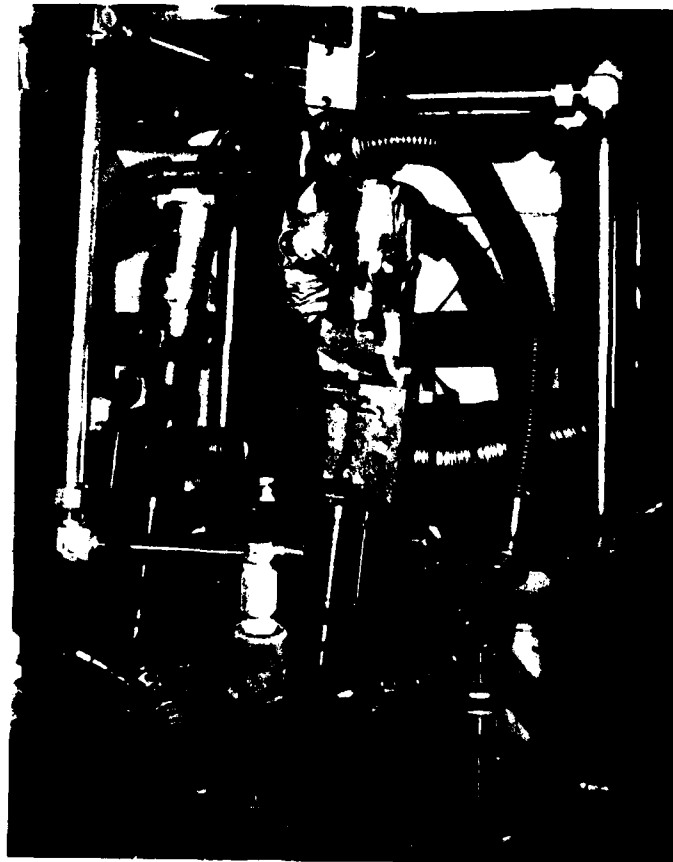ntrol unit is designed so that the execution of a particular command can be confirmed through the telemetry link with the payload. This characteristic is used to confirm that the three primary, or the three backup commands, that is, Fan On, Valve Open and Valve Closed-Fan Off are transmitted through the electronic system and are being acted on by the sampler package. The current delivered to the fan motor and to the motor-driven mechanical valve are also monitored and reported back to the ground station.

Five other parameters are recorded, namely, the level of the liquid helium in the sampler and four temperature readings taken at (1) the liquid helium boil-off vent, (2) the liquid nitrogen boil-off vent, (3) the surface of the sampler (away from the vents), and (4) the surface of the gondola, or, as in the latest flights, the air temperature.

The sensing probe is composed of six resistors placed at the 1 1/4, 5 1/2, 12 1/2, 21, 31 1/2, and 41 1/2 liter levels in the liquid helium dewar. The sensitivity circuit is designed to use as little power as possible (milliwatts) to detect the resistance change. From the value of each resistor, at each moment, the circuit forms a single unit of data, reflecting the amount of liquid helium remaining in the dewar. The temperature sensors used were two thermistors and two silicon unijunction transistors. Ambient temperature and pressure measurements are also available from radiosonde units attached to the gondola for each flight.

A valve-position indicator is used with the motor driven mechanical valve which provides the ground station with positive confirmation that the vacuum sampling system is open. The position indicator involves a slide motion variable resistor which parallels the motion of the mechanical valve. A zero voltage reading indicates the valve is open and a reading of 1.20 to 1.40 V indicates a closed valve. The voltage value of the closed position is deliberately set to a different value for each valve, in order to be identified with that particular valve, providing another cross check on which valve has opened. The greatest use made of the sensors was for in-flight decision making. The sensors are also important indicators of certain conditions that would cause abortion of the mission.

5. FIELD PROGRAM

5.1 Flight Package

The gondola system, described in Section 4, is joined to the parachute and balloon as illustrated in Figure 7. A 200-ft load line (100 ft for air recovery packages) serves to isolate the gondola from the parachute and balloon, minimizing the risk of outgassing from these large surfaces being ingested by the sampling tube. An electrical cable for balloon control parallels the load line and is fastened to it. The system is designed so that a valve located on top of the balloon can be commanded to open, release helium and so control descent rate. Following completion of sampling, a termination command causes balloon destruct and separation from the parachute. The gondola descends on the parachute and at impact, special switches on the gondola base close, activating an explosive separation of the parachute; this minimizes dragging of the experiment across the terrain.

**TYPICAL BALLOON SYSTEM
FOR WHOLE AIR SAMPLING FLIGHT
TO 20km ALTITUDE**

274,000 cu ft
BALLOON — 126 ft

48 ft diameter
PARACHUTE — 60 ft

10,000 lb Test
NYLON LOAD LINE — 200 ft

SELF-RIGHTING GONDOLA — 9 ft
CRYOGENIC SAMPLING PACKAGE
BY-PASS AIR IN-LET DUCT (3" O.D. SST)
BALLAST POUR TUBES (3" O.D. CANVAS) — 17 ft
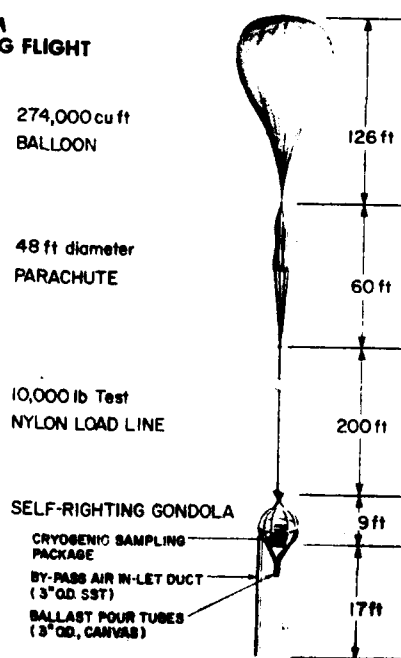
Figure 7. Flight Package

21

5.2 Countdown and Launch

Typically, the tri-sampler is removed from the vacuum system the second day before launch in order to permit a slow, uniform chilling. Outfitting of the gondola system is completed the day before launch, so that it may be weighed and suspended from the launch vehicle.

The intake tubing initially receives a thorough cleaning, and then a two-day trickle flow of gaseous helium provides the final flush. The tubing is encased in a polyethylene shroud which separates at launch.

Launch is usually scheduled for within one hour subsequent to ground sunrise principally for three reasons. Launch weather is generally more favorable and sampling will take place during daylight (a specification maintained for every flight, in order to minimize the additional variable of diurnal variations in oxides of nitrogen concentrations). Finally, adequate time is provided for daylight recovery following termination.

Final countdown procedures commence about five hours prior to the scheduled launch time. Top-off of the tri-sampler cryogens and a complete electronic check and interface take place. Completion of the flight package continues on the flight line. The complete package, prior to launch, is shown in Figure 8. To minimize risk, power to the tri-sampler package is not turned on until just prior to launch.
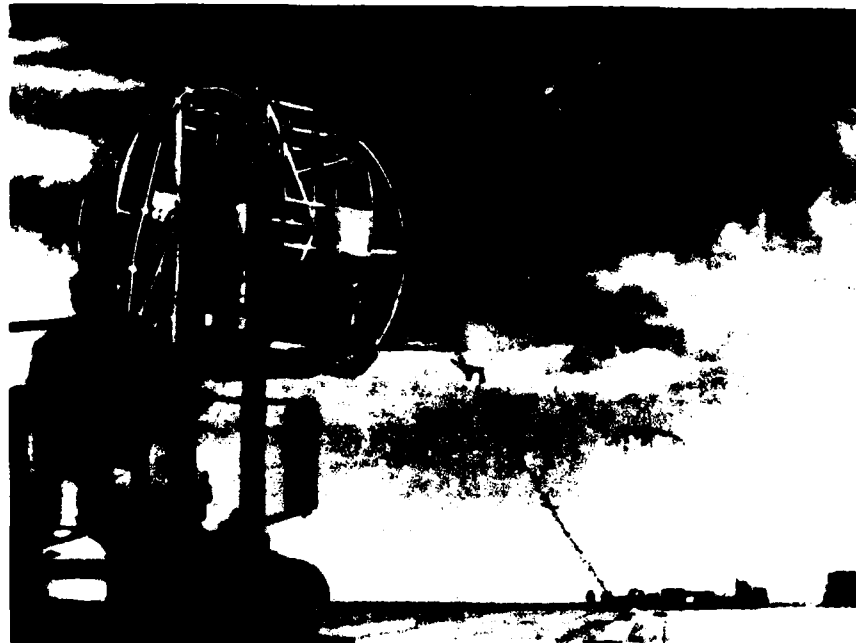
Figure 8. Ground Recovery Gondola Ready for Launch

