



Survey and analysis of halogenated compounds in the atmosphere by gas chromatography/high resolution mass spectrometry
by Mark A. Engen

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry
Montana State University
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Abstract:

The application of a dual-sector high resolution mass spectrometer (HRMS) to the detection of halogen-containing compounds in the Earth's atmosphere is demonstrated. By this technique, the contents of air samples collected in remote areas surrounding Bozeman, Montana, are introduced to the HRMS by a cryogenic concentration method followed by gas chromatography. The HRMS is tuned to the exact masses of the ions expected in the electron impact ionization mass spectrum of each compound. Due to the large ion optic system of the mass spectrometer used here, any level of mass resolution that is required for the complete separation of hydrocarbon-based from halocarbon-based ions of the same nominal mass can be achieved while maintaining a high level of ion throughput to the detector. By this technique, the analysis of compounds identified in background air while monitoring either of the ions, CF_3^+ or Br^+ will be discussed. Compounds identified while monitoring the Br^+ ion include CH_3Br , CH_2BrCl , CH_2Br_2 , CHBr_3 , CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, and CF_2BrCl . Those identified while monitoring the CF_3^+ ion are CF_4 , CF_3H , CF_3Cl , $\text{CF}_3\text{CF}_2\text{Cl}$, CF_3Br , and CF_3CFH_2 . Most of these compounds are present in background tropospheric air at the low to sub parts-per-trillion by volume (pptv) level. To our knowledge, this is the first time CF_3H and CF_2Br_2 have been detected in background tropospheric air.

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IN THE ATMOSPHERE BY
GAS CHROMATOGRAPHY / HIGH RESOLUTION MASS SPECTROMETRY

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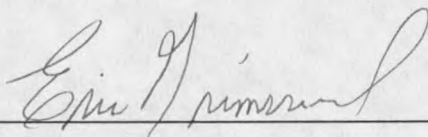
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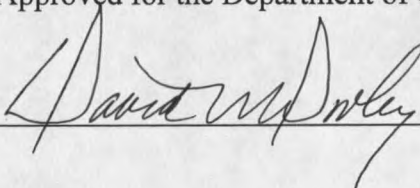
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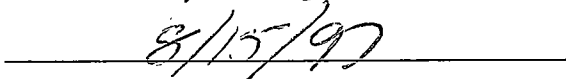


TABLE OF CONTENTS

	Page
INTRODUCTION	1
Atmospheric Chemistry	11
Troposphere	11
Stratosphere	15
The Antarctic Ozone Hole	22
Arctic Polar Vortex Chemistry	23
The Mesosphere	24
EXPERIMENTAL PROCEDURES	26
Sample Collection	26
Sample Concentration and Clean-up	27
Concentration Method 1	27
Concentration Method 2	29
Chromatography	31
Methods for GS-Q Capillary Column	31
Methods for DB-VRX Column	32
Detection	33
The Mass Spectrometer	33
Selected Ion Monitoring Procedure	35
Standards	40
Low Concentration Standards	42
High Concentration Standards	42

RESULTS AND DISCUSSION	44
Qualitative Determinations by GC-HRMS	44
Compounds indicated by monitoring the CF_3^+ ion	44
Compounds indicated by monitoring the Br^+ ion on the GS-Q Capillary Column	52
Compounds indicated by monitoring the Br^+ ion using the DB-VRX Capillary Column	65
Quantitative determinations by GC-HRMS	78
Quantitative Analysis of CF_3^+ and Br^+ Compounds with GS-Q Capillary Column	79
Quantitative Analysis of Br^+ Compounds with DB-VRX Capillary Column	83
Detection Limits	90
Analysis of Select Bromocarbons from December 1996 to April 1997	91
Conclusion	92
SUMMARY	94
REFERENCES	99
APPENDIX	108

LIST OF TABLES

Table		Page
1.	Perfluorinated and other long lived atmospheric species.	4
2.	Hydrofluorocarbons and hydrochlorofluorocarbons; the replacement refrigerants.	5
3.	Brominated and iodinated compounds.	6
4.	Exact masses of most abundant nuclides of carbon, hydrogen, fluorine, chlorine, bromine, oxygen, nitrogen, and sulfur.	9
5.	Atmospheric concentration of compounds analyzed with GS-Q column.	81
6.	Measurements of CF_2ClBr by NOAA/CMDL.	84
7.	Relative responses of select brominated compounds to CF_2ClBr	88
8.	Atmospheric concentration of brominated compounds analyzed with DB-VRX column.	88

LIST OF FIGURES

Figure		Page
1.	Physical description of the atmosphere.	12
2.	Schematic presenting the chemical interactions in the stratosphere.	18
3.	Schematic diagram of the sample introduction system.	30
4.	Electron impact mass spectrum of the mass calibration gas, n-dodecane.	37
5.	Mass spectrum of a mixture of n-C ₁₂ H ₂₆ and CF ₂ ClBr over the mass range, m/z = 80 to 88, with the resolution of the mass spectrometer set to R = 2,000.	41
6.	CF ₃ ⁺ single ion chromatograms using three different resolution settings. In each chromatogram the relative responses are normalized to the maximum response observed under each condition. The amount of air sampled is 340 atm-cm ³	54
7.	CHF ₃ ³⁷ Cl ⁺ single ion chromatograms using two different resolution settings. The expected GC retention time of CHF ₂ Cl is indicated in chromatogram A.	55
8.	Single ion chromatograms using two ions expected in the electron impact spectrum of CF ₄ . The expected retention time of CF ₄ is indicated in chromatogram A.	56
9.	Single ion chromatograms and expected retention time for CHF ₃	57

10. Single ion chromatograms and expected retention time for CF_3Cl . The isotopic pairs of ions in chromatograms B and C were simultaneously measured in a single analysis. The value of A_r in chromatogram C is the ratio of this peak area to that in chromatogram B. 58

11. Single ion chromatograms and expected retention time for $\text{CF}_3\text{CF}_2\text{Cl}$. Chromatograms B and C and chromatograms E and F (isotopic pairs) were simultaneously determined. A_r values are the ratios of the responses to the minor and major isotopic ions. 59

12. Single ion chromatograms and expected retention time for CF_3Br . The responses to the isotopic pairs of ions in chromatograms B and C, D and E, and F and G were simultaneously determined. A_r values are the ratios of the responses of the minor ^{81}Br -containing ion to that of the major ^{79}Br -containing ion. 60

13. Single ion chromatograms and expected retention time for $\text{CF}_3\text{CH}_2\text{F}$ 61

14. $^{81}\text{Br}^+$ single ion chromatograms using four different resolution settings. The amount of air sampled is 340 atm-cm^3 62

15. Single ion chromatograms and expected retention time for CH_3Br . The responses to the isotopic pairs of ions in chromatograms A and B and chromatograms C and D were simultaneously determined. A_r values are the response ratios of the ^{81}Br -containing and the ^{79}Br -containing ions. 63

16. Single ion chromatograms and expected retention time for CF_2BrCl . The responses to the isotopic sets of ions in chromatograms A and B, C and D, E and F, and G, H, and I were simultaneously determined. 64

17.	$^{81}\text{Br}^+$ single ion chromatograms using three different resolution settings. In each chromatogram the relative responses are normalized to the maximum response observed under each condition. The amount of air sampled is 340 atm-cm^3	69
18.	Single ion chromatogram monitoring $^{81}\text{Br}^+$ at resolution of 2000. Eight brominated compounds have been identified in rural Montana background air; CF_3Br , CF_2ClBr , CH_3Br , CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, CH_2ClBr , CH_2Br_2 , CHBr_3	70
19.	Single ion chromatograms identifying the compound CF_2ClBr , $R = 2000$, $\text{RT} = 4:00$	71
20.	Single ion chromatograms identifying CF_2Br_2 , $R = 2000$, $\text{RT} = 6:20$	72
21.	Single ion chromatograms identifying $\text{CF}_2\text{BrCF}_2\text{Br}$, $R = 2000$, $\text{RT} = 8:10$	73
22.	Single ion chromatograms identifying CH_3Br , $R = 2000$, $\text{RT} = 4:42$	74
23.	Single ion chromatogram identifying CH_2Br_2 , $R = 2000$, $\text{RT} = 13:50$	75
24.	Single ion chromatograms identifying CH_2ClBr , $R = 2000$, $\text{RT} = 11:00$	76
25.	Single ion chromatograms identifying CHBr_3 , $R = 2000$, $\text{RT} = 18:20$	77
26.	Tropospheric concentration of CF_2ClBr measured at Niwat Ridge, Boulder, CO by NOAA/CMDL from 1989 through 1995.	86

27.	(Top) Tropospheric concentrations of CF_2ClBr and CH_2Br for the sampling period, December 1996 through April 1997. (Bottom) Tropospheric concentrations of CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, CH_2Br_2 , and CHBr_3 for the sampling period of December 1996 through April 1997 in the area of Bozeman, MT.	93
28.	EI mass spectrum of CF_2HCl	109
29.	EI mass spectrum of CF_4	110
30.	EI mass spectrum of CF_3H	111
31.	EI mass spectrum of CF_3Cl	112
32.	EI mass spectrum of CF_3Br	113
33.	EI mass spectrum of $\text{CF}_3\text{CF}_2\text{Cl}$	114
34.	EI mass spectrum of CF_3CFH_2	115
35.	EI mass spectrum of CF_2ClBr	116
36.	EI mass spectrum of CF_2Br_2	117
37.	EI mass spectrum of $\text{CF}_2\text{BrCF}_2\text{Br}$	118
38.	EI mass spectrum of CH_3Br	119
39.	EI mass spectrum of CH_2ClBr	120
40.	EI mass spectrum of CH_2Br_2	121
41.	EI mass spectrum of CHBr_3	122

ABSTRACT

The application of a dual-sector high resolution mass spectrometer (HRMS) to the detection of halogen-containing compounds in the Earth's atmosphere is demonstrated. By this technique, the contents of air samples collected in remote areas surrounding Bozeman, Montana, are introduced to the HRMS by a cryogenic concentration method followed by gas chromatography. The HRMS is tuned to the exact masses of the ions expected in the electron impact ionization mass spectrum of each compound. Due to the large ion optic system of the mass spectrometer used here, any level of mass resolution that is required for the complete separation of hydrocarbon-based from halocarbon-based ions of the same nominal mass can be achieved while maintaining a high level of ion throughput to the detector. By this technique, the analysis of compounds identified in background air while monitoring either of the ions, CF_3^+ or Br^+ will be discussed. Compounds identified while monitoring the Br^+ ion include CH_3Br , CH_2BrCl , CH_2Br_2 , CHBr_3 , CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, and CF_2BrCl . Those identified while monitoring the CF_3^+ ion are CF_4 , CF_3H , CF_3Cl , $\text{CF}_3\text{CF}_2\text{Cl}$, CF_3Br , and CF_3CFH_2 . Most of these compounds are present in background tropospheric air at the low to sub parts-per-trillion by volume (pptv) level. To our knowledge, this is the first time CF_3H and CF_2Br_2 have been detected in background tropospheric air.

INTRODUCTION

During the last two decades, a great deal of attention has been focused on the environmental significance of a variety of halogenated compounds known to be present in the Earth's atmosphere. Since 1962, when Rachel Carson wrote her landmark book *Silent Spring* (1), public concern regarding the effects and fates of the many halogenated compounds in the environment has steadily increased. Carson's book brought to the forefront the detrimental effect DDT was having on the bird population. Shortly thereafter, DDT was found to be toxic to human populations, so it was removed from use in this country. During the 1960's and 1970's a growing concern with pollution of our environment developed.

In 1971, James Lovelock, developer of the electron capture detector, detected chlorinated compounds in all background air samples he analyzed. One of the compounds he identified was CFCl_3 (CFC-11), a man-made compound used as a refrigerant. In 1975, Grimsrud and Rasmussen detected and

measured CF_2Cl_2 (CFC-12) and CH_3Cl in background air (2,3). These were the first mass spectrometry based analyses of halocarbons in background air, and the first time methyl chloride had been detected in background air.

Sherwood Rowland and Mario Molina in 1974, suggested that chlorofluorocarbons may cause destruction of stratospheric ozone. With increasing concern and public awareness of the possible effects CFC's might be having on the ozone layer, aerosol canisters which used CFC's as propellants were removed from the market in 1978. Researchers first discovered the Antarctic Ozone Hole in 1985 (4). This discovery accelerated policy changes which would lead to a reduction in anthropogenic chlorine (CFC's) and bromine (Halons) to the atmosphere. In 1987, many countries in the world convened and drafted a proposal to eliminate CFC's and Halons, which has become known as the Montreal Protocol. The Montreal Protocol has since been amended twice, in 1990 and 1992, in order to speed the reduction of halogenated species in the atmosphere. With the 1992 amendments it is estimated that chlorine and bromine levels will decrease to levels such that the

Antarctic Ozone Hole will no longer be present around the year 2050. In 1995, P. Crutzen, M. Molina, and S. Rowland were awarded the Nobel Prize in Chemistry for their early work in stratospheric chemistry linking CFC's to the destruction of stratospheric ozone, further reinforcing the importance of studying the effects of anthropogenic chemicals in our natural environment.

Halogenated compounds containing chlorine, bromine, or iodine atoms have been extensively investigated with respect to their potential for destroying ozone in the stratosphere (5 - 11), see Tables 1, 2, and 3. Also, halogenated compounds, including those containing only fluorine atoms, have been studied with respect to their effects on radiative cooling of the Earth's surface (12 - 15). In the course of these investigations, the presence of numerous halogenated compounds in background air samples have been reported, some of which are thought to have natural as well as anthropogenic sources. With increased use of partially halogenated hydrocarbons as replacements for the fully halogenated species, whose use has been discontinued, the chemical means by which halogen atoms are transported

throughout the atmosphere promises to become increasingly complex in the next several decades.

Table 1. Perfluorinated and other long lived atmospheric species.

<u>Compound</u>	<u>Common</u>	<u>Tropospheric</u>	<u>Atmospheric</u>	<u>Ozone</u>
	<u>Name</u>	<u>Concentration</u>	<u>Lifetime</u>	<u>Depleting</u>
		<u>(pptv)</u>	<u>(years)</u>	<u>Potential</u>
CF_2Cl_2	CFC-12		120	0.9
CFCl_3	CFC-11		60	1
C_4F_{10}			2600 (15)	0
CF_4	CFC-14	80 (16)	>50,000 (15)	0
C_2F_6	CFC-116	3 (16)	>10,000 (15)	0
$\text{C-C}_4\text{F}_8$			3200 (15)	0
$(\text{CF}_3)_2\text{C-C}_4\text{F}_6$			2900 (15)	0
C_5F_{12}			4100 (15)	0
C_6F_{14}			3100 (15)	0
$\text{C}_2\text{F}_5\text{Cl}$	CFC-115	4 (17)	1700 (15)	0.4
$\text{C}_2\text{F}_4\text{Cl}_2$	CFC-114	5 (17)	300 (15)	0.7
CF_3Cl	CFC-13	10 (16)	640 (15)	
SF_6		0.8 (35)	3200 (15)	0

In studying the atmospheric chemistry of individual halogenated compounds, a challenging aspect has been and will continue to be the means by which these compounds are detected and quantified in real air samples. The most widely-used methods (19) are currently based on the

separation of compounds of interest by gas chromatography with detection either by electron capture detector (ECD) (22-27) or by mass spectrometer (MS) (28,24,2,3).

Table 2. Hydrofluorocarbons and hydrochlorofluorocarbons; the replacement refrigerants.

<u>Compound</u>	<u>Common</u>	<u>Tropospheric</u>	<u>Atmospheric</u>	<u>Ozone</u>
	<u>Name</u>	<u>Concentration</u>	<u>Lifetime</u>	<u>Depleting</u>
		<u>(pptv)</u>	<u>(years)</u>	<u>Potential</u>
CHFC_2Cl_2	HCFC-21	0.1-2.5 (20)	2-3 (6)	
CHF_2Cl	HCFC-22	80 (17)	15 (21)	0.053 (21)
$\text{CH}_3\text{CF}_2\text{Cl}$	HCFC-142b		21 (21)	0.059 (21)
CH_3CFCl_2	HCFC-141b		8 (21)	0.081 (21)
CF_3CHCl_2	HCFC-123		2 (21)	0.016 (21)
CF_3CHClF	HCFC-124		8 (21)	0.019 (21)
CF_3CHF_2	HFC-125		35 (21)	0 (21)
$\text{CF}_3\text{CH}_2\text{F}$	HFC-134a		21 (21)	0 (21)
CF_3CH_3	HFC-143a		50 (21)	0 (21)
CHF_2CH_3	HFC-152a		2 (21)	0 (21)
CF_3H	HFC-23			0
$\text{C}_3\text{HCl}_2\text{F}_2$	HCFC-225ca			
$\text{C}_3\text{HCl}_2\text{F}_2$	HCFC-225cb			
$\text{C}_2\text{HF}_3\text{BrCl}$	HCFC-123B1			

The GC-MS approach is almost equally applicable to all halogenated compounds because the electron impact (EI)

ionization process, on which it is based, provides almost uniform ionization efficiency for all compounds.

Table 3. Brominated and iodinated compounds.

<u>Compound</u>	<u>Common</u>	<u>Tropospheric</u>	<u>Atmospheric</u>	<u>Ozone</u>
	<u>Name</u>	<u>Concentration</u>	<u>Lifetime</u>	<u>Depleting</u>
		<u>(pptv)</u>	<u>(years)</u>	<u>Potential</u>
CH ₃ Br		11 (29)	1.7 (6)	0.1-0.6 (6)
CH ₂ BrCH ₂ Br		1-37 (29)		
CHBr ₃		2-46 (29)		
CH ₂ Br ₂		3-60 (29)		
CF ₃ Br	H-1301	2 (30)	72-107 (6)	8-16 (6)
CF ₂ Br ₂	H-1202		1.5 (6)	0.3 (6)
CF ₂ ClBr	H-1211	2 (30)	12-18 (6)	2.2-3.5 (6)
CF ₂ BrCF ₂ Br	H-2402	0.5-1.0 (30)	23-28 (6)	5-6 (6)
CHF ₂ Br	H-1201		7 (6)	0.4-1.8 (6)
CH ₂ BrCl		2.5 (31)		
CH ₃ I		1.04 (32)	4 days (32)	
CH ₂ ClI				
CH ₂ I ₂		0.46 (32)		
C ₂ H ₅ I		2 (32)		
CF ₃ I				
CH ₂ BrI				

However, for those compounds that have large rate constants for thermal electron attachment, the ECD generally provides better sensitivity than the MS. For this reason, the ECD has been the method of choice for the quantitative analysis

of atmospheric halocarbons, such as CF_3Br (19), that have very low atmospheric concentrations and very large electron attachment rate constants.

In the present study, we report the use of a GC-high resolution mass spectrometer (HRMS) for the identification and quantitative analysis of atmospheric halocarbons. High resolution should provide considerable assistance in the analysis of halogenated compounds, primarily because of the exact masses of the nuclides of carbon, hydrogen, and the halogens listed in Table 4. Inspection of this table indicates that ions that originate from molecules containing only hydrogen and carbon will have exact masses that are somewhat greater than their nominal (nearest integer) mass values. Those ions containing only carbon and halogen atoms will have exact masses that are somewhat less than their nominal mass values. Ions that contain either chlorine or bromine atoms will tend to have particularly large mass deficiencies. In Table 4, it is noted that hydrocarbon derivatives containing nitrogen atoms will also have exact masses greater than the nominal value. The nuclides of oxygen and sulfur have relatively large negative mass

deficiencies and could interfere with the analysis of halogenated compounds. The atmospheric compounds that contain these elements are generally much more polar than halogenated compounds, and therefore are easily separated from the halogenated compounds by the gas chromatographic column.

With a mass spectrometer capable of moderate to high resolution, the mass differences shown in Table 4 are sufficient to allow complete separation of hydrocarbon-based and halocarbon-based ions of the same nominal mass, thereby eliminating hydrocarbon-based interference and noise. With the use of low resolution mass spectrometers, the exact mass differences shown in Table 4 are not sufficient to separate hydrocarbon-based and halocarbon-based ions of the same nominal masses. As a result, the multitude of hydrocarbons present in an air sample, in the GC flow gases, and in the residual vapors of a mass spectrometer itself, typically provide the major source of chemical interference and noise in the atmospheric analyses of halogenated compounds by GC-MS.

Table 4. Exact Masses of Most Abundant Nuclides of Carbon, Hydrogen, Fluorine, Chlorine, Bromine, Oxygen, Nitrogen, and Sulfur.

<u>Nuclide</u>	<u>Exact Mass^a</u>	<u>Δm^b</u>
¹² C	12.0000	0
¹³ C	13	+0.00335
¹ H	1.01	+0.00783
¹⁹ F	19	0
³⁵ Cl	34.97	-0.03
³⁷ Cl	36.97	-0.03
⁷⁹ Br	78.92	-0.08
⁸¹ Br	80.91	-0.08
¹⁴ N	14	0
¹⁶ O	15.99	-0.01
³² S	31.97	-0.03

^a Taken from the Handbook of Chemistry and Physics, 69th Edition, CRC Press, Boca Raton, FL, 1989.

^b Mass excess or deficiency relative to the nominal mass value.

If the high resolution mass spectrometer also has a large ion optic system, it can achieve these required levels of resolution while maintaining high ion throughput to the detector. In this way, the principal limitation of the conventional GC-MS technique described above should be overcome with GC-HRMS, leading directly to superior detection and identification capabilities for all

atmospheric halocarbons. The realization of these expectations is demonstrated here using a HRMS-based atmospheric analysis system recently assembled in our laboratory.

In this initial use of our HRMS-based analysis system, we have somewhat arbitrarily chosen to focus on two groups of low-level atmospheric halocarbons that are detected when either of the ions, CF_3^+ or Br^+ , is monitored while an air sample is introduced by high resolution gas chromatography.

Following the detection of a compound by the above procedure; additional GC-HRMS analyses are conducted using most of the other major ions expected in the electron impact ionization spectrum of the suspected compound. Definitive proof for the presence of each compound is thereby obtained.

Two of the compounds identified in the present study, CF_3H and CF_2Br_2 have not been previously detected in background air. A possible source of CF_3H is suggested from the analyses of air samples obtained from a fume hood of an aluminum smelter. A source for the compound CF_2Br_2 has not been determined, but the compound is almost certainly of anthropogenic origin. Before describing experimental

procedure, a brief discussion of fundamental atmospheric chemistry, pertinent to the compounds in this study, is presented.

Atmospheric Chemistry

During the process of developing an instrument, developing methods, and detecting and measuring some of the trace components of the atmosphere, I have become increasingly interested in the complex chemical processes that take place in the Earth's atmosphere. I would like to present some basic atmospheric chemistry as it applies to the halogenated compounds in this study, starting with reactions involving hydroxyl radical in the troposphere.

Troposphere

The troposphere is the layer of the atmosphere that is nearest to the Earth and extends up to around eleven kilometers (Figure 1).

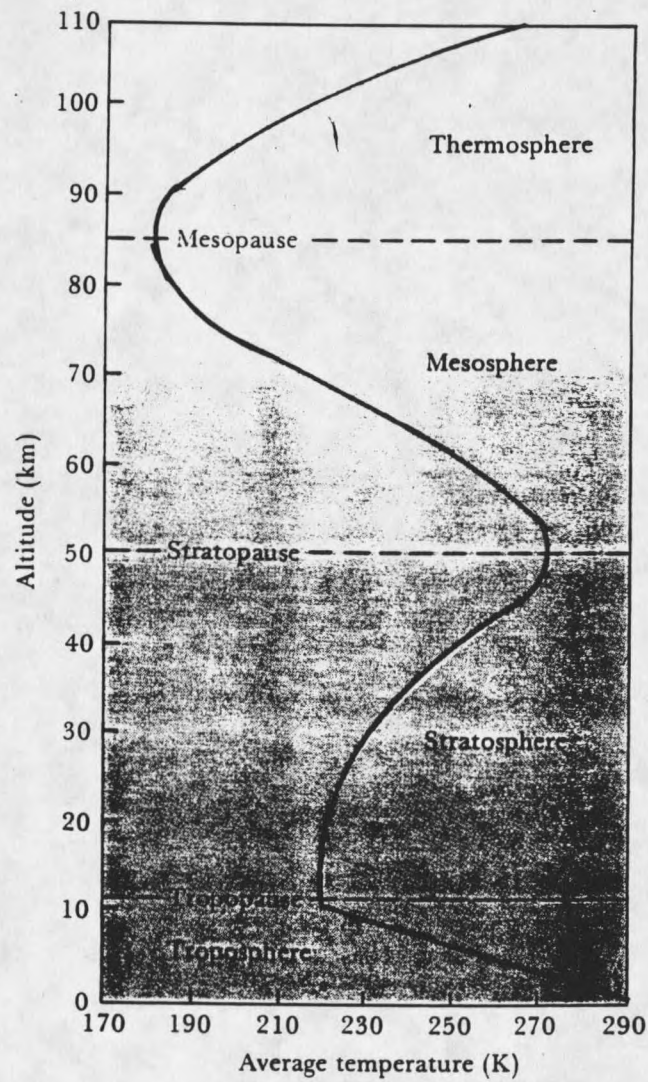
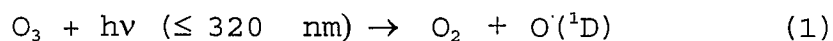
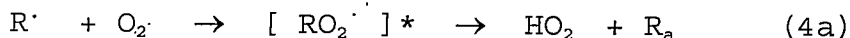
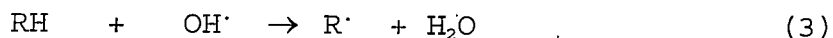


Figure 1. Physical description of the atmosphere.

