Data Quality Control, Format, and Availability. Each of the Electrochemical Concentration Cell (ECC) oxidant meters was checked on a monthly basis against a calibrated ozone source. This source had been checked against the ECC meter with which it would be used before being deployed to the field location. Through this procedure a check on the absolute accuracy of the ECC meters was maintained to within ±10 percent of the original calibration during the year.

A computer processes the data from the mean hourly data submitted by each observing location to the Techniques and Standards Group. An example of the computer printout for a month's data for Boulder is shown in figures 15 and 16. The format of figure 15 includes the mean hourly surface amounts, the daily average, and the largest of the hourly values for each day. The form shown in figure 16 includes the daily average amounts, the daily maximum, the time of the maximum, and the duration of any peaks of 100 nanobars or more.

Currently, copies of the computer printout of the partial pressure of surface ozone are available through the Techniques and Standards Group, ARL, NOAA, Boulder, Colo. The processed data are also contained on computer punch cards.

Plans for 1974. In addition to the present ECC meter measurements at the GMCC locations, the McMillan Electronics Corporation chemiluminescent ozone meter is being used at Boulder and the South Pole. This instrument is being tested as a possible second method for measuring surface ozone at the GMCC observations. It operates on the principle of the photometric detection of the chemiluminescence resulting from the flameless reaction of ethylene gas with ozone. Tentative plans are also, to conduct tests on a Dasibi Corporation ultraviolet absorption ozone photometer; it measures ozone by detecting the absorption by ozone of ultraviolet light at 253.7 nm.

The various measuring techniques will also be compared with the 1 percent, neutral buffered potassium iodide method of measuring ozone, in order to establish a summary standard against which all instruments will be compared.

4.1.4 Freon-11 (CCl₃F)

An objective of the GMCC program is to assess the relative contributions of natural sources and of man-made sources to the background concentrations of trace constituents. Separating most of the climatically active gases into these two sources is very difficult. CO_2 , O_3 , and NH₃ are all produced by man and by nature. The sources are unevenly distributed and of varying strengths. Further, the sinks and removal processes are highly variable. As one example, CO_2 uptake by biota is much more efficient in the Northern Hemisphere than in the Southern Hemisphere because of more biota mass and is further complicated by the temperature dependent behavior of the oceanic source-sink.

