

## 8. Nitrous Oxide and Halocarbons Group

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### 8.1. CONTINUING PROGRAMS

#### 8.1.1. FLASK SAMPLES

##### *Sampling and Instrumentation*

During 1988, air samples were collected in pairs of 0.3-L, Summa-treated, stainless steel cylinders each week at BRW, NWR, MLO, and SMO. The samples at SPO were collected each week only during January, November, and December, when the Antarctic interior was accessible by aircraft. In addition, a new flask sampling effort was instituted at the Alert (ALT) station of the Canadian Atmospheric Environment Service, in the Northwest Territories, where flask pairs were filled with air on a 1-2 week schedule beginning in February. All flask samples were shipped to our central laboratory in Boulder, Colorado, where they were analyzed by EC-GC for  $N_2O$ , CFC-12 ( $CCl_2F_2$ ), and CFC-11 ( $CCl_3F$ ).

Primary calibration tank no. T3088 was retired from service in December 1987 and was replaced by aluminum cylinder 62631 that had been treated with Aculife (Scott Specialty Gases, Plumsteadville, Pennsylvania) and filled with dried air from NWR.  $N_2O$ , CFC-12, and CFC-11 concentrations in the new tank were compared with those in T3088 in September and October 1987, and again in May 1988. No significant drift was apparent from these intercomparisons.

An automated flask analysis system was designed, and construction of it was begun in 1988. In the past, each flask was analyzed manually on one GC system, but with this new system, up to 10 flasks can be analyzed in any sequence, and reference gases can be interspersed as needed. Three GCs will be used to analyze  $N_2O$  (affected by  $CO_2$ ),  $N_2O$  (unaffected by  $CO_2$ ), CFC-12, CFC-11, CFC-113 ( $CCl_2F-CClF_2$ ), chloroform ( $CHCl_3$ ), methylchloroform ( $CH_2CCl_3$ ), and carbon tetrachloride ( $CCl_4$ ). A desk-top computer will be used to control the chromatographic system as well as to collect, analyze, and store the data. The hardware has been purchased, and most of the controlling software has been written.

Some unusual samples were collected or reported in 1988. The first came from the second boat pit of Khufu's pyramid in Egypt in October 1987. *Tans et al.* [1988] explained the air sampling procedure and measurement results. It was hoped that the chamber would contain ancient air, but the halocarbon composition showed that the pit was not sealed with respect to the outside atmosphere. A stability study was initiated using various types and sizes of containers (aluminum and stainless steel) to find a suitable generic flask for all compounds measured by GMCC for ambient levels of  $CO_2$ ,  $CH_4$ ,  $N_2O$ , CFC-11, and CFC-12 over time. The electropolished stainless steel and aluminum flasks were stable for ambient levels of CFC-11 and CFC-12 for storage under 35 days, but all other compounds showed significant loss or gain with time for these unusually wet samples [*Tans et al.*, 1988].

The second set of unusual samples was collected at SPO on

January 24, 1988. The samples in two 1.0-L flasks were pressurized to 150 kPa, returned to Boulder, and sealed in a time capsule in the foundation of the new CIRES building on the University of Colorado campus. These samples will be recovered in 50-100 years for reevaluation of their contents.

##### *Results*

Data from flasks collected at BRW, NWR, MLO, SMO, and SPO from 1977 through 1988 show a mean, global growth rate of  $0.68 \text{ ppb yr}^{-1}$  for  $N_2O$  (Figure 8.1),  $16.1 \text{ ppt yr}^{-1}$  for CFC-12 (Figure 8.2), and  $9.8 \text{ ppt yr}^{-1}$  for CFC-11 (Figure 8.3). Preliminary 1988 monthly mean data are tabulated in Table 8.1. The CFC-11 and CFC-12 data show that concentrations are rising over the past few years at a rate stronger than that seen in the earlier record. Since calibration gas standards have been changed in this period and insufficient time has gone by to determine calibration tank long-term stability or drift characteristics, it is uncertain whether the stronger rise is real, being a response to increased chemical usage and release into the atmosphere, or a vagary of the new standard.

Data from flasks collected at ALT were often erratic; many pairs did not match well. This was worse for CFC-11 than it was for CFC-12. Consequently, only flask pairs with concentrations that agreed have been retained for subsequent analysis. Results from ALT compare favorably with those from BRW, although there are slight differences (Figure 8.4). These differences can be ascribed to the large distance between the stations and the different air masses that move in and across the Arctic basin.

#### 8.1.2. RITS CONTINUOUS GAS CHROMATOGRAPH SYSTEMS AT GMCC BASELINE STATIONS

##### *Sampling and Instrumentation*

In-situ measurements of CFC-11, CFC-12, CFC-113,  $N_2O$ ,  $CH_2CCl_3$ , and  $CCl_4$  were made 8 times per day at three GMCC baseline stations, BRW, MLO, and SMO, and 12 times per day at SPO. Instrumental precision has consistently been better than 0.3% for  $N_2O$  and between 0.5 and 2% for the rest of the compounds. In mid-1987 measurements of  $N_2O$  were begun using a Porapak Q column, and the precision has been greatly improved because there is no known  $CO_2$  effect, and no interfering peaks on the chromatogram (Figure 8.5).

