

NBS standard by about 5% over a wide range of ozone values, and higher by about 2% over the range from an ozone partial pressure of about 20 to 70 nanobars, which includes almost all the data from the GMCC observatories.

#### 4.1.4 Halocarbons

The weekly exposure of an evacuated stainless steel cylinder has continued at Barrow, Mauna Loa, and Samoa throughout 1976. In addition, a set of special flask samples was taken at these stations during late October and early November in cooperation with the NASA Latitude Survey.

A dual evacuated cylinder program was instituted at Niwot Ridge, Colorado, in January and continued through the year. INSTAAR, which has facilities on Niwot Ridge, was under contract to expose the pair of flasks each week.

A dual cylinder pump-up system was tested during January at the South Pole station.

#### Instrumentation

A number of changes and additions helped improve the quality of the data. During March 1976, the Hewlett-Packard chromatograph was electronically modified according to the manufacturer's recommendations. This permitted the variable frequency mode of operation to be used with ultrapure nitrogen carrier gas. The change brought about a sensitivity increase of 2.5. The Idaho Falls detector and fixed-pulse electronics were no longer used. A mass flow controller was installed in the carrier gas line in April to reduce flow fluctuations and their effect on detector response. Negative chromatogram peaks were observed and found to be caused by halocarbons in the carrier gas despite the ultrapure (99.999%) nitrogen used. In August, a Supelco Gas Purifier was installed in the carrier gas line which reduced halocarbon impurities to an amount below their detectable limit.

The cylinder pump-up tests run in January at South Pole showed unfavorable results. Following a critical review of the flasks and pump system, changes are being made to improve the sampling system. Our stainless steel cylinders are being passivated by the SUMMA electropolishing process developed by Moleetrics, Inc., of Englewood, California. It is believed this will minimize cylinder wall effects that cause modification, adsorption or desorption of collected trace halogens. The cylinders are being equipped on both ends with all stainless steel Nupro type SS-4H bellows valves. These valves contain no elastomers or polymers that could serve as halocarbon sources or sinks. After chemical cleaning, the cylinders are evacuated while heating, then filled with zero air. Chromatographic purity checks are made a day and at least a month later by sampling the zero air.

The dual cylinder pump-up system has been simplified. The pump system contains a 7-micron all stainless steel filter at the inlet to the stainless steel bellows pump. At the outlet of the pump, the gas flows through a relief valve, then through both cylinders which are parallel. The inlet of the pump system is connected through a short section of stainless steel tubing to the gas stack manifold at each station.

#### Future Program Developments

The dual cylinder pump-up system described in the previous section will be tested at the South Pole facilities during 1977. Samples taken in January and February will be used to assess the quality of the system and the value of deploying similar systems to all of the baseline stations. Cylinder pairs will also be pumped up monthly through the rest of 1977 to test for long-term sample stability.

A major emphasis during the coming year will be developing reference gases for chromatograph calibration. Large cylinders will be pressurized with background air, and reference values of halocarbons will be determined through interlaboratory and standard gas comparisons.

Analysis for other halocarbons, such as dichlorodifluoromethane (F-12) and nitrous oxide ( $N_2O$ ), will be possible when reference gases become available.

#### Data

Our complete 1976 data base for trichlorofluoromethane (F-11) is presented in Table 9. These data are graphically presented with earlier data in Figure 11. The scatter in the data and the standard deviations have decreased. This is partly due to increased control of parameters in the chromatographic analysis. Also, the evacuation of sampling flasks has been monitored more closely.

Of the three baseline stations Barrow has the highest concentrations, Samoa the lowest, and Mauna Loa is in between. This is what is expected. However, a phase difference is also likely but is not readily apparent from the graphs. In fact, the concentrations appear to have risen and peaked together. Whether the rise and fall is a true annual cycle will need at least another year's data to determine.

Niwot Ridge samples were taken in pairs of flasks. Most of these pairs showed coincidence. Early in the sampling, one pair consistently was not coincident and had F-11 concentrations higher than expected. That pair was considered contaminated and was withdrawn from the sampling rotation scheme in early June.

A plot of the Niwot Ridge data indicates close agreement with the Mauna Loa data.