22

Figure 9 shows balloon release. Gondola release is activated when the balloon is approximately over the launch vehicle. Figure 10 shows the ascending package.
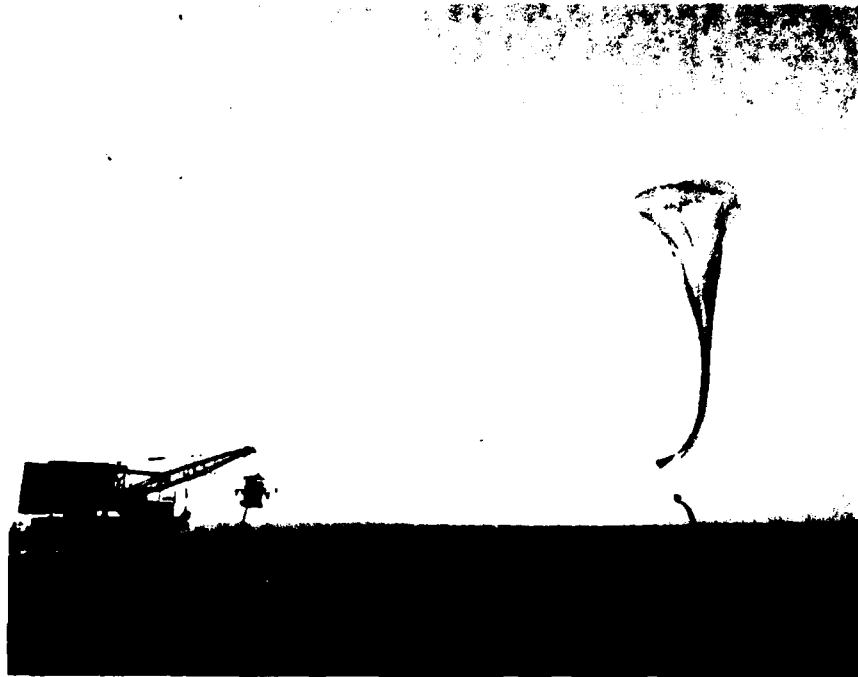
Figure 9.   Balloon Release

5.3   Flight Profile

The ascent to float altitude averages one hour. Valving of helium is commanded to initiate a descent rate of 100 ± 50 ft/min/ (~ 30 m/min). This procedure, sampling only during descent, is to minimize sampling of air that may have become contaminated by contact with the package. Only unperturbed air from several meters below the package will be sampled. The fan is commanded "on" several minutes prior to the tri-sampler "valve open" or sampling command. Based on the measured descent rate and the specified sampling time, the altitude at which sampling commences is chosen so that the "official" altitude becomes the median altitude sampled. Typically, a 1- to 2-km altitude increment is covered for one sample. After "valve closed" and "fan off" commands, balloon valving and ballasting, as needed, are initiated to accelerate descent to the second sampling altitude. The slower descent

23
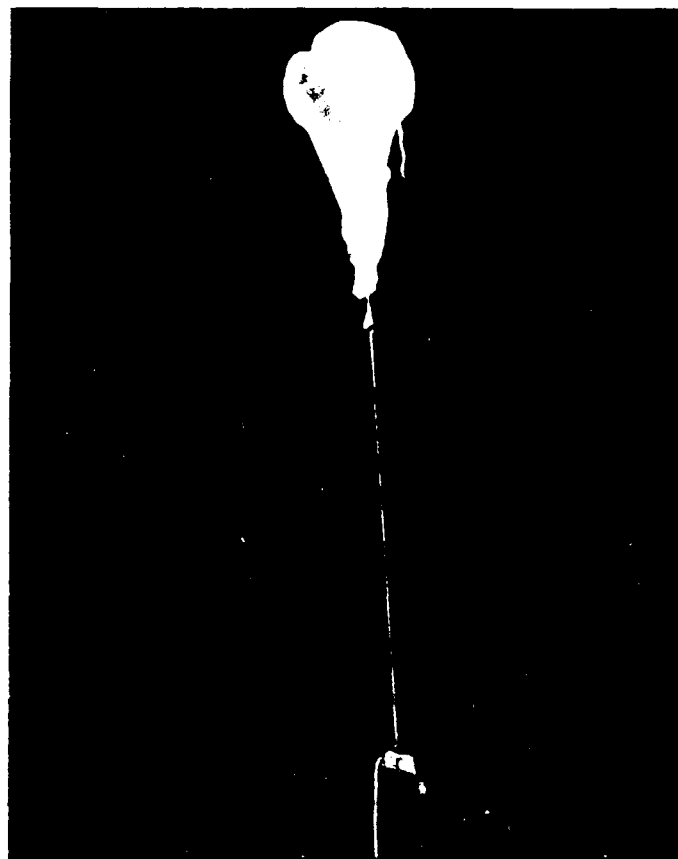
Figure 10. Package on Ascent

rate is resumed for the second sample, and the procedure again repeated for the third sample. Figure 11 illustrates typical measured flight profiles from three latitudes. The individual sampling tubes are designed to obtain a one-mole sample in 50 min but actual sampling times are based on laboratory calibrations of rates for each tube. In Figure 11, the Holloman profile shows that sampling at 30 km was twice interrupted. This was done in each case because the descent rate was drifting outside the desired range, calling for adjustment. Sampling is never conducted during helium valving or glass bead ballasting. A similar situation can be seen on the Panama profile at 25 km. After the three samples have been obtained, termination is commanded. Balloon destruct and separation occur, and the gondola descends on parachute for recovery.

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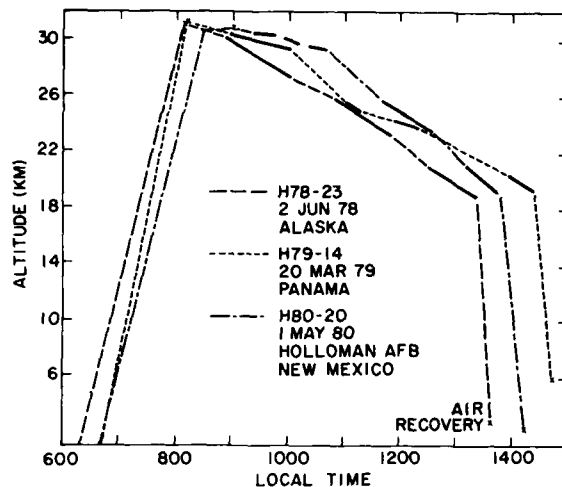
Figure 11. Typical Flight Profiles

5.4 Recovery

In most cases, ground recovery is employed. The gondola described in Section 4.2 is utilized and has always come to rest in an upright position, minimizing cryogen losses. Crews are guided to the impact area by a spotter plane. Cryogens are replenished on site and the package subsequently returned to the field laboratory.

Air recovery, employed when available, is mandatory for Alaska and Panama flights where inhospitable surface conditions prevail. An Air Force C-130 aircraft is used. Hooks attached to a nylon cable snag the descending parachute and a winch system aboard the aircraft is used to reel in the package. This more expensive recovery method is faster and it avoids the risk of damage to the package upon ground impact. Figure 12 contains the surface projections for the 1980 flights where air recovery provided prompt recovery. The lower altitude flight of 28 April 1980 required the obtaining of the 12-km sample in a 140 mph (225 km/hr) jet stream wind, with termination occurring hundreds of kilometers from the launch site. The retrieved package is shown in Figure 13 on the C-130 upon arrival back at the launch site. The opening on the aircraft requires that a gondola without roll bars be used for such flights.

5.5 Record of Flights

Twenty-two sampling flights have been conducted with whole air samples obtained on all flights. Most flights were launched from Holloman AFB, New Mexico, but the program included five launch sites, located from 9° N to 65° N.

