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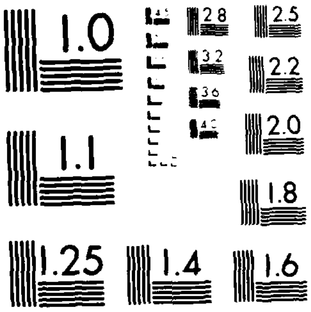
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Observations of Major Stratospheric Chlorine Species

CHARLES C. GALLAGHER
CHARLES A. FORSBERG

24 October 1983

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A cryogenic whole air sampler (Tri-Sampler) and a Direct Flow Sampler (DFS), a motor-driven filter sampler, are used simultaneously on a balloon platform with the goal of sampling all significant stratospheric chlorine compounds to permit determination of total chlorine content in the lower stratosphere. Gas chromatographic techniques are applied to the retrieved whole air samples to determine volume mixing ratios of CF_2Cl_2, $CFCl_3$, CH_3Cl, CH_3CCl_3, and CCl_4. Specially treated filters are used with the DFS to capture all acidic and particulate chlorine compounds. The filter samples are

20. (contd)

analyzed using wet chemistry and neutron-activation analysis techniques. The filter sampling effort was conducted in cooperation with other experimenters. It will be reported in more detail in a separate publication that will also include the total chlorine summations. Three balloon flights were conducted during 1981—1982 from Holloman AFB, ~~New Mexico (33°N)~~, and simultaneous samplings were obtained at various altitudes from 15 to 30 km. ClO studies are not included in the measurements program; this species contributes to total chlorine content only down to about 30 km. Mixing-ratio lapse rates for the species analyzed by gas chromatography are consistent with those species being of tropospheric origin. Also, stratospheric abundances of $CFCl_3$ and CF_2Cl_2 exhibited minimal changes over several years, although the tropospheric abundances of these species are known to increase at about 10 percent per year in the northern hemisphere.

Preface

The authors wish to thank Rocco S. Narcisi for initiating the study and for his continued encouragement; Allen Mason for his generous assistance in formulating the effort; Bruce Gandrud and Eugene Mroz for filter preparation and chemical analysis; Hans Laping, John Borghetti, Edward Mansfield, Ronald Lavigne, and the many others within LKD, Det. 1, LC, and SU who provided continuing support.

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1. INTRODUCTION

Determination of total stratospheric chlorine is essential to complete the picture of the chlorine cycle and its effect on stratospheric ozone content.

Although many experiments have been conducted to determine stratospheric concentrations of several chlorine compounds, there have only been limited efforts at simultaneous determination of all chlorine compounds. This is partly because a variety of diagnostic tools is needed for the various species. Berg et al[1] sampled stratospheric air by employing ultra-pure activated charcoal traps aboard aircraft and balloon platforms. Neutron activation techniques were developed to analyze the retrieved samples and provided the first measurements of total stratospheric chlorine content, with a typical value of 3 ppbv obtained at 20 km. This method, however, does not provide a species-by-species breakdown of chlorine content.

This report primarily addresses the acquisition of stratospheric whole air samples and the subsequent gas chromatographic analyses of these samples to determine abundances of the five most significant chlorine-containing species exclusive of acidic or particulate species. Acidic and particulate species were gathered on treated filters coincident with some of the whole air samples. Summations of

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(Received for publication 20 October 1983)

[1] Berg, W.W., Crutzen, P.J., Grahek, F.E., Gitlin, S.N., and Sedlacek, W.A. (1980) First measurements of total chlorine and bromine in the lower stratosphere, Geophys. Res. Lett. 7:937-940.

the results from both efforts provides values for total stratospheric chlorine content for the altitudes sampled.

The filter-based samplings and analyses depended, in part, on outside support. A separate paper is being prepared, in cooperation with the other contributors, that will describe the acidic and particulate chlorine studies in more detail and will contain the total chlorine summations.

2. BACKGROUND

Environmental concerns arising from the release of large quantities of chlorinated fluorocarbons into the atmosphere stimulated interest in stratospheric chlorine chemistry. Chlorinated fluorocarbons and other chlorinated compounds of both natural and artificial origin are photolyzed in the stratosphere and enter into catalytic cycles postulated to destroy ozone.