In November 1988, the MLO and SMO systems were modified so that all three columns could be backflushed. Previously, only the  $N_2O$  GC was equipped for backflush operation. The backflush modifications at BRW will be completed in early 1989. Backflushing the columns should improve the precision of the measurements by allowing 30-min runs instead of 60-min runs. Along with the backflush modifications, an HP hierarchical filing system was installed to speed up data storage. It is anticipated that 30-min runs will begin early in 1990.

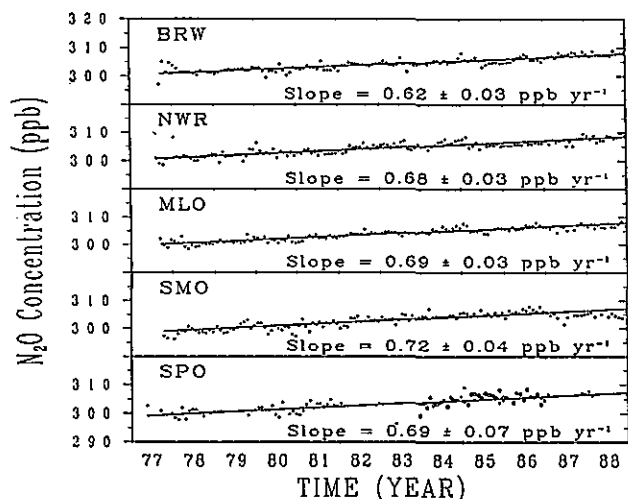


Fig. 8.1. Monthly mean concentrations of  $N_2O$  from the NOAA/GMCC flask (+) network ( $CO_2$  and  $H_2O$  corrected). The SPO plot also shows monthly means (o) from the old GMCC in-situ GC. The trends and  $\pm 2$  standard deviations are also shown.

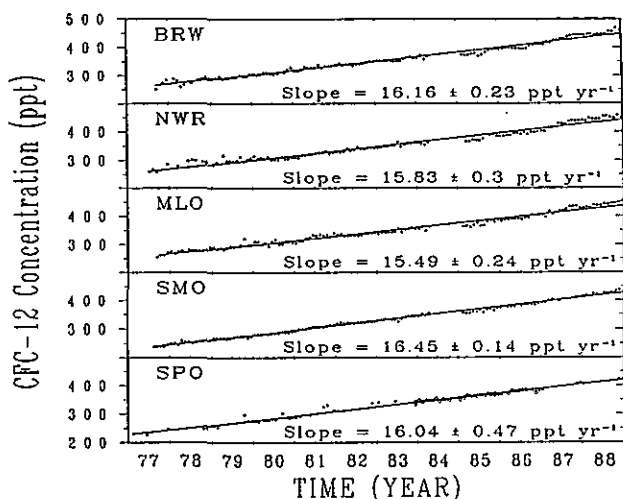


Fig. 8.3. Monthly mean concentrations of CFC-11 from the NOAA/GMCC flask (+) network. The SPO plot also shows monthly means (o) from the old GMCC in-situ GC. The trends and  $\pm 2$  standard deviations are also shown.

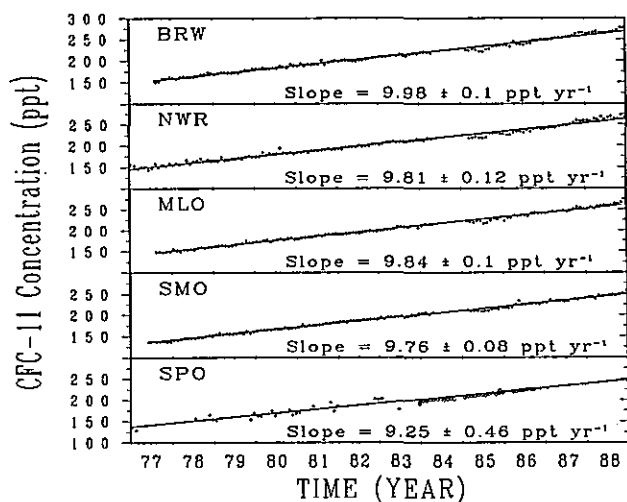


Fig. 8.2. Monthly mean concentrations of CFC-12 from the NOAA/GMCC flask (+) network. The SPO plot also shows monthly means (o) from the manually operated GMCC in-situ GC. The trends and  $\pm 2$  standard deviations are also shown.