This region experiences significant mixing, both horizontally and vertically, as is apparent from the variety of weather produced in the troposphere. A chemical species released at ground level can be transported to the upper troposphere in a matter of hours, and if the compound has a significantly long atmospheric lifetime, it will become evenly distributed throughout the troposphere (at least hemispherically) in a relatively short period of time (32). The tropospheric chemistry most pertinent to this work is associated with reactions involving the hydroxyl radical. In the troposphere the first step in the production of hydroxyl radical is the photolysis of ozone to oxygen, shown in Equation 1. The atomic oxygen then reacts with water molecules to produce hydroxyl radicals (Equation 2) (2,33).



For compounds containing a carbon hydrogen-bond reaction with hydroxyl radical predominantly determines the lifetime of these species in the atmosphere. As can be seen in Equation 3, hydrogenated compounds react with the hydroxyl radical to form water and a reactive radical ($\text{R}^\bullet$) (33).



The reactive radical will then react with oxygen to form an oxygenated radical intermediate in the excited state $[\text{RO}_2\cdot]^*$. The excited state intermediate can be collisionally stabilized (Eq. 4b), then the oxygenated radical product ($\text{RO}_2\cdot$) can then proceed through a variety of reaction pathways. Otherwise, the reactive intermediate will dissociate to HO_2 and a neutral compound (Eq. 4a). In general, hydrogenated compounds will react with hydroxyl radical to form water soluble oxygenated compounds.

Because of the reactions initiated by hydroxyl radical (Equations 3 and 4), the compounds used as replacements for CFC's contain at least one hydrogen atom per molecule. Hydrogenation decreases the compound's atmospheric lifetime by allowing for a removal mechanism in the troposphere; therefore, a lower percentage of the replacement compounds are expected to reach the stratosphere. For example, the atmospheric lifetime of CF_3Cl (CFC-13) is 640 years,

compared to that of CHF_2Cl (HCFC-22) at 15 years (see Tables 1 and 2).

Stratosphere

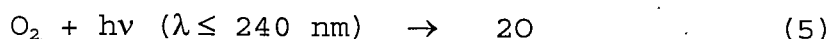
The stratosphere extends from the tropopause at about eleven kilometers to the stratopause at about 50 km. Mixing in the stratosphere takes place horizontally with chemical species diffusing up through the stratosphere very slowly. It can take 50 to 60 years for a compound to reach the upper stratosphere.

The concern regarding ozone in the Earth's stratosphere stems from the ability of ozone to protect the Earth's surface from harmful ultraviolet radiation. Only ozone strongly absorbs in the UV-B region of the spectrum (280 - 320 nm), radiation which is particularly damaging to DNA in living systems.

The amount of ozone in the stratosphere is far from constant; it varies monthly, yearly, and from place to place. This natural variation can be as large as 25% at high latitudes. Factoring in seasonal variations, the eleven-year solar cycle, and other complicating variables,

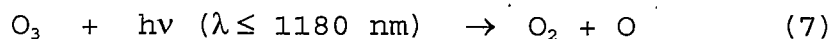
atmospheric scientists use statistical methods to reveal the long-term global thinning of ozone believed to be caused by halogen-catalyzed reactions with ozone.

Ozone is produced in the upper stratosphere where ultra violet radiation dissociates molecular oxygen to atomic oxygen (Eq. 5). The atomic oxygen then reacts with molecular oxygen to form ozone, as shown in Equation 6 (4,8,14).



These reactions occur rapidly in the stratosphere over the tropics where solar radiation is most intense. Because the circulation of the upper atmosphere constantly moves away from the equator towards the poles, ozone concentrations are generally greater at the higher latitudes.

Ozone is destroyed when it absorbs radiation that would otherwise reach the Earth's surface (Eq. 7).



There is no net reduction in ozone because atomic oxygen is formed (Eq. 6). The atomic oxygen can then react

with molecular oxygen to reform ozone. Also, ozone is continually destroyed through reactions with families of naturally occurring radicals that contain chlorine, bromine, nitrogen, hydrogen, or oxygen atoms, see Figure 2 (4,10).

The above mentioned production and destruction mechanisms lead to a relatively steady-state concentration of ozone in the stratosphere, that is until the last several decades. With the widespread use of chlorofluorocarbons (CFC's) as refrigerants and Halons (fluorocarbons that contain bromine) in fire extinguishers, significant amounts of chlorine and bromine have been introduced into the atmosphere by the escape or discharge of these chemicals into the environment. Because CFC's do not react with hydroxyl radical they are inert to the oxidative processes of the troposphere. As a result, they are efficiently transported to the stratosphere and are primarily responsible for the increase of chlorine in the stratosphere from about 0.8 ppbv fifty years ago to around 4.0 ppbv in 1990 (8). Current levels of bromine in the stratosphere due both to natural and anthropogenic sources are between 10 and 20 pptv (5) or about 0.5% as abundant as chlorine.

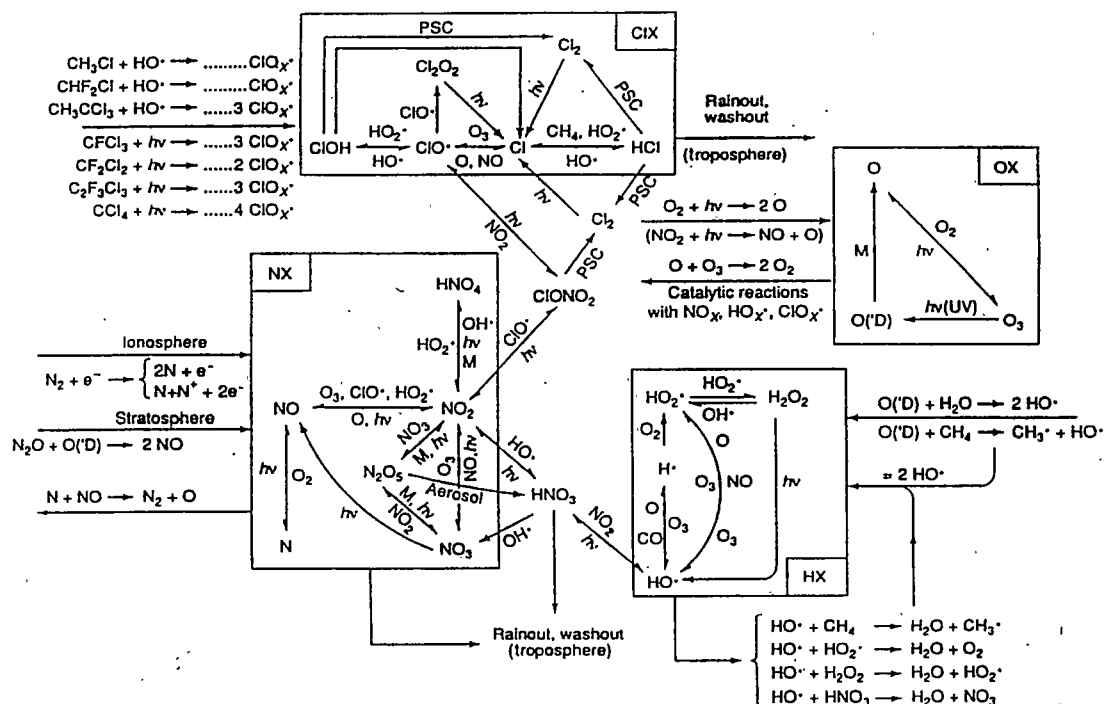
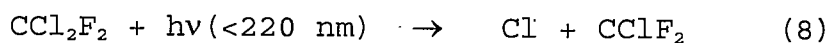


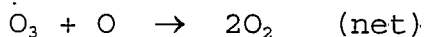
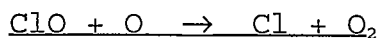
Figure 2. Schematic presenting the chemical interactions in the stratosphere.

Even though bromine concentration is significantly less than that of chlorine, bromine's synergistic effect with chlorinated compounds (Eq. 14) in the catalytic destruction of ozone accounts for approximately 25% of ozone destruction due to halogenated compounds. Bromine was implicated to account for as much as 35% of the chemical loss of ozone in the arctic polar vortex in the winter of 1991-1992 (34). What are the mechanisms by which chlorine and bromine destroy ozone?

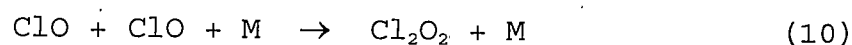
Once CFC's and Halons rise above the bulk of the ozone layer, which lies between 15 and 30 km altitude depending on latitude, they are photolyzed by ultraviolet light producing halogen atoms. For Example (8):



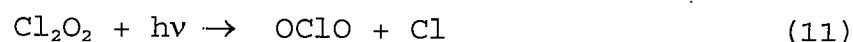
The atomic chlorine, bromine, or iodine can then participate in catalytic cycles which destroy ozone. For example, chlorine atoms will react with ozone as follows:



Also, the ClO radical can react with another ClO radical (Eq. 10),

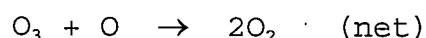
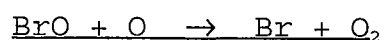


to produce Cl_2O_2 , which if radiated by UV light (Eq. 11)



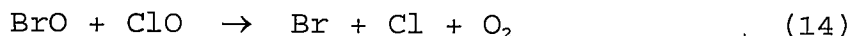
regenerates chlorine atoms (Eq. 12). A more comprehensive explanation of chlorine's role in the stratosphere can be seen in the schematic shown in Figure 2.

Similar to Equation 9, atomic bromine has the net effect of reducing ozone to molecular oxygen:



There are two primary reactions that make bromine a better catalyst at destroying ozone than chlorine.

First, the fast synergistic reaction between the much more abundant ClO radical and the BrO radical (Eq. 14) producing atomic chlorine and bromine.



The atomic halogens then continue the catalytic destruction of ozone (Equations 9 and 13). Secondly, the sink (a stable nonreactive species in the stratosphere that will eventually diffuse back into the troposphere where it is removed from the atmosphere via various pathways) for bromine is not nearly as stable as its chlorine counterpart. The stratospheric sink for chlorine involves ClO radical reacting with NO₂ to form the stable product ClONO₂ (Eq. 15).

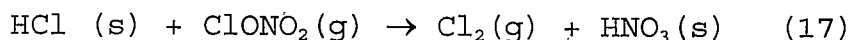


Chloronitrate is stable in the stratosphere except in special cases where heterogeneous chemical reactions occur (35). The reaction between BrO and NO₂ produces bromonitrate (Eq. 16), but BrONO₂ is not nearly as stable as chloronitrate and the equilibrium lies to the left (Eq. 16) with the reactive species BrO being an abundant species of bromine in the stratosphere (36,37).



The Antarctic Ozone Hole

The Antarctic ozone hole is due to a special case in stratospheric chemistry where the generally nonreactive forms of chlorine (ClONO_2 and HCl) are converted to reactive species by heterogeneous chemical reactions. During the polar winters, an isolated air mass is formed (polar vortex), and within the polar vortex polar, stratospheric clouds (PSC's) will form during the cold, dark, polar winters. PSC's form in the lower stratosphere when temperatures drop below -77°C and sufficient amounts of HNO_3 and water condense on sulfate particles (4). Hydrochloric acid will freeze on the surface of these particles and then will react with gaseous chloronitrate in a surface-assisted reaction producing solid nitric acid and chlorine gas molecules (Equation 17) (5,38).



When the sun returns in the spring and the polar vortex is still in place, the molecular chlorine is photolyzed to atomic chlorine.



The atomic chlorine can then react with ozone in catalytic cycles (Eq. 9-12,14). With little NO_2 present, the terminating step to the catalytic cycle (Eq. 15) is ineffective. In this case, heterogeneous chemistry causes a denitrification process which releases chlorine from its normally stable reserve to reactive chlorine (Eq. 17). This process causes an unrestrained destruction of ozone that can go on for several weeks, until the air masses are warmed sufficiently to break up the polar vortex. Calculations of global ozone thinning contribute about 3% of the 6% to 8% per decade loss of ozone to this heterogeneous chemistry (14).

Arctic Polar Vortex Chemistry During the arctic winters when the polar vortex is in place, the same chemical species are formed and in approximately the same concentrations as in the Antarctic. Why is it then that the ozone hole only forms at the south pole? It is primarily due to the fact that arctic winters are slightly warmer than those at the south pole, allowing warm spring air masses to push into the north polar region and break up the arctic

polar vortex before the sun returns in spring. Therefore, it is probable that in the next several decades, while the levels of chlorinated species are still elevated, we will experience a colder and longer winter than average. In this event, if the arctic polar vortex were to remain in place for several weeks after the polar sun rise we would probably experience an arctic ozone hole due to the same catalytic cycles as in the south pole.

The Mesosphere

As can be seen in Figure 1, the mesosphere extends from the stratopause at about 50 km to the mesopause at around 85 km. The mesospheric chemistry of interest to the present study is associated with the extremely stable perfluorinated compounds (PFC's). PFC's are not effected by either, the oxidative properties of the troposphere or the photolytic properties of the stratosphere. Ravishankara et al. (15) has suggested that the major means of destruction for PFC's will result from the absorption of Lyman- α radiation ($\lambda = 121.6$ nm), in the mesosphere. As a result of the inertness of PFC's, they have extremely long lifetimes ($>10,000$ years,

see Table 1) allowing these green house gases (15,39) to accumulate for millennia.

It can be speculated that some of the new CFC replacement compounds, such as CF_3CFH_2 (HFC-134a), will find their way to the mesosphere. Even though HFC's will be quite reactive to the oxidative properties of the troposphere (Eq. 3), a percentage will reach the stratosphere. Once in the stratosphere, it is likely that the hydrofluoro compounds will not be very photolytically active, and in the absence of hydroxyl radical may find their fate in the mesosphere.

EXPERIMENTAL PROCEDURES

Sample Collection

Air samples were collected in a variety of rural and mountainous areas within a 10-mile radius of Bozeman, Montana. It has been assumed here that the samples collected in these local areas are representative of background tropospheric air of this region of North America. Sample containers are commercially-purchased stainless-steel vessels whose interior surfaces have been electropolished. The air to be sampled was first forced through these containers for at least 30 minutes at a rate of about 5 liters per minute by a DC-powered diaphragm pump (KNF Neuberger, model N05SVI). The containers were then filled to above-ambient pressure levels prior to transport to the Mass Spectrometry Facility at Montana State University.

Sample Concentration and Clean-up

Two methods were used to concentrate the analytes of interest from whole air samples. Method 1 was developed to trap the very volatile highly fluorinated compounds (boiling points between -165 and -25 °C). Method 2 was necessary to assure quantitative desorption of less volatile compounds from the trap.

Concentration Method 1

Air samples were introduced into the GC-HRMS by the sampling system represented in Figure 3. Sample sizes of up to 1000 atm-cm^3 of whole air can be concentrated with the typical sample size being 340 atm-cm^3 . After the connection of a flask containing an air sample, the transfer line and the approximately 13 liter expansion volume (EV) were evacuated with a rotary pump. A metering valve (MV) and a six-port valve (6PV) then allowed the air sample to pass through a freeze-out loop (FOL), which was submerged in liquid nitrogen, and into the evacuated volume. The

freeze-out loop consisted of a fused-silica capillary column, (J&W GS-Q 0.53-mm ID) of approximately twenty centimeters in length. The transfer lines to and from the freeze-out loop were made from uncoated, deactivated, 0.53-mm ID fused-silica capillary column. The rate of air sample flow through the freeze-out loop was regulated (approximately $50 \text{ cm}^3 \text{ min}^{-1}$) for all samples by opening the metering valve until the pressure read at the pressure gauge (PG) reached some preselected value. The water content of the air was removed prior to the freeze out loop by passing the air through a drying tube (DT). The drying tube was constructed of 0.25-in OD stainless steel tubing, approximately four centimeters in length, packed with coarsely ground $\text{Mg}(\text{ClO}_4)_2$. A particle filter (PF) was placed in line after the drying tube to remove particles greater than ten micrometers. The amount of air taken from the sampling flask was deduced by the change in pressure read on the Baratron pressure gauge (BPG) and the known internal volume of the concentration system. The internal volume, of the expansion volume and all transfer lines between valve A and the Baratron pressure gauge, is 13.3

liters, see Figure 3. Once the desired amount of sample had passed through the freeze-out loop valve A was closed, then valve C was closed. Next, valve D was opened and the freeze-out loop is pumped down to a pressure of 0.05 mbar. This process helps to remove most of the excess nitrogen and oxygen from the freeze-out loop. Finally, the 6-port valve was rotated and the freeze-out loop was heated by a heat gun set at 400 degrees Fahrenheit. The analytes were desorbed onto the analytical column and the temperature program for the GC was started.

Concentration Method 2

Concentration method 2 follows the same procedures as method 1. The only difference being the freeze-out loop, which was constructed of 1/8-in OD stainless steel tubing packed with silanized glass beads of 60/80 mesh. After desorption from the FOL, the analytes were refocused on the head of the capillary column by cooling a short piece of the analytical column to liquid nitrogen temperatures. The cryogenically focused analytes were then flash heated with warm air and the temperature program for the GC was started.

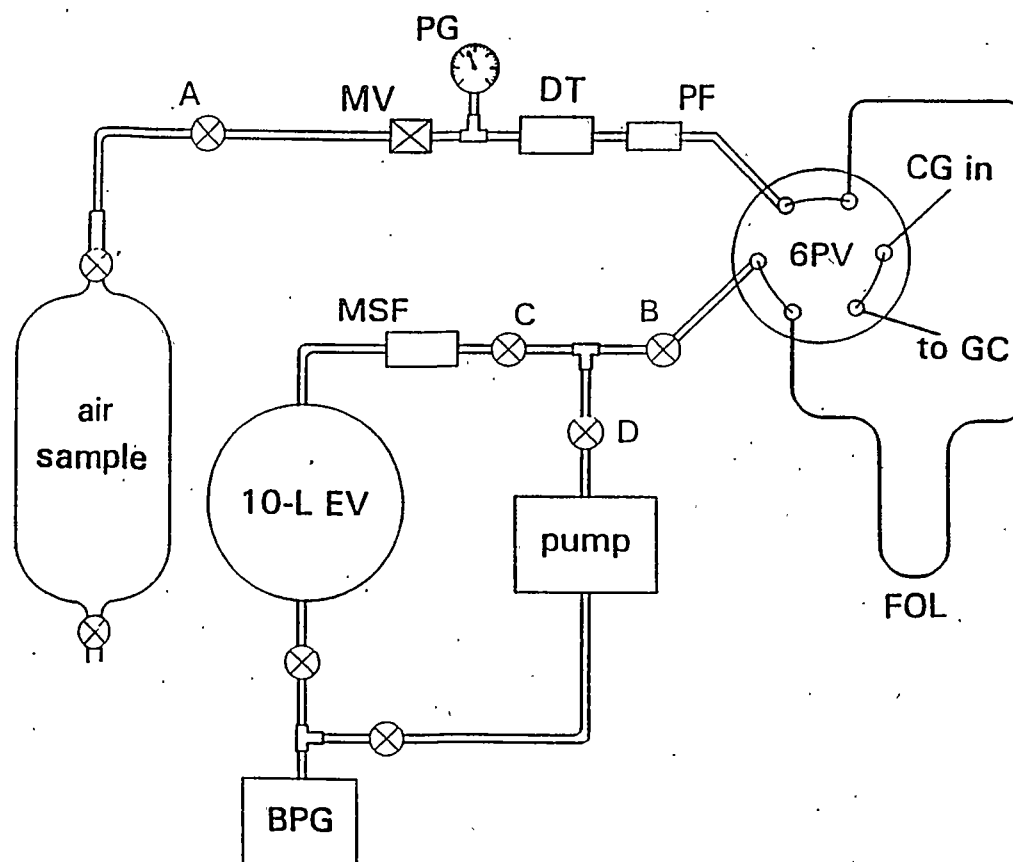


Figure 3. Schematic diagram of the sample introduction system.

Chromatography

Two primary chromatographic methods were used in order to achieve optimum chromatographic resolution and separation. Chromatography of the highly fluorinated compounds proved especially challenging.

Methods for GS-Q Capillary Column

A J&W GS-Q gas-solid, porous layer open tubular (PLOT) column of 30 meters length and 0.32 mm ID was used for separation of the perfluorinated and highly fluorinated compounds; all compounds which contained the CF_3^+ fragment ion. This column was designed specifically for very volatile compounds. The chromatographic resolution of this column was quite poor, but it was the only capillary column tried in which separation of the most volatile compounds was achieved. Two temperature programs were followed.

Temperature program 1 was used for CF_3Cl , CF_3Br , $\text{C}_2\text{F}_5\text{Cl}$, and CF_3CFH_2 . The initial GC temperature was held at 30°C for 2 minutes, then the oven was ramped up at 25°C per minute to 220°C and held for 12 minutes. Temperature program 2, used

for CF_4 and CF_3H , was the same except for an initial temperature of -10°C .

The flow rate of helium through the GC column was set so that an unretained compound (such as nitrogen) had an initial linear velocity of 25 cm sec^{-1} through the column with a constant head pressure of 60 kPa.

Methods for DB-VRX Column

The DB-VRX column was used for the analysis of all of the brominated compounds except CF_3Br (CF_3Br was analyzed on the GS-Q). The GC contained a J&W DB-VRX column 60 meters in length by 0.25 mm ID with a film thickness of 1.4 microns. A combination of temperature and pressure programs were used to obtain optimum separation and resolution. The oven was initially held at 30 degrees Celsius for 5 minutes followed by a temperature ramp of 15 degrees-per-minute to 220°C . The temperature was maintained at 220°C for the remainder of the 25 minute run time. A pressure program was used to reduce the time necessary for moving the analytes from the FOL to the point of cryofocusing. The initial head pressure was set at 200 kPa and held for 0.5 minutes, then

the pressure was ramped downward at 10 kPa per minute to 100 kPa and maintained for the remainder of the run. The exit end of the capillary GC column was threaded directly into the ion source of the mass spectrometer.

Detection

The Mass Spectrometer

The instrument used for this work was a VG ZAB-2F (VG Instruments) high resolution mass spectrometer. Originally purchased by Battelle Northwest Research Laboratories in 1978, this instrument was granted to MSU in 1992. At MSU, the instrument was thoroughly refurbished and numerous component parts were either replaced or upgraded. A new HRMS data system (Fisons, model VG OPUS) and a new gas chromatograph (Hewlett-Packard, model 5890 Series II Plus, with liquid N₂ oven cooling) were added. The ZAB-2F mass spectrometer is a dual (magnetic/ electric) sector instrument with maximum ion acceleration voltage of +8.0 kV. The relatively large ion optic system of the ZAB-2F provides continuously variable levels of mass resolution up to

100,000 and an unusually high efficiency for ion transmission to the detector at any selected resolution. Its present detector is an electron multiplier of the discreet dynode type (ETP Scientific, Inc. , model AF130) which is mounted 90° off the axis of the ion beam. A stainless-steel conversion dynode (where positive ions are converted to electrons) is also located at 90° off axis and is negatively biased up to -5.0 kV. The mass resolution of the instrument is conveniently selected by externally-controlled variations of the source and detector slits. Any level of resolution ($M/\Delta m$, where M is the mass of an ion and Δm is the peak width at half height) from a minimum value of about 1000 up to about 100,000 can be selected. Since the efficiency of ion throughput to the detector is increased with use of wider slits, maximum slit widths, providing the minimum level of required resolution, are typically used. Since being refurbished, this mass spectrometer has been used only for the analysis of relatively clean air and gas samples.

Selected Ion Monitoring Procedure

In order to monitor the intensity of an ion of interest while maintaining moderate or high resolution conditions, it is necessary to continuously calibrate the controlling fields of the mass spectrometer to insure that it focuses precisely at the exact mass of interest when instructed to do so by the data system. For this purpose n-dodecane is continuously introduced to the ion source via the heated gas expansion volume. As shown in Figure 4, the electron impact spectrum of n-dodecane consists of numerous fragment ions and a molecular ion of nominal $m/z = 170$. The identities and exact masses of all of the major ions are known (for example, the exact mass of the molecular ion is 170.20358). In preparation for a specific analysis, a mass calibration file is first made by performing a voltage scan in which the accelerating voltage (initially set at 8.0 kV) and electric sector field are scanned downward in unison while the magnetic sector field is held constant. This scan must be performed over a narrow mass range that begins and ends with any two of the reference ions in the spectrum of n-dodecane (Figure 4). The mass range must be narrow so

that the accelerating voltage does not decrease to a value of less than 5 kV, where an unacceptable loss of sensitivity would occur.

Using this calibration file, the data system then instructs the mass spectrometer to jump between any one selected ion of n-dodecane and any other exact mass or set of exact masses within the calibrated range. A duty cycle of 0.5 seconds was typically used here during which the mass spectrometer spent 0.10 second on the selected reference ion and divided the remaining 0.40 seconds among the set of ions selected for observation. The settling time between voltage jumps is very fast (about 10 ms) and this accounts for our strong preference for electric field rather than magnetic field control of the instrument.