Berg et al[1] pointed out that observations of total chlorine as a function of space and time should be made in conjunction with measurements of major stratospheric chlorine species in order to

(1) explore any chlorine species variability when all chlorine species are trapped and accounted for,

(2) ensure that there has been an adequate accounting of all significant chlorine species vis a vis chlorine-ozone photochemistry, and

(3) establish needed values for global limits on stratospheric chlorine for photochemical modeling efforts.

An ongoing AFGL interest in measuring stratospheric fluourocarbon content was initiated originally to determine potential effects of AF operations on stratospheric ozone content. This program was later expanded to determine total stratospheric chlorine content because the chlorine freed by solar ultraviolet-induced dissociation of the fluourocarbons would, of course, contribute to the overall chlorine cycle.

A study was initiated at AFGL to identify all of the more significant chlorine-containing species in the stratosphere. The results, described in an internal report[2] and compiled as an addendum to that report, also indicated the need for three diagnostic methods to both identify and quantify all relevant species.

Five of the key species are best suited for gas chromatographic investigation. These include fluorocarbons 11 and 12, species already being studied at AFGL, plus methyl chloride (CH_3Cl), methyl chloroform (CH_3CCl_3), and carbon tetrachloride (CCl_4). Second, analyses by both wet chemistry and neutron-activation

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[2] Mason, A.S. (1979) Stratospheric Total Chlorine Sampling Study, Mobilization Augmentee Progress Report to AFGL/LKD.

methods would be performed on acidic and particulate species captured on treated filters. Acidic species would be captured only on base treated segments; particulate species would be captured on both neutral and base-treated filter segments. Principal species of interest that would be captured only on base treated segments are Cl^-, chlorine nitrate ($ClONO_2$), hydrochloric acid (HCl), and hypochlorous acid ($HOCl$). The only significant particulate species would be sodium chloride ($NaCl$). The third diagnostic method would be needed to measure atomic chlorine, and, more importantly, chlorine oxide (ClO). Stratospheric chlorine oxide content has been investigated using microwave,[3] optical,[4] and resonance fluorescence[5] methods, and its contribution to total stratospheric chlorine content is significant only down to about 30 km altitude. Such measurements are not included in our program; however, three of our four filter samplings were obtained at or below 20 km, altitudes where the ClO contributions would be negligible.

3. EXPERIMENTAL PROGRAM

Experience in obtaining whole air samples at stratospheric altitudes was gained at AFGL through a series of balloon flights that commenced in 1975.[6] Although a few grab samples were obtained using previously evacuated spheres, most sampling was done cryogenically, primarily with a liquid-helium cooled dewar that contained 3 evacuated 2-liter-volume cylinders. This tri-sampler is illustrated in Figure 1. The remotely activated valves had the scientific and economic advantages of obtaining whole air samples at 3 altitudes on a single balloon flight. Detailed descriptions of the tri-sampler, the flight package, and the overall field program are given elsewhere.[6] Tri-samplers were used to obtain all the whole air samples reported herein.

Filter based samplings were accomplished simultaneously with some of the whole air samplings in 1981 and 1982 with a Direct Flow Sampler (DFS) mounted on the same gondola that contained the tri-sampler. The DFS, on loan from the

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3. Waters, J.W., Gustincic, J.J., Kakar, R.K., Roscoe, H.K., Swanson, P.N., Phillips, T.G., de Gtaauw, T., and Kerr, A.R. (1979) Aircraft search for millimeter-wavelength emissions by stratospheric ClO, J. Geophys. Res. **84**:7034-7040.

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6. Gallagher, C.C., Forsberg, C.A., Pieri, R.V., and Faucher, G.A. (1981) Stratospheric Trace Gas Composition Studies Utilizing in situ Cryogenic, Whole-Air Sampling Methods, Tech Report AFGL-TR-81-0071, AD A104375.