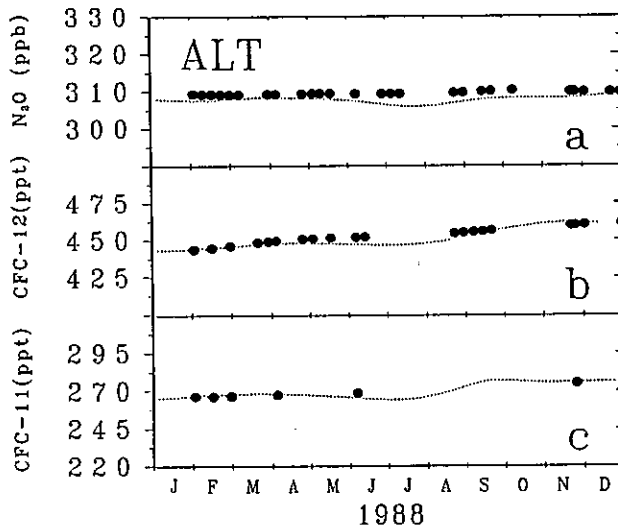


Fig. 8.4. Average concentrations for (a)  $N_2O$ , (b) CFC-12, and (c) CFC-11 from flask pairs collected at ALT. The dotted line is a spline fit to BRW flask data for comparison.

New regulators were purchased and installed in 1988, solving many of the contamination problems. A contaminant still elutes between  $CH_3CCl_3$  and  $CCl_4$  on the SP2100 GC column in one of the BRW standards, and one of the MLO standards has a large amount of CFC-113. The major problem with the contaminants is that they make it difficult to integrate the chromatogram peaks consistently, and the precision suffers as a result. The precision can be improved for  $CH_3CCl_3$  and  $CCl_4$  by calculating concentrations from peak heights instead of from peak areas. In the future, both peak heights and peak areas will be computed and stored for all components measured by the RITS GC system, and old data will be reintegrated and both areas and heights will be stored.

A modified RITS GC was set up and tested at SPO in February. The system consisted of two Shimadzu Mini-2 GCs that measure the concentrations of  $N_2O$ , CFC-12, CFC-11,  $CH_3CCl_3$ , and  $CCl_4$  on an hourly basis. An IBM XT clone computer was set up to allow automated data transfer from the two HP3390 integrators to a floppy disk. Data from the disk are then transferred weekly via satellite to Boulder.

#### Results

In 1987 an apparent increase of 18 ppt yr<sup>-1</sup> was reported for CFC-12 at BRW (Figure 8.6a). It is now apparent that this was the result of seasonal fluctuations in the CFCs, perhaps from European air masses. The seasonal variation at BRW is also more apparent in the CFC-11 data (Figure 8.6b).

TABLE 8.1. 1988 Monthly Mean Concentration for N<sub>2</sub>O (ppb by mole fraction in dry air), CFC-12 (ppt), and CFC-11 (ppt) from Flask Pairs Collected at BRW, NWR, MLO, SMO, and SPO

1988	N <sub>2</sub> O					CFC-12					CFC-11				
	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO	BRW	NWR	MLO	SMO	SPO
Jan.	308.7	309.5	307.2	305.4	308.0	443.9	440.9	428.3	415.7	405.1	263.5	260.3	248.8	242.7	
Feb.	308.1	308.3	308.1	305.8	306.4	444.2	437.2	433.1	418.8		265.3	258.5	254.2	243.9	
March	309.8	309.8	306.5	304.3		446.6	447.8	430.9	415.4		266.3	263.5	250.3	238.0	
April	308.6	307.5	308.0			447.8	444.6	438.1	424.1		268.5	262.1	256.2	247.0	
May	308.4	308.1	307.2	305.1		443.8	445.8	438.3	421.3		265.6	269.4	256.9	243.7	
June	308.1	307.7	306.8			446.8	445.6	438.6			266.1	263.8	257.9		
July	307.5	309.2	308.3	304.3		446.8	454.2	442.8	426.9		265.6	267.9	257.7	246.2	
Aug.	306.9	309.0	307.0	305.5		448.6	455.4	442.0	426.8		267.3	270.0	259.1	249.2	
Sept.	308.9	308.1	306.7	304.6		457.0	450.9	445.7	427.3		268.6	264.5	261.8	245.8	
Oct.	308.5	308.8	307.9	304.1		456.7	448.5	446.0	433.5		271.9	263.8	262.0	249.9	
Nov.	309.0	310.4	308.9	303.7		469.6	459.1	449.2	437.7	423.4	277.7	272.7	266.9	251.5	246.9
Dec.	309.6	309.6	307.3	306.2	307.1	462.0	451.2	453.7	434.0	423.1	277.3	268.0		258.3	244.6

These data are provisional, pending final calibration.

The year 1988 was the first complete year of CH<sub>3</sub>CCl<sub>3</sub>, and CCl<sub>4</sub> measurements from the GMCC baseline observatories. Although it has been possible to calculate crude atmospheric growth rates from this limited data set, the results should be considered tentative until measurements over a larger time span are obtained. Also, some analytical problems, which may have an effect on the overall accuracy of these numbers, are still being resolved.