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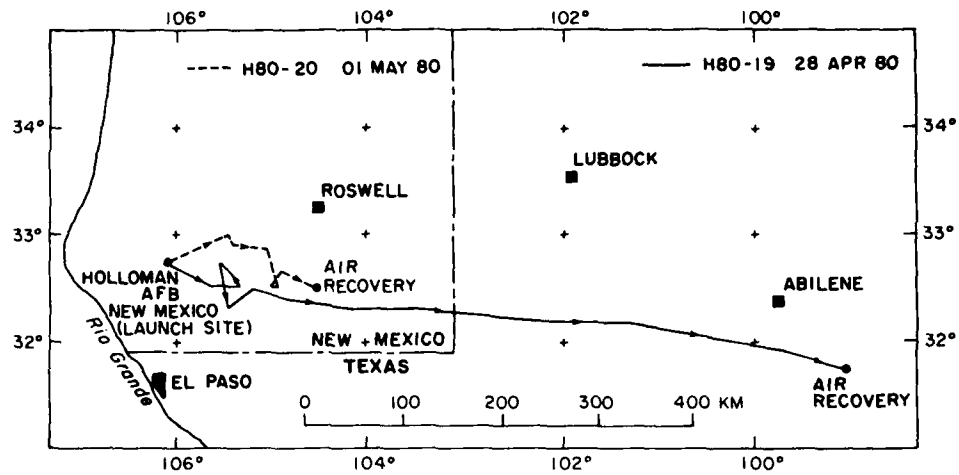
Figure 12. Surface Projections of Holloman 1980 Flight Profiles
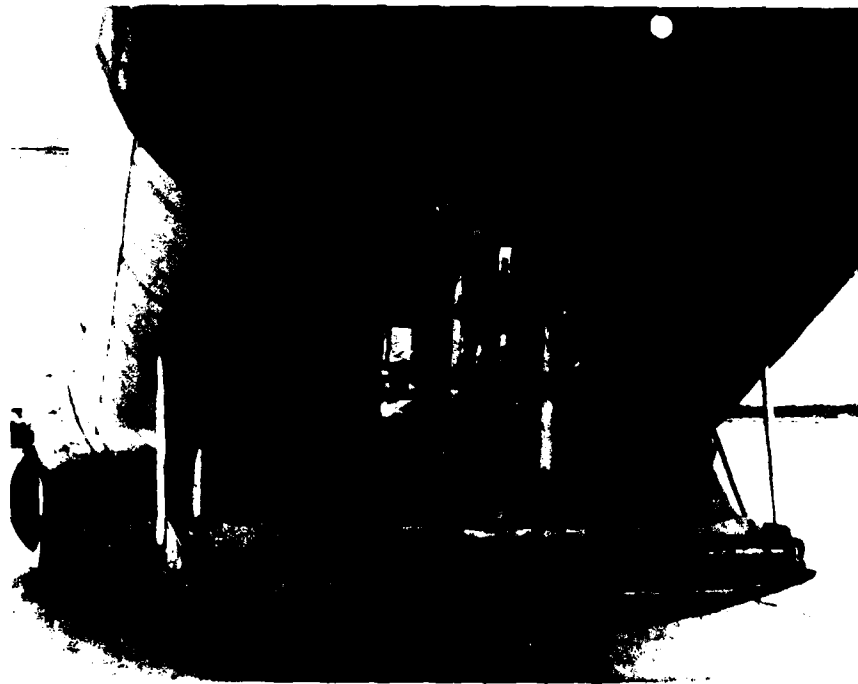
Figure 13. Air Snatch Gondola on AF C-130 Aircraft Following Retrieval

26

Table 2 summarizes the more important flight parameters from all twenty-two flights. Flight numbers for the present program, whole air sampling (WAS), are listed along with the corresponding AFGL Aerospace Instrumentation Division (LC) flight numbers. Gross weight includes completely rigged gondola, ballast, parachute and balloon. Local surface conditions require air recovery for Alaska and Panama flights, as previously indicated. Air recovery is employed at other sites as scheduling and economics permit. Grab sampling was utilized on the first Panama flight to permit shorter sampling periods and thereby avoid intruding on restricted air space as forecast for a tri-sampler flight trajectory. For the other instances of grab sampling, substitution was made because of damage to a cryogenic sampler in shipment to the field site (indicative of very rough handling en route). The stainless steel sampling spheres were 15 to 22 liters in volume, with internal surfaces passivated with either gold or hexamethyldisilazane. The valves were controlled in the same manner as on the tri-samplers. Diagnostics for grab samples would be by gas chromatography only.

Specific flight dates were a function of several factors. Launch dates from Holloman 33° N and Chico 40° N were chosen to include investigation of potential seasonal variations in stratospheric trace gas composition. On three flights, a very long lateral trajectory occurred, necessitating omission of the third sample in order to avoid the risk of losing the communication link. The few other missing samples are due to valving, or vacuum problems occurring on one of three chambers.

6. DIAGNOSTIC METHODS

6.1 Post-Flight Procedures

The air samples are maintained frozen until just prior to analysis, in order to minimize potential sample alterations. In preparation for sample warm-up, transfer and analysis, the tri-sampler is connected to the manifold illustrated in Figure 14. The pump-out valve on each sample chamber is connected to a stainless steel sphere and to the manifold; each sphere has been passivated and then evacuated to 10^{-9} mm on a separate vacuum system. The passivation procedure minimizes trace species absorption on the sphere surface. Gold and hexamethyldisilazane (HMDS) were used on alternate spheres. The use of HMDS was first reported elsewhere[16] and sample behavior relative to both surface treatments has been studied in detail by Dr. Joseph Calo, Princeton University, under AF Contract No. F19628-77-C-0071.

16. Schmeltekopf, A. L., Goldan, P. D., Harrop, W. J., Thompson, T. L., Albritton, D. L., McFarland, M., Sapp, A. E., and Henderson, W. R. (1976) Balloon-borne stratospheric grab-sampling system, Rev. Sci. Instrum. 47:1479-1485.

Table 2. Flight Records

WAS Flight Number	AFGL Flight Number	Date	Location	Latitude	Gross Weight lb	Balloon Volume M cu ft	Float Altitude k ft	Recovery Method	Sampling Method	Altitudes Sampled km
1	C75-10	05 Jun 75	Chico	40° N	1193	0.274	67.1	Ground	Cryo	20
2	C75-11	26 Jun 75	Chico	40° N	1193	0.274	66.5	Ground	Cryo	20
3	H76-3	27 Jan 76	Holloman	33° N	991	0.274	69.4	Ground	Cryo	20
4	H76-4	06 Feb 76	Holloman	33° N	1583	2.010	102.3	Ground	Cryo	30
5	H76-6	12 Feb 76	Holloman	33° N	683	0.075	51.2	Air	Cryo	15
6	H76-24	14 May 76	Alaska	65° N	831	0.274	69.1	Air	Grab	20
7	H76-38	19 May 76	Alaska	65° N	939	0.803	62.3	Air	Grab	15
8	H77-8	05 Feb 77	Holloman	33° N	2291	2.900	101.9	Ground	Cryo	30, 25, 20
9	H77-10	16 Feb 77	Holloman	33° N	1589	0.355	66.3	Ground	Cryo	18, 15
10	H77-20	30 Mar 77	Panama	9° N	1491	2.010	102.7	Air	Grab	30, 20
11	H77-59	08 Oct 77	Chico	40° N	2725	2.900	101.1	Ground	Cryo	30
12	H77-63	17 Oct 77	Chico	40° N	1963	0.803	77.7	Ground	Cryo	18, 15
13	H78-23	02 Jun 78	Alaska	65° N	2147	2.900	102.0	Air	Cryo	30, 25, 20
14	H78-26	07 Jun 78	Alaska	65° N	1366	0.355	69.3	Air	Cryo	15, 12
15	W78-35	19 Aug 78	So. Dakota	45° N	1579	0.355	66.0	Ground	Cryo	15, 12
16	W78-36	29 Aug 78	So. Dakota	45° N	2083	2.900	103.4	Ground	Cryo	30, 25, 20
17	H79-11	15 Mar 79	Panama	9° N	1349	0.274	65.0	Air	Cryo	18, 15
18	H79-14	20 Mar 79	Panama	9° N	2141	2.900	103.0	Air	Cryo	30, 25, 20
19	H79-30	21 Jun 79	Holloman	33° N	2152	2.900	102.5	Ground	Cryo	30, 25, 20
20	H79-31	25 Jun 79	Holloman	33° N	1309	0.628	62.8	Ground	Grab	18, 15, 12
21	H80-19	28 Apr 80	Holloman	33° N	1740	0.629	74.4	Air	Cryo	18, 15, 12
22	H80-20	01 May 80	Holloman	33° N	2436	2.940	100.7	Air	Cryo	30, 25, 20

KIN TEK NO CALIBRATION SYSTEM

THERMO ELECTRON MOD 12A NO$_x$ ANALYZER

KIN TEK NO$_2$ CALIBRATION SYSTEM

MONITOR LABS MOD 8440 NO$_x$ ANALYZER

1 OF 3

22 LITER EXPAN- SION SPHERE

PRESSURE TRANSDUCER

TRI SAMPLER STRATOSPHERIC SAMPLES 3 ALTITUDES

LIQUID HELIUM TRANSFER STILL

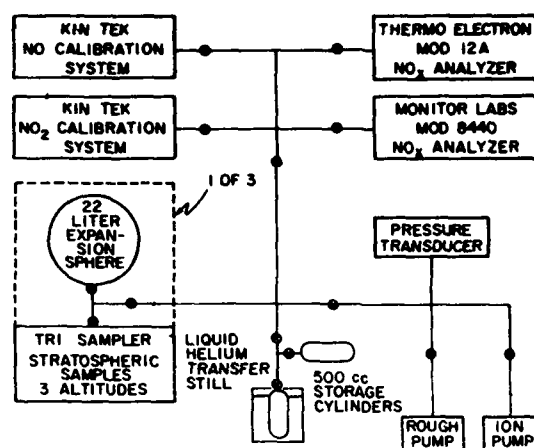500 cc STORAGE CYLINDERS

ROUGH PUMP

ION PUMP

Figure 14. Post-Flight Sample Transfer System

Dr. Calo's studies indicate that both surface treatments are acceptable for the present application but with preference to HMDS. The manifold is then evacuated while the tri-sampler and sphere valves remain closed. Each sample chamber-sphere combination is then valved off from the manifold before being opened to each other. The tri-sampler guard vacuum is then released to accelerate cryogen boil-off. The sample eventually returns to the gaseous state, filling the sphere. Only gold seal valves and gold plated copper gaskets are used with the stainless steel manifold. Generally, the small portion of the manifold seen by the sample at this time is also gold plated. A flow of slightly warmed air is directed into the emptied liquid helium chamber until a thermocouple indicates that the sample chamber has achieved room temperature. This is to ensure that high boiling point species such as $CFCl_3$ are completely regenerated. The warm-up consumes several hours. Each sample is now at approximately 700 mm pressure. At this pressure, the theoretical analysis described in Section 3.1 indicates that measurements of NO and NO_2 content can be made up to 24 hours subsequent to sample regeneration (interpreted to start at the "whoosh" heard shortly after liquid helium depletion). Shortly after room temperature is achieved, analysis commences. The highest altitude sample is opened, first, to the pressure transducer for confirmation of sample quantity. Then, sample flow is directed to the chemiluminescent analyzers whose operation will be described in Section 6.2. This analytical procedure typically consumes about one-third of the available sample. Early in the program this sphere-chamber combination would then be valved off from the manifold to await gas chromatography studies. Since then, the procedure has been to transfer the remainder of the sample into a somewhat smaller, stainless steel cylinder utilizing cryogenic methods. The sample, subsequently regenerated, is allowed to expand into a second cylinder which serves as a backup sample source while providing a