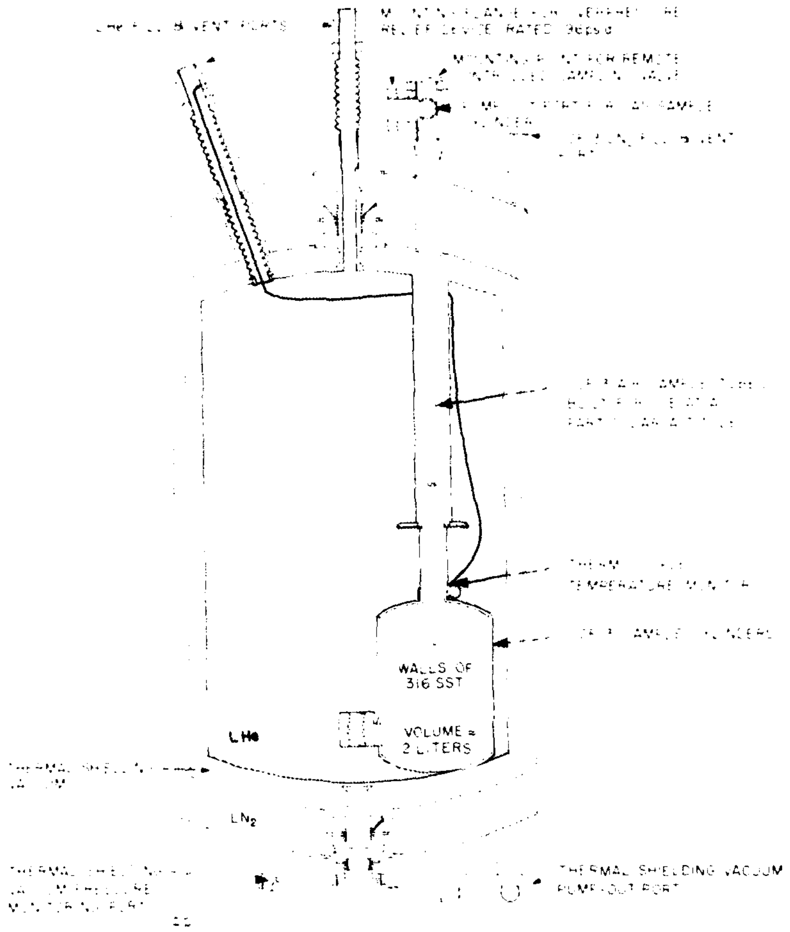

Figure 1. Tri-Sampler Cross Section. The unit is of stainless steel construction, of 127 cm overall height, and the nested chambers enclosing vacuum and liquid nitrogen regions provide a 28-h hold time for the 42-liter capacity liquid helium chamber under static conditions

Department of Energy, is shown in Figure 2. It uses a 1/2-hp Westinghouse aircraft motor to power a Torrington blower and draw air at high velocity through 1 ft^2 of filter paper. Sampling is remotely activated. Volume flow is measured by a propeller-anemometer flowmeter, and the output signal is included in the general TM transmission package. The system can sample, for example, approxi-