On the basis of only 1 year of observations at MLO (Figure 8.7), the concentration of atmospheric CCl<sub>4</sub> does not appear to be increasing significantly; CH<sub>3</sub>CCl<sub>3</sub>, however, does seem to be growing at about 4% per year, a finding that is confounded by a contaminant interfering with the measurement of this com-

pound. As for the CFC-113 estimates, the estimated growth rates for CCl<sub>4</sub> and CH<sub>3</sub>CCl<sub>3</sub> will be refined considerably as our in-situ systems remain on line long enough to collect a few years' data and as lingering contamination problems are resolved.

### 8.1.3. LOW ELECTRON ATTACHMENT POTENTIAL SPECIES

A temperature-programmable, dual-channel, EC-GC was purchased and installed for the measurement of LEAPS gases, specifically HCFC-22 (CHClF<sub>2</sub>), CFC-113, and the Halons, H-1301 (CBrF<sub>3</sub>) and H-1211 (CBrClF), in our Boulder laboratory. The GC was fitted with a programmable cryofocus-

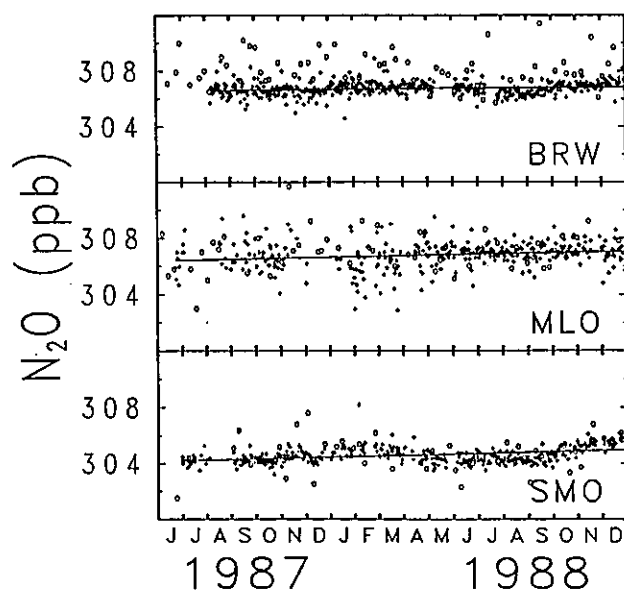


Fig. 8.5. N<sub>2</sub>O concentrations from flask pair samples (o) and daily means from the in-situ RITS GC (+), at BRW, MLO, and SMO.

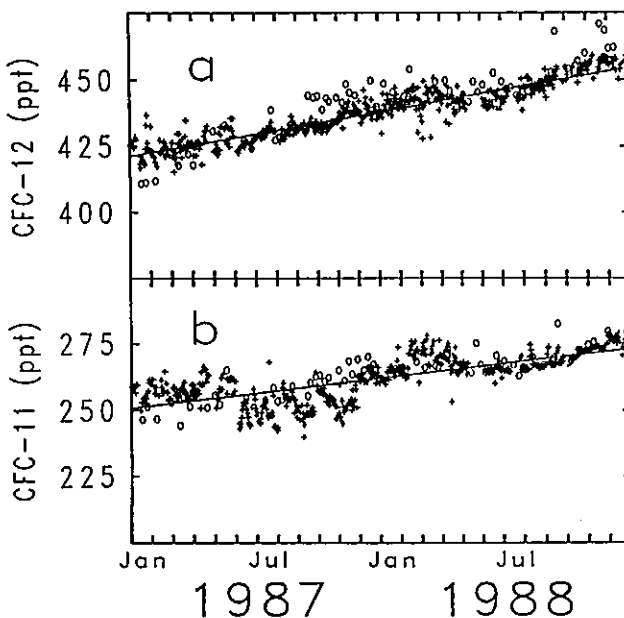


Fig. 8.6. (a) CFC-12 and (b) CFC-11 concentrations (ppt) at BRW from the in-situ RITS GC. Note the apparent elevation in CFC concentration from late October to late May.

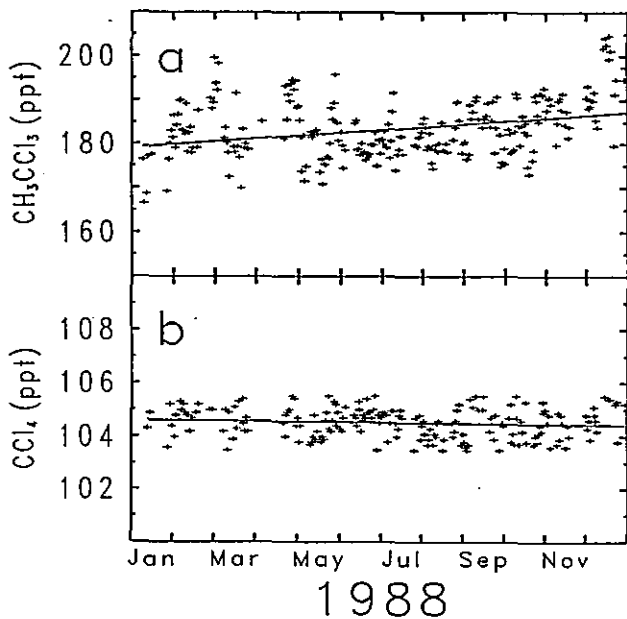


Fig. 8.7. (a)  $\text{CH}_3\text{CCl}_3$  and (b)  $\text{CCl}_4$  concentrations at MLO in 1988 from the in-situ RITS GC.

ing unit for concentrating and injecting atmospheric gases. This unit, designed for injecting gases adsorbed to packed tubes, was modified to allow the direct injection of up to 500 mL. As a result, electrophilic gases can be measured to levels as low as 1 ppt.