		Ц	ΔΚΥΙΔΙ	PRESS	URE OF	SURFA	CF NZN	HE IN	NAN193	¥5			
		5	r a t j d m	ROJL	DE⊇								
		м	ONTH	JUNF		YEAR	1973						
		ε	UN L P MÉ	MT EC	C								
GYT	1	2	3	4	5	ĥ	7	Ą	Э	10	11	12	13
DATE	•	,	2		5		·			1		L /2	15
1	46.7	38.0	26.8	37.5	47.7	40.9	34.0	38.4	34.1	27.7	19.5	16.0	15.0
2	36.4	35.5	35.0	32-1	23.7	28.2	24.8	21.9	18.9	19.4	13.6	13.6	14.6
З	39.9	37.4	25.7	53.3	5.4.5	26.7	28.2	25.9	29.2	29.7	33.1	33.1	36.0
4	30.2	59.3	20.9	16.1	12.2	50.9	22.4	20.4	16.5	17,0	19.0	26. R	26.8
5	39.1	35.5	24.4	36.1	39.5	34.7	34.3	35.7	35,9	36.9	40,7	41.2	75.9
6	18.6	20.0	15.1	5,15	24.4	25.9	26.9	26.4	26.4	7K,4	53.0	51.1	15.6
7	25.5	22.5	18.1	26.0	29.4	31.9	33.8	33.R	32.9	31.4	30.4	29.5	29.0
А	33.4	55.6	20.5	24.0	25.5	27.0	26.5	26.0	26.5	26.5	22.0	17.6	25.6
9	65.9	47.3	31.1	33.6	36.6	34.2	30.8	25,9	24.4	25.0	22.0	17.5	20.6
10	42.0	34.9	32.9	27.9	25.8	50.6	51.2	22.3	51.3	53.9	55.8	25.5	25.6
11	36.7	33.1	28.9	23.5	13.9	15.6	18.3	20.5	22.7	23.3	26.5	29.3	25.1
12	39.2	35.4	31.0	20.5	20.5	23.9	24.5	27.4	28.5	28.5	28.1	27.5	15.3
13	36.7	35.0	26.4	17.9	22.5	15.0	15.8	19.7	16.8	18.0	20.4	18.1	15.8
14	27.3	24.4	17.3	18.5	19.1	19.7	19.5	19.8	16.2	16.4	16.3	14.5	12.7
15	30.1	30.2	23.4	53.4	31.5	34.1	33.5	33.6	32.4	30.5	29.3	28.7	25.7
16	56.0	55.5	55.0	54.4	55.1	60.5	60.5	59.9	59.9	59.9	66.0	54.2	49.0
17	42.3	43.3	40.4	36.5	39.0	35.4	33.1	39.1	34.2	39.2	38.2	37.8	32.3
) F:	د.35	43.4	45.0	44.5	44.1	45.2	43.7	40.7	37.7	41.3	41.4	43.0	41.5
19	42.4	41.9	38.4	40.0	43.7	46.4	47.5	45.0	39.3	40.4	39.9	39.0	37.5
20	35.8	34.5	27.5	26.5	29.8	25.6	18.1	18.1	24.0	25.1	23.5	24.1	19.8
51	43.9	43.0	31.0	36.4	30.0	23.6	28.4	31.2	32.3	32.9	31.8	30.9	27.1
22	30.5	30.4	28.2	25.5	25.4	23.2	21.0	51.1	23•1	26.9	25.2	23.1	21.9
53	37.7	22.1	21.5	17.6	50.1	51°1	51.1	53.0	23.5	23,5	23.5	25.0	23.0
24	34.7	27.3	18.3	24.9	23.7	29.7	30.7	30.7	33.6	33.5	33.6	33.6	31.6
25	34.5	27.1	16.9	18.3	23.7	30.6	31.6	34.0	33.5	28.7	32.1	28.7	29.7
56	63.3	25.9	21.0	24.9	28.3	29.2	29.8	29.8	26.4	28.3	28.8	51.3	21.5
27	39.6	29.3	22.5	51.0	21.5	23.4	23.4	24.9	23.5	22.5	21.5	18.1	18.1
28	50.8	52°9	19.1	11*5	15.7	19.2	20.2	50.5	19.3	20.3	50.3	16.9	14.5
29	21.5	22.5	21.5	18.1	12.7	11.2	14.2	10.3	15.5	18.5	16.1	18.1	18.6
30 31	44.1	37.7	32.3	39.2	32.8	26.5	23.0	20.6	20.5	19.5	22.1	13•1	15.7
MEAN	36.7	33.1	27.4	27.7	28.6	23.3	28.4	28.4	27.8	28.1	27.8	27.0	24.7

Figure 15. Example of one month's surface ozone data at Boulder, Colo.