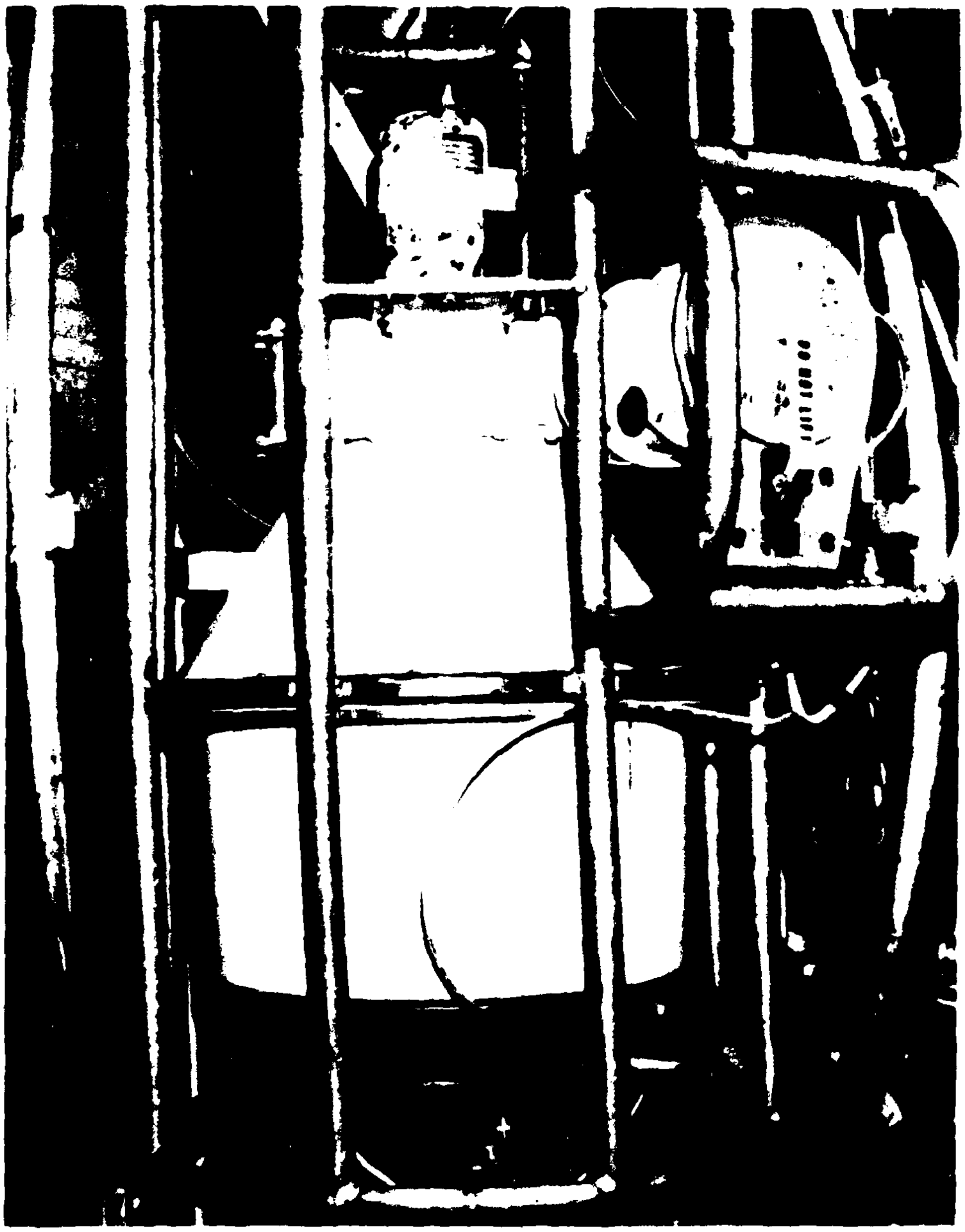

Figure 2. Direct Flow Sampler. In preparation for flight, the unit is shown mounted in a small cage attached to a larger gondola. The filter (not visible) is mounted in the horizontal plane at the junction between the cylindrical and conical sections. The motor is on the top, and the flowmeter is in the exhaust tube (upper right). Pneumatically operated doors are opened on the inlet (bottom) and exhaust just before sampling. An inlet tube (not yet attached) extends below the gondola

mately 700 ambient cfm at 20 km altitude. The filter treatment for each flight is described briefly in Section 5.

4. DIAGNOSTICS

4.1 Gas Chromatography

The cryogenic samples were analyzed at AFGL using gas chromatography. Two gas chromatographs (GC) were utilized: a Perkin Elmer Model 3920B optimized for fluorocarbon detection, and a Hewlett Packard (H-P) Model 5733A optimized for methyl chloride detection.

Operating parameters for the Perkin Elmer GC are the same as those used for the previous samples, namely:

(1) a 12-ft length, 1/8-in-diam nickel column packed with Porasil C (mesh range 80/100), a spherical, siliceous packing material;
(2) a nickel 63 electron capture detector; and
(3) ultra-high purity (UHP) nitrogen carrier gas.

A heated gas inlet system that has vacuum capability and is operated in conjunction with a heated, 10-port sampling valve provides reliable injections of both calibration and stratospheric gas samples.

The H-P instrument became operational late in 1981. Because methyl chloride was expected to be the most abundant of the newly investigated stratospheric species, the new CG was optimized for detection of this compound. Operating parameters for the H-P GC are the following:

(1) a 10-ft length, 1/8-in-diam nickel column packed with Porasil B (mesh range 80/100);
(2) a nickel 63 electron capture detector; and
(3) UHP nitrogen carrier gas containing 0.3 percent oxygen.

Porasil B is similar to Porasil C but has a larger surface area per gram and a smaller pore diameter. The carrier gas mixture was suggested by Rasmussen et al[7] among others to provide enhanced response for weak electron-capturing species.

