

normally set at a value of 520,000 counts so that the display then reads out the approximate ozone amount directly in partial pressure, although in the somewhat unwieldy units of 10^3 nanobars (1 microbar).

4.1.4 Halocarbons

PROGRAM

Although the project leader for the GMCC Freon-11 program relocated to the Techniques and Standards Group in 1974, actual flask preparation and analyses were continued at the Air Resources Laboratory's Field Research Office at Idaho Falls, Idaho, until the middle of May 1975. Sampling continued at Barrow, Mauna Loa, and Samoa with stainless steel flasks. Outlined below are the operating conditions of the Electron Capture Chromatograph used at Idaho Falls to analyze the flask samples:

Detector:	15 millicuries Nickel 63
Detector Temperature:	30°C
Column:	10'x $\frac{1}{4}$ " Carbowax 400/Porasil F
Column Temperature:	30°C
Carrier Gas:	Ultra-pure nitrogen
Flow Rate:	50 cc/min
Electronics:	Fixed pulse mode
Pulse width:	2 microseconds
Pulse period:	200 microseconds
Pulse height:	-20 volts
Sample Volume:	5 cc

A Hewlett-Packard variable frequency gas chromatograph was received in April 1975 and put into operation at the Techniques and Standards Laboratory in Boulder, Colorado. The operating conditions of this instrument were:

Detector:	15 millicuries Nickel 63
Detector Temperature:	100°C
Column:	10'x $\frac{1}{8}$ " Carbowax 400/Porasil F
Column Temperature:	40°C
Carrier Gas:	95% Argon--5% Methane
Flow Rate:	15 cc/min
Electronics:	Variable frequency mode
Sample Volume:	1 cc

Transfer of the complete halocarbon program took place in mid-May and the stations were instructed to send all exposed flasks to Boulder for analysis. Cross comparisons were made of the Idaho Falls system and Boulder system by analysis of the same samples at both locations.

As flasks were analyzed in Boulder, it became apparent that the sensitivity of the Hewlett-Packard chromatograph was too low because of certain limiting design features. For partial correction of this deficiency, the Idaho Falls detector and electronics were transferred to Boulder. A duplicate of the electronics was fabricated and, together with the detector, was

installed in the Hewlett-Packard chromatograph to continue the analysis. This configuration was used through the remainder of the year. The operating conditions were:

Detector:	15 millicuries Nickel 63
Detector Temperature:	150°C
Column:	10'x1/8" Carbowax 400/Porasil C
Column Temperature:	70°C
Carrier Gas:	Ultra-pure nitrogen
Flow Rate:	20 cc/min.
Electronics:	Fixed pulse mode
Pulse width:	2 microseconds
Pulse period:	200 microseconds
Pulse height:	-20 volts
Sample Volume:	1 cc

Tests on the Hewlett-Packard chromatograph were continued to determine whether the sensitivity of the instrument could be increased under variable frequency operating mode. The manufacturer has recommended certain electronic modifications to the instrument which will be attempted in 1976.

INSTRUMENT DEVELOPMENT

A. Gas Dilution Apparatus

The Idaho Falls chromatograph system was initially calibrated for Freon-11 on the basis of coulometry and this calibration was transferred to Boulder by sample comparisons. A number of errors can arise using such an approach. Implementation of an independent calibration gas method was, therefore, considered.

Because of simplicity of design, a static gas dilution system was built. In the design stage, the virial coefficient gas law was used and an error analysis made using manufacturer's commonly quoted accuracies and precisions for temperature and pressure measurements. A schematic diagram of this system is shown in Figure 19.

The operational procedure is for pure Freon-11 (sample) gas to be introduced into an evacuated volume of approximately 10 cc where the gas is isolated and its temperature and pressure measured. The small gas volume is now expanded into a large volume of 10,000 cc and a dilution gas introduced. Temperature and pressure are again measured. With the resulting 1000:1 volume ratio and a 10:1 pressure ratio, a dilution of 10^4 is possible. If the mixture is then reintroduced into the smaller volume and the large volume again evacuated, the procedure can be repeated again and again to reach any desired sample gas concentration.