29

more acceptable pressure for safety reasons. Both cylinders were baked and pumped to a high vacuum prior to the transfer. The cylinders are allowed to re-main open to each other in excess of 24 hours after removal from the manifold. They are oscillated frequently during this period to enhance sample mixing. For the 1980 samples, a slug was added to each cylinder as an additional mixing aid. New storage cylinders are attached and the manifold is re-evacuated in preparation for the second sample. The analytical and transfer procedures are identical for the second and third samples. The storage cylinders have been previously evacu-ated on a separate vacuum system as were the spheres. The three chemilumi-nescent analyzer measurements have always been obtained within the 24-hr limit. The foregoing procedure is conducted first for the high altitude tri-sampler and, second, for the low altitude unit.

Samples within the 500 cc storage cylinders are used, subsequently, for gas chromatography studies (see Section 6.3) and the remainder is included in a library that contains portions of all samples gathered to date.

6.2 Chemiluminescence

Determinations of nitric oxide and nitrogen dioxide would be made by chemi-luminescence methods. Two commercial NO_x analyzers were procured for this purpose. The initial instrument, Thermo Electron Corp. Model 12A, was modified in-house to provide greater resolution and accuracy at the lower end of the operat-ing range (that is, for low parts per billion concentrations). The standard output was replaced by a Keithley Model 640 vibrating capacitor electrometer; zero current balance would be achieved using a Keithley Model 261 picoampere source. Subsequently, a Monitor Labs Model 8440 NO_x analyzer was acquired, and it also was modified to optimize low concentration measurements. At the manufacturer's suggestion, the internal pump was replaced with an external direct drive pump and the internal flow orifices replaced with smaller diameter components.

In addition to the usual gain in measurement precision afforded by use of two instruments, an additional precaution against detection of a second chemilumi-nescence reaction is achieved, since separate optical wavelengths are utilized for detection by the two instruments.

Originally all calibrations were achieved through dynamic dilution of separate purchased standards of NO and NO_2 in N_2 or He, utilizing a Thermo Electron Corp. Series 101 dynamic NO - NO_2 - O_3 calibrator supplied with smaller than standard control orifices. Ultra-high purity nitrogen (99.999 percent) was used as the mixing gas. Various dilutions were successively produced. A portion of the sample was continuously diverted to vent, through a flowmeter, in order to provide the recom-mended pressure drop for proper use of the dilution device. Standard gas mixtures

were acquired, stored in aluminum cylinders with an aluminum oxide surface, enhanced by an anodizing process that eliminates pinhole porosity. An additional proprietary step has been taken to improve further the stability of the gas mixture (Airco Corp., Spectra Seal Cylinders).

Periodically, only a flow of the nitrogen is directed into the analyzers to check for possible NO_x content in the mixing gas. A second calibration method was phased into the system in 1978, and chosen as the sole method in 1980. The new method is based on the permeation of the test gas through a teflon membrane into a flow of ultra-high purity nitrogen. Separate units were incorporated for NO and NO_2 (Kin Tek Corp. Models 570 and 670). Calibration plots are achieved for the NO_x analyzers through successively varying permeation tube temperature and nitrogen flow rate. A portion of the mixture flows to vent through a flowmeter in order to maintain the required pressure drops. Dilutions to approximately one part per billion have been achieved and with the instruments initially balanced for zero input, both were found to be linear in NO to zero concentration and very slightly nonlinear in NO_2 at the lowest concentrations. Frequent calibrations reveal only a slight long-term drift in analyzer response. The error in the calibration plots is considered negligible as compared to other sources of error. The calibrations indicate that for NO the TE12A reads high by about the same percentage that the ML8440 reads low, largely canceling analyzer error in the averaged values. Total error from all sources is estimated to be 25 percent for readings greater than 1 PPB, increasing to 50 percent below 0.5 PPB. For NO_x, both instruments read low by an average of less than 5 percent and with the over-all uncertainty in NO_x values estimated at ± 25 percent. Not all of the previously referenced papers indicated the accuracy of measurement, but where stated, the range was between about 35 percent and 50 percent.

6.3 Gas Chromatography

Nitrous oxide and fluorocarbon measurements were made by gas chromatography. The principal instrument used is a Perkin Elmer Model 3920B with a Nickel 63 electron capture detector. All chromatography based results, except as noted, were obtained with this gas chromatograph (GC). The carrier gas is ultra-high purity nitrogen. A 12 ft long, 1/8 inch diam Porasil C column was used. Initially, stainless steel column tubing was used but later replaced by the more inert nickel tubing to increase peak resolution and to minimize chances for alteration of the gas species. Porasil is a spherical, siliceous column packing. Mesh range is 80/100. A heated, gas inlet system and heated 10-port sampling valve are used for injection as illustrated in Figure 15.
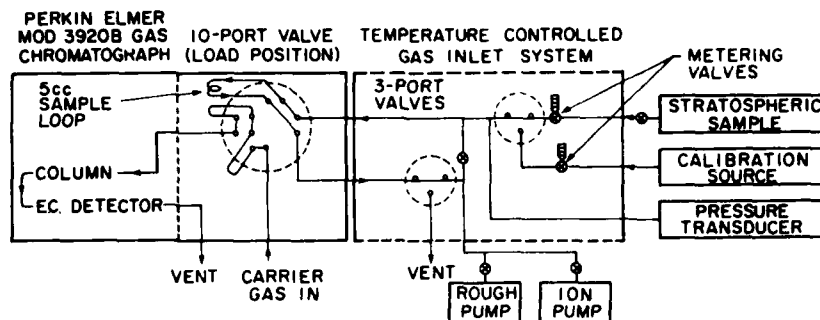
31

Figure 15. Chromatograph Input System

The valve is shown in the load position. Initially, the stainless steel system is evacuated and then either the sample or calibration gas introduced. For sample introduction, an aliquot of air is transferred from the cylinder into a section of gold plated stainless steel tubing and subsequently bled into the 5 cc loop to the desired pressure. After injection, the system is re-pumped and a fresh aliquot of sample obtained from the cylinder. For each sample, several such injections are made at various column and detector temperatures, in order to obtain the most accurate results. For injection of calibration gases, a similar pumpout situation exists, but the metering valve is used to obtain the desired pressure under dynamic flow conditions. The flow can be maintained either to vent or through the forepump. The two-port valve which parallels the 10-port sampling valve is opened only during pumpout and it is included in order to provide a more efficient pumpout of the upper portion of the system. Typically, the injection valve is maintained at 150° C and the inlet system at up to 100° C. The heaters and temperature sensors are not shown in Figure 15. Most data have been obtained with a carrier gas flow rate of 40 cc/min. The flowmeter for the carrier gas is calibrated using a precision bubble flowmeter. This precision flowmeter is used also to calibrate all other flow systems in the experiment.

Initially, calibration mixtures were prepared with purchased primary standard mixtures and further diluting them in ultra-high purity nitrogen using a titration tube mixing system (see Thermo Electron Corp. Model 101 description in Section 6.2). Calibration plots were obtained for various combinations of column and detector temperatures (column T from 40° to 100° C and detector T from 225 to 325° C) and always for three filling pressures (100, 200 and 500 or 700 mm). Plots remained linear throughout the range of mixing ratios of interest. Some extrapolation was required for the lowest observed mixing ratios of the fluorocarbons. The primary standards are replaced periodically, even though only a small portion of

32

the cylinder contents have been consumed, and a minimum of two such fresh standards are available at all times. Later, precision, electronic, mass flow controllers (Matheson Model 8240) were acquired and calibration curves similarly prepared using the same purchased standards. The two sets of plots provide close agreement. Then, a permeation tube system of the type used with the chemilumi- nescent analyzers was added and all three methods are currently in use. The permeation tubes provide dilutions down to the 1 PPT range for the fluorocarbons and as low as needed for nitrous oxide. The permeation system calibration plots agree with the titration system plots to within 2 percent for N_2O and 4 percent for $CFCl_3$. The CF_2Cl_2 permeation system was more erratic, but with recent data agreeing with the titration system results to within 10 percent. Only dilution based calibrations are used for the listed CF_2Cl_2 mixing ratios. Some injections are made with the loop under vacuum. This is a good check for possible desorption from the system walls of previously absorbed components. The results are favorable, that is, negligible desorption, due in part to the heating of the injection system. The large sample quantities obtained with cryogenic sampling permit an almost un- limited quantity of GC runs to be obtained from a single sample, if desired. The over-all accuracy (including sampling, storage, transfer and measurement system errors) is estimated to be 5 percent for N_2O and 10 percent for the fluorocarbons, except increasing to 10 percent for N_2O and 15 percent for the fluorocarbons at the lowest mixing ratios measured. For the oldest data (1976 and 1977), add an addi- tional 5 percent to the previously quoted values.