The chromatograph responses were calibrated frequently using both dilution and permeation methods to produce the reference gas standards for all species investigated. Most dilution calibrations were carried out using purchased primary standard mixtures (typically at 1 ppmv in UHP nitrogen) and further diluting them in UHP nitrogen through use of a precision titration-tube mixing system. Addi-

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[7] Rasmussen, R.A., Rasmussen, L.E., Khalil, M.A.K., and Dalluge, R.W. (1980) Concentration distribution of methyl chloride in the atmosphere, J. Geophys. Res. **85**:7350-7356.

tional dilutions using the primary standard mixtures and UHP nitrogen with electronic, mass flow controllers were prepared periodically. Independent of these, a method based on the temperature dependent permeation of the test gas through a Teflon membrance into a stream of UHP nitrogen was also utilized. For each method, a succession of mixing ratios was produced to enable generation of plots of GC responses. All calibration gases flow directly to the GC input. The systems are described in more detail elsewhere.[6]

4.2 Wet Chemistry and Instrumental Neutron Activation Analysis

Because significant quantities of chlorine were found to be embedded in the fiber material of the filters, an extraction process was performed on the retrieved filters before analysis to obtain a solution containing the chlorine species. Half of the solution was then analyzed using a wet chemistry technique developed by Lazrus et al.[8] The remaining half experienced neutron activation analysis at the Massachusetts Institute of Technology (MIT),[9] with all irradiations carried out in the pneumatic facility (1PH1) of the MIT-RR, whose thermal neutron flux is at the nominal value of 5×10^{12} n cm^{-2} s^{-1}.

5. FLIGHT SCHEDULE AND SAMPLES OBTAINED

Twenty-five balloon flights, commencing in 1975 and terminating in 1982, were conducted in the series. One or more stratospheric whole air samples were obtained on every flight, and the results from the first 22 flights have already been reported.[6, 10] The final three flights were conducted primarily to determine total stratospheric chlorine content, and details of these samplings, analyses, and results are reported herein.

Flight parameters are contained in Table 1. The format of Table 1 is identical with that of Table 2 in AFGL Report TR-81-0071,[6] and the combination of the two tables provides a consistent and complete tabulation of all the more relevant flight parameters for all flights in the series. On Flight 23, a filter sample was obtained coincident with the 20-km whole air sample. On Flight 24, a single filter

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8. Lazrus, A. L., Gandrud, B. W., Woodward, R. N., and Sedlacek, W. A. (1976) Direct measurements of stratospheric chlorine and bromine, J. Geophys. Res. 81:1067-1070.

9. Janghorbani, M. (1983) Development of Analytical Methodology for the Measurement of Chlorine and Bromine in the Stratosphere, Tech Report AFGL-TR-83-0142, AD A132640.

10. Gallagher, C. C., Forsberg, C. A., and Pieri, R. V. (1983) Stratospheric N_2O, CF_2Cl_2, and $CFCl_3$ composition studies utilizing in situ cryogenic, whole air sampling methods, J. Geophys. Res. 88:3798-3807.

Table 1. 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
23	H81-14	31 May 81	Holloman	33 N	2304	0.804	75.6	Ground	Cryo	20, 15, 12
24	H81-5	4 Jun 81	Holloman	33 N	2307	3.69	104.4	Ground	Cryo	30, 25, 20
25	H82-07	6 Apr 82	Holloman	33 N	2629	0.804	70.3	Ground	Cryo	20, 15

sample was obtained over the 30-km to 25-km band, that is, coincident with both the 30- and 25-km cryogenic samples as well as during the time between them. Separate filters and DFS units were used to sample coincident with the 20- and 15-km cryogenic samplings on Flight 25.

Filter preparation and wet chemistry analyses for Flights 23 and 24 were performed at the National Center for Atmospheric Research. The filters were wholly base-treated, thus providing the total acidic and particulate chlorine content. For Flight 25, filter preparation and wet chemistry analyses were performed at the Los Alamos Scientific Laboratory. These filters were prepared with separate neutral and base-treated segments, thus permitting resolution of particulate and acidic chlorine content. In all cases, the neutron activation analyses were conducted at MIT.[9]

6. GAS CHROMATOGRAPHIC ANALYSES AND RESULTS

6.1 1981 Flights

The six whole air samples were returned to AFGL as cryofrosts within the two tri-samplers for subsequent warm-up and analyses. Chemiluminescence analysis to determine oxides of nitrogen content (to be reported separately) preceded the gas chromatographic analysis on the Perkin Elmer GC. Values obtained for fluorocarbons 11 and 12 are given in Table 2. Because values for nitrous oxide (N_2O) content have always been obtained, they are included as well. The overall uncertainty in the mixing ratios quoted is estimated to be 5 percent for nitrous oxide and 10 percent for the fluorocarbons.