During December several attempts were made to achieve a three-stage dilution into the parts-per-trillion range using fluorocarbon-11 and nitrogen. Successive batches of the gas mixtures did not show repeatability, probably because of container wall effects. Further tests are in progress.

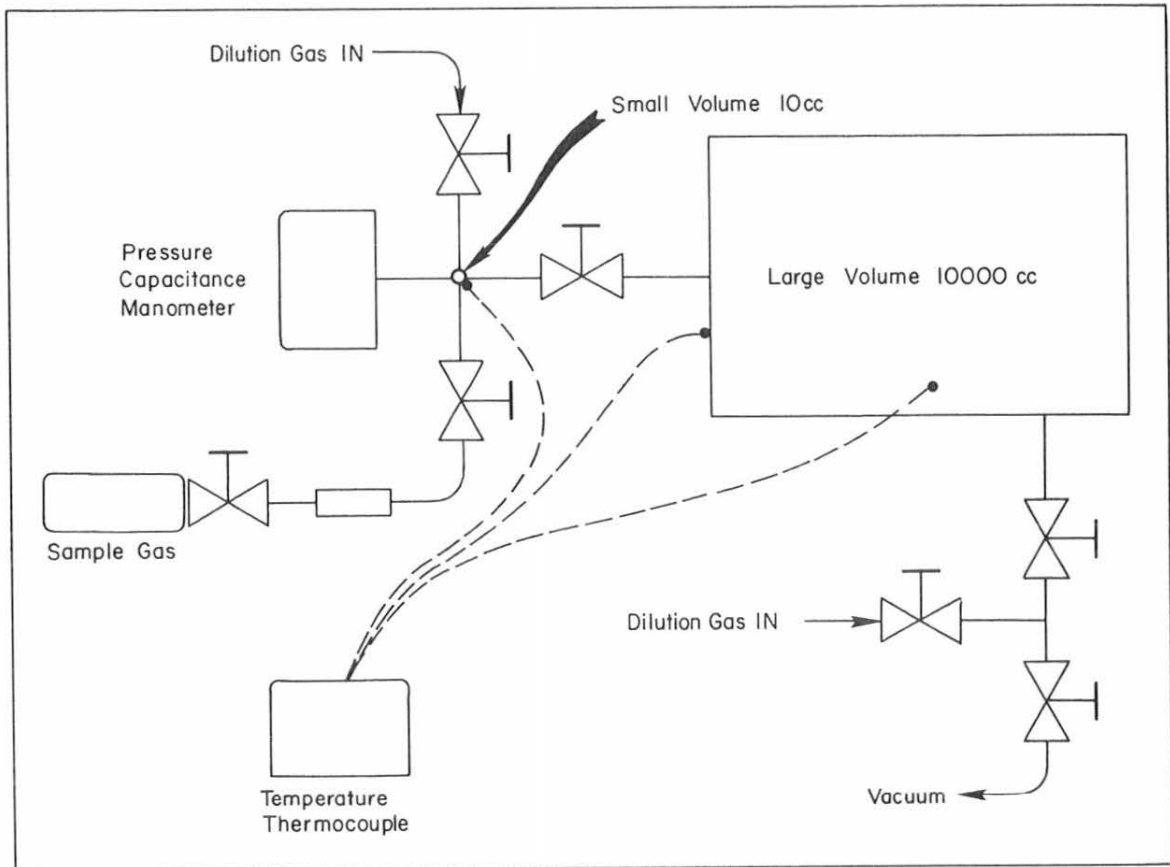


Figure 19. Diagram of gas dilution apparatus.

B. Cylinder Pump-Up System

A preponderance of apparently contaminated (high-reading) fluorocarbon-11 samples collected at the GMCC field stations during 1975 indicated the need for an improved sampling technique. To eliminate problems inherent in sampling with stainless steel flasks, a decision was made to collect air samples pressurized to an overpressure of about 10 psi above ambient air pressure. A prototype flask pump-up apparatus, shown in Figure 20, was therefore built and tested. First field use of the unit will be at South Pole Station in January 1976.