		5	VCITAT	BOJL	DER								
		м	ONTH	JUNE		YEAR	1973						
		5	ALLEDVE	NT EC	c								
		t	001240	NI EC	C.								
GMT	14	15	15] 7	19	19	20	21	22	23	24	MEAN	XAP
DATE													
1	22.4	35.0	45.2	49.1	-1.0	-1.0	-1.0	55.9	60.7	62.2	45.7	38.3	62.2
2	15.5	17.4	20.9	22.3	21.4	28.2	32.1	34.5	39.3	36.4	34.5	26.1	39.3
3	40.4	42.9	42.8	40.9	38.0	33.1	38.0	40.4	36.0	27.3	27.3	33.5	42.8
4	22.4	23.3	25.4	31.5	33.1	33.1	36.5	41.9	40.3	37.9	36.4	26.6	41.8
5	33.4	35.9	33.5	29.5	28.7	25.3	23.8	25.8	26.3	21.5	19.0	32.0	41.2
6	15.7	27.5	28.0	28.5	28.5	26.5	26.5	26.5	26.5	25.1	19.2	23.9	23.5
7	28.5	32.4	34.9	33.9	36.4	39.9	29.5	29.1	27.1	28.1	27.1	30.0	38.9
R	13.7	19.1	53.5	44.7	49.6	56.9	46.1	52.0	59.4	62.3	73.1	35.5	73.1
9	30.7	42.3	39.8	41.9	61.7	56.3	80.7	70.7	56.5	46.9	40.4	41.0	P0.7
10	25.0	5.9.5	29.4	28.4	36.9	35.9	38.0	37.6	37.6	35.6	38.3	59.9	\$2.0
11	19.5	15.8	23.0	24.6	30.7	32.4	33.6	34.2	35.3	36.5	36.6	26.6	36.7
15	15.2	50.9	26.5	58.9	48.2	44.9	38.1	32.5	28.5	33.7	35.5	29.4	48.2
13	17.5	26.9	32.8	33.4	37.5	55.3	73.0	73.7	62.6	55.5	39.1	32.7	73.7
14	10.3	11.5	16.4	21.9	21.9	28.0	28.7	33.0	33.7	33.1	30.1	21.2	33.7
15	27.6	38.9	41.5	37.1	35.9	39.1	41.1	48.7	50.1	50.2	40.0	35.3	50.2
16	49.1 27.9	53.4	53.4	52.8	50.1	47.4	46.9	47.3	46.8	42.7	41.2	53.6	49.6
17	42.0	31.9	33.9	41.5	48.5	48.6	46.1	44.7 47.]	46.2	43.8	35.2 43.6	39.3	50.1
18	35.4	43.1	42.2	35.6	44.3 32.5	47.0	33.2	36.9	38.5	39.7	35.5	38.7	47.5
20	19.9	24.2	30.7	38,9	41.5	43.2	38.9	37.9	42.2	40.7	41.8	30.4	43.2
21	21.2	25.0	26.1	36.5	47.5	45.4	44.9	45.4	45:4	36.5	34.9	34.7	47.5
22	18.2	28.9	31.4	38.0	50.1	47.4	49.8	51.2	62.3	59.6	47.2	34.2	42.3
23	23.5	27.4	33.7	29.9	29.9	33.3	35.3	36.3	40.2	36.2	37.2	23.0	5.04
24	30.6	36.0	41.7	38.0	35.5	35.5	36.0	34.5	35.9	33.5	34.4	32.7	41.9
25	18.9	18.9	35.5	53.2	50.8	34.1	33.7	31.2	29.8	32.7	28.8	30.7	53.2
26	28.3	29.8	33.2	32.2	33.2	32.2	34.7	33.7	38.1	38.5	42.0	30.3	42.0
27	16.1	18.5	24.7	29.9	33.7	39.1	41.6	47.9	39.2	37.1	34.2	27.9	47.9
28	17.9	24.3	30.7	33.7	32.2	26.8	35.7	40.1	30.4	28.9	28.5	24.4	40.1
29	20.5	25.9	43.7	41.5	70.9	97.1	75.6	61.9	60.5	55.6	54.6	34.5	c7.1
30	20.6	27.0	32.9	41.2	50.0	56.4	21.9	80.5	68.7	57.4	49.1	38.3	A1.9
31													
MEAN	24.3	28.9	34.1	36.1	39.9	41.4	43.1	43.8	42.9	40.2	37.7	32.8	51.4