Because of procurement problems, the H-P GC was not available for prompt analysis of the 1981 flight samples. The samples were cryogenically transferred to stainless steel cylinders subsequent to the June 1981 analyses, and these stored samples were analyzed on the H-P GC during February 1982, the earliest occasion after the instrument had been obtained and fully calibrated. Only samples obtained at altitudes where filter samplings also took place were analyzed at this time. Tests at AFGL and elsewhere have indicated that the samples could be expected to remain stable to within a few percent during the storage period.

Table 2. Nitrous Oxide and Fluorocarbon Results From 1981 Flights

FLIGHT DATE	SAMPLING ALTITUDE	TROPOPAUSE HEIGHT	N_2O	F12 (CF_2Cl_2)	F11 ($CFCl_3$)
4 June 1981	30 km	11.4 km	93 ppbv	79 pptv	5.5 pptv
"	25	"	110	101	10
"	20	"	178	175	91
31 May 1981	20	11.7 km	142	173	60
"	15	"	243	190	174
"	12		293	236	151

The results are contained in Table 3. The specifics for the analyses and calibrations appropriate to each of the quoted values follows.

Table 3. Volume Mixing Ratios of Other Major Stratospheric Chlorine Species From 1981 Flights (All Expressed in PPTV)

FLIGHT DATE	ALT. (km)	CH_3Cl	CH_3CCl_3	CCl_4
4 June 1981	30	200	58	24
"	25	378	47	39
31 May 1981	20	365	151	49

6.1.1 Methyl Chloride

Because response on the Perkin Elmer GC was weak and because the H-P GC operating conditions were optimized for detection of methyl chloride, the reported values are based exclusively on results obtained with the H-P GC. Methyl chloride is of natural origin. Both permeation and dilution methods were used for calibration standards and provided good agreement with one another. Also, methyl chloride should have maintained good stability during the 8 months of storage at the high cylinder pressures employed (typically ~200 psi).[7] Overall uncertainty of the quoted values is estimated to be 20 percent.

6.1.2 Methyl Chloroform

Methyl chloroform is of anthropogenic origin, manufactured primarily for use as an industrial degreasing solvent. Our GC response for this species is rather weak, and the reported values represent the average from analyses performed with both chromatographs. Tests at AFGL and elsewhere[11] have shown that the species stores well in stainless steel containers with an expected loss of less than 10 percent per year. However, the independent study indicates a relatively poor agreement among several laboratories (not including AFGL) who participated in an inter-laboratory comparison of a number of reference samples containing methyl chloroform at representative tropospheric and stratospheric mixing rations. The discrepancies appear to be due, to a significant degree, to the reliability of the calibration gas standards. As with the other species we investigated, our calibration gas standards were prepared using both dilution and permeation methods. Overall uncertainty of the reported values in Table 3 is estimated at 30 percent.

6.1.3 Carbon Tetrachloride

Carbon tetrachloride is wholly of anthropogenic origin, and mixing-ratio measurements as performed by various researchers suffer from serious inconsistencies in calibrations. For this reason, a somewhat more extensive calibration effort was undertaken in support of the values reported in Table 3. As usual, both dilution and permeation sources were used to produce the calibration standards. In addition, separate tests were performed to confirm the factory-supplied permeation rate data for the Kin Tek Corporation carbon tetrachloride permeation tube (S/N 0542). Tube emissions were monitored while the permeation system was being used to produce the reference calibration standards for the chromatographs. This monitoring was accomplished by measuring the weight loss from the tube during the test period. This was no simple task because weight losses in the low mg range have to be measured for a tube that weighs several hundred grams! For this purpose, a Mettler Corporation Model H315 Macro Analytical High Capacity Balance was acquired (weighing range 1001g, readability 0.1 mg, precision 0.1 mg). The permeation tube manufacturer states permeation (emission) rates in nanoliter/min at standard temperature and pressure for each operating temperature. These values were converted to g/min for the comparison, and the tests were conducted for permeations lasting anywhere from 1000 to 7000 min, sufficient periods to produce adequate weight losses and thus lower weighing errors. For each test, results remained within a few percent of the factory calibration values and, overall, bracketed these values. Therefore, the permeation system was considered reliable.