DATA

Table 10 lists the halocarbon-11 (CCl_3F) concentrations determined from flask air samples collected at the GMCC baseline stations. Indicated standard deviations were determined from the spread in repeated sample analyses. The overall uncertainty in the concentrations is estimated to be $\pm 25\%$ except for data obtained during October, November, and December 1975 in which flask contamination may have caused the unexpectedly high concentrations. The problem is under investigation.

Table 10. 1975 Data Base CCl₃F

Month	Day	BARROW		Day	SAMOA		Day	MAUNA LOA		
		F-11 Conc. (ppt)	σ		F-11 Conc. (ppt)	σ		F-11 Conc. (ppt)	σ	
Jan	16	120	5	4	155	7	3	142	4	
	28	137	7	14	164	21	10	149	13	
		21			941	44	17	118	14	
		31			170	21				
Feb	11	143	13				3	113	8	
	18	136	4				7	161	6	
	26	112	15				19	114	7	
							26	14628	221	
Mar	4	108	2	13	92	10	5	97	3	
	14	111	4	21	99	10	12	110	6	
	18	102	2	31	106	7	19	115	4	
	25	149	7				25	107	9	
Apr	1	142	3	10	116	4	9	105	3	
	15	99	8	18	145	10	16	1836	21	
	25	114	7				23	99	4	
							28	98	2	
May	1	119	3	6	5153	--	2	114	5	
	9	102	4	12	64	6	7	105	4	
	13	155	3	20	108	8	13	100	7	
	20	168	7				17	95	7	
	27	95	6				21	82	10	
							29	106	16	
Jun	5	103	4	8	109	6	7	134	10	
	10	106	5	8	83	5	12	85	10	
					21	85	5			
Jul	15	147	9	12	781	13	1	776	24	
	25	107	6							
Aug	3	117	15	1	260	7	8	185	22	
	14	105	7	14	598	6	14	106	18	
					22	233	9	21	278	20
								27	320	11
Sep	6	132	8	6	220	9	5	185	16	
	16	203	6	13	681	16	11	225	31	
	26	220	9				18	243	4	
							25	30353	--	
Oct	1	128	8	2	503	7	2	147	7	
	10	540	10	10	220	11	9	346	12	
	14	231	5	18	415	12	16	371	21	
	23	202	11	31	307	3	24	331	5	
Nov	12	272	6	8	284	1	6	370	8	
	19	132	5							
Dec	16	204	8	14	256	2				
	24	948	6							
	30	251	7							