A number of standard gases were tested on the GC with a silicone oil column (Chrompack CP-Sil-5, 1.2  $\mu\text{m}$ ) set to a temperature range of  $-60^\circ\text{C}$  to  $+110^\circ\text{C}$ . The column eluted all gases of interest from H-1301 (boiling point =  $-59^\circ\text{C}$ ) to  $\text{CCl}_4$  (boiling point =  $77^\circ\text{C}$ ), with reasonable separation of peaks. Peaks were identified and response factors determined for  $\text{N}_2\text{O}$ , H-1301, HCFC-22, CFC-12,  $\text{CH}_3\text{Cl}$ , HFC-134a ( $\text{C}_2\text{H}_2\text{F}_4$ ), H-1211, CFC-11, HCFC-123 ( $\text{CF}_3\text{CHCl}_2$ ),  $\text{CH}_2\text{Cl}_2$ , CFC-113,

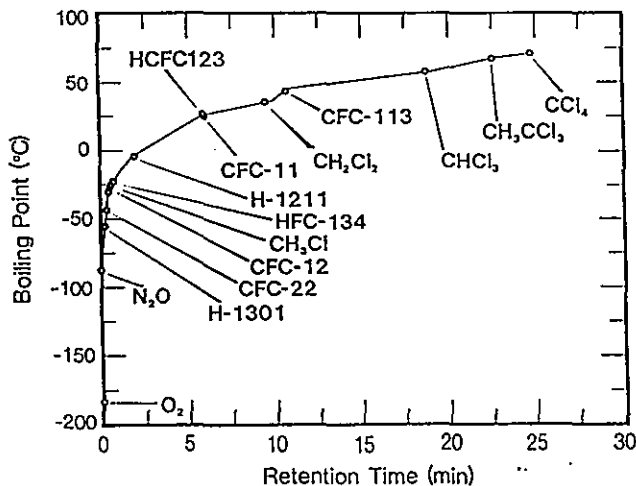


Fig. 8.8. Boiling point curve for the chromatographic separation of natural gases and halocarbons on a silicone oil-based, capillary column (Chrompack CP-Sil-5, 1.2  $\mu\text{m}$ ; 0.53 mm  $\times$  50 m). Note similar retention times for proposed replacement halocarbons (CFC-134a and HCFC-123) and the compounds they are to replace (CFC-12 and CFC-11).

$\text{CHCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ , and  $\text{CCl}_4$  (Figure 8.8). Two of these gases, HFC-134a and HCFC-123, have been proposed as replacement halocarbons for CFC-12 and CFC-11.

The first air samples for LEAPS gases were collected from NWR in November, beginning our long-term monitoring program for the four LEAPS gases. The GC has also been used to measure the composition and contamination of industrial solvents used for cleaning regulators and fittings purchased by our laboratory, and to identify contaminants in cylinders of commercial carrier gas, "zero air" collected at NWR, and standard gases filled at NWR. Evaluating alternative, analytical columns and installing new, high-pressure pumps at the observatories to provide sufficient samples for replicate mea-

TABLE 8.2. Summary of GMCC Gravimetric Standards Prepared in 1988

Set	Compounds	Quantity	Concentration Range	Prepared for
1	$\text{CO}_2, \text{N}_2\text{O}$	5	ppm	NOAA/RITS
2	CFC-12	8	ppm, ppb, ppt	NOAA/RITS
3	CFC-12, CFC-11, CFC-113, $\text{CH}_3\text{CCl}_3$ , $\text{CCl}_4$ , $\text{CHCl}_3$	3	ppb, ppt	NOAA/RITS
4	CFC-12, CFC-11, CFC-113, $\text{CH}_3\text{CCl}_3$ , $\text{CCl}_4$ , $\text{CH}_3\text{Br}$	3	ppt	NOAA/RITS
5	CFC-113	3	ppm, ppb, ppt	NOAA/RITS
6	CFC-113, Halon-1211, CFC-22	1	ppb	NOAA/LEAPS
7	$\text{CH}_4$	5	0.1 %	NOAA/FT-IR/CC
8	HFC-134a	7	ppm	NOAA/FT-IR
9	HCFC-123	1	ppm	NOAA/FT-IR
10	$\text{CO}_2$	4	ppb	NOAA/GMCC
11	Benzene, isoprene, pentane, $\alpha$ -pinene, m-xylene, 2,2-dimethylbutane	1	ppm	NOAA/JAL
12	Halon-1211	1	ppm	OGC
13	Halon-1211	1	ppm	NOAA/ARL/Idaho Falls

surement of LEAPS gases should lead to improvements in precision and accuracy of the LEAPS measurements.