An inherent limitation of the electric field control method for the analysis of GC effluents, that must be acknowledged, is in interpreting the signals obtained. Under this mode of operation the relative intensities of the different ions observed for a given compound are not expected to be the same as those appearing in a reference mass spectrum for that compound.

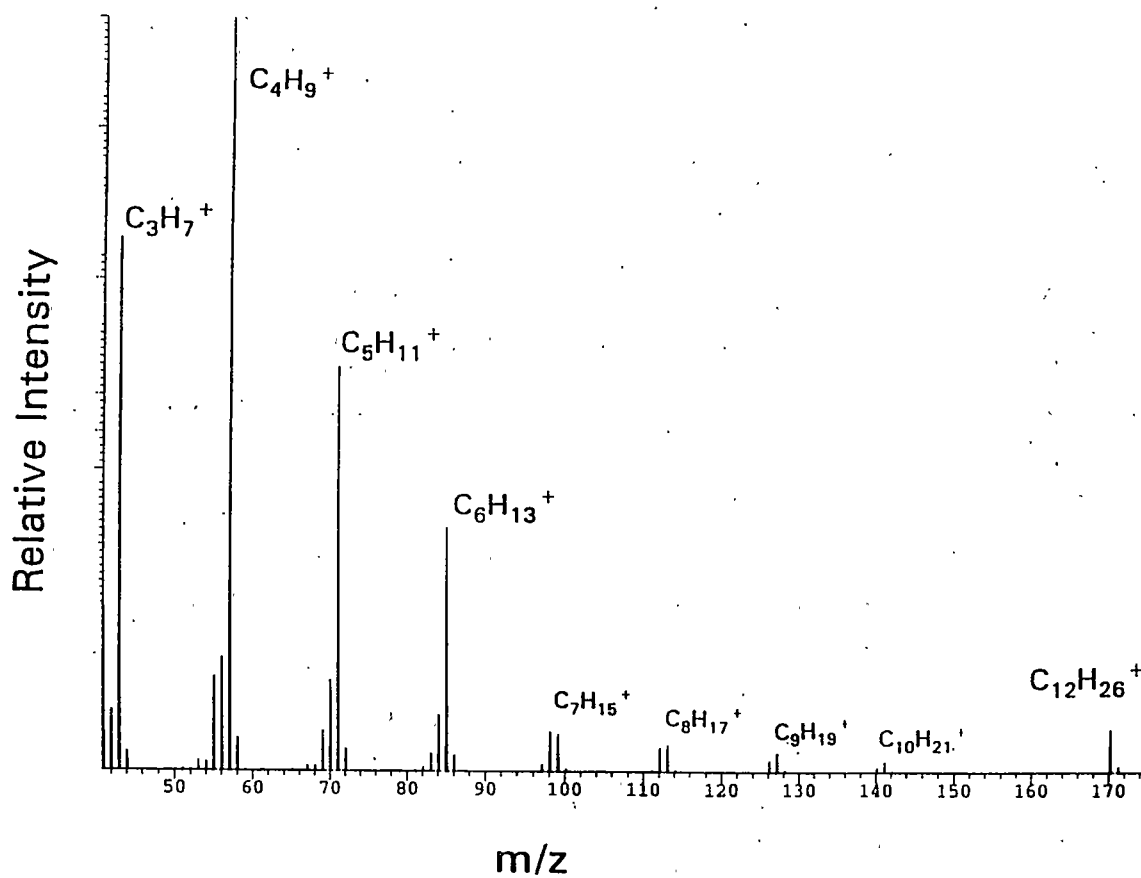


Figure 4. Electron impact mass spectrum of the mass calibration gas, n-dodecane.

This is because reference mass spectra are obtained by scanning the magnetic field while the electric fields are held constant. For example, when the individual ions within the $^{35}\text{Cl}/^{37}\text{Cl}$ and $^{79}\text{Br}/^{81}\text{Br}$ isotopic cluster groups are monitored by sequential, multiple jumps of the electric field, the measured relative intensities for the heavier isotopic ions will tend to be slightly less than expected from the known isotopic abundances. This is because a slightly lower accelerating voltage is used to bring the heavier isotopic ions into focus. This will slightly decrease both the efficiency of ion extraction from the ion source and the sensitivity of the detector to the more massive isotopic ion. This is due to ion optic properties of the magnetic sector, and as seen in Equation 19 mass is inversely proportional to accelerating voltage when describing the focusing properties of the magnetic sector (m = mass, z = charge, B = magnetic field, r = radius, V = accelerating voltage), therefore lower accelerating voltages are necessary to pass ions of increasing mass through the magnetic sector when it is operated at a constant field.

$$m/z = B^2 r^2 / 2V \quad (19)$$

In preparation for a given analysis, it was also necessary to know the minimum level of mass resolution that would provide good separation of the halocarbon ions of interest from hydrocarbon-based ions from all sources including those produced by the reference compound, n-dodecane, that was continuously present in the ion source. In addressing this issue, it is instructive to consider the abbreviated mass spectrum shown in Figure 5 of a mixture of n-dodecane and CF_2ClBr that was continuously bled into the ion source via the heated gas expansion volume. It is seen in this spectrum that a resolution setting of $M/\Delta m = 2,000$ provides good baseline separation of the two ions, CF_2Cl^+ and $\text{C}_{12}\text{H}_{25}^+$, that appear at nominal mass 85. The exact masses of these ions are 84.96885 and 85.10173, for which $m/\Delta m = 625$ (where m and Δm are the average and difference in mass, respectively). As illustrated in this case, the level of resolution required to provide baseline separation between halocarbon-based and hydrocarbon-based ions is about three times the $m/\Delta m$ value of the two ions to be separated. Of course, lower resolutions than this are sometimes

adequate in those fortuitous cases where no hydrocarbon interference's are present at the nominal masses of interest.

Standards

The preparation of standards is an integral part of all quantitative work and has proven to be an especially challenging aspect of this project. Low concentration standards were prepared in our laboratory with limited success (low to sub parts-per-trillion by volume levels). The highly fluorinated and low boiling compounds (boiling points $< 0^{\circ}\text{C}$) proved to be the most predictable and showed good stability when stored for extended periods of time. Hydrogenated compounds with boiling points greater than approximately 0°C and in particular the stability of methyl bromide (CH_3Br), stored in flasks, proved to be very unpredictable at low concentrations (concentrations below part-per-million levels).

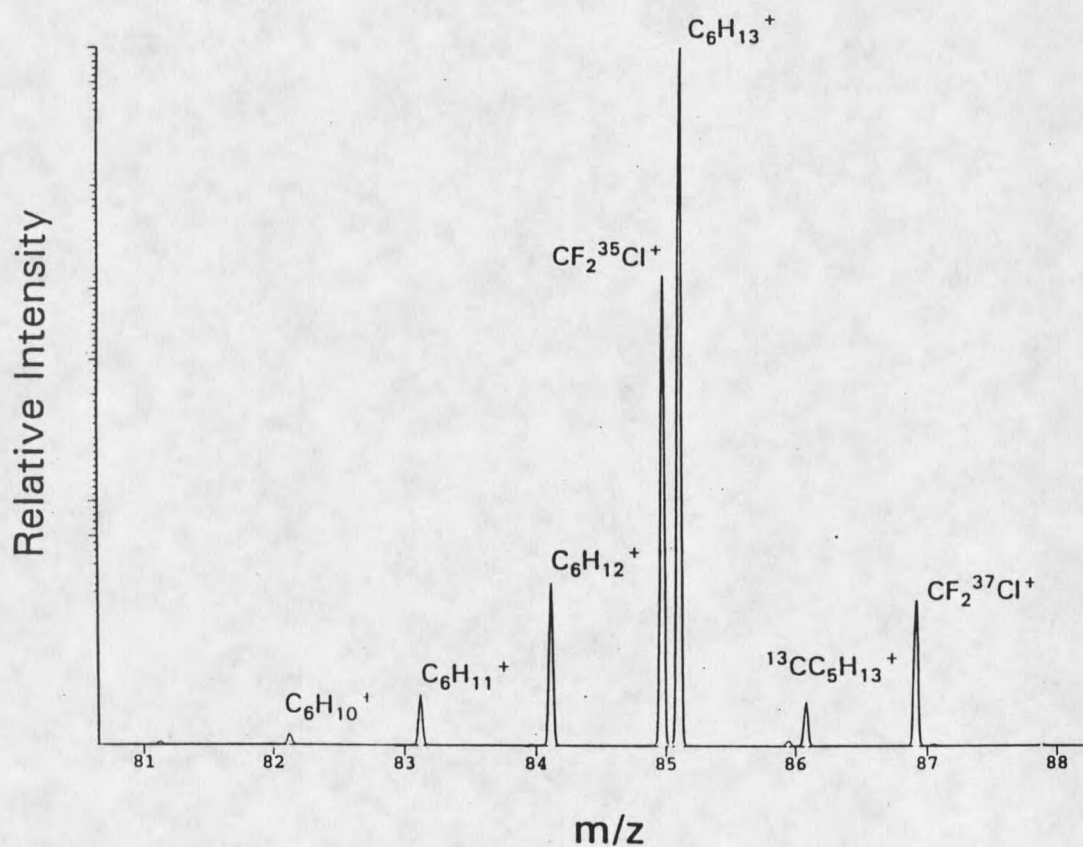


Figure 5. Mass spectrum of a mixture of n-C₁₂H₂₆ and CF₂ClBr over the mass range, m/z = 80 to 88, with the resolution of the mass spectrometer set to R = 2,000.

Low Concentration Standards

Low concentration standards (low to sub pptv) were prepared by the successive dilution of the pure gaseous substance of interest into a series of three twenty liter glass carboys. The carboys were pressurized to above ambient pressure with nitrogen gas that was void of the compounds of interest. For the most inert compounds (best behaved) standard preparation accuracy's achieved in our laboratory are estimated at $\pm 50\%$. In an analysis of the propagation of error associated with making 3 successive dilution's a relative error of $\pm 8\%$ can be assigned. The remaining error is attributed to wall effects, either adsorption onto the wall and/or contamination of the flask walls (40,41). Standards prepared from the compounds in the well behaved list include CF_4 , CF_3H , CF_3Cl , $\text{CF}_3\text{CF}_2\text{Cl}$, CF_3Br , CF_3CFH_2 , CF_2ClBr .

High Concentration Standards

Standard mixtures of approximately 200 ppmv concentration containing CH_3Br , CF_2Br_2 , $\text{C}_2\text{F}_4\text{Br}_2$, CH_2ClBr , CH_2Br_2 , CHBr_3 , and CF_2ClBr were prepared in our laboratory.

The mixture was prepared by injecting a pure aliquot of each compound into a five liter glass flask and then pressurizing the flask to above ambient pressures with nitrogen gas. The calculated relative error associated with this single dilution technique is $\pm 5\%$ and this is in agreement with the several standards produced in our laboratory. Wall effects have been reported to have less significance for gas standards in the high ppmv range (41). The high concentration mixture proved stable, although mixing was necessary before use. Mixing was accomplished by heating the outside of the flask with a heat gun.

RESULTS AND DISCUSSION

Qualitative Determinations by GC-HRMS

The discussions to follow will be facilitated by the fourteen electron impact ionization mass spectra shown in Figures 28-41, in the Appendix. Inspection of these spectra indicates that the first seven compounds have an ion of nominal mass 69 in their spectra and that all of the brominated compounds have ions of mass 79 and 81.

Compounds indicated by monitoring the CF_3^+ ion

Compounds identified in this study were analyzed using the GS-Q capillary column and concentration method 1. In Figure 6, three single ion chromatograms, analyzing 340 atm-cm³ of clean outdoor air, are shown where the mass spectrometer has been tuned to the exact mass, $m/z = 68.9952$, of the ion, CF_3^+ , using three different resolution settings. With use of the lowest resolution setting of our instrument ($R = 700$) in Figure 6A, a relatively high level

of baseline noise is observed. This is not surprising because the mass deficiency of the CF_3^+ ion is small and other hydrocarbon-based ions of nominal mass 69 would be expected to contribute to the baseline noise level at this resolution setting. As the resolution is increased to 2000, most of the chemical noise is removed. Further increase in resolution to 4500 results in the loss of the last peak at a retention time of 7.65 minutes, thereby indicating that the compound responsible for this response does not actually have the ion, CF_3^+ in its mass spectrum. The signal-to-noise response to the remaining CF_3^+ peaks is not actually as high in Figure 6C as in 6B. This is due to the expected reduction of ion throughput accompanying the use of increased resolution in Figure 6C relative to 6B. Therefore, a slight increase in the relative importance of residual instrumental noise is detectable in Figure 6C.

The typical method used to determine the identity of individual compounds is as follows. Each compound is identified by matching GC retention times to standards, detecting many of the major fragment ions present in the EI

mass spectrum, and by simultaneously monitoring isotopic clusters of ions in order to determine the isotopic abundance ratios (A_r).

The last peak shown in Figures 6A and 6B, corresponds to the compound CF_2HCl (HCFC-22). Verification of this compound is shown in Figure 7 where the exact mass of the ion $\text{CFH}^{37}\text{Cl}^+$ was monitored, $m/z = 68.9721$. This ion and the retention time indicated in Figure 7A were expected for the compound, CHF_2Cl , which is known to be present in the atmosphere at a concentration (about 125 pptv (42,43)) which is quite high relative to those of the compounds to be highlighted in the present study. As expected, the relative response to CHF_2Cl was greatly increased and that to CF_3 -containing molecules was greatly decreased as the resolution of the mass spectrometer was increased to $R = 4500$ in Figure 7B. It should be noted that the remarkable change in the two measurements shown in Figures 6C and 7B was caused by a change of only 0.02 mass units in the selected exact mass. This provides an excellent example of the increased utility of HRMS over that of low resolution MS

for the definitive analysis of multicomponent samples. This is also a good example of how a minor fragment ion of a trace atmospheric component (100 to 1000 pptv) can cause interference's in the analysis of ultra trace (<10 pptv) components of the atmosphere.

In Figure 8, another compound, CF_4 , known to be present in the atmosphere at levels in excess of the low pptv range has been identified. The only two ions (CF_3^+ and CF_2^+) of $m/z > 42$ having significant relative intensity in its mass spectrum were monitored (Fig. 29 in Appendix). Both ions expected for CF_4 are clearly evident in chromatograms 8A and 8B. CF_4 (CFC-14) is a by product of the industrial production of aluminum by the Hall-Heroult process (44-46,39).

In Figure 9, the expected retention time of CF_3H is noted and the three major ions (CF_3^+ , CF_2H^+ , and CF_2^+) in its mass spectrum (Fig. 30 in Appendix) have been monitored with detectable responses observed at each of these exact masses. The large response noted in Figure 9C and a minor one in Figure 9B at 7.6 minutes is due to CHF_2Cl (see mass

spectrum in Appendix, Fig. 28). The large peak in Figure 9B is due to CF_2Cl_2 whose presence in the atmosphere is known to be very high, about 540 pptv. The origin of the last peaks noted in Figures 9B and 9C is presently unknown. To our knowledge, the compound CF_3H has not been previously detected in background air. It seems reasonable to speculate that a source of this compound might be associated with the industrial production of aluminum by the Hall-Heroult process. The atmospheric presence of CF_4 and C_2F_6 has been associated with the production of aluminum (44,45,46,39). For this reason, two air samples collected from the ventilation exhausts of an aluminum plant were analyzed in our lab by GC-HRMS. Elevated levels of CF_3H , as well as CF_4 and C_2F_6 , were found in both samples.

In Figure 10, the expected retention time of CF_3Cl (CFC-13) is noted and three major ions (CF_3^+ , $\text{CF}_2^{35}\text{Cl}^+$, and $\text{CF}_2^{37}\text{Cl}^+$) in its spectrum (Fig. 31 in Appendix) have been monitored with detectable responses observed at each of these. For this compound, an isotopic pair of ions were simultaneously monitored in Figures 10B and 10C, so that the

relative intensities of these two responses could be determined. The area of the minor isotopic peak relative to that of the major ion is shown to be $A_r = 0.322$, in good agreement with the known isotopic ratio of 0.323. The very large responses observed in Figures 10B and 10C at about 6.6 minutes are due to CF_2Cl_2 , a major atmospheric halocarbon with a concentration of about 540 pptv (42).

In Figure 11, the expected retention time of $\text{CF}_3\text{CF}_2\text{Cl}$ (CFC-115) is indicated and six ions in its mass spectrum (Fig. 32 in Appendix) have been monitored with detectable responses noted at each of these. For the two isotopic pairs, 11B-11C and 11E-11F, that were simultaneously monitored, it is noted that the response ratios observed for these are in good agreement with the corresponding peak heights noted in the EI mass spectra for this compound. Also, it is noted that another compound with a retention time of about 7.8 minutes also produces an ion of composition, $\text{C}_2\text{F}_4\text{Cl}^+$. The origin of this signal is presently thought to be $\text{CF}_2\text{ClCF}_2\text{Cl}$ and not CF_3CFCl_2 due to the absence of a significant CF_3^+ response for this compound.

in chromatogram 11A. At a retention time of about 2.7 minutes, a response to C_2F_6 is also noted in chromatograms 11A and 11D while monitoring the ions CF_3^+ and $C_2F_5^+$.

In Figure 12, the expected retention time of CF_3Br (H-1301) is indicated and responses at all of the seven exact masses selected for this compound (see spectrum in the Appendix, Fig. 32) are observed. CF_3Br has been used extensively in fire extinguishers (22). Note that the ratios of responses observed for the three pairs of simultaneously measured bromine isotopic ions in Figures 12B-12C, 12D-12E, and 12F-12G are in good agreement with the expected ratio, 0.98. The additional peaks noted by monitoring the Br^+ ion in Figures 12B and 12C will be discussed below. The very large responses noted in Figures 12D and 12E at a retention time of about 3.3 minutes are due to Xe nuclides of $m/z = 128.9048$ and 130.9051 , respectively (the total concentration of the nine naturally occurring nuclides of Xe in the atmosphere is about 0.1 parts per million and these two nuclides have relative abundances of 26% and 21%, respectively (47)). It is noted in Figures

12F and 12G that monitoring either one of the molecular ions of CF_3Br provides an excellent response to this compound, in spite of the fact that the relative intensities of these ions in the mass spectrum shown in the Appendix are only about 10% that of the base peak at mass 69. This is due to the lower level of chemical noise encountered at the exact masses of these molecular ions.

In Figure 13, the expected retention time of $\text{CF}_3\text{CH}_2\text{F}$ (HCF-134a) is indicated and responses to three of the exact masses selected for this compound (Fig. 33 in Appendix) are observed. The large peak observed in Figure 13B at about 6.0 minutes is due to the CHF_2^+ ion of the compound CHF_2Cl (see Appendix). The origins of the responses observed at about 7.9 minutes in Figure 13B and at about 2.2 minutes in Figure 13C are unknown. This particular HFC is a replacement for CF_2Cl_2 (CFC-12) and CHF_2Cl (HCFC-22) in refrigeration, air conditioning, and in aerosol applications and is currently the most widely used HFC (28).

Compounds indicated by monitoring
the Br^+ ion on the GS-Q Capillary
Column

Compounds identified in this study were detected using the GS-Q capillary column and concentration method 1. In Figure 14, one of the isotopes of the Br^+ ion has been monitored using four different resolution settings. It is shown that the relative intensities of only three of the observed peaks remains constant as resolution is increased, thereby indicating that all other responses noted with low resolution are not actually due to the Br^+ ion. The brominated compound with a retention time of about 5.3 minutes is CF_3Br and has been previously identified in Figure 12.

In Figure 15, the expected retention time of CH_3Br is indicated and strong signals are observed at this time when each of the four major ions in the mass spectrum of CH_3Br (Fig.38 in Appendix) is monitored. Methyl bromide has been extensively studied in the last ten years and there are still many questions regarding the overall mass balance. At

present, there is a mass imbalance and the known sources do not add up to the known sinks (24,48,49). The principal sources of methyl bromide are oceanic, fires, fumigation, and auto emissions (24).

The expected retention time of CF_2BrCl (H-1211) is indicated in Figure 16 and responses are observed when nine of the ions in its mass spectrum (Fig. 35 in Appendix) of $m/z > 50$ are monitored. Note that the relative areas of the simultaneously-monitored isotopic cluster groups are in good agreement with the relative intensities indicated in the mass spectrum of this compound. Again, the origin of the large peaks in Figures 16C and 16D is CF_2Cl_2 and that of the large peaks in Figures 16E and 16F are isotopes of Xe. The origin of the peak at about 3.3 minutes is unknown as is the corresponding peak noted in chromatogram 16H.

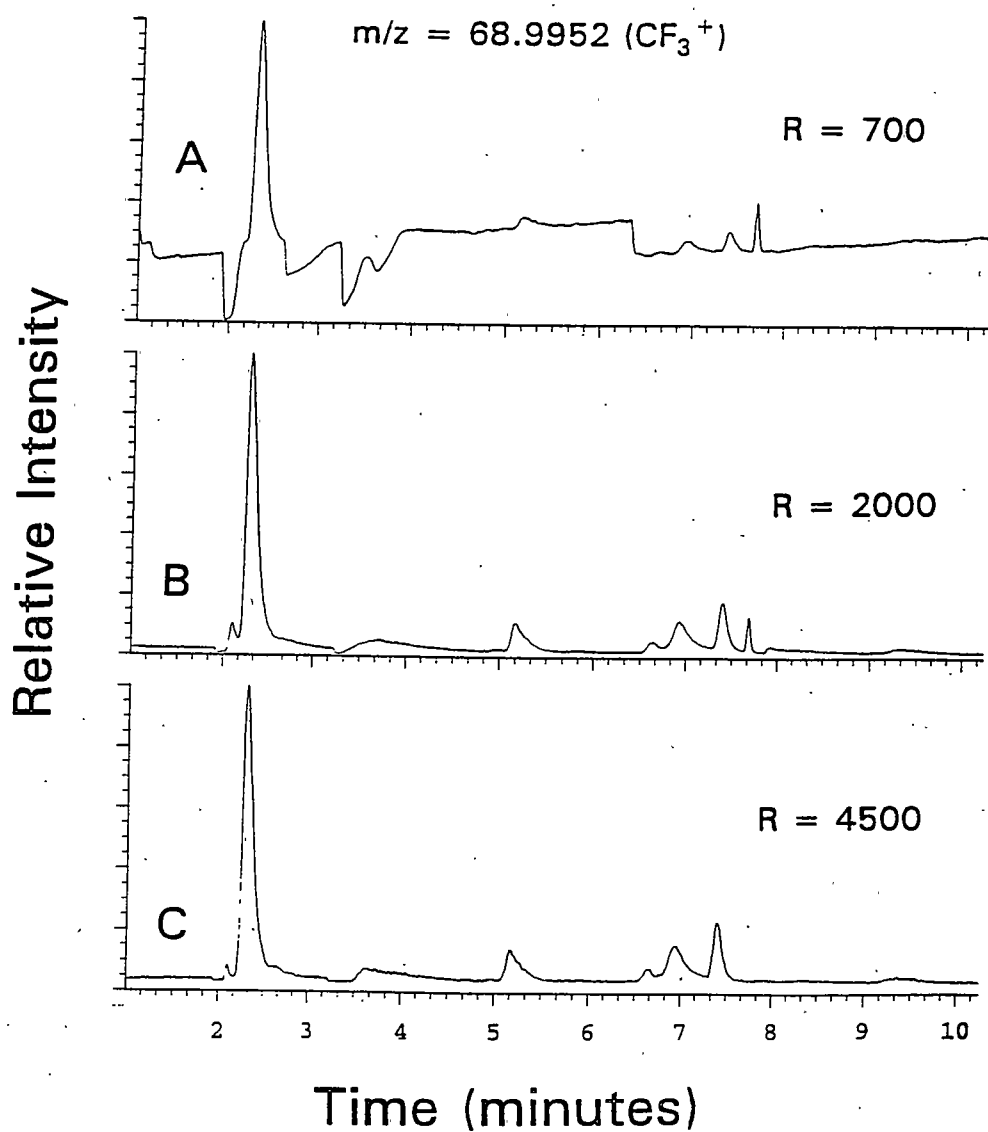


Figure 6. CF_3^+ single ion chromatograms using three different resolution settings. In each chromatogram the relative responses are normalized to the maximum response observed under each condition. The amount of air sampled is 340 atm-cm^3 .