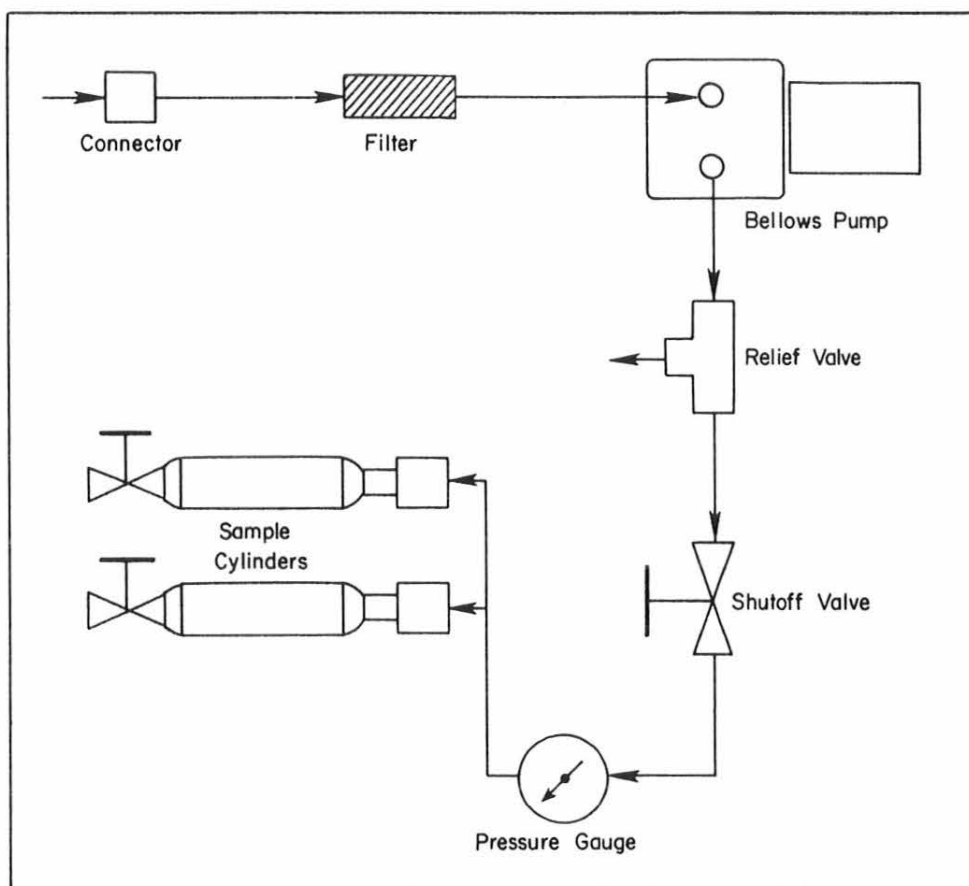


Figure 20. Diagram of cylinder pump-up system.

The 1975 data and all previously obtained data are graphically displayed in Figures 21, 22, and 23.

In a cooperative effort with Naval Research Laboratory, 18 stainless steel flask air samples were collected during Arctic flights in April and May 1975. CCl_3F analysis results for these samples are shown in Table 11.

4.2 Upper-Air Measurements Using Lidar

4.2.1 Aerosols

A major activity during 1975 was the continuing study of the enhanced stratospheric dust layer caused by the eruption of Fuego volcano in Guatemala during October 1974 (Fegley & Ellis, 1975). Observations were made during the evening hours, one day per week. Although this event was less significant in terms of stratospheric enhancement than the Agung volcano eruption during the

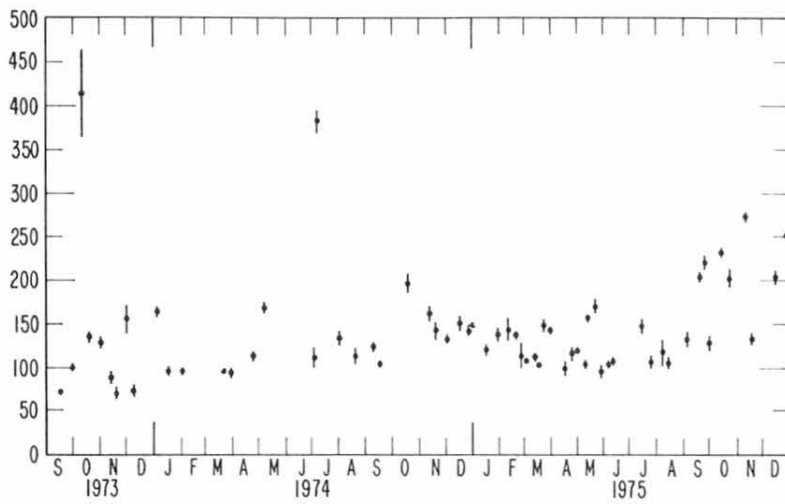


Figure 21. CCl_3F data for Barrow, Alaska.

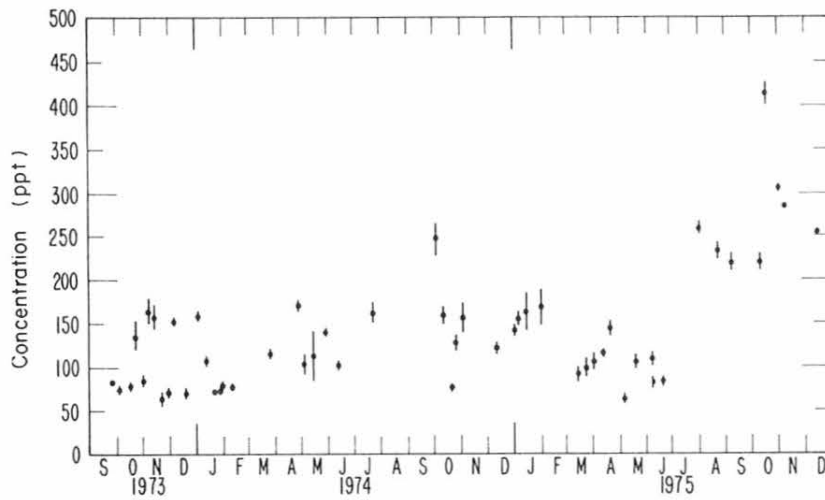


Figure 22. CCl_3F data for Cape Matatula, Samoa.