#### 8.1.4. GRAVIMETRIC STANDARDS

Our newly completed gravimetric standards laboratory is now capable of preparing gravimetric standards for a large variety of compounds at sub-percent, parts per million, parts per billion, and parts per trillion concentrations. Several sets of gravimetric standards were prepared for various projects such as RITS, LEAPS, and FT-IR, and other groups, including NOAA/ARL Idaho Falls, NOAA/AL, and OGC (Table 8.2).

Standard curves were constructed from gravimetric sets of  $N_2O$ , CFC-12,  $CH_3CCl_3$ , and  $CCl_4$ . The precision for these curves was 0.4 ppb, 1.6 ppt, 2.2 ppt, and 1.3 ppt, respectively, where precision is defined as the average difference between the gravimetric concentration and the concentration predicted by the standard curve (Figures 8.9-8.12). A set of CFC-11 and

CFC-113 standards will soon be prepared, and all RITS compounds will be reported on the NOAA scale. CFC-11 and CFC-12 are currently reported on the OGC scale of 1985. The nonlinear response of  $N_2O$  on an ECD was investigated by comparing  $N_2O$  gravimetric standards in a 290-ppb range. NIST SRMs and NOAA  $N_2O$  standards were used to construct a curve from 44 to 333 ppb (Figure 8.9). A linear extrapolation from a response of unity differed by as much as 12.5 ppb from the true curve in the 130 to 150 ppb range, but the difference was not as significant (less than 3 ppb) in the 280 to 320 ppb range.

Gravimetric standards of CFC-12 were prepared by two different methods. Pure CFC-12 gas was diluted to the parts per trillion level and compared with parts per trillion standards prepared from the dilution of pure CFC-12 liquid. Both sets of standards agreed within 1.6 ppt (Figure 8.10).

A dual-detector Shimadzu GC-8A with a flame ionization detector was purchased and will be used to compare standards at the parts per million levels. A Perkin-Elmer 3920B GC and a

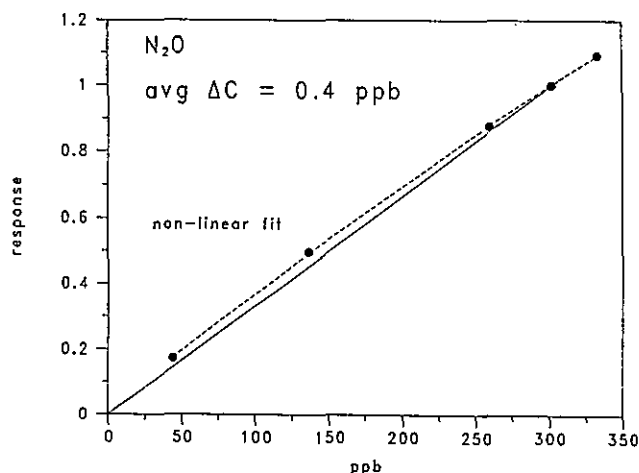


Fig. 8.9.  $N_2O$  standard curve prepared from NIST SRMs and NOAA gravimetric standards. A normalized detector response is plotted versus concentration.

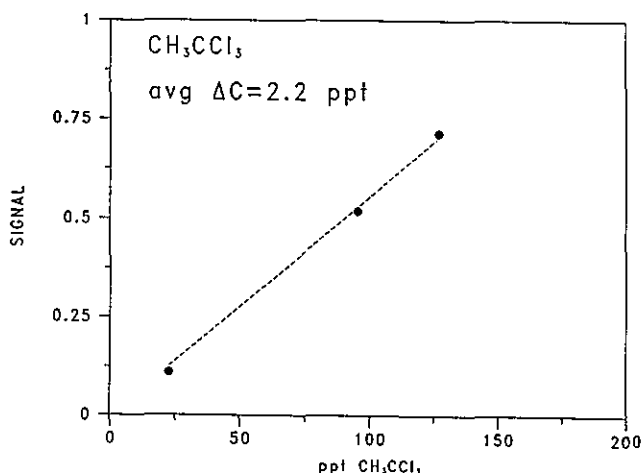


Fig. 8.11.  $CH_3CCl_3$  standard curve for parts per trillion levels.