7. RESULTS

7.1 Chemiluminescent Analyzer Measurements

Measurements of NO and NO_2 were obtained from all but the grab samples where sample quantities were too low for analysis on the chemiluminescent analy- zers. The results, shown in Table 3, represent the average of results from the two analyzers except as indicated. The Monitor Labs unit was under repair at the time of the 1979 series. All data are presented as measured. Calibrations are obtained always at the time of the stratospheric samples analyses and periodically between such series.

Table 3. Nitric Oxide and Nitrogen Dioxide Mixing Ratios

LKD Flight Number	Flight Date	Location	Sampling Altitude (km)	(PPBV) NO	(PPBV) NO_2	(PPBV) NO_x
11*	08 Oct 77	Chico	30	1.0 ± 0.3	0.7	1.7 ± 0.5
12*	17 Oct 77	Chico	18	1.3 ± 0.4	3.0	4.3 ± 1.1
13*	02 Jun 78	Alaska	30	8.6 ± 2.2	26.4	35.0 ± 9
			25	2.2 ± 0.6	13.0	15.2 ± 4
			20	1.8 ± 0.5	3.9	5.7 ± 1.5
14*	07 Jun 78	Alaska	15	2.1 ± 0.6	0.8	2.9 ± 0.8
			12	2.1 ± 0.6	4.0	6.1 ± 1.6
15	19 Aug 78	So. Dakota	15	2.3 ± 0.6	1.7	4.0 ± 1.0
			12	4.0 ± 1.0	2.8	6.8 ± 1.7
16	29 Aug 78	So. Dakota	30	12.0 ± 3.0	23.0	35.0 ± 9
			25	3.6 ± 0.9	4.1	7.7 ± 2.0
			20	3.2 ± 0.8	9.1	12.3 ± 3.1
17	15 Mar 79	Panama	18	1.9 ± 0.5	2.5	4.4 ± 1.1
			15	2.0 ± 0.5	3.8	5.8 ± 1.5
18	20 Mar 79	Panama	30	12.7 ± 3.2	7.1	19.8 ± 5
			25	3.2 ± 0.8	2.7	5.9 ± 1.5
			20	5.9 ± 1.5	4.8	10.7 ± 2.7
19*	21 Jun 79	Holloman	30	2.7 ± 0.9	0.5	3.2 ± 0.8
			25	1.8 ± 0.6	0.6	2.4 ± 0.6
			20	2.0 ± 0.7	0.9	2.9 ± 0.8
21	28 Apr 80	Holloman	18	0.6 ± 0.3	2.1	2.7 ± 0.7
			15	0.5 ± 0.3	2.4	2.9 ± 0.8
			12	0.5 ± 0.3	1.5	2.0 ± 0.5
22	01 May 80	Holloman	30	1.8 ± 0.5	16.9	18.7 ± 5
			25	0.4 ± 0.2	2.9	3.3 ± 0.8
			20	0.7 ± 0.3	3.3	4.0 ± 1.0

*Thermo Electron Model 12A only.

Flight numbers 1 through 10, preliminary data only. No data points for small cryogenic and grab samples.

NO_2 is not measured directly. The listed values are the calculated differences between NO_x and NO.

The results from the Holloman 1980 series are plotted in Figure 16. Comparison is made with both the model profiles of the unperturbed stratosphere developed by AFGL for the Environmental Impact Statements for the F-16 and KC-10A[17,18] as well as to representative models developed elsewhere.[19] Since the measured

(See References, page 49, for References 17, 18 and 19.)

34

concentrations generally exceed those predicted by the models, a given quantity of NO_x emissions should have even less of a potential effect on the stratosphere than would otherwise be predicted. However, such an effect could be either an increase or a decrease in O_3 depending on injection altitude.[7] As presented in Figure 16, NO_x, is defined in the more common manner:

$$NO_x = NO + NO_2 .$$

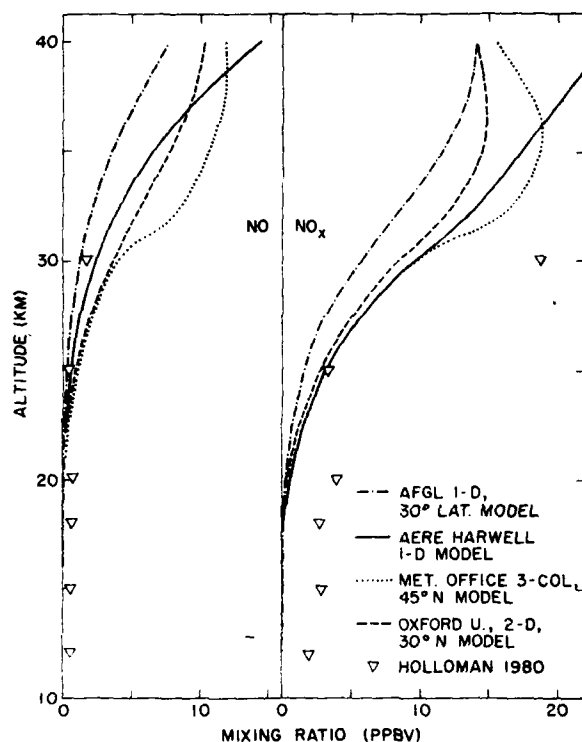Figure 16. Oxides of Nitrogen, Holloman, 1980 and Various Model Profiles

The NO and NO_2 for the unperturbed model and the $NO + NO_2$ perturbations from a given injection are all presented as absolute concentrations in the initial report,[17] however, they have been converted to mixing ratios for the present comparison. The converted values are contained in Table 4. It is usually preferable to compare measurements with theoretical models for NO_x, not only to somewhat iron out diurnal variations in NO and NO_2 but, also, for the case of retrieved air samples to offset potential NO to NO_2 conversions in storage and transfer procedures. For the AF model, the perturbed stratosphere profile was developed, assuming F-16 NO_2 emissions at $1.2 \cdot 10^8$ molecules cm^{-3}/year at a 15-km injection altitude.

35

Table 4. Theoretical Values for Mixing Ratios of Both the Unperturbed and Perturbed Stratosphere for NO, NO_2 and the NO_x Perturbation

Altitude km	Total Density (cm^{-3}) (10^{18})	Unperturbed NO (PPBV) (10^{-2})	Unperturbed NO_2 (PPBV) (10^{-2})	Perturbed NO (PPBV) (10^{-2})	Perturbed NO_2 (PPBV) (10^{-2})	Perturbation $NO + NO_2$ (PPBV) (10^{-5})	Unperturbed $NO + NO_2$ (PPBV)
0	24.110	1.599	5.908	1.599	5.908	0	0.07507
2	21.050	1.182	2.830	1.182	2.830	0	0.04012
4	16.510	0.864	1.425	0.864	1.425	0	0.02289
6	13.400	0.668	0.789	0.668	0.789	0	0.01457
8	10.880	0.715	0.567	0.715	0.567	0	0.01282
10	8.7330	0.862	0.510	0.862	0.510	0	0.01372
12	6.9130	1.736	0.844	1.738	0.845	3	0.02580
14	5.9310	3.502	1.289	3.507	1.291	7	0.04791
16	4.1030	8.147	3.907	8.157	3.912	15	0.12055
18	2.8240	10.868	14.143	10.873	14.149	11	0.25012
20	2.0000	13.194	28.619	13.197	28.625	9	0.41813
22	1.4290	17.189	51.558	17.192	51.565	10	0.68747
24	1.0320	25.530	91.741	25.534	91.751	14	1.17271
26	0.74450	44.215	170.450	44.220	170.477	32	2.14665
28	0.54230	76.921	292.753	76.928	292.772	26	3.69674
30	0.39700	130.866	448.892	130.877	448.942	61	5.79758
32	0.29240	202.565	613.611	202.579	613.646	49	8.16176
34	0.21590	299.875	756.276	299.893	756.322	64	10.5615
36	0.16040	428.379	822.195	428.404	822.256	86	12.5057
38	0.11980	592.805	780.559	592.838	780.601	75	13.7336
40	0.08999	780.587	640.471	780.620	640.505	67	14.2106