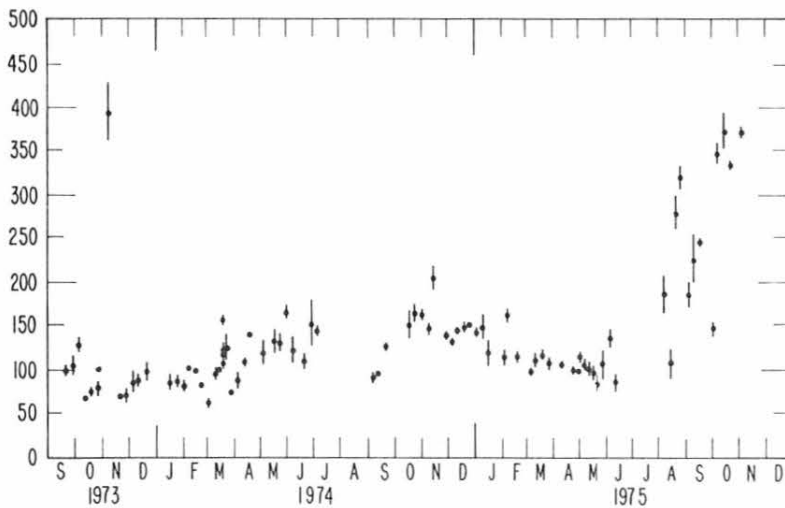


Figure 23. CCl_3F data for Mauna Loa, Hawaii.

Table 11. CCl_3F Values from NRL Cooperative Program

Date 1975	Sample No.	Altitude (feet)	F-11 Conc. (ppt)	Position
4-17	2	1000	110.2	85°46'N 40°00'W
17	4	1000	103.5	84°39'N 67°12'W
18	6	1000	90.2	85°48'N 20°49'W
18	8	1000	970.8	85°25'N 40°33'W
19	10	1000	107.5	85°29'N 25°26'W
21	12	1000	94.1	85°09'N 24°39'W
23	14	1000	105.4	81°39'N 61°57'W
28	19	1000	108.9	82°55'N 58°46'W
29	22	1000	98.5	87°14'N 25°28'W
5- 1	25	1000	131.1	87°25'N 27°42'W
2	27	22000	86.3	82°37'N 56°55'W
2	29	1000	113.2	86°07'N 77°58'W
2	31	27000	78.9	86°10'N 44°52'W
3	33	1000	111.6	86°11'N 87°03'W
5	35	1500	111.6	84°03'N 48°03'W
5	37	20000	101.9	89°29'N 28°22'W
5	39	20000	61.3	87°46'N 18°44'E
5	41	1000	116.9	82°56'N 20°08'E

mid-1960's, it remains one of the better studied events by the use of advanced monitoring systems such as lidar and stratospheric research vehicles (Rosen et al., 1975; Elterman, 1975).

Figure 24 summarizes the 1975 study of the Fuego event. It is a plot of the integral of the backscatter coefficient throughout the depth of the stratospheric cloud. Weekly values are shown rather than monthly averages. The dust layer first appeared at Mauna Loa on October 8, 1974, as a clearly defined layer slightly above the tropopause. Its intensity increased such that by November 5 the layer was easily visible to the eye as a widespread cirrus-like layer. As the layer continued to diffuse both horizontally and vertically, it became less prominent. (Originally the layer was less than 1 km thick but gradually thickened to 3 to 4 km toward mid-1975.) The layer was much more horizontally uniform after about March 1975 and generally weakened until finally resembling the normal Junge layer of late 1973. During 1974 the stratosphere had become extremely clean with scattering ratios