PARTIAL PRESSURE OF SURFACE OZONE IN NANOBARS

Figure 15. Example of one month's surface ozone data at Boulder, Colo. — continued. PARTIAL PRESSURE OF SUPPACE JZONE IN NANORARS STALLON ROLLOFR MONTH JUNE YF 1 7 1 9 7 3 EQUIPAENT FCC MEAN MAXON TIPE DURATIONS UNY (GAT) (414) 38.7) 74.3 2305 47.8 > 26.1 1655 3 33.5 44.4 1950 2225 25.6 42.H 4 5 32.0 44.4 0345 35.3 5 53.9 1540 7 30.0 44.9 1330 92.9 5 35.4 2330 4 41.0 94.9 1925 10 24.9 46.1 0045 11 25.6 37.9 0005 29.4 56.7 1745 12 32.7 80.2 13 2000 14 21.2 36.2 1950 55.2 15 2205 35.3 67.2 15 53.6 1045 50.1 11 19.3 1850 13 43.4 52.7 1705 19 38.7 51.7 0625 20 30.4 45.9 1905 57.4 <1 34.7 1820 22 34.2 65.2 2250 23 59.0 46.8 0005 24 32.7 MSG 59.6 25 30.7 1645 44.4 45 30.7 2340 27 27.9 53.3 2030 24.4 42.6 29 2030 69 34.5 121.1 10 1758 30 38.3 96.6 1945 31 MEAN 32.8 57.6 "" OTHER DESERVATIONS OF 100NB OR MORE DAY ANOUNT TIME DURATION. 29 110.4 1940 10 29 168.9 1905 5 * DUPATION GIVEN FOR VALUES OF LOONA OF MORE

Figure 16. Example of surface ozone data summary.

To disentangle these relationships, we need global measurements of an inert tracer whose source is wholly anthropogenic or wholly natural and whose production is known, quantitatively, with some precision.

Candidate materials should be relatively inert, minimally soluble in sea water with the resulting long (10 years or greater) residence time in the atmosphere. Further, if the tracer is sampled in remote locations, extremely low concentration must be detectable. Dr. James E. Lovelock (1971, 1972, 1973) has suggested Freon-11 (CCl₃ F) as such a tracer.

A collaborative program in the Air Resources Laboratories was established to build and operate electron capture gas chromatographic detectors (Lovelock et al., 1971). Dr. Lovelock provided the initial system and consultation on methods. The gas chromatographic (GC) equipment is operated by the Air Resources Laboratories Field Research Office at Idaho Falls, Idaho, under the direction of Messrs. Thayne Thompson and C. Ray Dickson in support of a variety of tracer experiments. The material is apparently only man made and as such represents a unique identification of man's activities. Its production in 1973 was about 2.5×10^{11} g annually and to date approximately 2×10^{12} g have been produced. Approximately 98 percent of this material is produced and released in the Northern Hemisphere. Thus, it is a unique tracer especially for identifying inter-hemispheric transport. A program was begun in September 1973 to collect samples of Freon-11.

Lovelock et al. (1971) have determined that the background concentration of Freon-11 in the Eastern Atlantic was about 65 x 10⁻¹² parts per part. Measurements in uncontaminated air above the Los Angeles inversion indicate approximately a 70 x 10^{-12} concentration. Collection and detection of these very low concentrations creates many expected and unexpected difficulties. Table 6 shows the individual flask concentrations measured at the three locations in September through December 1973. The data record appears to be very "noisy," and we have not to date separated real signals from possible sampling contamination or analysis uncertainties. However, the lowest values observed do not seem to be too different from background levels observed elsewhere. Two special points should perhaps be made. Most of the sampling at Mauna Loa has been done in the late forenoon or early afternoon. These times are typical of an upslope flow that often comes from the populated regions of Hawaii. Thus, the possibility of sampling locally released Freon-11 has not been eliminated. (Sampling in the nighttime downslope air should assist in clarifying this situation.) High values have been observed at Barrow, Alaska, with concentrations $> 120 \times 10^{-12}$. However, recent work by the Naval Research Laboratory (Wilkniss, 1974) has shown that high concentrations of Freon-11 penetrate well into the Arctic, so that the possibility of trans-polar transport cannot be ruled out. A duplicate flask sampling program to test the sampling procedure is being instituted at selected stations in 1974 and a revised procedure to collect pressurized flask samples is being developed.