Table 9. 1976 Data Base for CCl<sub>3</sub>F

Month	Barrow		Mauna Loa			Niwt Ridge				Samoa				
	Day	Conc. (pptv)	σ	Day	Conc. (pptv)	σ	Day	Conc. (pptv)	σ	Day	Conc. (pptv)	σ		
Jan	6	361	2	9	1878	3	16	152	2	153	2	25	218	3
	19	241	6	17	216	2	23	144	1	146	2			
				25	171	2								
Feb	17	274	6	13	117	2	7	131	1	145	4	19	167	1
	25	169	5				24	460	-	778	-			
Mar	13	130	2	11	136	2	7	900	-	723	-	9	263	1
	19	139	4	23	189	2	10	137	3	168	4	18	622	13
	23	130	1	30	121	1	18	108	1	117	1	26	102	1
							24	118	2					
Apr	2	138	2	16	250	3	2	122	1	122	1	2	118	2
	19	120	2	24	38000	-	8	131	2	129	1	7	256	5
	28	161	2				15	115	2	123	2	15	131	1
							30	150	1	138	1	24	123	2
May	6	630	14	5	123	2	5	119	1	122	3	9	459	6
	12	195	1	14	113	2	14	118	1	118	2	15	101	2
	21	127	2	26	104	2	24	119	3	121	2	29	108	1
	25	125	1											
Jun	3	143	6	3	122	5	2	194	1	174	1	6	122	3
	9	135	1	10	121	3	8	120	1	120	1	10	106	1
	19	124	1	17	113	3	16	118	3	117	1	19	113	3
							24	118	2	123	1	24	112	3
							30	1434	19	1672	13			
Jul	3	143	2	1	124	5	7	131	1	130	2	3	111	1
	7	365	-	9	125	1	22	125	4	125	1	8	113	1
	13	139	2	22	126	4	30	122	2	123	1	15	117	2
	21	141	1	29	126	2						22	116	2
	27	187	3									29	119	3
Aug	12	127	2	3	119	1	4	117	2	120	4	5	117	1
	25	157	1	12	120	1	12	119	3	119	1	12	124	1
				18	302	5	20	127	1	132	1	19	121	2
				25	571	4	26	133	2	132	1	26	133	3
				30	143	2								
Sep	7	165	4	10	143	1	5	146	2	145	1	2	129	1
	15	434	3	15	149	1	10	151	1	151	2	8	132	2
	22	159	2	21	145	2	24	142	1	142	2	23	136	1
	29	173	1	28	155	2						30	131	1
Oct	5	235	1	6	154	1	5	152	1	153	1	7	144	1
	15	188	1	12	162	1	14	175	2	174	1	13	153	1
	19	205	2	20	179	2	23	186	1	184	2	21	155	1
	27	247	3	29	153	2	28	186	1	185	1	27	172	1
	29	204	2											
		204	2											
Nov	2	202	1	1	192	2	4	178	1	177	1	4	175	2
	16	265	3	5	188	2	12	185	1	-	-	8	165	1
				10	207	1	19	173	2	171	1		174	1
				16	172	1	24	174	2	175	1		165	1
				22	177	2						11	156	1
				29	177	2						18	162	1
												25	176	3
Dec	3	205	2	9	172	2	3	183	1	182	5	1	158	1
	8	196	2	15	177	3	9	169	1	168	1	16	160	2
	15	256	2	22	170	2	22	171	1	171	1	30	154	1
	20	193	1	29	170	2	29	171	1	172	1			
	28	193	2											

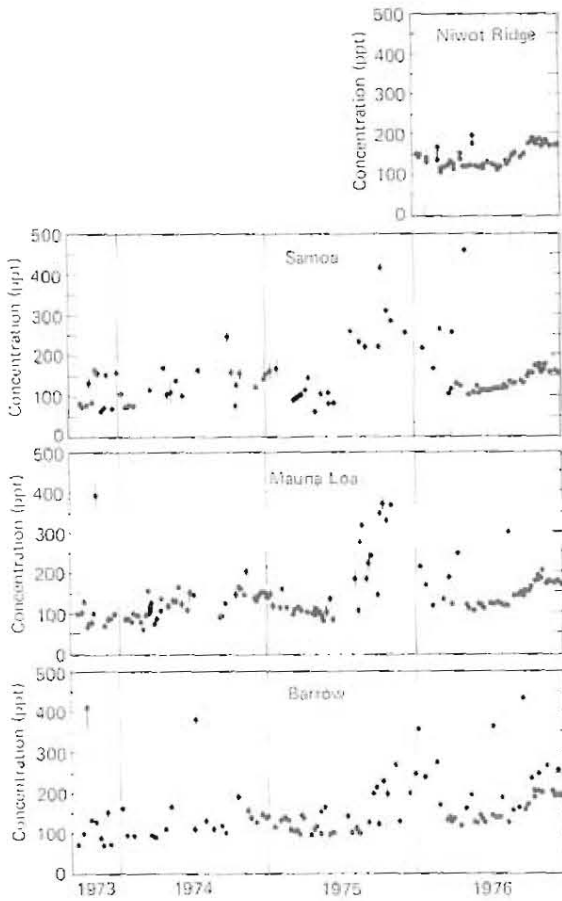


Figure 11.  $CCl_3F$  concentrations at four GMCC observatories.

#### 4.2 Stratospheric Aerosol Measurements Using Lidar

Since the last report, monitoring of stratospheric aerosols over Mauna Loa has remained the major activity. Data were taken at Mauna Loa 20 times during 1976. In general, the trend during this period was a return to a clean stratosphere after the volcanic injection by the de Fuego volcano in Guatemala during October 1974 (Fegley and Ellis, 1975 a,b; Russell and Hake, 1977). However, on January 24, 1977, a new, intense volcanic-like cloud was detected at the tropopause above Mauna Loa. To our knowledge, as of the date of this writing (3/77) the cloud has not been detected at other locations. It seems to have density comparable with that of the de Fuego cloud, but it is more patchy, disappearing and reappearing every few days.