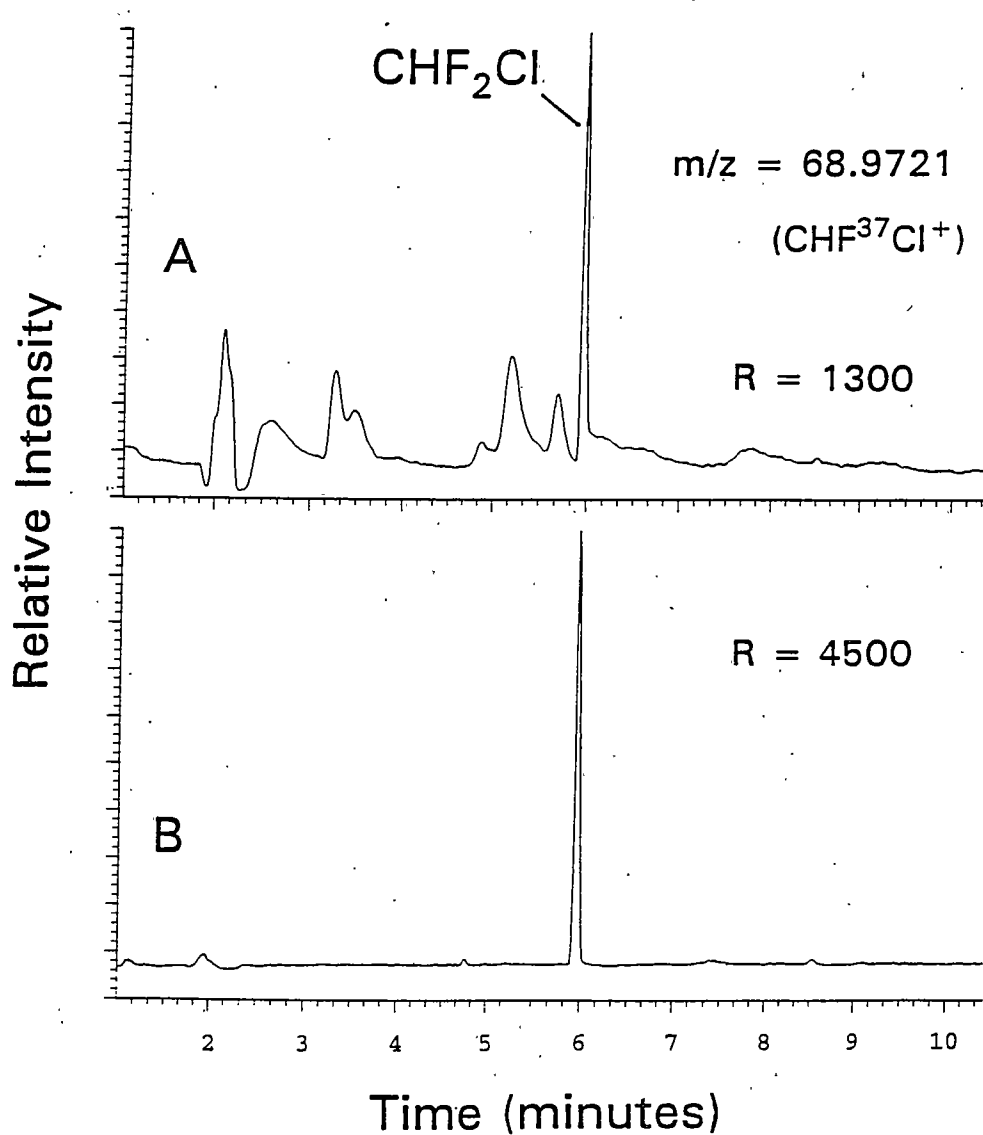


Figure 7. $\text{CHF}^{37}\text{Cl}^+$ single ion chromatograms using two different resolution settings. The expected GC retention time of CHF_2Cl is indicated in chromatogram A.

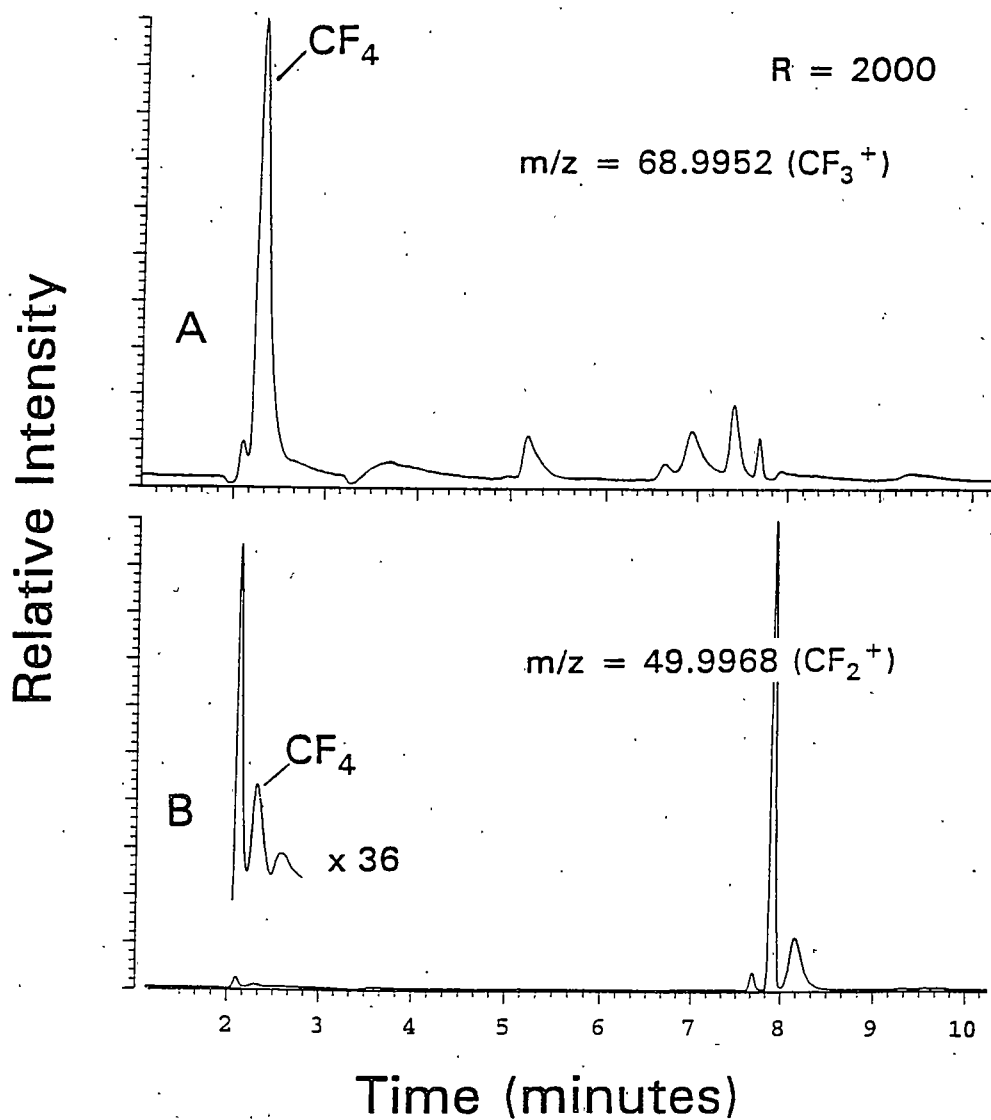


Figure 8. Single ion chromatograms using two ions expected in the electron impact spectrum of CF_4 . The expected retention time of CF_4 is indicated in chromatogram A.

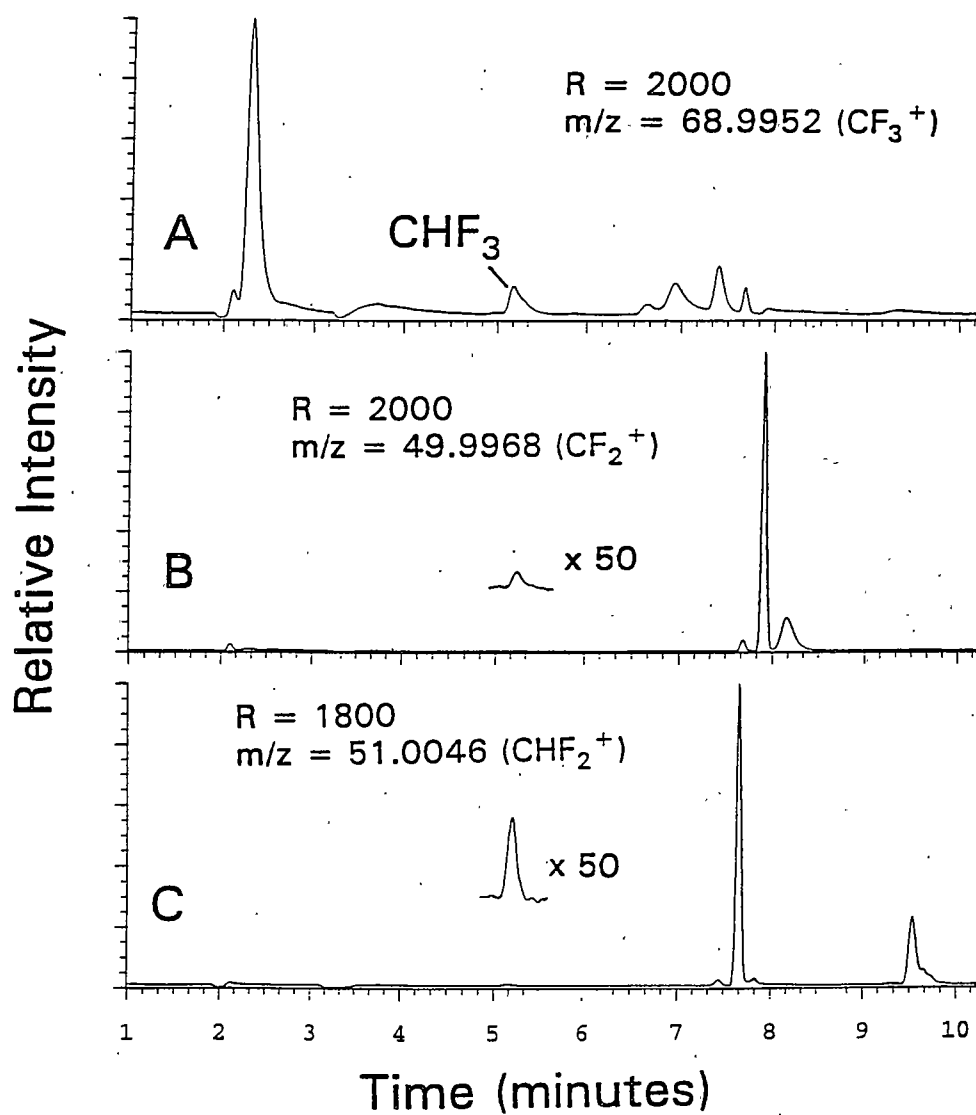


Figure 9. Single ion chromatograms and expected retention time for CHF_3 .

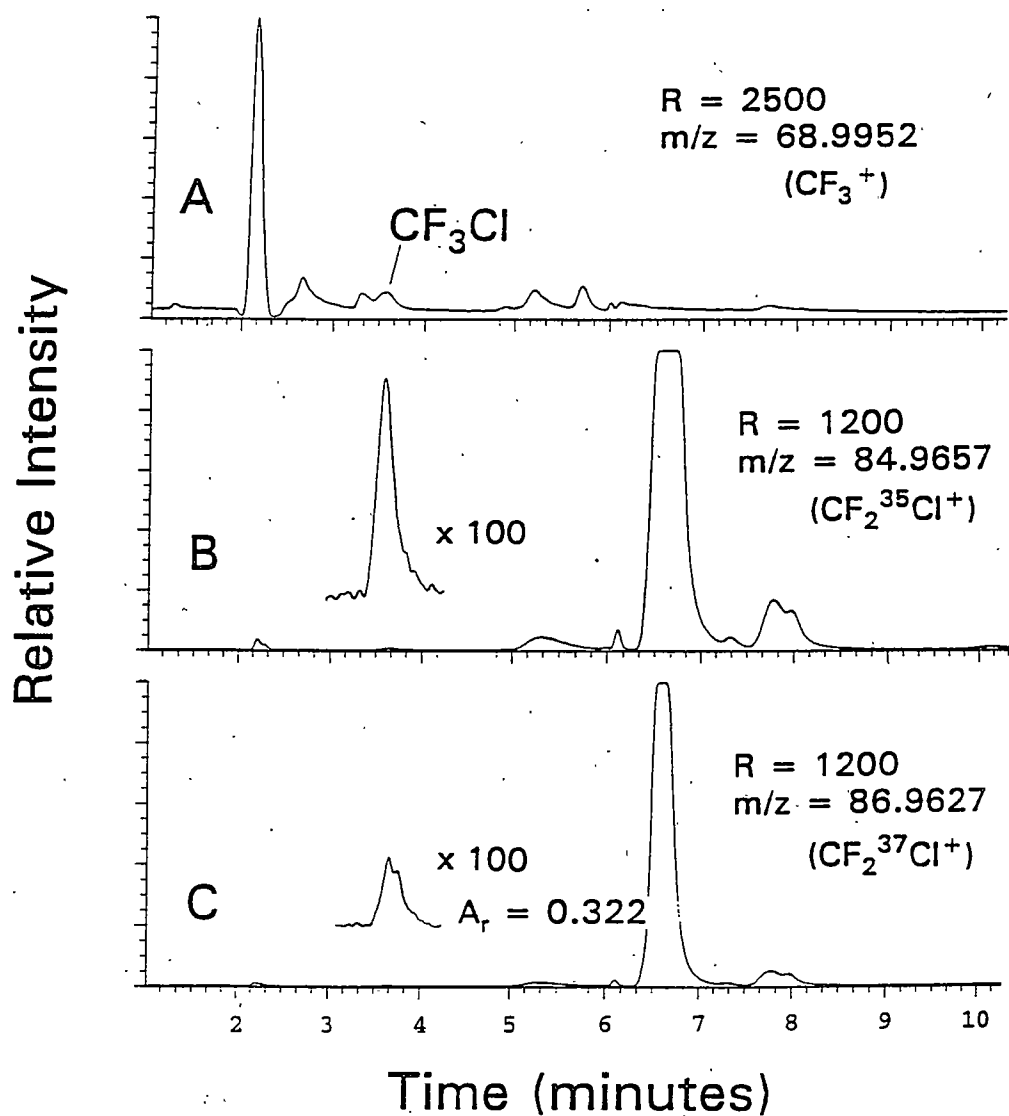


Figure 10. Single ion chromatograms and expected retention time for CF_3Cl . The isotopic pairs of ions in chromatograms B and C were simultaneously measured in a single analysis. The value of A_r in chromatogram C is the ratio of this peak area to that in chromatogram B.

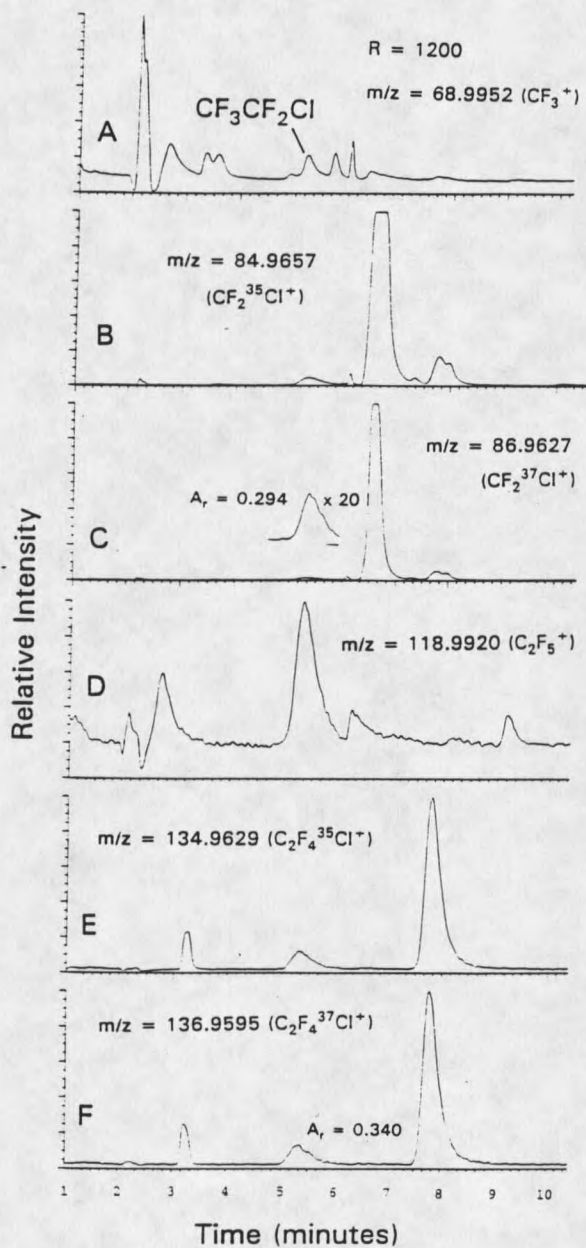


Figure 11. Single ion chromatograms and expected retention time for $\text{CF}_3\text{CF}_2\text{Cl}$. Chromatograms B and C and chromatograms E and F (isotopic pairs) were simultaneously determined. A_r values are the ratios of the responses to the minor and major isotopic ions.

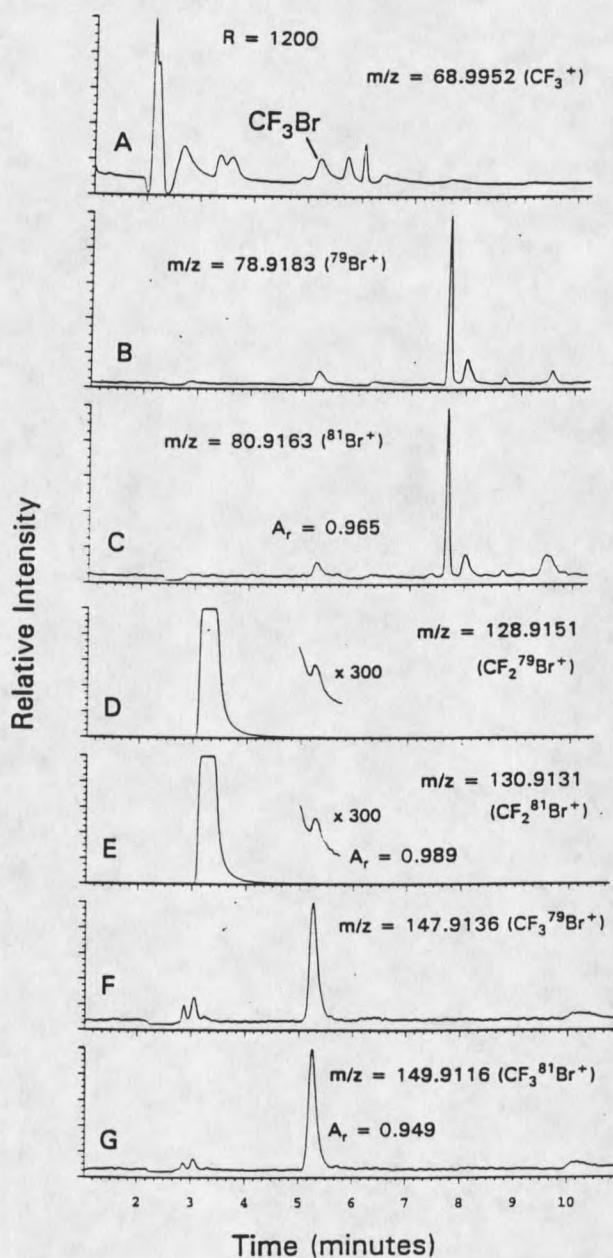


Figure 12. Single ion chromatograms and expected retention time for CF_3Br . The responses to the isotopic pairs of ions in chromatograms B and C, D and E, and F and G were simultaneously determined. A_r values are the ratios of the responses of the minor ^{81}Br -containing ion to that of the major ^{79}Br -containing ion.

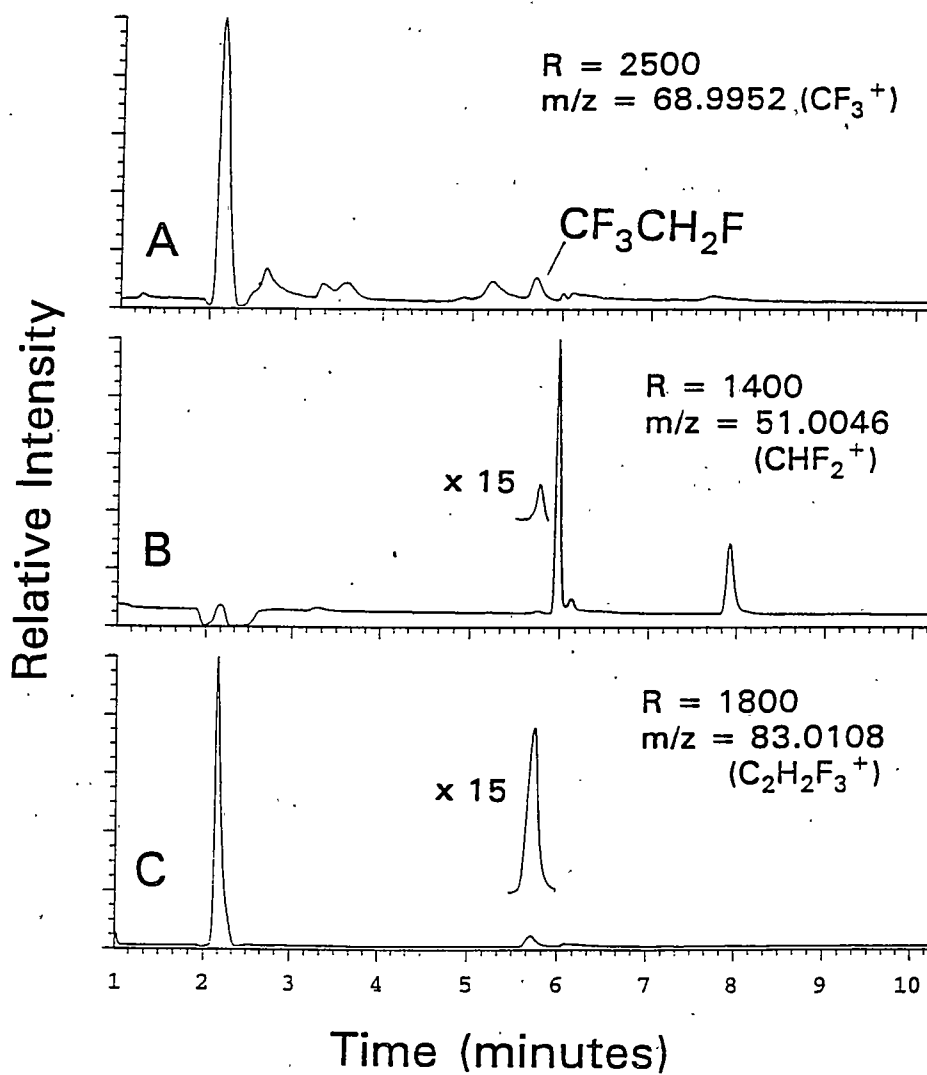


Figure 13. Single ion chromatograms and expected retention time for $\text{CF}_3\text{CH}_2\text{F}$.

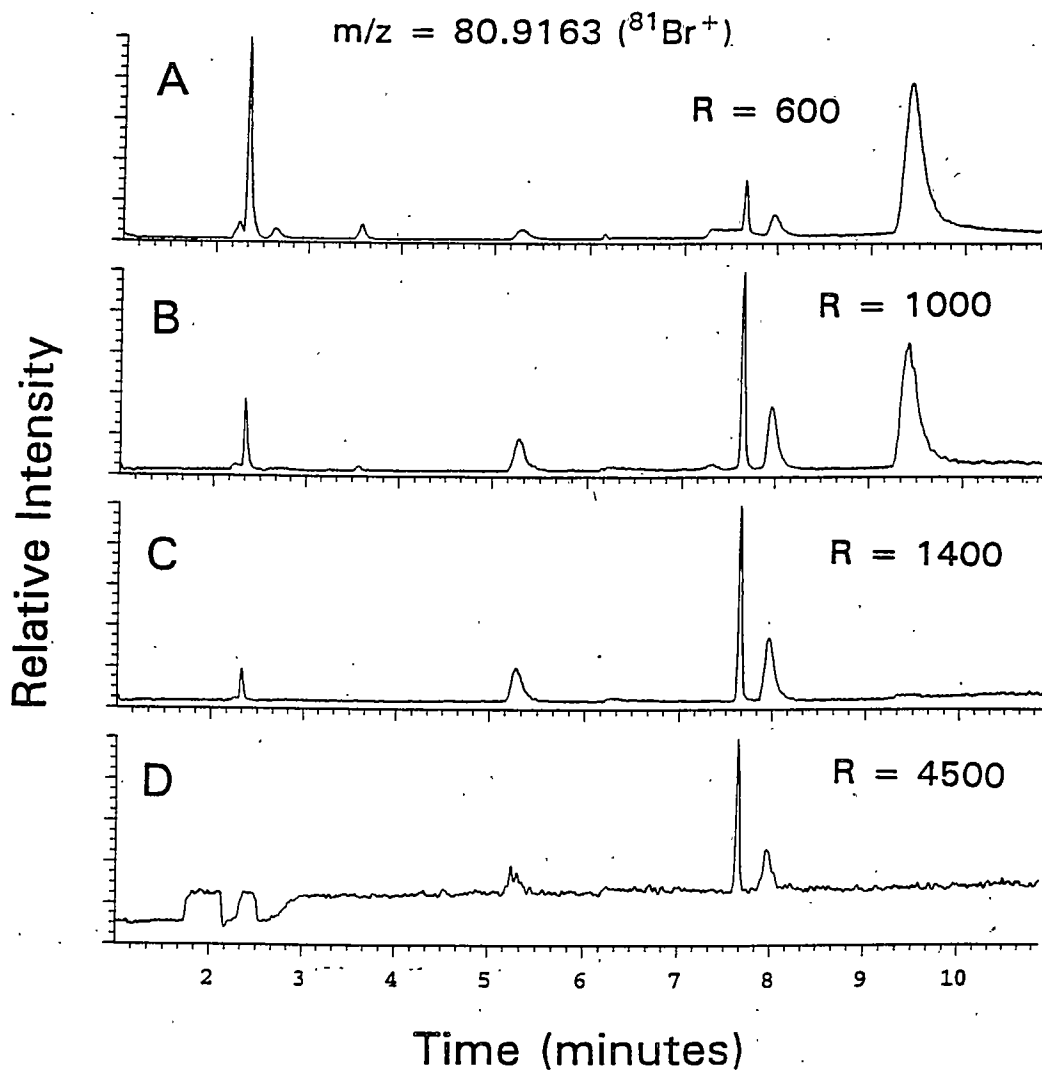


Figure 14. $^{81}\text{Br}^+$ single ion chromatograms using four different resolution settings. The amount of air sampled is 340 atm-cm^3 .