Date		Freon-11 Concentration pptV	σ	CCl. Concentration σ pptV				
		В	arrow, Alasi	ka				
Sept.	16	69.5	1.6	42.2	2.2			
Oct.	29 11	99.8 412.7	4.0 52.4	107.2 53.7	3.1 4.2			
UCL.	19	133.0	4.9	138.4	2.7			
Nov.	2	128.1	5.5	69.8	2.5			
	13	86.6	7.9	52.7	4.5			
	20	67.8	6.7	22.1	3.8			
Dog	30 8	152.7	18.0	57.2	3.6			
Dec.	0	70.7	7.5	62.9	4.0			
		Cape	Matatula, S	Samoa				
Sept.	25	84.0	2.0	50.4	7.0			
Oct.	4	75.1	3.6	52.7	3.3			
	15	79.2	4.6	55.2	3.0			
	23 30	135.8 84.1	15.6	109.5	12.0			
Nov.	7	164.9	15.2	70.3 79.9	10.7 3.8			
	14	157.6	14.1	72.1	7.8			
	21	63.7	10.6	66.8	5.2			
	2.8	71.3	5.4	71.0	3.7			
Dec.	5	154.4	4.5	119.8	6.0			
	19	71.2	6.6	76.3	4.3			
		Μ	auna Loa, H	awaii				
Sept.	19	100.0	4.7	42.2	4.1			
1913 - Million B (Million) - College	28	103.9	11.4	N.D.	-			
Oct.	5	129.4	7.2	150.3	8.2			
	12	66.4	1.8	75.2	4.5			
	19 26	73.6 78.2	4.1 6.9	39.2 40.7	3.9 5.2			
	29	100.2	1.6	40.7	2.0			
Nov.	7	395.2	32.9	14.1	0.7			
	23	69.2	3.3	61.2	4.3			
	26	69.5	6.5	59.3	6.8			
Dec.	7	85.5	10.5	67.4	9.4			
	12 21	87.5 98.6	7.1 8.9	64.3 N.D	5.2			
	21	30.0	0.9	N.D.				

Table 6. Station Data Results 1973

N.D. = not detected < 5 ppt

A summary of the 1973 program, equipment, analysis, and results follows.

Three sampling stations were chosen to represent different latitudes: Pt. Barrow, Alaska at 72°N; Mauna Loa, Hawaii at 19°N; and Cape Matatula, American Samoa at 14°S.

The sampling method collects ambient air in stainless steel flasks with high purity shut-off valves. Six flasks are assigned to each station to accommodate a rotation scheme. On a weekly basis, a flask is sent in padded mailing tubes with data sheets to the stations. The flask is then opened to the ambient air, resealed, and returned to Idaho for Freon-11 and CC14 analysis. Upon completion of five replicate chromatographic determinations, each flask is cleaned, numbered, re-evacuated, and returned to the station. This complete procedure requires 6 weeks.

In addition to this program, a cooperative effort with Dr. J. E. Lovelock has started to relate meteorological data to the Freon-11 concentrations measured at Adrigole, Ireland ($50^{\circ}51'N$, $9^{\circ}44'W$). The automated electron capture gas chromatograph of Dr. Lovelock provides daily observations of CCl₃F and CCl₄. Meteorological trajectories calculated backwards in time and space from Adrigole, Ireland, using a comprehensive data base supplied by the U.S. Air Force and a computer program developed by Mr. Jerome Heffter of the Air Resources Laboratories (the details of which will be reported in other publications) have been related to concentration data. Figure 17 shows the results of associating particular trajectories with specific concentration values. The very much higher concentration associated with transport from Europe as compared with the Eastern Atlantic background concentration levels (of order $65x10^{-12}$) lends confidence to the trajectory computations. The

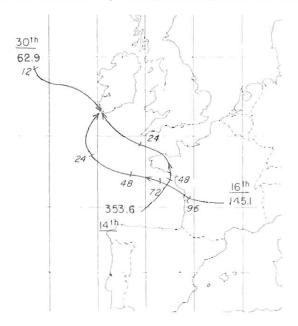


Figure 17. Concentration of CCl₃F (x10⁻¹²) as given trajectory (data underlined) at Adrigole, Ireland, August 1973.