The NO_x profile from the latest series has been compared with the longer term average as shown in Figure 17. The latest profile averages a lower mixing ratio than the average. The data spread does not permit such a claim to be conclusive but certainly indicates no increase with time. Data for NO_x were obtained from the first two Holloman series (1976 and 1977), although not included herein as the NO_x analyzer/calibration system was in a preliminary stage at that time.
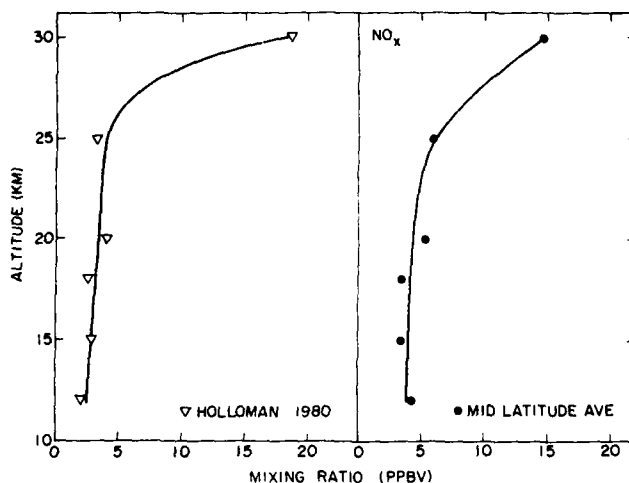

Figure 17. NO_x as a Function of Time

The mid-latitude profile is compared with the high and low latitude results in Figure 18. Initially, all data are shown relative to sea level but then the Alaska and Panama data are referenced to the mean, measured mid-latitude tropopause of 13 km (see Table 5). Latitudinal dependence is observed and is seen to be reduced when the adjustment is made. Such treatment is likely of greater significance when species of tropospheric origin, such as the fluorocarbons, are studied. Some latitudinal dependence of NO_x has been predicted.[20] Since there is only one set of NO_x data for Panama and similarly for Alaska, one cannot preclude other variables such as air mixing during a given series, with its possible effect on the profile. Such mixing could contribute to the fact that the desired descent profile is achieved with greater difficulty on some flights than on others. Although solar heating of the helium in the balloon affects balloon control, there is the likelihood of vertical air movements at times (see Section 7.2).

20. Wofsy, S. C. (1978) Temporal and latitudinal variations of stratospheric trace gases: A critical comparison between theory and experiment, J. Geophys. Res. 83:364-378.

Table 5. Tropopause Heights for Sampling Flights

| WAS Flight Number	AFGL Flight Number	Date	Location	Tropopause km	Height Above Tropopause km					
					"30"	"25"	"20"	"18"	"15"	"12"
1	C75-10	05 Jun 75	Chico	14.3	-	-	5.7	-	-	-
2	C75-11	26 Jun 75	Chico	11.5	-	-	8.5	-	-	-
3	H76-3	27 Jan 76	Holloman	10.9	-	-	9.1	-	-	-
4	H76-4	06 Feb 76	Holloman	10.2	19.8	-	-	-	-	-
5	H76-6	12 Feb 76	Holloman	11.4	-	-	-	-	3.6	-
6	H76-24	14 May 76	Alaska	8.5	-	-	11.5	-	-	-
7	H76-38	19 May 76	Alaska	10.3	-	-	-	-	4.7	-
8	H77-8	05 Feb 77	Holloman	10.0	20	15	10	-	-	-
9	H77-10	16 Feb 77	Holloman	12.8	-	-	-	5.2	2.2	-
10	H77-20	30 Mar 77	Panama	17.6	12.4	-	2.4	-	-	-
11	H77-59	08 Oct 77	Chico	11.8	18.2	-	-	-	-	-
12	H77-63	17 Oct 77	Chico	10.4	-	-	-	7.6	4.6	-
13	H78-23	02 Jun 78	Alaska	8.5	21.5	16.5	11.5	-	-	-
14	H78-26	07 Jun 78	Alaska	9.1	-	-	-	-	5.9	2.9
15	W78-35	19 Aug 78	So. Dakota	16.1	-	-	-	-	(-1.1)	(-4.1)
16	W78-36	29 Aug 78	So. Dakota	12.1	17.9	12.9	7.9	-	-	-
17	H79-11	15 Mar 79	Panama	17.3	-	-	-	0.7	(-2.3)	-
18	H79-14	20 Mar 79	Panama	17.6	12.4	7.4	2.4	-	-	-
19	H79-30	21 Jun 79	Holloman	15.8	14.2	9.2	4.2	-	-	-
20	H79-31	25 Jun 79	Holloman	15.8	-	-	-	2.2	(-0.8)	(-3.8)
21	H80-19	28 Apr 80	Holloman	13.4	-	-	-	4.6	1.6	(-1.4)
22	H80-20	01 May 80	Holloman	9.6	20.4	15.4	10.4	-	-	-
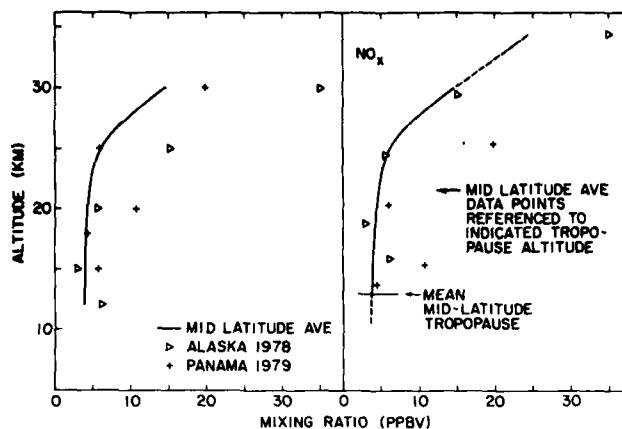
Figure 18. NO_x as a Function of Latitude

7.2 Gas Chromatograph Measurements

Gas chromatograph measurements were obtained for samples from all twenty-two flights. The results are contained in Table 6. Only data from three early flights are omitted. The first two flights served primarily to test the engineering and sample handling procedures, whereas the fourth sample became contaminated. Only slight latitudinal variations were noted for data obtained between 33° and 45° N and all such data will be categorized as mid-latitude data. Measurements for flights 3, 5, 6 and 7 were made on a Becker, Model 417, gas chromatograph at NOAA, Boulder.[21]

Mid-latitude nitrous oxide results are shown in the top graph in Figure 19 and a median profile was established. The Holloman 1979 series exhibited folded profiles, and the data are not included in Figure 19. In the lower graph the mid-latitude profile is compared with the Alaska and Panama data. The mixing ratio lapse rate as a function of altitude is seen to increase with latitude. Since normal diffusion from the troposphere to the stratosphere, across the tropopause, is known to be very slow, it has been postulated that the principal mechanism is an upwelling to the stratosphere in the tropics followed by a gradual diffusion northward. More recently, reports indicate that comparisons such as in Figure 19 might exaggerate the latitudinal dependence and that the data should more appropriately be plotted relative to the tropopause.

Figure 20 shows the same mid-latitude data plotted relative to the tropopause altitude. The profile becomes somewhat smoother and converges around the nominal tropospheric mixing ratio of 320 PPBV.

21. Gallagher, C.C., Pieri, R.V., and Goldan, P.D. (1977) Stratospheric measurements of N_2O, $CFCl_3$ and CF_2Cl_2, J. Atmos. Sciences 34:1481-1482.

Table 6. Nitrous Oxide and Fluorocarbon Mixing Ratios

LKD Flight Number	Flight Date	Location	Sampling Altitude (km)	Sampling Method	(PPBV) N_2O	(PPTV) CF_2Cl_2	(PPTV) $CFCl_3$
3*	27 Jan 76	Holloman	20	Cryo	280	-	56
5*	12 Feb 76	Holloman	15	Cryo	270	-	69
6*	14 May 76	Alaska	20	Grab	218	100	42
7*	19 May 76	Alaska	15	Grab	300	100	-
8	05 Feb 77	Holloman	30	Cryo	67 ± 11	62 ± 12	8 ± 2
			25		130 ± 17	65 ± 13	3 ± 1
			20		120 ± 17	125 ± 20	32 ± 7
9	16 Feb 77	Holloman	18	Cryo	-	150 ± 23	64 ± 13
			15		315 ± 32	173 ± 26	115 ± 20
10	30 Mar 77	Panama	30	Grab	160 ± 20	78 ± 15	24 ± 5
			20		290 ± 29	185 ± 28	43 ± 9
11	08 Oct 77	Chico	30	Cryo	115 ± 17	54 ± 11	6 ± 2
12	17 Oct 77	Chico	18	Cryo	242 ± 25	113 ± 20	90 ± 17
			15		285 ± 29	148 ± 24	178 ± 27
13	02 Jun 78	Alaska	30	Cryo	23 ± 3	11 ± 2	7 ± 2
			25		113 ± 11	62 ± 9	28 ± 5
			20		175 ± 11	163 ± 17	90 ± 12
14	07 Jun 78	Alaska	15	Cryo	216 ± 11	211 ± 22	-
			12		269 ± 14	179 ± 18	-
15	19 Aug 78	So. Dakota	15	Cryo	278 ± 14	205 ± 21	132 ± 15
			12		303 ± 16	-	-
16	29 Aug 78	So. Dakota	30	Cryo	37 ± 4	50 ± 7	-
			25		182 ± 11	71 ± 10	42 ± 7
			20		240 ± 12	166 ± 17	90 ± 12
17	15 Mar 79	Panama	18	Cryo	316 ± 16	304 ± 31	124 ± 15
			15		342 ± 18	254 ± 26	174 ± 18
18	20 Mar 79	Panama	30	Cryo	204 ± 11	133 ± 15	12 ± 2
			25		220 ± 11	143 ± 16	63 ± 9
			20		319 ± 16	-	-
19	21 Jun 79	Holloman	30	Cryo	141 ± 12	84 ± 11	48 ± 8
			25		137 ± 11	58 ± 8	9 ± 2
			20		219 ± 11	114 ± 14	118 ± 15
20	25 Jun 79	Holloman	18	Grab	257 ± 13	216 ± 22	200 ± 20
			15		319 ± 16	279 ± 28	178 ± 18
			12		300 ± 15	267 ± 27	163 ± 17
21	28 Apr 80	Holloman	18	Cryo	233 ± 12	136 ± 15	77 ± 11
			15		276 ± 14	148 ± 17	94 ± 13
			12		348 ± 18	180 ± 18	127 ± 14
22	01 May 80	Holloman	30	Cryo	62 ± 7	32 ± 5	1 ± 1
			25		154 ± 11	91 ± 12	23 ± 4
			20		177 ± 11	113 ± 14	47 ± 8