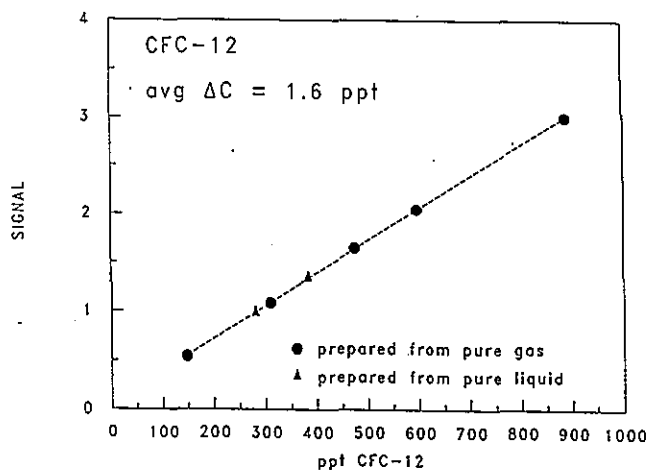


Fig. 8.10. CFC-12 standard curve for parts per trillion concentration levels, showing good agreement between two methods of preparation.

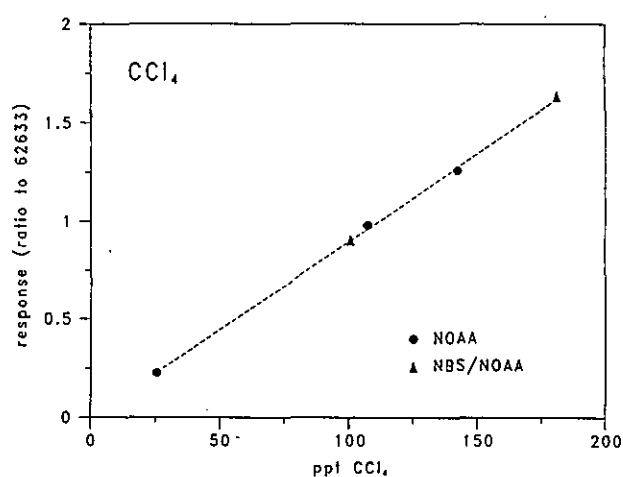


Fig. 8.12.  $CCl_4$  standard curve for parts per trillion levels showing good agreement between NOAA and NIST standards.

Spectro-Physics SP7100 GC with electron capture detectors will be used to compare standards at parts per billion and parts per trillion level. This set of GCs will allow us to examine our standard sets more closely at each step in the dilution process.

## 8.2. SPECIAL PROJECTS

### 8.2.1. SOVIET-AMERICAN GAS AND AEROSOL EXPERIMENT II

SAGA II in 1988 emphasized filtering and reducing the CFC,  $N_2O$ ,  $CO_2$ , and  $CH_4$  data collected by automated GCs during the 3-month cruise. The results were evaluated and presented at professional meetings, and a data report describing our analytical methods, data reduction, and results was published in December [Butler *et al.*, 1988]. Manuscripts for publication in professional journals were begun once the data were finalized.

### 8.2.2. FT-IR SPECTROMETER ARCHIVE PROJECT

As discussed in section 8.1.1., the goal of finding a generic flask for all compounds measured by GMCC has been elusive. The FT-IR spectrometer permits archiving the IR absorption of atmospheric trace gases for future analysis of compounds not currently analyzed by GMCC. A solar tracker that permits the spectrometer to follow the sun was designed in 1988. It is anticipated that the FT-IR archive project will begin in 1990.

The principal goal in 1988 was measuring laboratory spectra of many important RITS gases, including  $CH_4$  and the new substitute CFCs. These spectra are required to calibrate the instrument for atmospheric measurements. The spectra were also useful in verifying our methods for the preparation of gas standards. Figure 8.13 shows a laboratory infrared spectrum between 600 and 1500  $cm^{-1}$  for one of the proposed replacement halocarbons, HFC-134a, measured for a sample containing 1021 ppm in air in a 15-cm-long gas cell at 300 K. Figure 8.14 shows a Beer's law plot for the  $\nu_4$  fundamental band of  $CH_4$  at various temperatures, where the slope of the line yields the band strength value for the compound. For both  $CH_4$  and HFC-134a,

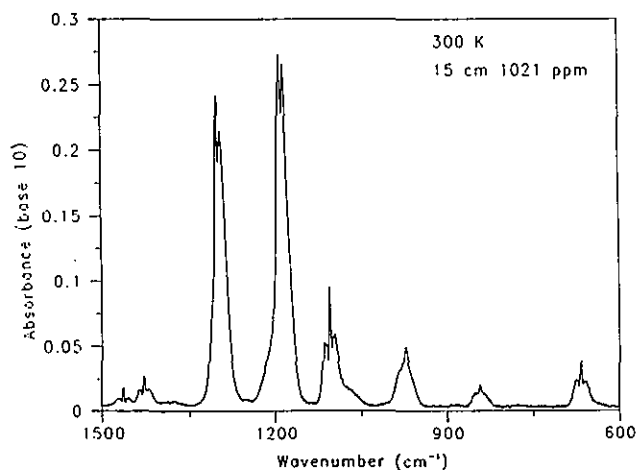


Fig. 8.13. Infrared absorption by one of the proposed replacement halocarbons (HFC-134a).