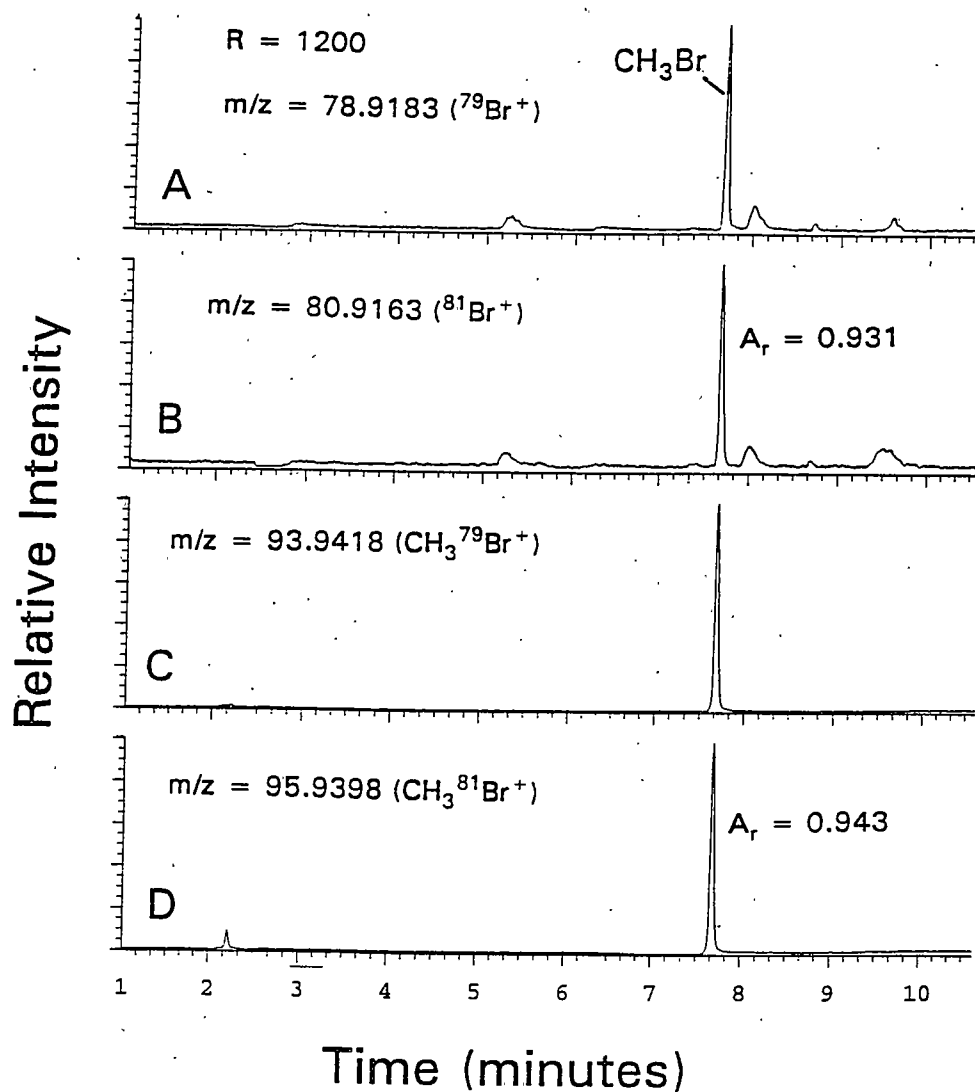


Figure 15. Single ion chromatograms and expected retention time for CH_3Br . The responses to the isotopic pairs of ions in chromatograms A and B and chromatograms C and D were simultaneously determined. A_r values are the response ratios of the ^{81}Br -containing and the ^{79}Br -containing ions.

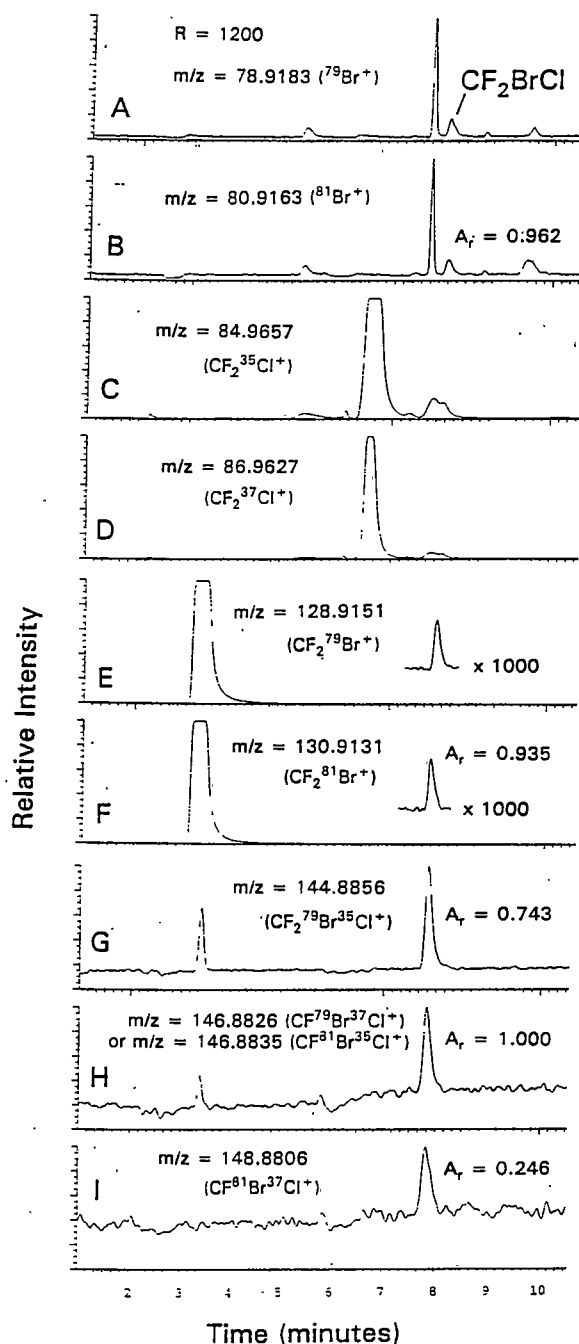


Figure 16. Single ion chromatograms and expected retention time for CF_2BrCl . The responses to the isotopic sets of ions in chromatograms A and B, C and D, E and F, and G, H, and I were simultaneously determined.

Compounds indicated by monitoring
the Br^+ ion using the DB-VRX
Capillary Column

Compounds identified in this part of the study, were detected using the DB-VRX capillary column chromatography procedures and concentration method 2. In Figure 17, three single ion chromatograms are shown where the mass spectrometer has been tuned to the exact mass, $m/z = 80.9163$, of the ion, $^{81}\text{Br}^+$, using three different resolution settings. With the use of a low resolution setting of our instrument ($R = 1000$) in Figure 17, at least fourteen distinct peaks are observed, with a coelution of two compounds at approximately four minutes. With increasing resolution only eight of the original fourteen peaks persist, indicating that these compounds are almost certainly bromine containing. The best signal-to-noise while maintaining sufficient resolution was determined to be $R = 2000$, see Figure 18. In Figure 18, the eight brominated compounds detected in background Montana air, while monitoring the $^{81}\text{Br}^+$ fragment ion, are shown. All of the

following chromatograms, Figure 19 - Figure 25, were obtained using a resolution setting of 2000.

In Figure 19, the compound CF_2ClBr has been identified at a retention time of about 4 minutes. Most of the major fragment ions present in the EI mass spectrum of this compound have been detected (Fig. 35 in Appendix). Commonly known as Halon-1211, this compound has been used extensively as a fire extinguishent (30,50). Each compound was identified by matching retention times to standards, detecting many of the major fragment ions present in the EI mass spectrum, and by simultaneously monitoring isotopic clusters of ions in order to verify the correct isotopic abundance ratios (A_r). In Figure 19, $A_r = 0.92$, which agrees well with the known isotopic abundance of 0.97 when taking into account that the A_r value will be slightly lower do to the use of the voltage jumping technique described earlier.

In Figure 20, four of the most abundant fragment ions have been detected for the compound CF_2Br_2 (see mass spectrum in Fig. 36, Appendix) at the expected retention time of 6:20. The A_r value is slightly higher than expected

for the Br^+ isotopes due to the low signal-to-noise for the $^{79}\text{Br}^+$ isotope. This is the first time CF_2Br_2 has been detected in the atmosphere and its source is unknown, but is very likely of anthropogenic origin.

In Figure 21, the compound $\text{CF}_2\text{BrCF}_2\text{Br}$ (H-2402) has been identified by monitoring four of the major ions in its mass spectrum (Fig. 37 in Appendix) at a retention of 8:10. H-2402 was produced in Japan and used in the former Soviet Union (53). A_r for the Br^+ isotopic pair is low due to a coelution of an unknown compound in the $^{79}\text{Br}^+$ chromatogram.

In Figure 22, at a retention time of 4:42 methyl bromide (CH_3Br) is identified (mass spectrum in Appendix, Fig. 38). As mentioned earlier, methyl bromide is produced naturally in the oceans (49,18) and during the burning of biomass (51). It is also released into the atmosphere during its use as a fumigant for strawberries and grains (48). The contribution to atmospheric CH_3Br from anthropogenic release is not well known (24,48,49,52) due to uncertainties in our knowledge of the natural sources and sinks.

In Figure 23, the compound CH_2Br_2 has been detected at a retention time of about 13:50 minutes and seven of the major fragment ions have been monitored (Fig. 40 in Appendix). Dibromomethane is produced naturally in the oceans (22,29) and has industrial sources (24).

In Figure 24, at a retention time of 11:00 minutes bromochloromethane has been identified by monitoring nine fragment ions (mass spectrum in Appendix, Fig. 39). CH_2ClBr is also thought to be primarily from natural sources (22,29).

In Figure 25, bromoform has been detected at a time of 18:20 and nine of the major fragment ion in its mass spectrum have been monitored (Fig. 41 in Appendix). CHBr_3 has also been shown to have natural oceanic sources (22,24,52).

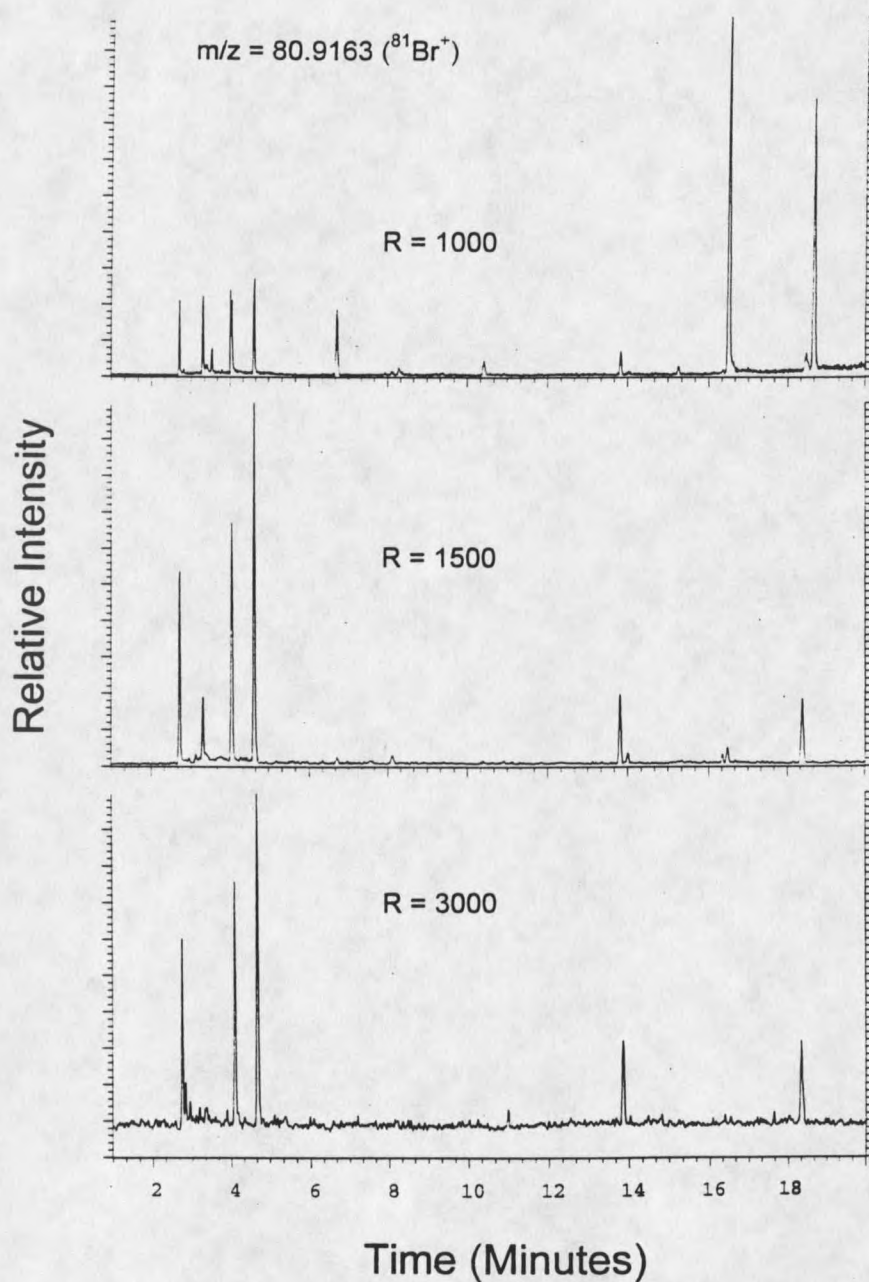


Figure 17. $^{81}\text{Br}^+$ single ion chromatograms using three different resolution settings. In each chromatogram the relative responses are normalized to the maximum response observed under each condition. The amount of air sampled is 340 atm-cm^3 .

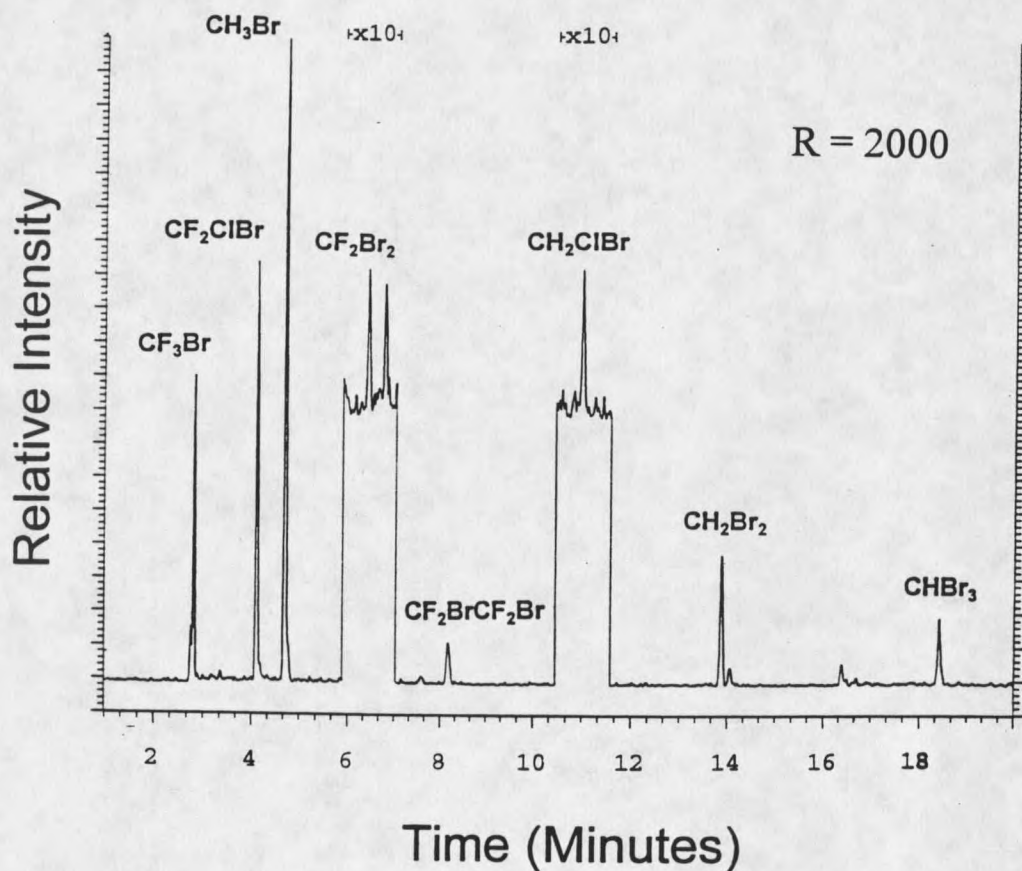


Figure 18. Single ion chromatogram monitoring $^{81}\text{Br}^+$ at resolution of 2000. Eight brominated compounds have been identified in rural Montana background air; CF_3Br , CF_2ClBr , CH_3Br , CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, CH_2ClBr , CH_2Br_2 , CHBr_3 .

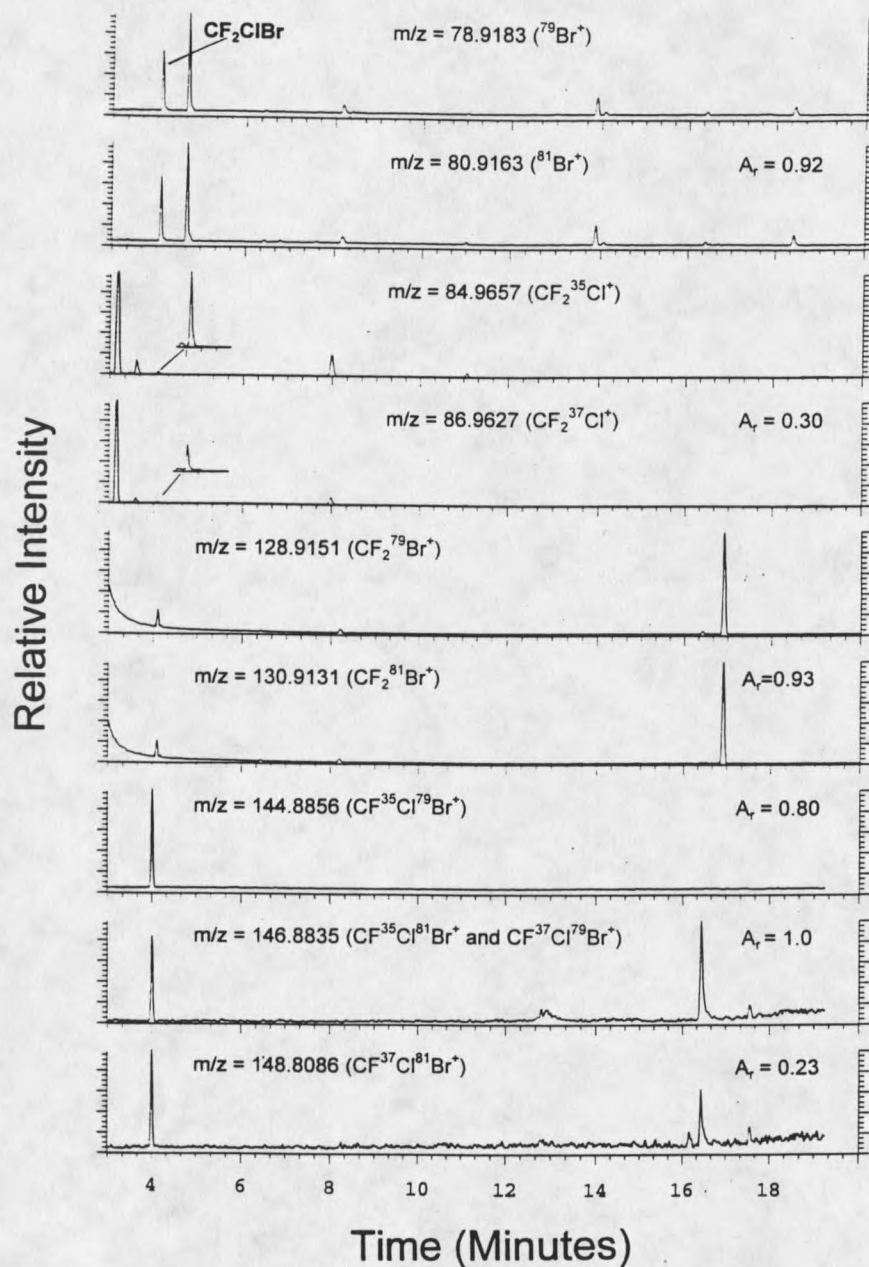


Figure 19. Single ion chromatograms identifying the compound CF₂ClBr, R = 2000, RT = 4:00.

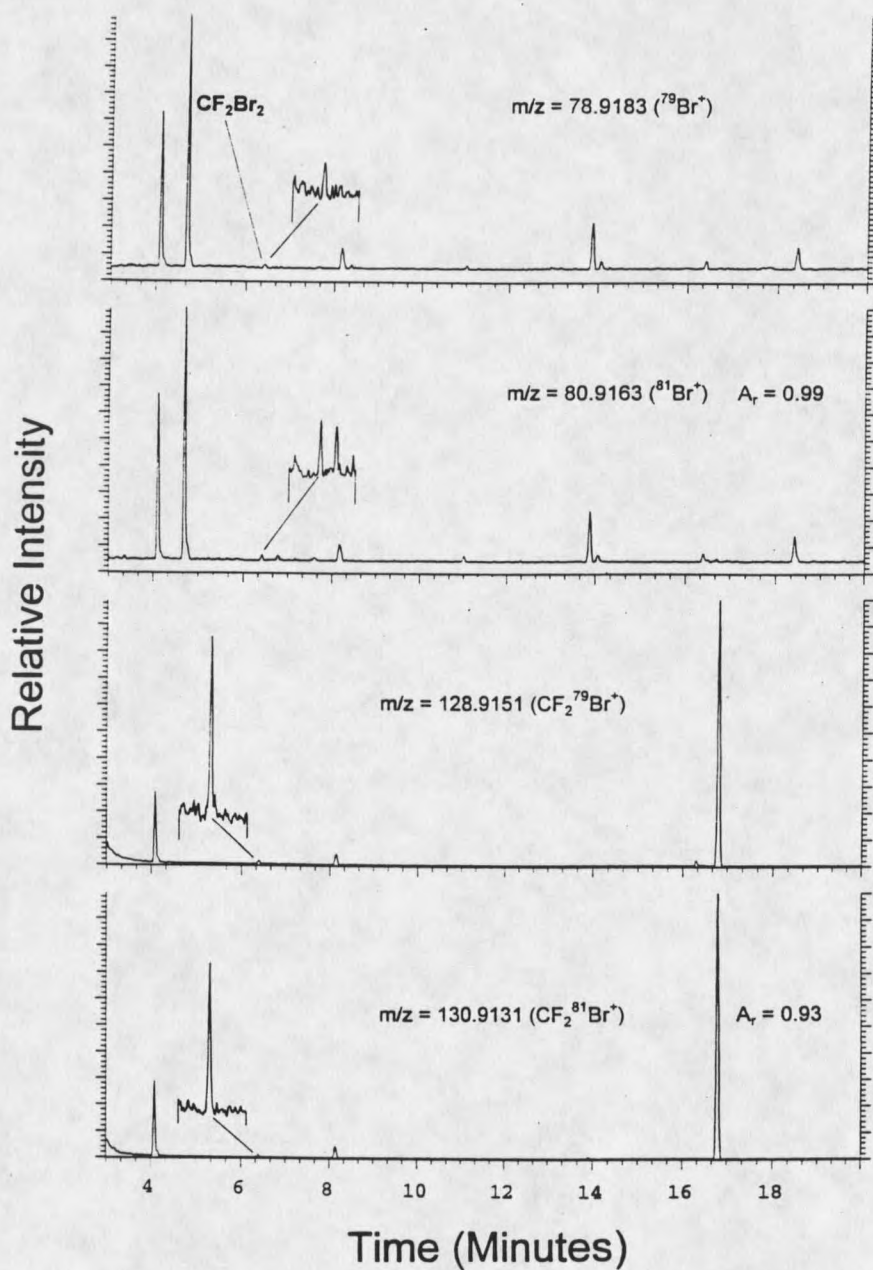


Figure 20. Single ion chromatograms identifying CF_2Br_2 ,
 $R = 2000$, $\text{RT} = 6:20$.