*Measured on NOAA - Gas Chromatograph
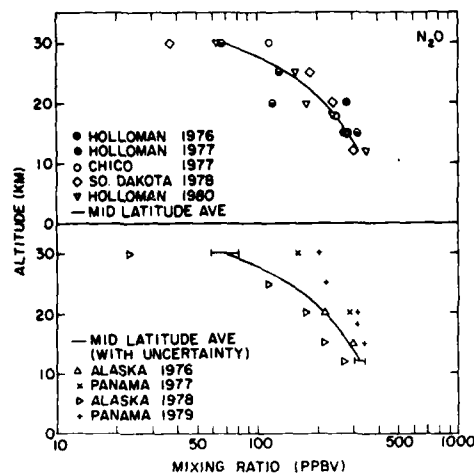
Flight Nos. 1, 2, and 4: No data, see text.

40

Figure 19. N₂O as a Function of Latitude

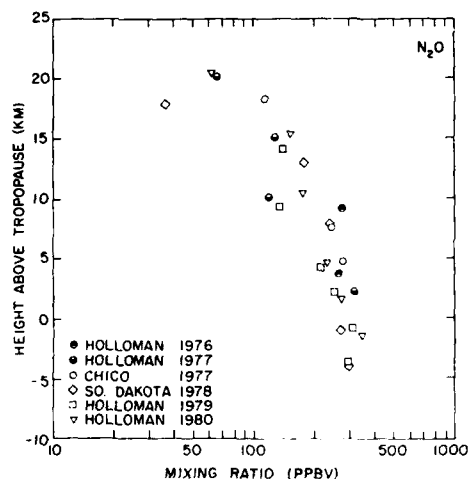Figure 20. Mid-Latitude N₂O Relative to Tropopause

These data were replotted as simple dots for clarity in Figure 21 and again compared with the Alaska and Panama data. Any latitudinal variations become much less discernible, but there is still indication that the low latitude mixing ratio, lapse rate is slightly slower, and as such, is consistent with the tropical upwelling theory. Middle and high latitude profiles become essentially indistinguishable from each other.

A similar set of comparisons was made for fluorocarbon 12 (that is, CF_2Cl_2). Figure 22 shows the mid-latitude data, the median profile, and in the lower graph, a comparison with Alaska and Panama results. All of the Panama and all but two

41

of the Alaska data points are consistent with the tropical upwelling and northward diffusion theory.
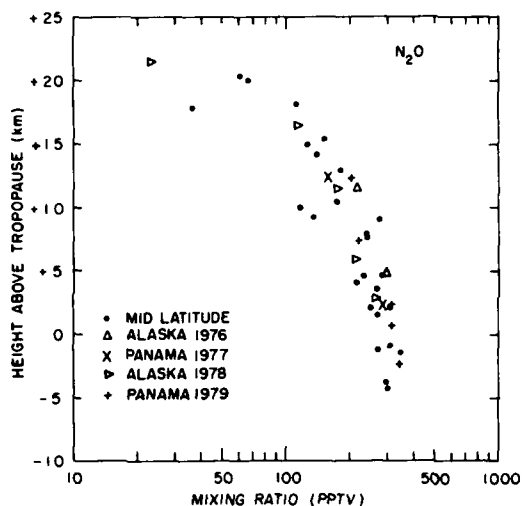
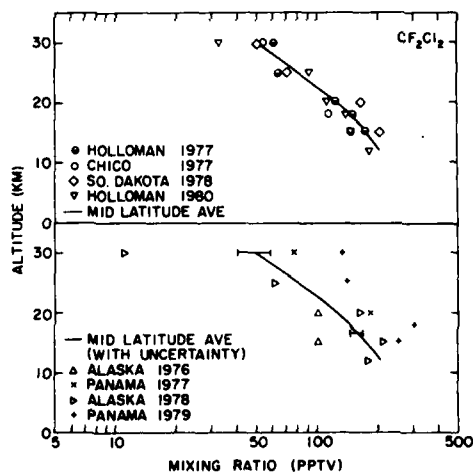Figure 21. All N_2O Results Relative to Tropopause

Figure 22. Fluorocarbon 12 as a Function of Latitude

The mid-latitude data, relative to tropopause height, are plotted in Figure 23. The folded profile data from the Holloman 1979 series are included. Figure 24 contains the mid-latitude data (dots) as well as the Alaska and Panama results. As with N_2O, the Panama CF_2Cl_2 profile shows a slightly slower mixing ratio lapse

42

rate than does the middle and high latitude data. The middle and high latitude profiles are about coincident. The slower mixing ratio lapse rate at low latitudes was also observed for N_2O and CF_2Cl_2 by Goldan et al at NOAA.[22]
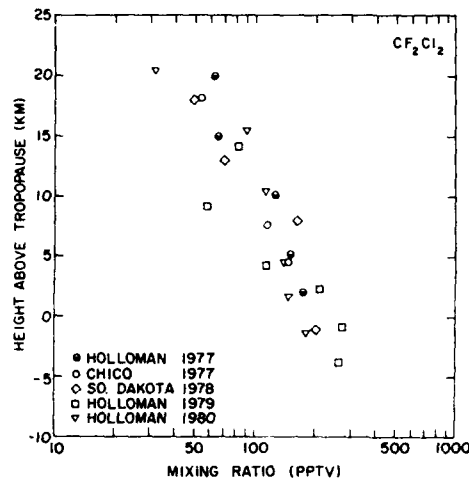

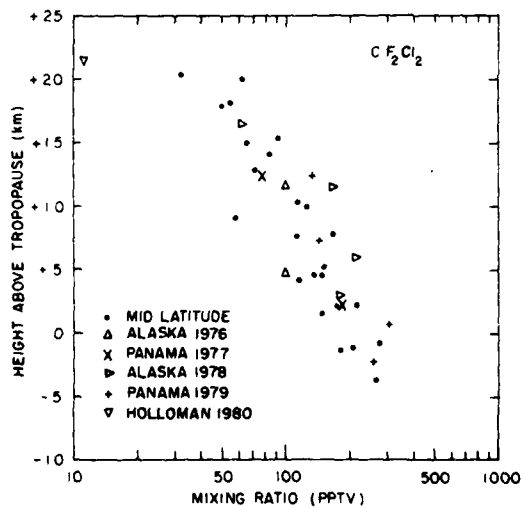Figure 23. Mid-Latitude Fluorocarbon 12 Relative to Tropopause

Figure 24. All Fluorocarbon 12 Results Relative to Tropopause

22. Goldan, P. D., Kuster, W. C., Albritton, D. L., and Schmeltekopf, A. L. (1980) Stratospheric $CFCl_3$, CF_2Cl_2 and N_2O height profile measurements at several latitudes, J. Geophys. Res. 85:413-423.

43

Figure 25 contains the fluorocarbon 11 ($CFCl_3$) data, again establishing a mid-latitude profile and comparing it to Alaska and Panama measurements. The profile readily extrapolates to a nominal tropospheric mixing ratio of 135 PPTV. For this species, only the Panama data exhibit a profile separate from that for the mid-latitudes.
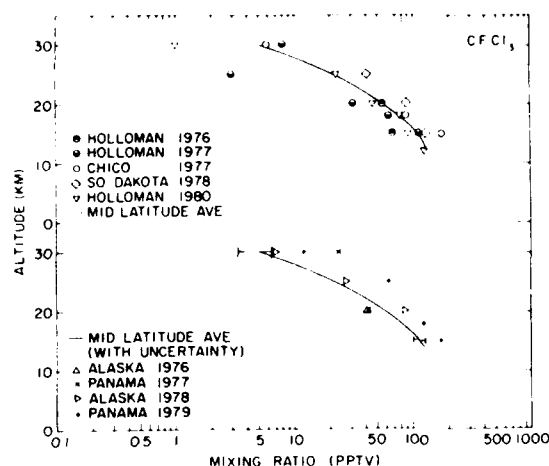

Figure 25. Fluorocarbon 11 as a Function of Latitude

Figure 26 contains the mid-latitude mixing ratios versus height above tropopause; Figure 27 includes all latitudes, plotted individually and exhibiting independence of latitude. This is similar to behavior reported by NOAA[22] and, as in their case, the lack of discernible latitude dependence is believed due largely to the greater measurement uncertainty in these, the lowest mixing ratios among the species studied. Also, with the greater lapse rate, uncertainties in tropopause determinations become more significant and so Figure 25 is probably the more reliable indicator of $CFCl_3$ behavior. Fabian et al obtained a $CFCl_3$ profile at a mid-latitude location.[23] Results are plotted relative to sea level but with the tropopause altitude indicated on their graphs.