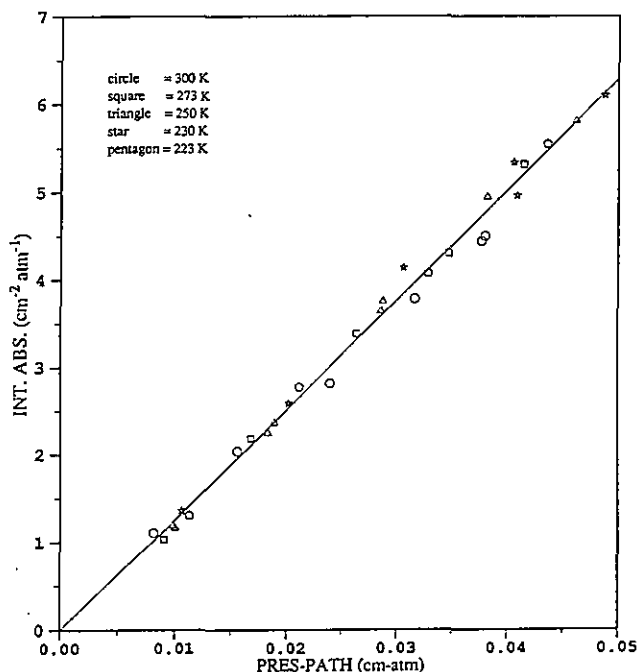


Fig. 8.14. Beer's law plot of integrated absorbance versus pressure-pathlength for the  $\nu_4$  band of  $CH_4$  at various temperatures.

band strength values were not a function of temperature, but the band shape was definitely affected by temperature; the band was narrower and absorption greater at lower temperatures. Table 8.3 shows a summary of all band strength measurements in 1988. The GMCC band strength for the  $\nu_4$  band of  $CH_4$  is identical to the value of Varanasi *et al.* [1983]. The measured total band strengths for HFC-134a and HCFC-123 are comparable with total band strengths for the compounds that they are replacing, CFC-12 and CFC-11. Since the atmospheric lifetimes of the replacement CFCs are shorter (~15 years for HFC-134a and ~2 years for HCFC-123) than that of the CFCs (~100 years), the potential for the replacement CFCs to produce the greenhouse effect is greatly reduced.

TABLE 8.3. Summary of Band Strength Measurements for RITS Gases

Compound	Formula	Total Band Strength ( $cm^{-2} atm^{-1}$ at 300 K)	Reference
<i>Methane</i>			
$\nu_4$ band	$CH_4$	125	This report
$\nu_4$ band	$CH_4$	126	Varanasi <i>et al.</i> , 1983
<i>CFC and Substitutes</i>			
HFC-134a	$C_2H_2F_4$	3147	This report
CFC-12	$CCl_2F_2$	3271	Elkins <i>et al.</i> 1986
HCFC-123	$C_2HCl_2F_3$	2379	This report
CFC-11	$CCl_3F$	2417	Elkins <i>et al.</i> , 1986

### 8.2.3. AIRBORNE GAS CHROMATOGRAPH

A Shimadzu Mini-2 gas chromatograph was modified for use aboard the NOAA King Air research aircraft. The GC was designed for measuring halocarbons in the atmosphere at the parts per trillion level at 4-min intervals in a pressurized aircraft. The GC was configured with a 0.6-m Porasil B main column and a 0.3-m Porasil B backflush column. A carrier gas makeup

stream and two absolute backpressure regulators were installed at the outlet of the detector to compensate for changes in atmospheric pressure.

One test flight was conducted over eastern Colorado on December 6, 1988. CFC-12 was measured at various altitudes, and flask samples were collected and compared with the GC data. Figure 8.15 shows CFC-12 as a function of altitude. This test flight provided valuable preliminary information regarding the capabilities and limitations of an airborne EC-GC.

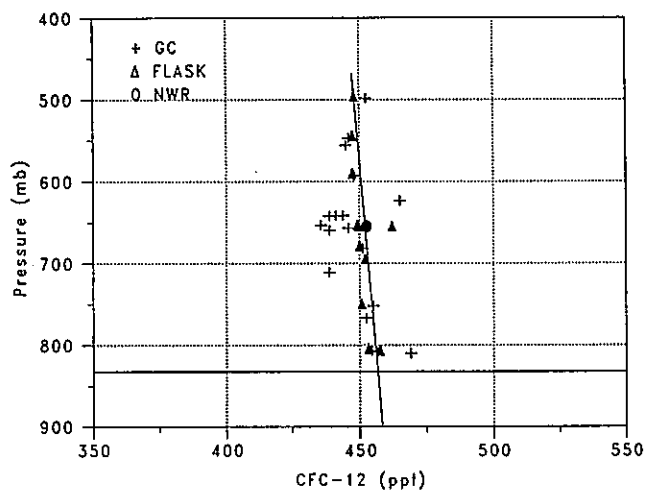


Fig. 8.15. CFC-12 variation with altitude over eastern Colorado on December 6, 1988.

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