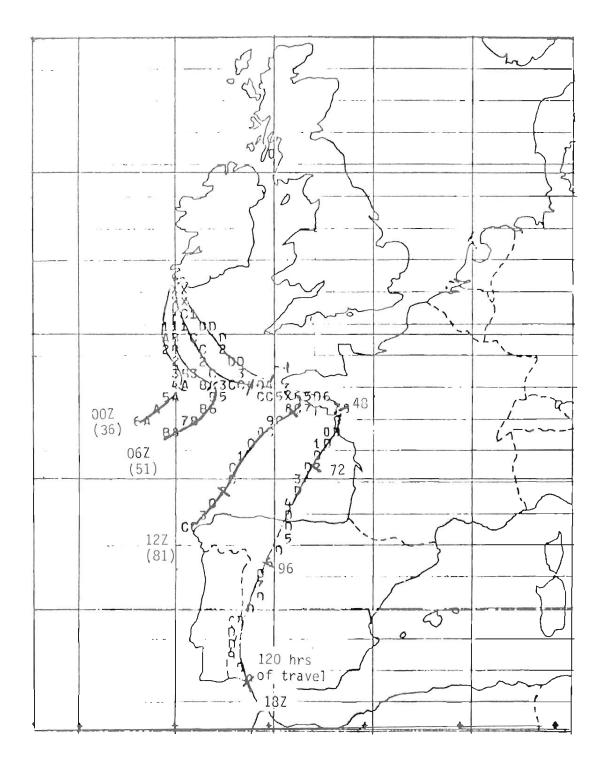


Figure 18. Computer produced trajectories for September 8, 1973.

study is only in its initial stages; however, tentative conclusions are that more than a single concentration measurement is required within a 24-hour period since the meteorological trajectories may originate from a wide distribution of potential sources. A portion of the day may represent air from clear areas, although the remainder may be from populated areas. Figure 18 shows the computed produced trajectories for September 8, 1973, which illustrate the shift from "clean" to "polluted" sources.

Equipment. The flasks were factory cleaned in trichloroethane vapor and the cleaning procedure used before initial station use is a 2-hour immersion in 5 molar phosphoric acid, distilled water rinse, ethanol rinse, and ultra purity nitrogen purge. They are then evacuated to 50 Microns of mercury pressure using a Precision Scientific, Model 25, vacuum pump and Cenco thermocouple gage No. 94178.

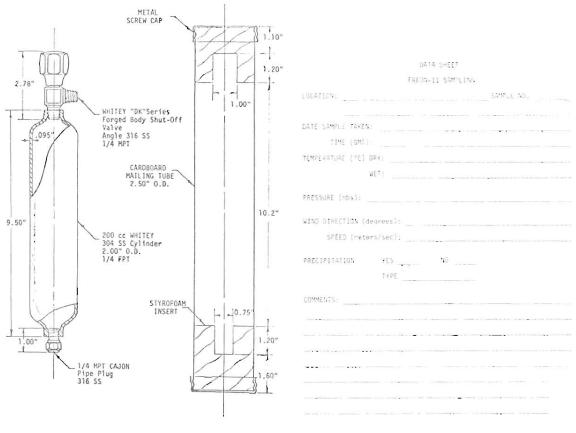
Figure 19 shows the sampling flask and mailing apparatus. The valve inlet has a plastic protective cap over it during shipment.

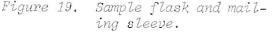
Figure 20 is the data sheet sent with each cylinder. It is completed in duplicate at the time of sampling; one is retained for the station records, the other returned with the cylinder.

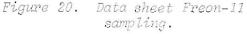
Figure 21 is a diagram of the electron capture chromatograph. Specific components (see numbers on fig. 21) follow:

- Ultra high purity nitrogen supplied by Liquid Air, Inc., in 2400 psi cylinders.
- High purity two-stage stainless steel regulator Series 3800, Matheson Gas Products.
- Micro-volume valve supplied by Carle Instruments, Inc., of Fullerton, California. Catalog No. 2016 which has two sample loops, 1/16 inch (0.16 cm) gas connections, and purge manifold. 5 cc sample loops are used.
- Swagelok reducing union from 1/4 FPT to 1/6 inch (0.16 cm) tube.
- Hoke shut-off valve connected by 1/4 inch (0.64 cm) stainless tubing to a Precision Scientific Model 25 vacuum pump and Cenco thermocouple vacuum gage No. 94178.
- 6. Fine metering valve, Series S, with 1/8 inch (0.32 cm) Swagelok inlet and outlet and vernier handle, by Nupro Company, Cleveland, Ohio.