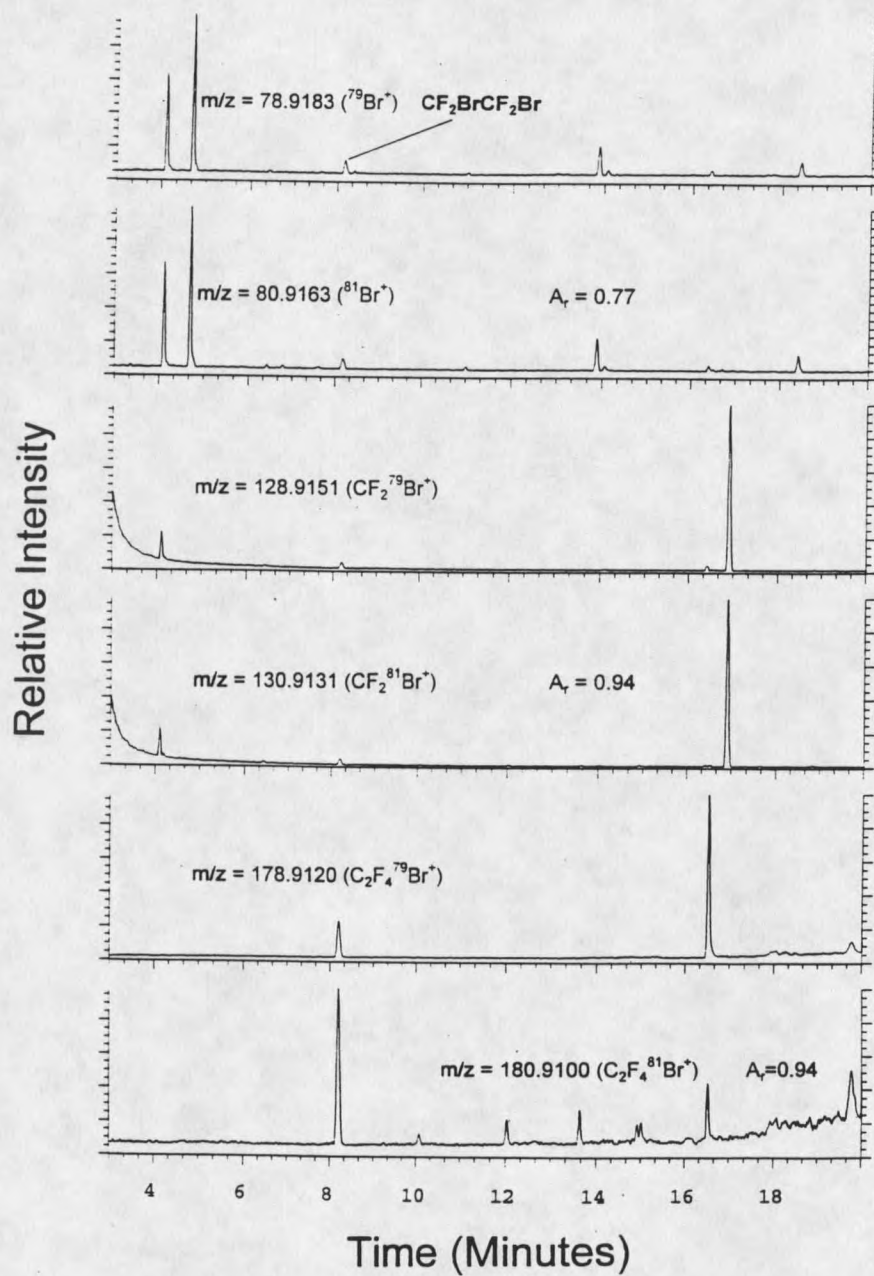


Figure 21. Single ion chromatograms identifying $\text{CF}_2\text{BrCF}_2\text{Br}$, $R = 2000$, $\text{RT} = 8:10$.

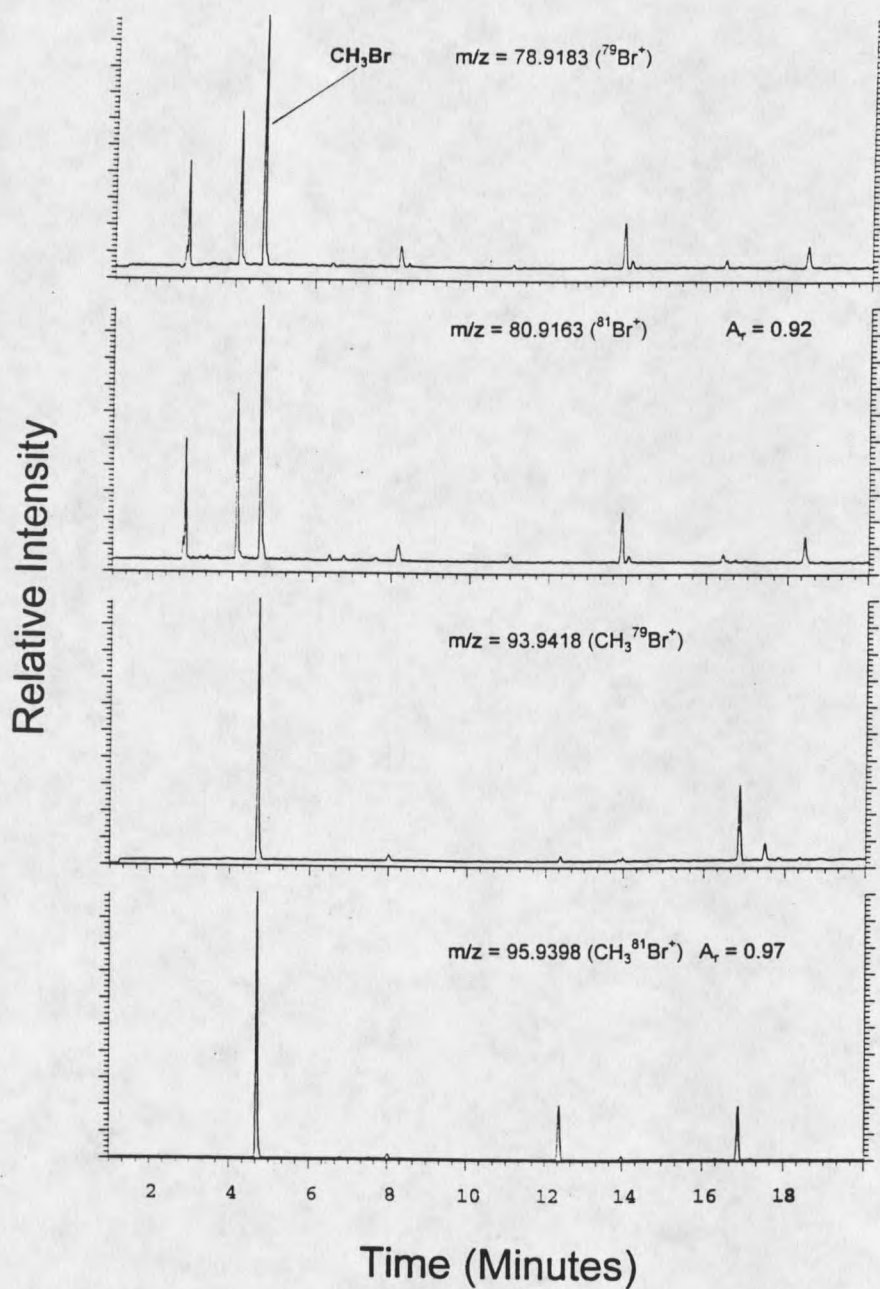


Figure 22. Single ion chromatograms identifying CH₃Br, R = 2000, RT = 4:42.

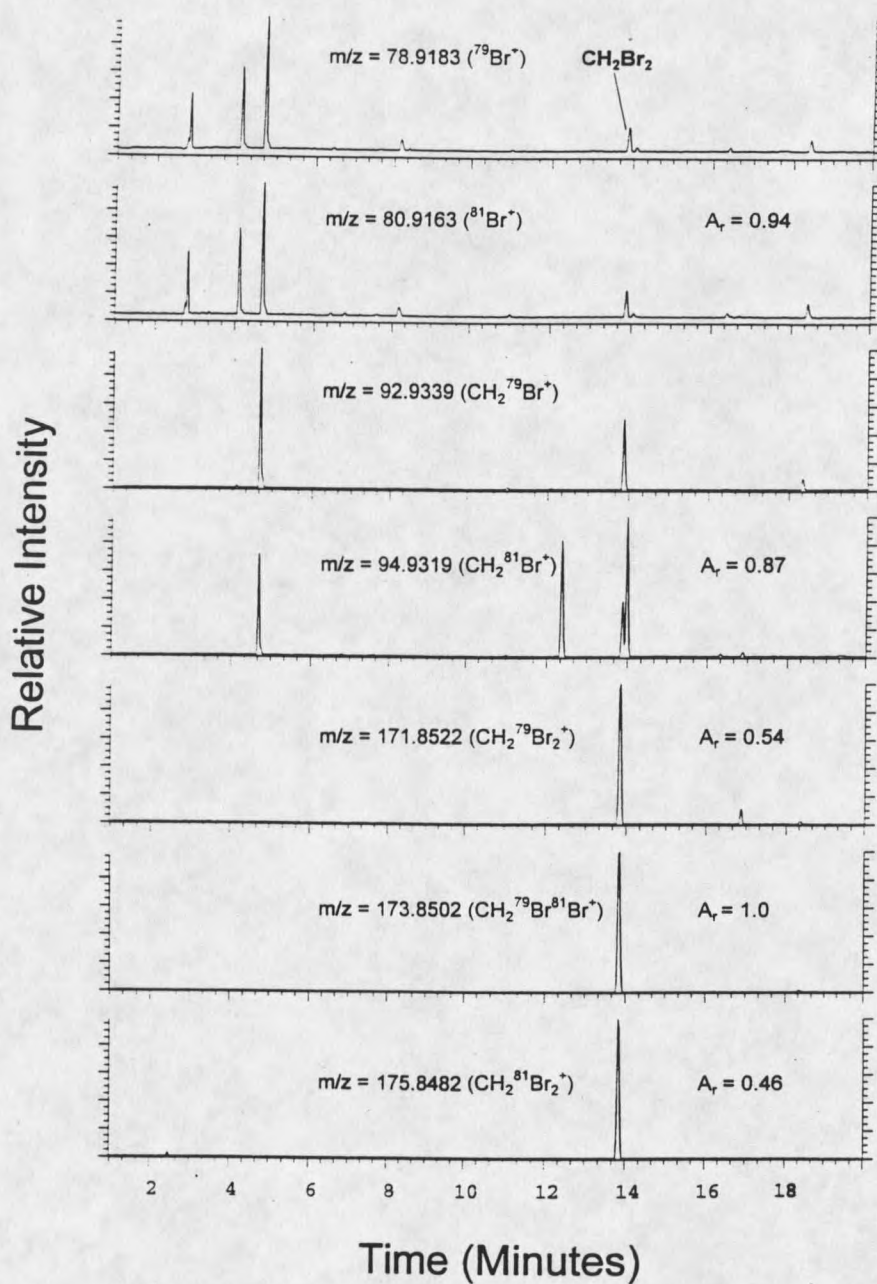


Figure 23. Single ion chromatogram identifying CH_2Br_2 ,
 $R = 2000$, $\text{RT} = 13:50$.

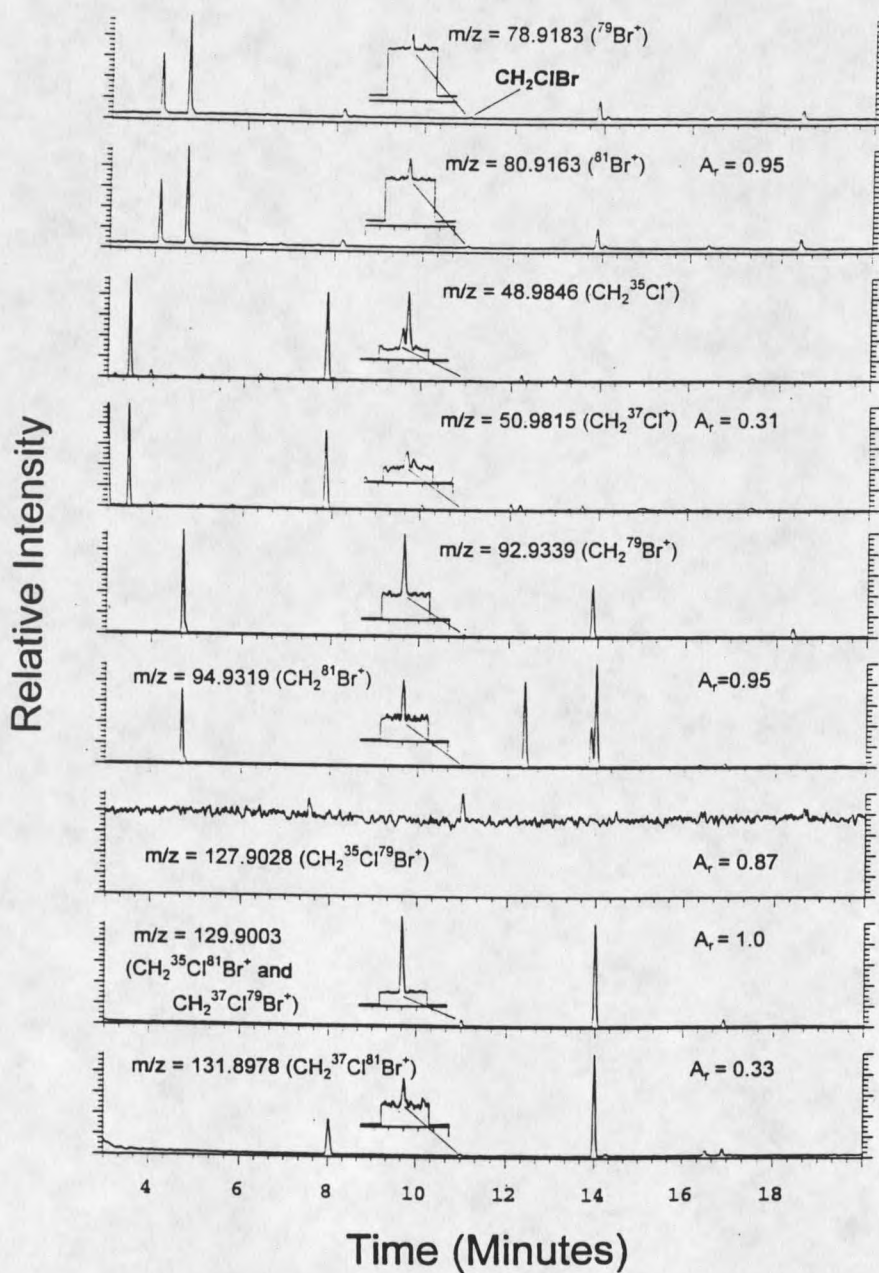


Figure 24. Single ion chromatograms identifying CH_2ClBr , $R = 2000$, $\text{RT} = 11:00$.

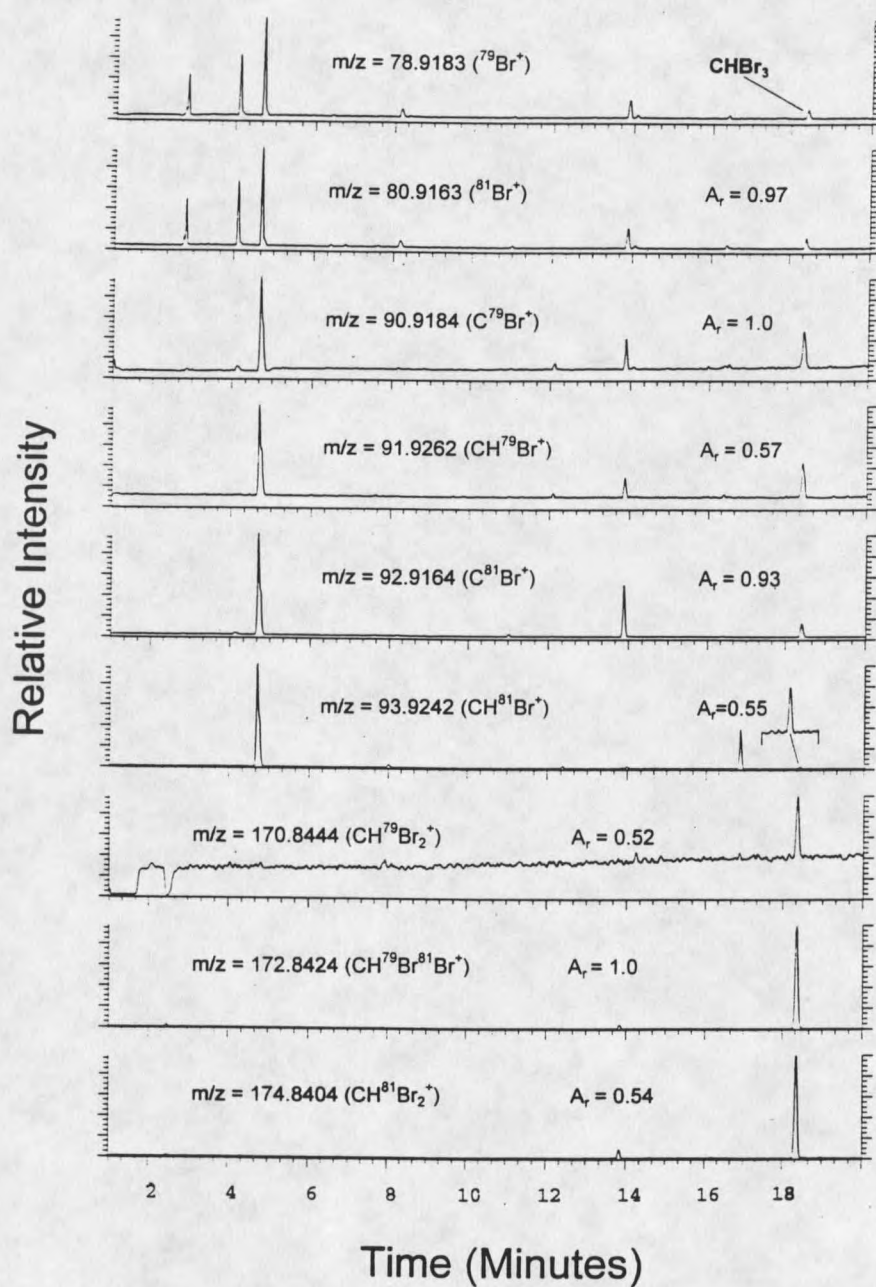


Figure 25. Single ion chromatograms identifying CHBr_3 ,
 $R = 2000$, $\text{RT} = 18:20$.

Quantitative determinations by GC-HRMS

Two quantitative methods were used to determine the atmospheric concentration of selected halocarbons. Because of the difficulty in making low concentration standards (discussed in the standard preparation section), all reported measurements are relative to measurements or standards made by others.

Quantitation is not a difficulty isolated to this study, but is an issue for all those making measurements at very low levels. In a review article discussing concentrations, lifetimes, and trends of CFC's, Halons, and related species in the atmosphere (22), it was stated "Calibration issues continue to limit our understanding of the global atmospheric distributions and trends of these species. Most activities undertaken to resolve this important issue are unsatisfactory at this stage". It was also stated that uncertainties in atmospheric concentrations of species like CFC-12 (CF_2Cl_2), reported to have an tropospheric concentration of 480 pptv, are estimated to be

less than 5%. But, for compounds at lower concentrations the uncertainty levels increased dramatically. CFC-113 ($\text{CCl}_2\text{FCClF}_2$) has been measured at levels of 71 pptv with an uncertainty of 20%, and H-1301 (CF_3Br) is reported to have an atmospheric concentration of 1.2 to 2.2 pptv and an estimated uncertainty of 80%. The concentration values and uncertainties given above are from 1990 annual means reported in the NASA Ref. Pub. 1339, 1994 (22).

Quantitative Analysis of CF_3^+ and Br^+ Compounds with GS-O Capillary Column

For the compounds analyzed in the CF_3^+ study, the GS-Q capillary column was used for chromatography and concentration method 1 (described earlier) was used to concentrate the air samples. The reproducibility of a given analysis has been very high. For example, the analysis of CF_3Br shown in Figure 12G was repeated 8 times over a 10-hour period. The standard deviation of the peak areas thereby recorded was less than 1%. In addition, estimated detection limits can be very low. For example, the signal-to-noise ratios of the two responses to CF_3Br shown

in Figures 12F and 12G are greater than 300. This leads to an estimated detection limit for this compound of about 30 parts-per-quadrillion.

The sample, whose analysis results are given in Table 5, was collected in a remote mountainous region about 8 miles east of Bozeman, MT, and is representative of numerous samples collected in local, rural and mountainous areas during the months of August and September of 1996.

The measured tropospheric concentrations listed in Table 5 were determined using a low concentration standard (approximately 6 pptv) and a single point calibration curve. The accuracy of our low concentration standards were discussed previously. The standard mixture contained the compounds listed in Table 5 and was checked against a standard containing CF_4 , provided to us by Indaco Air Quality Services, Inc., giving good agreement for CF_4 concentrations. This was the only low concentration calibration standard mixture produced in our laboratory which allowed us to measure mixing ratios similar to the mixing ratios reported by other groups. While good agreement was observed between these measurements and those

reported by other groups with this standard, this good agreement could be fortuitous. Comparison with other calibration standards prepared in our laboratory leads to uncertainties of about 50% in actual concentration.

Table 5. Atmospheric Concentration of Compounds Analyzed with GS-Q Column.

<u>Compound</u>	<u>Measured Conc.^a</u> <u>(pptv)</u>	<u>Ion Monitored</u> <u>(m/z)</u>
CF ₄	60	69
CF ₃ H ^b	7.2	51
CF ₃ Cl	2	85
CF ₃ CF ₂ Cl	5	85
CF ₃ Br	3	148, 150
CF ₃ CH ₂ F	4.1	83
CH ₃ Br	11	79
CF ₂ ClBr	3.2	81, 145

^a Uncertainties of 50% have been assigned.

^b Detected and measured for the first time.

Comparison of the response observed at $m/z = 68.9952$ with that of a calibration standard indicated that the concentration of CF₄ (CFC-14) in the air sample was 60 pptv. Previously reported determinations of this compound in background air samples are 67 (55), 60-65 (54), and 58 pptv (56).

Comparison of the response observed at $m/z = 51.0046$ with that of the calibration standard indicated that the concentration of CF_3H in the air sample was 7.0 pptv.

By comparison of the response observed at $m/z = 84.9657$ with that of the calibration standard, a CF_3Cl concentration of 2.0 pptv in the air sample was deduced. Previously reported determinations of this compound in background air are 4 (16) and 2 pptv (20).

Comparison of the response to CF_3CF_2Cl at $m/z = 84.9657$ to that of the calibration standard indicated a CF_3CF_2Cl concentration of 5.0 pptv in the air sample. A previously reported determination of this compound in background air is 5 pptv (55).

Comparison of the response to CF_3Br at the m/z value of either of these two molecular ions to that of the calibration standard indicated a concentration of 3.0 pptv in the air sample. CF_3Br has been used extensively in fire extinguishers. Previously reported determinations of this compound in background air are 1.7 (57), 1.7 (30), and 2.3 pptv (42).

Comparison of the response to $\text{CF}_3\text{CH}_2\text{F}$ at $m/z = 83.0108$ to that of the calibration standard indicated a concentration of 4.1 pptv in the air sample. A previously reported determination of this compound in background air is 3 pptv (42,28).

Comparison of the response to CH_3Br at $m/z = 78.9183$ to that of the CF_2BrCl calibration standard indicated a concentration of 11 pptv in the air sample. Previously reported determinations of this compound in background air are 12-15 (58), 10 (60), 14 (61), and 12 pptv (59).

Comparisons of the responses to CF_2BrCl at $m/z = 80.9163$ and $m/z = 144.8856$ to those obtained from the calibration standard indicated a concentration of 3.2 pptv in the local background air sample. Previously reported determinations of this compound in background air are 2.0 (57), 2.1 (30), and 3.5 pptv (42).

Quantitative Analysis of Br^+
Compounds with DB-VRX Capillary
Column

For the study of brominated compounds in the atmosphere concentration method 2 (described earlier) was used along

with chromatographic methods developed for the DB-VRX capillary column. Because of the difficulties in preparing low to sub parts-per-trillion standards (59) we have elected to associate our measurements, in this study of the bromine-containing compounds, with those of Montzka *et al.*, 1996 by way of the compound CF_2ClBr . CF_2ClBr will be used as an internal standard. Given the long atmospheric lifetime of CF_2ClBr (50,17), it will be fairly uniformly distributed throughout the troposphere of the northern midcontinental United States. As can be seen in Table 6, measurements of this long lived halocarbon are consistent to within ± 0.1 pptv throughout the northern hemisphere.

Table 6. Measurements of CF_2ClBr by NOAA/CMDL

<u>Location</u>	<u>Sampling Date</u>	<u>Concentration^a</u> (pptv)
Alert, NWT, Canada	Dec. 1995	3.4
Pt. Barrow, AK	Dec. 1995	3.44
Niwat Ridge, CO	Dec. 1995	3.5
Mauna Loa, HI	Dec. 1995	3.58
Cape Matatula, Samoa	Dec. 1995	3.39
Cape Grim, Australia	Nov. 1995	2.98
South Pole	Nov. 1995	3.16

^a Data retrieved from NOAA/CMDL data base
file://ftp.cmdl.noaa.gov/noaa/halons/h1211_96.txt

Therefore, measurements of CF_2ClBr (H-1211) made in Boulder, CO by (42) can be used, in conjunction with relative responses of H-1211 to other brominated compounds, to estimate the atmospheric concentration of the brominated compounds in this study (Tables 7 and 8). In Figure 26, CF_2ClBr has been tracked at Niwat Ridge (outside Boulder, CO) from 1989 to early 1996. I have extrapolated the data to include the sampling period of our study. With the apparent leveling off (slowed rate of increase) of the H-1211 concentration data collected at Niwat Ridge, a relatively constant tropospheric concentration of 3.5 pptv, for CF_2ClBr was assumed. Based on this value of CF_2ClBr , and knowing the response efficiencies of the other compounds relative to CF_2ClBr (Table 7) allowed CF_2ClBr to be used as an internal standard. This internal standard method was then used to determine the atmospheric concentration of the other six brominated compounds measured in this study, see Table 8. Relative responses were determined in our laboratory by making an approximately 200 ppmv concentration mixture containing CH_3Br , CF_2Br_2 , $\text{C}_2\text{F}_4\text{Br}_2$, CH_2ClBr , CH_2Br_2 , and CHBr_3 , and CF_2ClBr .