23. Fabian, P., Borchers, R., Weiler, K.H., Schmidt, U., Volz, A., Ehhalt, D.H., Seiler, W., and Müller, F. (1979) Simultaneously measured vertical profiles of H_2, CH_4, N_2O, $CFCl_3$ and CF_2Cl_2 in the mid-latitude stratosphere and troposphere, J. Geophys. Res. 84:3149-3154.
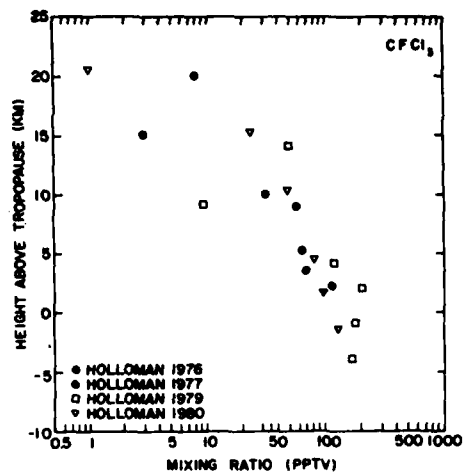
Figure 26. Mid-Latitude Fluorocarbon 11 Relative to Tropopause
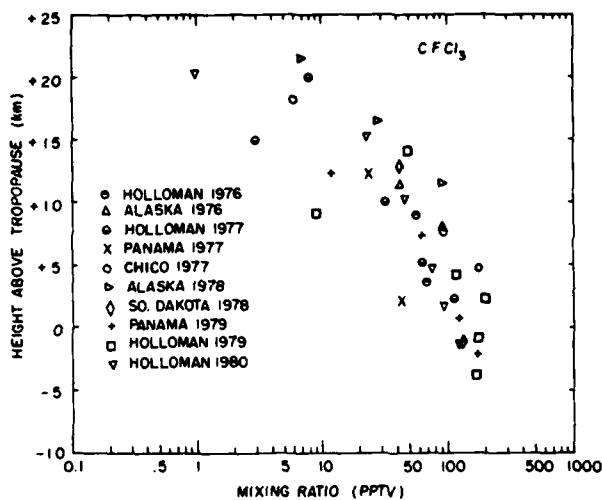

Figure 27. All Fluorocarbon 11 Results Relative to Tropopause

An error factor in plots of mixing ratio versus height above tropopause is the uncertainty in determining the mean tropopause altitude at the time of the sampling flight. It has been shown that through confusing temperature profiles in the tropo-pause region, considerable uncertainty as to the tropopause altitude can readily occur. Goldan et al. prefer to utilize the mean tropopause for the specific latitude and season in evaluating their results,[22] although this approximation does not, of course, eliminate the problem. Figure 28 shows the temperature profiles from a sensor on board the Holloman 1980 flights. The "official" tropopause altitudes are

indicated by the "hash" marks. These are supplied from Air Force rawinsonde flights conducted just before or after the sampling flights. Several criteria apply, but basically the base of the tropopause is determined by a change in the temperature lapse rate. As can be seen from the example in Figure 28, good agreement exists between the independent measurements; however, on the 1 May 1980 profile, other significant variations occur and so, although the defined tropopause altitude has been accurately determined, it may not be the most significant altitude vis a vis stratospheric trace gas behavior.

As alluded to earlier, the Holloman 1979 data exhibited folded profiles; that is, the mixing ratio lapse rates reversed at one or more altitudes, indicative of an anomaly in the stratosphere on that day. Folded profiles have been attributed to vertical air motions. Similar phenomena have been reported elsewhere.[22] It is likely that small vertical air motions existed at the time of other flights, contributing to data spread in the various graphs.
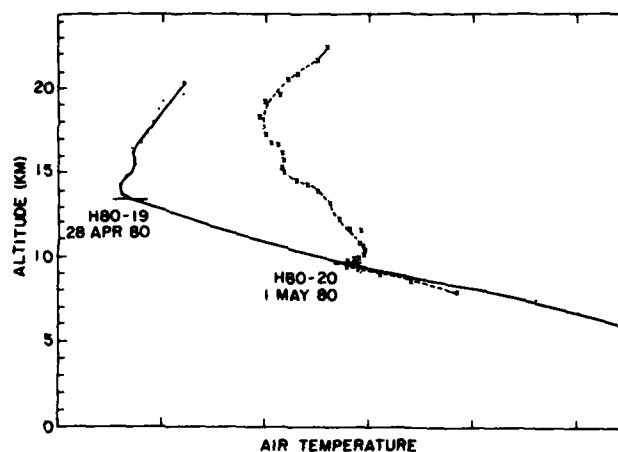

Figure 28. Stratospheric Temperature Profile, Holloman 1980

Finally, the relevant mixing ratio profiles obtained from the Air Force stratospheric model[17] have been compared with the mid-latitude observations (Figure 29). The measured lapse rates are seen to equal or exceed the theoretical values, indicating less than predicted intrusions of these species into the stratosphere. Also, the tropospheric values used in the model could be updated to reflect increased mixing ratios of these species as measured by several experiments and so would

46

shift the stratospheric model curves farther to the right of the observations. Fluoro-carbons 113 and 114 were not detected.
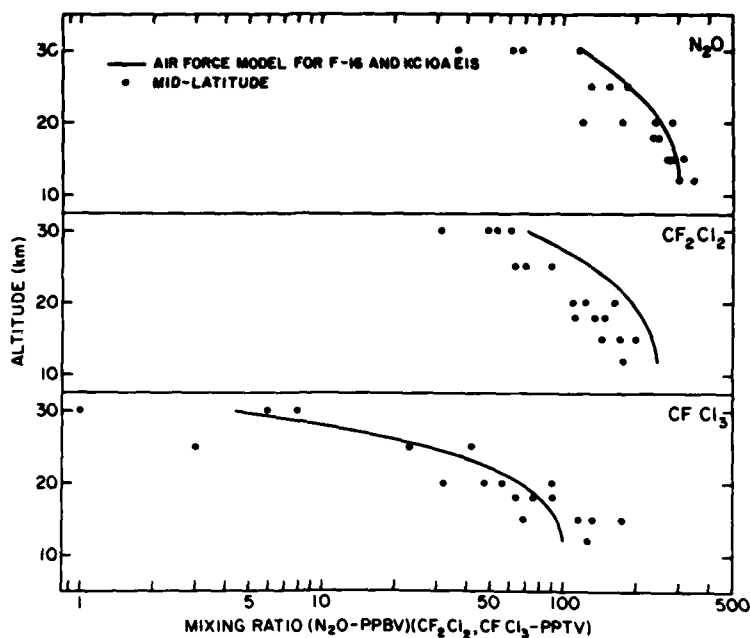

Figure 29. Comparison of Measured and Air Force Model
Profiles of Nitrous Oxide and Fluorocarbons 11 and 12

8. CONCLUSIONS

The goal of achieving measurements of mixing ratios of several stratospheric trace gas species of importance to the ozone budget has been satisfied. Coverage of several altitudes and latitudes permits comparison with and possible revision of stratospheric models relative to transport and chemistry. With limited stratos-pheric flights to date, the measured NO_x values can be interpreted as baseline values and being larger than predicted by theory, they suggest that for a given NO_2 injection the percentage change in stratospheric NO_x from such a perturbation should be even less significant (be it plus or minus).

The obtained profiles of nitrous oxide and the fluorocarbons indicate lapse rates with altitudes that vary with latitude and the particular gas species. Within the accuracy of the measurements the stratosphere exhibits no increase of the mixing

47

ratios as a function of time. This is similar to conclusions reached by NOAA,[22] but for the region just below the tropopause, however, it has been shown elsewhere[22] that $CFCl_3$ and CF_2Cl_2 mixing ratios do increase with time, about 10 percent per year, and with N_2O increasing at up to 2 percent per year. Since our intent has been to obtain measurements in the stratosphere, we have few data points in the troposphere. However, if we accept such rates of increase, it seems likely that, with time, increases in stratospheric mixing ratios should be observed. Leifer et al. recently reported measurements showing an increase in stratospheric $CFCl_3$ during the period 1974 to 1976.[24]

Thus, although mixing ratios of the various species studied have yet to exhibit increases in stratosphere values over the duration of the measurements, increased aircraft emissions and the subtropopause buildup in some species of interest suggest the importance of maintaining stratospheric measurements, in order to record promptly and disseminate any such changes at these altitudes.

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