Calibration plots generated using both permeation and dilution methods were in good agreement. The stability of carbon tetrachloride standards stored in small,

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[11] Rasmussen, R.A., and Khalil, M.A.K. (1981) Interlaboratory comparison of fluorocarbons -11, -12, methylchloroform and nitrous oxide measurements, Atmos. Environ. 15:1559-1568.

stainless steel cylinders has been demonstrated to be acceptable.[11] Indeed, AFGL tests of sample stability during storage indicate that sample acquisition and analysis errors dominate over any error resulting from the delayed analysis of this species. The CCl_4 results reported in Table 3 were obtained with the H-P GC, with the overall uncertainty estimated to be 20 percent.

6.2 1982 Flight

The two whole air samples were returned to AFGL for prompt analysis. Each chlorine species was investigated on the same chromatograph(s) used for the species for the 1981 samples. The results for the five species of principal interest are contained in Table 4. Calibration procedures were similar to those applied to previous analysis; *however, refinements to the methods* and the prompt analyses of all reported species resulted in some improvements in overall uncertainty-estimates for the tabulated results. Fluorocarbon values remained at 10 percent; methyl chloride improved to 10 percent; methyl chloroform improved to 20 percent; and carbon tetrachloride improved to 15 percent. Tropopause height at Holloman AFB on flight day was 13.5 km.

Table 4. Results From 6 April 1982 Flight (All Expressed in PPTV)

ALT. (km)	CF_2Cl_2	$CFCl_3$	CH_3Cl	CH_3CCl_3	CCl_4
20	158	52	177	157	19
15	329	184	403	164	58

Limited data has been obtained for other stratospheric chlorine species, particularly, fluorocarbons 21, 22, 113, and 114. Calibration gas response plots were generated for these species. Flight sample GC responses to these species were consistently weak at best, and so their combined contributions to total stratospheric chlorine content would be small.

The generally accepted northern hemisphere mixing ratios of the major chlorine species have been compiled in Table 5 as a guideline to evaluation of their overall lapse rates. The data were obtained from a recent World Meteorological Organization Report[12] that utilized results from several sources to provide both *1981 values and projected growth rates.*

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12. The Stratosphere 1981, Theory and Measurements, World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 11, 1-1—1-19.

Table 5. Northern Hemisphere Tropospheric Mixing Ratios (All Expressed in PPTV)

YEAR	CF_2Cl_2	$CFCl_3$	CH_3Cl	CH_3CCl_3	CCl_4
1981	300	190	650	165-180	135
1982	330	207	650	178-193	135-142

7. CONCLUSIONS

The expansion of our gas chromatography capability has permitted determination in this manner of stratospheric abundances of five important chlorine species: fluorocarbons 11 and 12, methyl chloride, methyl chloroform, and carbon tetrachloride. Combining the results with coincident measurements of acidic and particulate chlorine content using available filter preparation, sampling, and analytical techniques has provided sufficient data for summations of total chlorine content in the lower stratosphere, as will be reported shortly. Also, it should be noted that the stratospheric mixing-ratio lapse-rate profiles obtained for the newly investigated species support the general view that these species are of tropospheric origin, and, on that premise, the values are consistent with the accepted values for their tropospheric abundances. In addition, a fairly wide range of GC operating conditions have been explored without indication of the presence of additional chlorine species of abundance significant enough to materially affect summations of total stratospheric chlorine content.

Lastly, the fluorocarbon results reported herein add to the data base which permits evaluation of possible annual increases in stratospheric fluorocarbon content. In an earlier report,[10] we stated that, within the accuracy of the measurements, no annual increases in stratospheric fluorocarbon content were evident. The new data strengthens this claim for fluorocarbon 11. For fluorocarbon 12, careful evaluation of all mid-latitude data from 1977 to 1982 suggests an average annual increase of 1—2 percent. Within the uncertainty of the measurements, such a claim cannot be conclusive; however, even if true, it would still be far below the approximately 10 percent-per-year increase noted for tropospheric values of both fluorocarbons 11 and 12. Thus, although tropospheric fluorocarbon abundances are increasing at a significant rate, the increases are not reflected in the stratospheric concentrations. Therefore, fears expressed by DOD[13] and others[14] that fluorocarbon usage was endangering the environment may have been excessive.

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[13] Aerosol Ban Would Harm Defense, Pentagon Claims, Federal Times, Sept. 1977

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

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