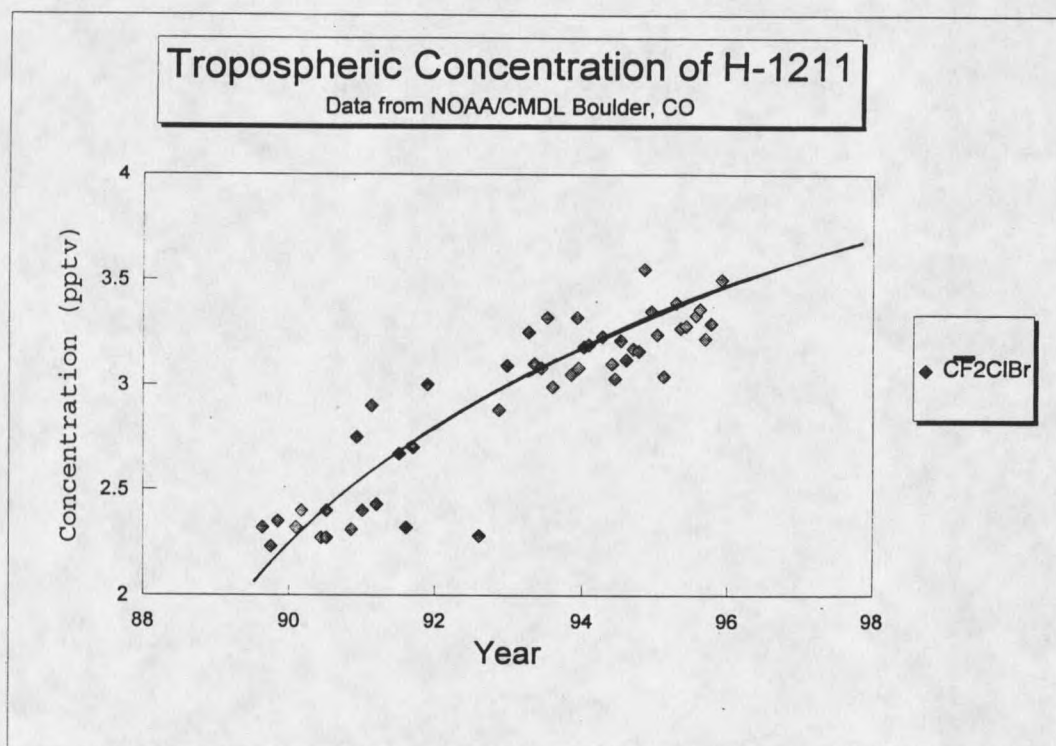


Figure 26. Tropospheric concentration of CF₂ClBr measured at Niwat Ridge, Boulder, CO by NOAA/CMDL from 1989 through 1995.

The mixture was then analyzed to determine the relative response of each compound to CF_2ClBr while monitoring both isotopes of the Br^+ fragment ion, see Table 7. Relative responses were also determined for CF_2ClBr , CF_2Br_2 , and $\text{CF}_2\text{BrCF}_2\text{Br}$ with respect to the CF_2Br^+ ions (Table 7).

Atmospheric concentrations in Table 8 were determined from the average of a number of samples collected between December 1996 and April 1997. The concentration of individual compounds were determined using the following equation (Eq. 20).

$$C_{\text{BC}} = ((C_{\text{IS}} * A_{\text{BC}}) / (RR * A_{\text{IS}})) \quad (20)$$

C_{BC} is the concentration of the brominated compound to be determined. C_{IS} is the concentration of the internal standard (CF_2ClBr) and has been determined to be 3.5 pptv. RR is the relative ratio from Table 7 for the brominated compound being analyzed. A_{BC} and A_{IS} are the chromatographic areas, for the brominated compound of interest and CF_2ClBr respectively. Areas are determined by monitoring Br^+ or CF_2Br^+ , after the introduction of an air sample into the analysis system.

Table 7. Relative Responses of select Brominated Compounds to CF_2ClBr .

<u>Compound</u>	<u>Br^+ ion</u>	<u>CF_2Br^+ ion</u>
CF_2ClBr	1.0	1.0
CH_3Br	0.60	
CF_2Br_2	2.1	6.4
$\text{CF}_2\text{BrCF}_2\text{Br}$	1.0	3.0
CH_2ClBr	1.4	
CH_2Br_2	2.9	
CHBr_3	5.1	

Table 8. Atmospheric Concentration of Brominated Compounds analyzed with DB-VRX Column.

<u>Compound</u>	<u>Measured^a</u>	<u>Detection^b</u>	<u>Ion used</u>
	<u>Conc.</u>	<u>Limit</u>	<u>for DL</u>
	<u>(pptv)</u>	<u>(ppqv)</u>	<u>(m/z)</u>
CF_2ClBr	3.5 ^c	19	85
CH_3Br	10.8	29	96
CF_2Br_2	0.04	11	131
$\text{CF}_2\text{BrCF}_2\text{Br}$	0.32	15	179
CH_2ClBr	0.07	11	130
CH_2Br_2	0.43	1	174
CHBr_3	0.20	1	173

^a A relative uncertainty of plus-or-minus 16% has been assigned to these measurements.

^b For 340 cc sample

^c Adjusted so that atmospheric concentration of CF_2BrCl is in agreement with Montzka et al., 1996, 3.5 pptv.

The estimated tropospheric concentration of CH_3Br by comparison of the response of CH_3Br at $m/z = 80.9163$ to that of CF_2BrCl indicated an average concentration of 11 pptv in the air samples. Previously reported determinations of this compound in background air are 12-15 [(58), 1985, N.Hem] 10 [(60), 1992] 14 [(61), 1992] and 12 pptv [(59), 1995].

The estimated tropospheric concentration of CH_2Br_2 by comparison of the response at $m/z = 80.9163$ to that of CF_2BrCl indicated an average concentration of 0.4 pptv in the air samples. Previously reported determinations of this compound in background air are 0.5-1 [(22), 1994, Inland], 3-60 [(29), Arctic], 2.5 [(31), 1984, Arctic], 2.7 [(58), 1985, N. Hem.], 2 [(24), 1996, oceanic].

The estimated tropospheric concentration of CH_2ClBr by comparison of the response at $m/z = 80.9163$ to that of CF_2BrCl indicated an average concentration of 0.07 pptv in the air samples. Previously reported determinations of this compound in background air are 2 [(31), 1984, Arctic]

The estimated tropospheric concentration of CHBr_3 by comparison of the response at $m/z = 80.9163$ to that of

CF_2BrCl indicated an average concentration of 0.2 pptv in the air samples. Previously reported determinations of this compound in background air are 0.2-0.5 [(22), 1994, Inland], 2-46 [(29), 1982, Arctic], 0.85 [(58), 1985, N. Hem.] 1-2 [(24), 1996, Oceanic].

The estimated tropospheric concentration of CF_2Br_2 by comparison of the response at $m/z = 128.9151$ to that of CF_2BrCl indicated an average concentration of 0.04 pptv in the air samples. To our knowledge this is the first time this compound has been detected in the atmosphere.

The estimated tropospheric concentration of $\text{CF}_2\text{BrCF}_2\text{Br}$ by comparison of the response at $m/z = 80.9163$ and at $m/z = 128.9151$ to that of CF_2BrCl indicated an average concentration of 0.3 pptv in the air samples. Previously reported determinations of this compound in background air are estimated at 0.5-1 [(53), 1992].

Detection Limits A detection limit for each compound was estimated based on a 3:1 signal-to-noise ratio for the ion of each compound that gave the highest signal-to-noise ratio, see Table 8. Detection limits as low

as 1 part-per-quadrillion by volume were achieved (ppqv) for sample sizes of 340 atm-cm³. This compares to 50 ppqv for 800 atm-cm³ samples, while a similar concentration method with analysis by GC/MS was used. (28).

Analysis of Select Bromocarbons from December 1996 to

April 1997 Samples collected from December 1996 through April 1997 and were analyzed for the brominated compounds CF₂ClBr, CF₂Br₂, CF₂BrCF₂Br, CH₃Br, CH₂Br₂, and CHBr₃. Tracking these compounds over this relatively short time period revealed fairly stable concentrations of all compounds, see Figure 27. Figure 27 (Top) shows the two compounds with concentrations greater than 1 pptv, CH₃Br and CF₂ClBr. CF₂ClBr was used as the internal standard and its concentration is assumed to have remained constant at 3.5 pptv over the sampling period. Figure 27 (Bottom) shows the compounds with tropospheric concentrations less than 1 pptv, CF₂BrCF₂Br, CF₂Br₂, CH₂Br₂, and CHBr₃.

Conclusion

The high potential of GC-HRMS for the trace analysis of halocarbons in the atmosphere has been demonstrated here. The increased specificity provided by exact mass monitoring with high resolution greatly increases the confidence with which positive identifications of sought-for-substances can be made. If the HRMS has a large ion-optic system, as in the present study, the high level of sensitivity inherent in GC detection by MS is also maintained. The results by GC-HRMS reported here verify the presence of CF_4 , CHF_2Cl , CF_3Cl , CHF_3 , $\text{CF}_3\text{CF}_2\text{Cl}$, CF_3Br , $\text{CF}_3\text{CH}_2\text{F}$, CH_3Br , $\text{CF}_2\text{BrCF}_2\text{Br}$, CF_2Br_2 , CH_2Br_2 , CHBr_3 , CH_2ClBr , and CF_2BrCl in background air samples of rural Montana. The compounds CF_3H and CF_2Br_2 were detected and identified for the first time in background air.

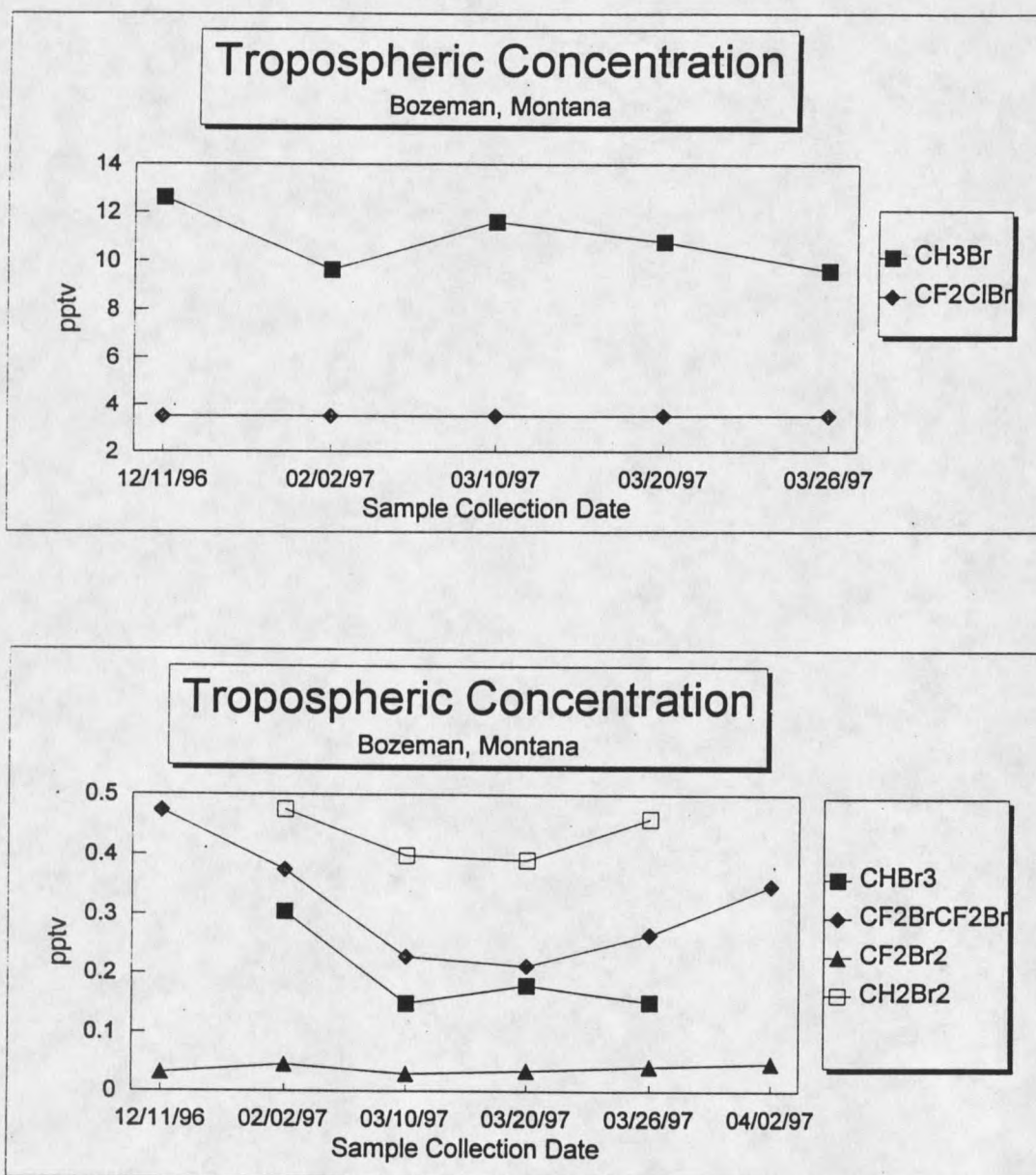


Figure 27. (Top) Tropospheric concentrations of CF₂ClBr and CH₂Br for the sampling period, December 1996 through April 1997. (Bottom) Tropospheric concentrations of CF₂Br₂, CF₂BrCF₂Br, CH₂Br₂, and CHBr₃, for the sampling period of December 1996 through April 1997 in the area of Bozeman, MT.

SUMMARY

The objective of this project was to develop a method for the ultra trace detection and analysis of halogenated compounds in the atmosphere. The analysis of brominated and perfluorinated species were of particular interest to us and the atmospheric chemistry community, in general. This is because of the limited data available regarding atmospheric mixing ratios of these low level (low pptv to sub pptv) atmospheric constituents.

Much of the recent work in the field of atmospheric chemistry has been focused on the design and testing of models which are used to predict the cumulative effects of the many minor chemical components of the atmosphere. Of particular concern are the compounds of anthropogenic origin linked to global warming and stratospheric ozone depletion. Also, in order to design a model one first has to know what chemical species are present and secondly, measurements are necessary to determine the accuracy of a proposed model.

We have developed what we believe is the most sensitive and compound-specific instrument ever dedicated to the analysis of halogenated compounds in the atmosphere. The development of this instrument started by refurbishing a high resolution mass spectrometer (VG-ZAB 2F) that had been donated to the MSU Mass Spectrometry Facility in an inoperable condition by Battelle Northwest Laboratories. The mass spectrometer was thoroughly overhauled, including the replacement of many of the electronic components. Once the mass spectrometer was operational, a new gas chromatograph and new data system were interfaced to the instrument. Additionally, an air-sampling system was developed and assembled in our laboratory. This system will allow volumes up to 1000 atm-cm³ of air to be preconcentrated and injected onto a capillary GC column.

Additionally, a system was designed and constructed for remote air sampling. A 12-volt diaphragm pump allowed us to collect samples in electropolished stainless steel canisters from remote locations. The samples were pressurized to approximately 35 psi and then transported to the MSU Mass Spectrometry Facility for analysis by GC-HRMS.

Two primary groups of compounds were analyzed in this work. First, the compounds containing a CF_3^+ fragment ion with a boiling point less than -26°C , and chromatographed on a J&W GS-Q capillary column. Second, bromine containing compounds eluting from a J&W DB-VRX capillary column and detected while monitoring the Br^+ fragment ion. The compounds were positively identified by monitoring most of the major peaks expected in the electron ionization mass spectrum of each compound and by matching retention time to that of a standard.

The compounds detected and then identified from the CF_3^+ single ion monitoring experiments are CF_4 , CF_3H , CF_3Cl , CF_3Br , $\text{CF}_3\text{CF}_2\text{Cl}$, and CF_3CFH_2 . Those compounds detected and then identified from the Br^+ monitoring experiments are as follows; CF_2ClBr , CH_3Br , CF_2Br_2 , $\text{CF}_2\text{BrCF}_2\text{Br}$, CH_2ClBr , CH_2Br_2 , and CHBr_3 . To our knowledge this is the first time CF_3H or CF_2Br_2 have been detected and identified in background air. A likely source of CF_3H is associated with the production of aluminum. A gas sample was provided to us from the fume hoods of an aluminum manufacturer, where elevated levels of CF_4 and C_2F_6 were detected, as expected, along with elevated

levels of CF_3H . The source of CF_2Br_2 is unknown at the present time, but it can be speculated that it is a byproduct or contaminant associated with one of the other halons, such as CF_3Br or CF_2ClBr .

The initial phase of this project was to develop the instrumental capabilities to detect and identify atmospheric halocarbons at very low concentrations (< 5 pptv). We have demonstrated the high sensitivity of our instrumentation by achieving estimated detection limits almost two orders of magnitude lower than similar, current GC/MS methods. Also, the stability of the instrumentation was demonstrated by analyzing a sample 8 times over the course of a 10 hour period with less than a 1% deviation in peak area detected.

The quantitative aspects of this project have proven extremely challenging. We have been unsuccessful at making low level calibration standards (low pptv) with a high level of accuracy. This was expected, due to the well-known difficulty, if not the impossibility, of making accurate gas standards below the ppmv range (40,41). All quantitative data reported are linked to measurements made by other groups (see Tables 5 and 8). Therefore, no claims as to the

absolute atmospheric concentrations of the chemical species reported here can be made.

The future of this project lies in developing superior methods of quantitation. The difficulties encountered in preparing low pptv gas standards are predominantly due to the uncertainties related to wall effects in the storage vessels. One way to reduce the significance of wall effects is to use larger storage vessels. For example, the volume of a sphere increases in proportion to radius cubed, whereas the surface area increases proportional to radius squared. Therefore, a larger container will have proportionally less surface area and should minimize the uncertainties related to surface effects. Also, if the container is significantly large ($>25 \text{ m}^3$), one could use the method of standard additions for quantitation. The method of standard additions has the added benefit of accounting for sample matrix effects, because the calibration standard is added directly to the sample and will undergo all sample processing procedures. This may be the only way one could report absolute atmospheric halocarbon concentrations with high level of accuracy.

REFERENCES

1. Carson, R. , Silent Spring, The Riverside Press, 1962.
2. Grimsrud, E.P. and Rasmussen, R.A. , Analysis of chlorofluorocarbons in the troposphere by gas chromatography - mass spectrometry, Atmos. Environ. , 9, 1014-1017, 1975a.
3. Grimsrud, E.P. and Rasmussen, R.A. , Survey and analysis of halocarbons in the atmosphere by gas chromatography - mass spectrometry, Atmos. Environ. 9, 1010-1013, 1975b.
4. Crutzen, P.J. , My Life with O₃, NO_x, and Other YZO_x Compounds (Nobel Lecture), Angew. Chem. Int. Engl. , 35, 1758-1777, 1996.
5. McElroy, M.B. and Salawitch, R.J. , Changing composition of the global stratosphere, Science, 243, 763-770, 1989.
6. Solomon, S. , Mills, M. , Heidt, L.E. , Pollock, W.H. and Tuck, A.F. , On the evaluation of ozone depletion potential, J. Geophys. Res. 97, 825-842, 1992.
7. Fisher, D.A. , Hales, C.H. , Filkin, D.L. , Ko, M.K.W. , Dak.Sze, N. , Connell, P.S. , Wuebbles, D.J. , Isaksen, I.S.A. and Stordal, F. , Model calculations of the relative effects of CFC's and their replacements on stratospheric ozone, Nature 344, 508-512, 1990a.
8. Rowland, F.S. , Stratospheric Ozone In the 21st Century The Chlorofluorocarbon Problem, Environ. Sci. Technol. 25, 622-628, 1991.
9. Rodriguez, J.M. , Probing Stratospheric Ozone, Science 261, 1128-1158, 1993.
10. Anderson, J.G. , Toohey, D.W. , and Brune, W.H. , Free Radicals Within the Antarctic Vortex: The Role of CFC's in Antarctic Ozone Loss, Science 251, 39-46, 1991.
11. Cicerone, R.J. , Fires, Atmospheric Chemistry, and the Ozone Layer, Science 263, 1243-1244, 1994.

12. Hileman, B. , Storm Warnings Rattle Insurers, C&EN, April 14, 28-31, 1997..
13. Schneider, S.H. , The Greenhouse Effect: Science and Policy, Science **243**, 771-779, 1989.
14. Fisher, D.A. , Hales, C.H. , Wang, W.C. , Ko, K.W. , and Sze, N.D. , Model calculations of the relative effects of CFC's and their replacements on global warning, Nature **344**, 513-516, 1990.
15. Ravishankara, A.R. , Solomon, S. , Turnipseed, A.A. and Warren, R.F. , Atmospheric lifetimes of long-lived halogenated species, Science, **259**, 194-199, 1993.
16. Fabian, P. , Borchers, P.R. , Penkett, S.A. , and Prosser, N.J.D. , Halocarbons in the stratosphere, Nature **294**, 733-735, 1981..
17. Prather, M.J. and Watson, R.T. , Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine, Nature, **344**, 729-734, 1990.
18. Singh, H.B. , Salas, L.J. , and Stiles, R.E. , Methyl Halides in and Over the Eastern Pacific (40°N-32°S), Journal of Geophysical Research **88**, 3684-3749, 1983.
19. Thompson, T.M. , Elkins, J.W. , Butler, J.H. , Montzka, S.A. , Myers, R.C. , Baring, T.J. , Cummings, S.O. , Dutton, G.S. , Gilligan, J.M. , Hayden, A.H. , Lobert, J.M. , Swanson, T.H. , Hurst, D.F. and Volk, C.M. , Nitrous oxide and halocarbon division, in Climate Monitoring and Diagnostics Laboratory, Report No. 22, Department of Commerce, 72-91, 1993.
20. Borchers, R. , Fabian, P. , Singh, O.N. , Lal, S. and Subbaraya, B.H. , Ozone in the Atmosphere (Bojkov, R.D. and Fabian, P. (eds.), pp. 290-293, A. Deepak Publishing, VA, 1988.

21. Fisher, D.A. , Hales, C.H. , Wang, W. , Ko, M.K.W. and Dak Sze, N. , Model calculations of the relative effects of CFC's and their replacements on global warming, Nature **344**, 513-516, 1990b.
22. Kaye J.A. , Penkett S.A. , Report on the Concentrations, Lifetimes, and Trends of CFC's, Halons, and Related Species, NASA Ref. Pub. 1339, 1994.4. Molina, M.J. , Polar Ozone Depletion (Nobel Lecture), Angew. Chem. Int. Engl. , **35**, 1778-1785, 1996.
23. Jugern et al. , BLAST94: Bromine Latitudinal Air/Sea Transect 1994, NOAA Technical Memorandum ERL CMDL-10, 1996.
24. Butler, J.H. , and Rodriguez, J.M. , Methyl Bromide in the Atmosphere, The Methyl Bromide Issue, chapter 2, 1996.
25. Lovelock, J.E. , Atmospheric fluorine compounds as indicators of air movements, Nature, Lond. **230**, 379, 1971.
26. Lovelock, J.E. , Maggs, R.J. and Wade, R.J. , Halogenated hydrocarbons in and over the Atlantic, Nature, Lond. **241**, 194-196, 1973.
27. Grimsrud, E.P. and Miller, D.A. , Oxygen doping of the electron capture detector in measurements of halogenated methane's by gas chromatography with electron capture detection, Anal. Chem. **50**, 1141-1145, 1978.
28. Montzka, S.A. , Myers, R.C. , Butler, J.H. , and Elkins, J.W. , Observations of HFC-134a in the remote troposphere, Geophysical Research Letters **23**, 169-172, 1996.
29. Berg, W.W. , Heidt, L.E. , Pollock, W. , Sperry, P.D. , and Cicerone, R.J. , Brominated Organic Species in the Arctic Atmosphere, Geophysical Research Letters **11**, 429-432, 1984.
30. Butler, J.H. , Elkins, J.W. , Hall, B.D. , Cummings, S.O. and Montzka, S.A. , A decrease in the growth rates of atmospheric halon concentrations, Nature, **359**, 403-405, 1992.