- 2.5 meter long spiral wound column made of 1/4 inch (0.64 cm) stainless steel. The column packing is Carbowax 400/Porasil F "Low K" Durapak made by Waters Associates, Inc. of Farmington, Mass.
- Cylindrical ionization chamber (brass). Internal dimensions are 1.1 cm long with a 1 cm diameter. Ionization source is 15 mCi of Ni-63 electroplated on platinum foil.
- 9. Fischer and Porter low flow flowrator, Model 10A1339Ni2AXGM, calibrated for nitrogen gas.
- Temperature test chamber, Model 1060 RB2 by Delta Design, Inc., of San Diego, Calif. Faceplate modified to house chromatograph column and detector within. It is an air thermostat.
- 11. Note shown on the figure. Moseley Autograph dual pen recorder, model 7100B to record chromatograph output.







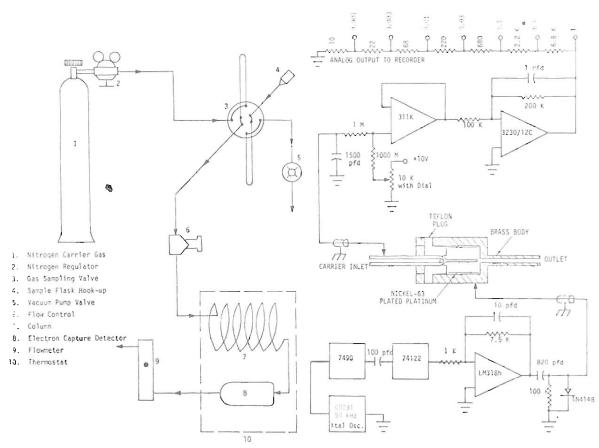


Figure 22 outlines the electronic package of the pulse model electron capture system.

Figure 21. Diagram of electron capture chromatograph apparatus.

Figure 22. Electron capture detector and electronics.

Data for 1973. On the chromatograph, data were extracted by hand measurements of peak height and width at half height then corrected to a Gaussian curve.

Dry air densities were determined from data sheet values of temperature and pressure and used to convert peak areas to parts per part by volume.

A typical clean air chromatogram is shown in figure 24.

Improvements for 1974. The increasing sample load requires many hours of hand extracting data from charts. The most accurate and time saving method of data handling is by electronic digital integrators. At the end of 1973, an integrating system (Autolab IV made by Spectra-Physics) was under trial examination.

During preliminary checks, cylinders gave consistent results when evacuated and opened to local air. However, because of the variability observed in the station samples, the sampling procedure will be changed.

4.2 Aerosols

4.2.1 MLO Ruby Laser Radar (LIDAR) System

During 1973, the MLO lidar continued in experimental and developmental phases. The lidar data have been useful in interpreting data collected by other observatory instruments, e.g., detection of a thin cirrus layer to determine its possible effect on radiometric data, or use of horizontal shots to measure aerosol spatial uniformity. These techniques were experimented with during 1973.

The primary purpose of the MLO lidar system is to accurately measure atmospheric scattering properties. These measurements, in addition to other MLO data, will lead to greater understanding of the physical and chemical dynamics of the atmosphere, e.g., the relationship of Junge layer strength and ozone levels (Fiocco and Grams, 1964; Rosen, 1968). Equally important are any trends that are observed; they may indicate a climatic change. For example, volcanoes injecting gasses and aerosols, aerospace operations, releasing contaminants, or man-made pollutants could all change the stratospheric albedo.

Lidar makes it possible to quickly measure the one-dimensional 180° backscatter properties of the atmosphere above the observatory. These measurements would be extremely difficult with direct sampling techniques.

Although the direct output of a lidar analysis is the atmospheric backscattering coefficient (BC), use of standard aerosol size distributions allows us to estimate aerosol number and mass density.