31. Rasmussen, R.A. , and Khalil, M.A.K. , Gaseous Bromine in the Arctic and Arctic haze, Geophysical Research Letters **11**, 433-436, 1984.
32. Solomon, S. , Garcia, R.R. , Ravishandara, A.R. , On the role of iodine in ozone depletion, Journal of Geophysical Research **99**, 20,491-20,499, 1994.
33. Atkinson, R. , Gas-Phase Tropospheric Chemistry of Organic Compounds: A Review, Atmospheric Environment **24A**, 1-41, 1990.
34. Salawitch et al. , Chemical Loss of ozone in the Arctic Polar Vortex in the Winter of 1991-1992, Science, **261**, 1993.
35. Toon et al. , Heterogeneous Reactions Probabilities, Solubility's, and the Physical State of Cold Volcanic Aerosols, Science, **261**, 1993.
36. Singh et al. , Measurements of atmospheric BrO_x radicals in the tropical and mid-latitude atmosphere, Nature, **334**, 1988.
37. Hills et al. , Kinetics of the BrO+ClO reaction and implications for stratospheric ozone, Nature, **328**, 1987.
38. Webster et al. , Chlorine Chemistry on Polar Stratospheric Cloud Particles in the Arctic Winter, Science, **261**, 1993.
39. Weston, Jr, R. E. , Possible greenhouse effects of tetrafluoromethane and carbon dioxide emitted from aluminum production, Atmos. Environ. , **30**, 2901-2910, 1996.
40. Denyszyn, R.B. , Sassaman, T. , Part Per Billion Gaseous Mixtures - A New Challenge, Pittsburgh Conference, 1986.
41. Nelson, G.O. , Gas Mixtures - Preparation and Control, Lewis Publishers, 1992.

42. Montzka, S.A. , Butler, J.H. , Myers, R.C. , Thompson, T.M. , Swanson, T.H. , Clarke, A.D. , Lock, L.T. and Elkins, J.W. , Decline in the tropospheric abundance of halogen from halocarbons: implications for stratospheric ozone depletion, Science, **272**, 1318-1322, 1996.
43. Montzka, S.A. , Myers, R.C. , Butler, J.H. , and Elkins, J.W. , Global Tropospheric Distribution and Calibration Scale of HCFC-22, Geophysical Research Letter **20**, 703-706, 1993.
44. Cicerone, R.J. , Atmospheric carbon tetrafluoride: a nearly inert gas, Science **206**, 59, 1979.
45. Rasmussen, R.A. , Penkett, S.A. and Prosser, N. , Measurement of carbon tetrafluoride in the atmosphere, Nature **277**, 549, 1979.
46. Penkett, S.A. , Prosser, N.J.D. , Rasmussen, R.A. and Khalil, M.A.K. , Atmospheric measurements of CF₄ and other fluorocarbons containing the CF₃ grouping, J. Geophys. Res. **86**, 5172-5168, 1981.
47. Windhlolz, M. , The Merck Index, 10th Edition, Merck & Co. , Inc. , Rahway, NJ. p. 1447, 1983.
48. Butler, J.H. , Methyl bromide under scrutiny, Nature **376**, 469, 1995.
49. Lobert, J.M. , Butler, J.H. , Montzka, S.A. , Geller, L.S. , Myers, R.C. , and Elkins, J.W. , A Net Sink for Atmospheric CH₃Br in the East Pacific Ocean, Science **267**, 1001-1005, 1995.
50. Lal, S. , Borchers, R. , Fabian, P. , and Krüger, B.C. , Increasing abundance of CBrClF₂ in the atmosphere, Nature **316**, 135-136, 1985.
51. Manö, S. , and Andreae, M.O. , Emission of Methyl Bromide from Biomass Burning, Science **263**, 1255-1257, 1994.

52. Cicerone, R.J. , Heidt, L.E. , and Pollock, W.H. , Measurements of Atmospheric Methyl Bromide and Bromoform, Journal of Geophysical Research 93, 3745-3749, 1988.
53. Butler et al. , A Decline in the Growth Rate of Atmospheric Halons, Submitted to Nature, 1992.
54. Fabian, P. , Borchers, R. , Kruger, C. and Lal, S. , CF₄ and C₂F₆ in the atmosphere, J.Geophys.Res. 92, 9831-9835, 1987.
55. Fabian, P. , in Handbook of Environmental Chemistry, Vol. 4A, Hutsinger (ed.), pp. 24, Springer, Berlin, 1986.
56. Zander, R. , Rinsland, C.P. , Farmer, C.B. and Norton, R.H. , Infrared spectroscopic measurements of halogenated source gases in the stratosphere with the ATMOS instrument, J.Geophys.Res. 92, 9836-9850, 1987.
57. Channin, M. , Ehhalt, D. , Fraser, P. , Frederick, J. , McCormick, M. , Megie, G. and Schoeberl, M. , Global trends, in WMO Global Ozone Research and Monitoring Project Report No. 20, pp. 162-281, 1990.
58. Penkett, S. , Jones, B. , Rycroft, B. and Simmons, D. , Interhemispheric comparison of the concentrations of bromine compounds in the atmosphere, Nature 318, 550-553, 1985.
59. Rhoderick, G.C. , Measurements of atmospheric methyl bromide using gravimetric gas standards, Environ. Sci. Technol. , 29, 2797-2800, 1995.
60. Rowland, R.S. , in Methyl Bromide Science Workshop Proceedings, Atmospheric and Environmental Research, Inc, Cambridge, MA, 1992.
61. Heidt, L.E., in Methyl Bromide Science Workshop Proceedings, Atmospheric and Environmental Research, Inc, Cambridge, MA, 1992.

62. Elkins, J.W. , Thompson, T.M. , Swanson, T.H. , Butler, J.H. , Hall, B.D. , Cummings, S.O. , Fisher, D.A. , and Raffen, A.G. , Slowdown in the Growth Rates of Atmospheric Chlorofluorocarbons 11 and 12: Result of the Montreal Protocol, Elkins et al. , 1992.
63. Khalil, M.A.K. , Rasmussen, R.A. , and Gunawardena, R. , Atmospheric Methyl Bromide: Trends and Global Mass Balance, Journal of Geophysical Research **98**, 2887-2896, 1993.
64. Shorter, J.H. , Kolb, C.E. , Crill, P.M. , Kerwin, R.A. , Talbot, R.W. , Hines, M.E. , and Harriss, R.C. , Rapid degradation of atmospheric methyl bromide in soils, Nature **377**, 717-719, 1995.
65. Toohey et al. , The Seasonal Evolution of Reactive Chlorine in the Northern Stratosphere, Science, **261**, 1993.
66. Lovelock, J.E. , Natural halocarbons in the air and in the sea, Nature **256**, 193-194, 1975.
67. Lobert, J.M. , Butler, J.H. , Montzka, S.A. , Geller, L.S. , Myers, R.C. , and Elkins, J.W. , A Net Sink for Atmospheric CH₃Br in the East Pacific Ocean, Science **267**, 1002-1005, 1995.
68. Schauffler, S.M. , Heidt, L.E. , Pollock, W.H. , Gilpin, T.M. , Vedder, J.F. , Solomon, S. , Lueb, R.A. , and Atlas, E.L. , Measurements of Halogenated Organic Compounds Near the Tropical Tropopause, Geophysical Research Letters **20**, 2567-2570, 1993.
69. Prather, M.J. , and Watson, R.T. , Stratospheric ozone depletion and future levels of atmospheric chlorine and bromine, Nature **344**, 729-734, 1990.
70. Harper, D.B. , Halomethane from halide ion-a highly efficient fungal conversion of environmental significance, Nature **315**, 55-57, 1985.

71. Goldstein, A.H. , Wofsy, S.C. , and Spivakovsky, C.M. , Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern midlatitudes, Journal of Geophysical Research **100**, 21,023-21,033, 1995.
72. Lefevre, C. , Ferrari, P. , Guenier, J.P. , and Muller, J. , Sampling and Analysis of Airborne Methylbromide, Chromatographia **27**, 37-43, 1989.
73. Sharp, G.J. , Yokouchi, Y. , Akimoto, H. , Trace Analysis of Organobromine Compounds in Air by Adsorbent Trapping and Capillary Gas Chromatography/Mass Spectroscopy, Environ. Sci. Technol. **26**, 815-816, 1992.
74. Rowland, F.S. , Stratospheric Ozone Depletion by Chlorofluorocarbons (Nobel Lecture), Angew. Chem. Int. Engl. , **35**, 1786-1798, 1996.
75. Wilson et al. , In Situ Observations of Aerosol and Chlorine Monoxide After the 1991 Eruption of Mount Pinatubo: Effect of Reactions on Sulfate Aerosols, Science, **261**, 1993.
76. Newman et al. , Stratospheric Meteorological Conditions in the Arctic Polar Vortex, 1991 to 1992, Science, **261**, 1993.
77. Proffitt et al. , Ozone Loss Inside the Northern Polar Vortex During the Winter of 1991-1992, Science, **261**, 1993.
78. Browell et al. , Ozone and Aerosol Changes During the 1991-1992 Airborne Arctic Stratospheric Expedition, Science, **261**, 1993.

APPENDIX

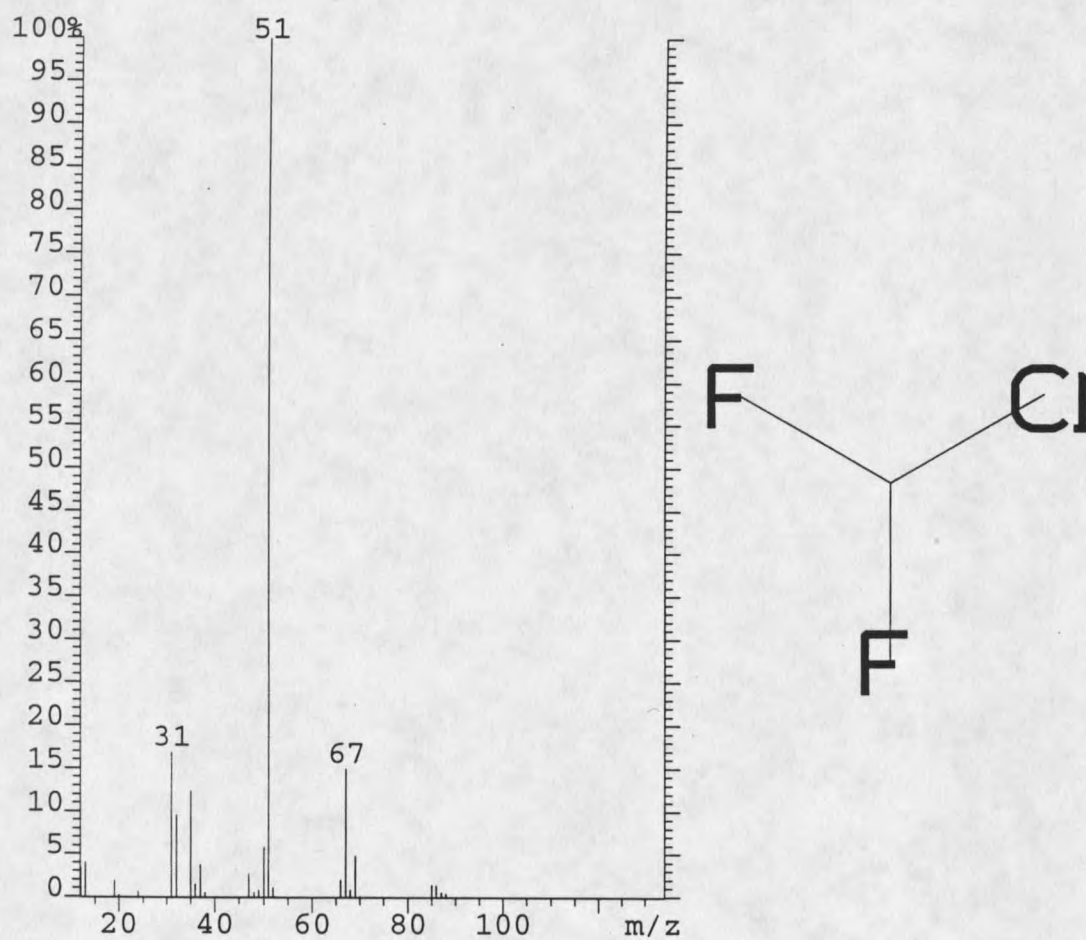


Figure 28. EI mass spectrum of CF_2HCl .

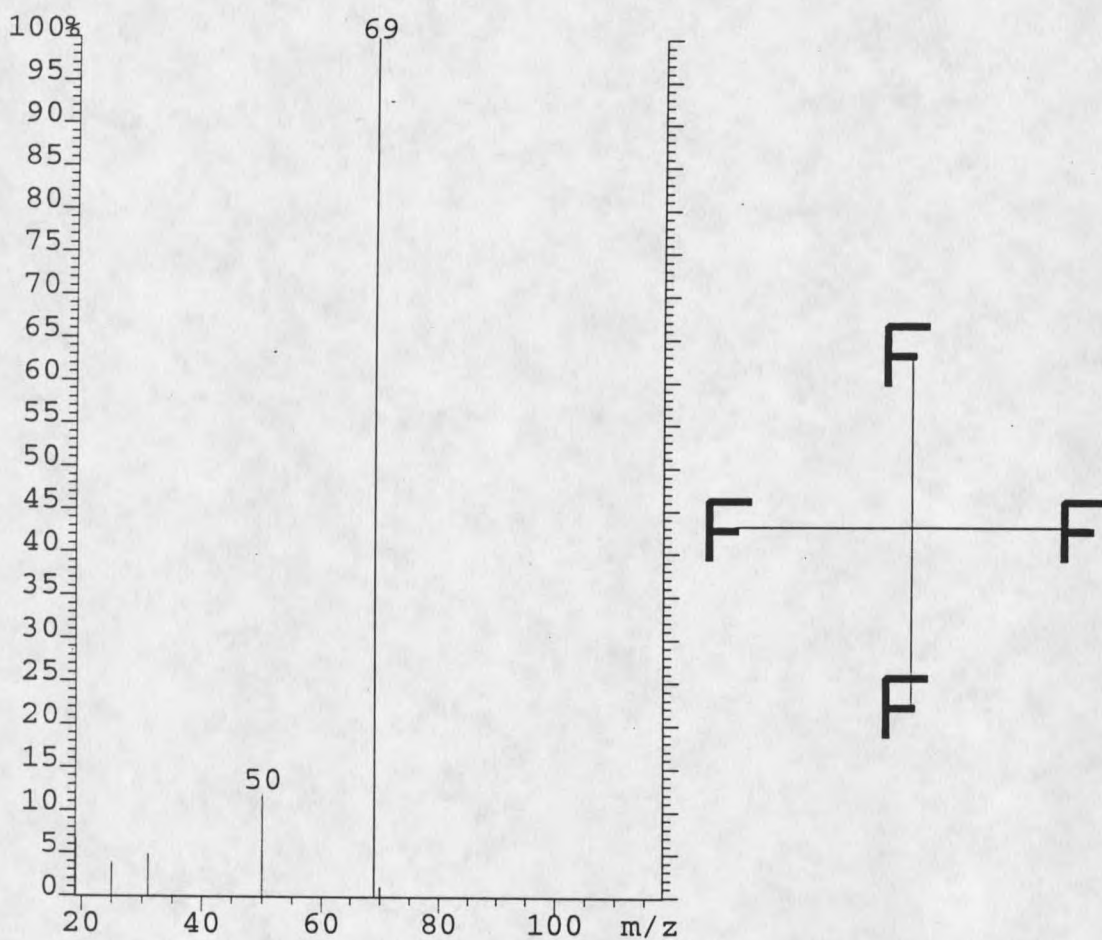


Figure 29. EI mass spectrum of CF_4 .

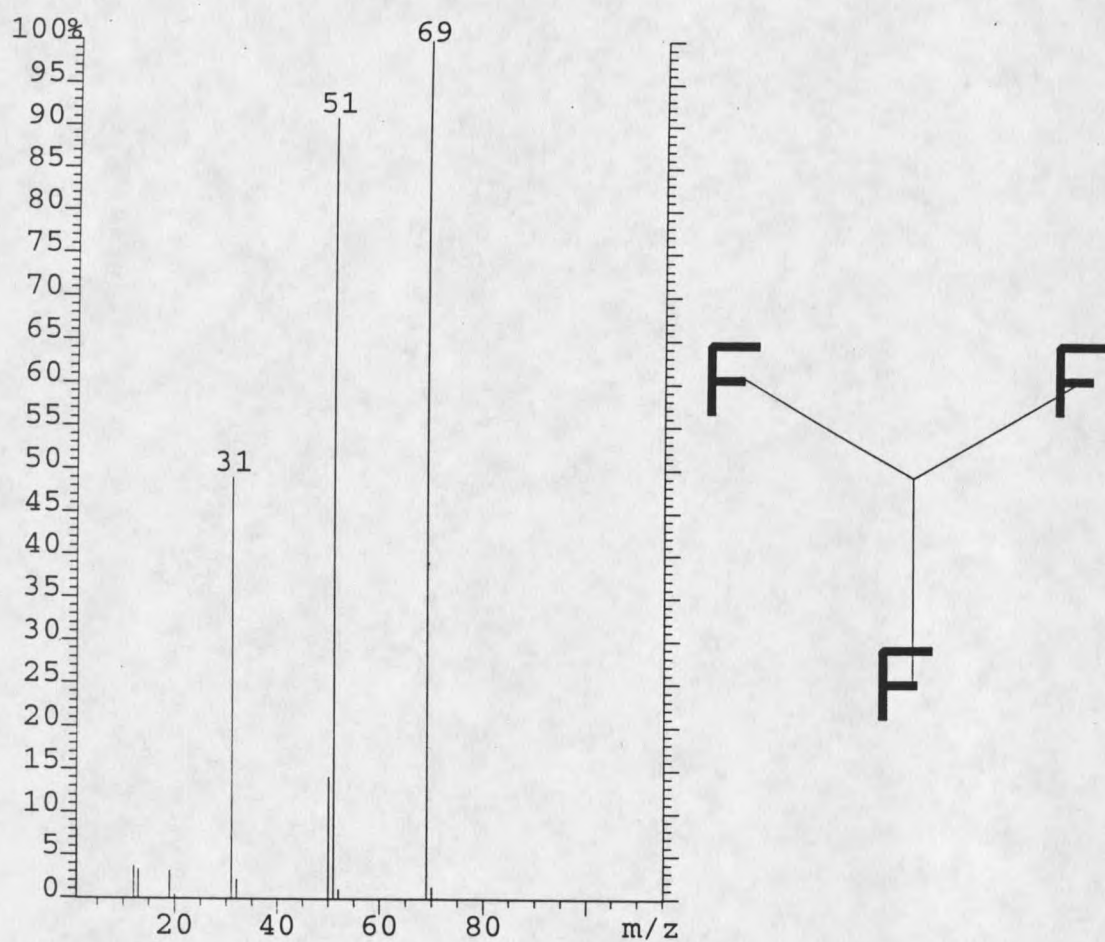


Figure 30. EI mass spectrum of CF_3H .

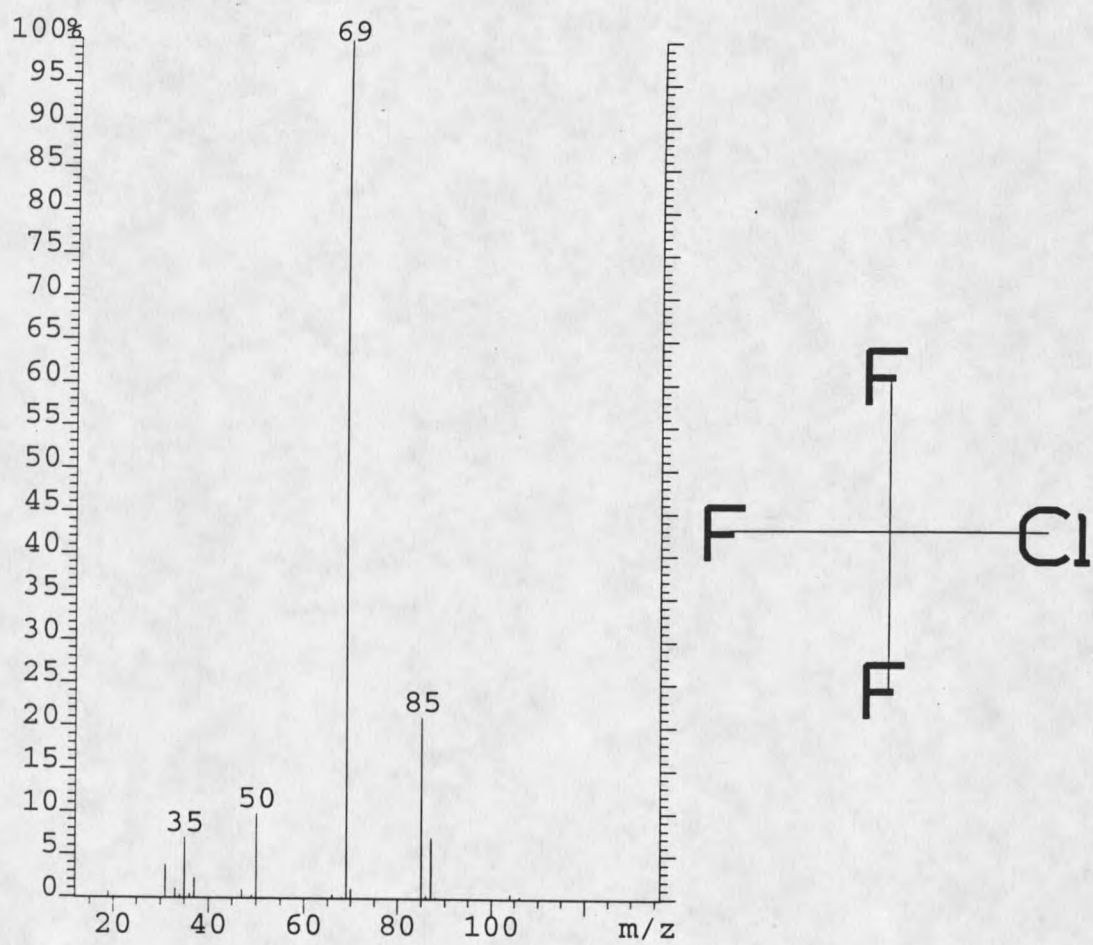


Figure 31. EI mass spectrum of CF_3Cl .

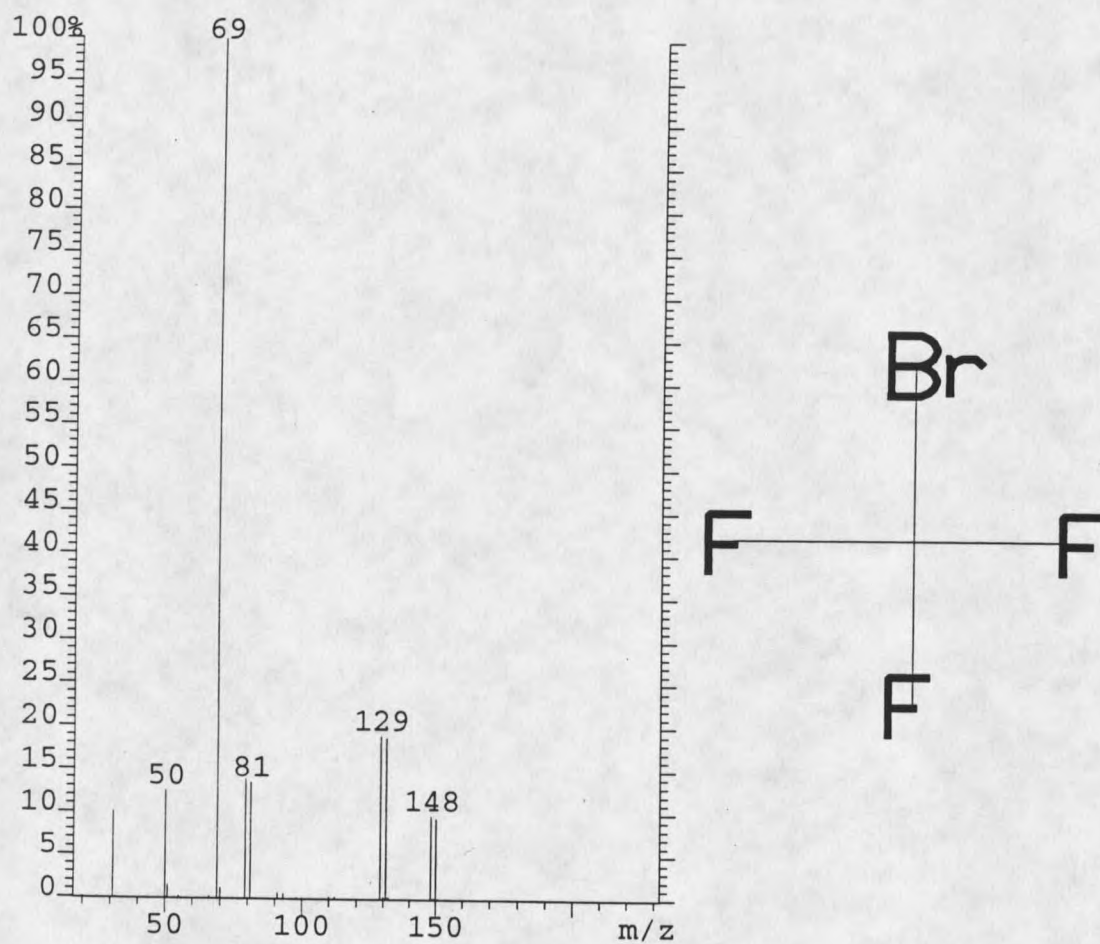


Figure 32. EI mass spectrum of CF₃Br.

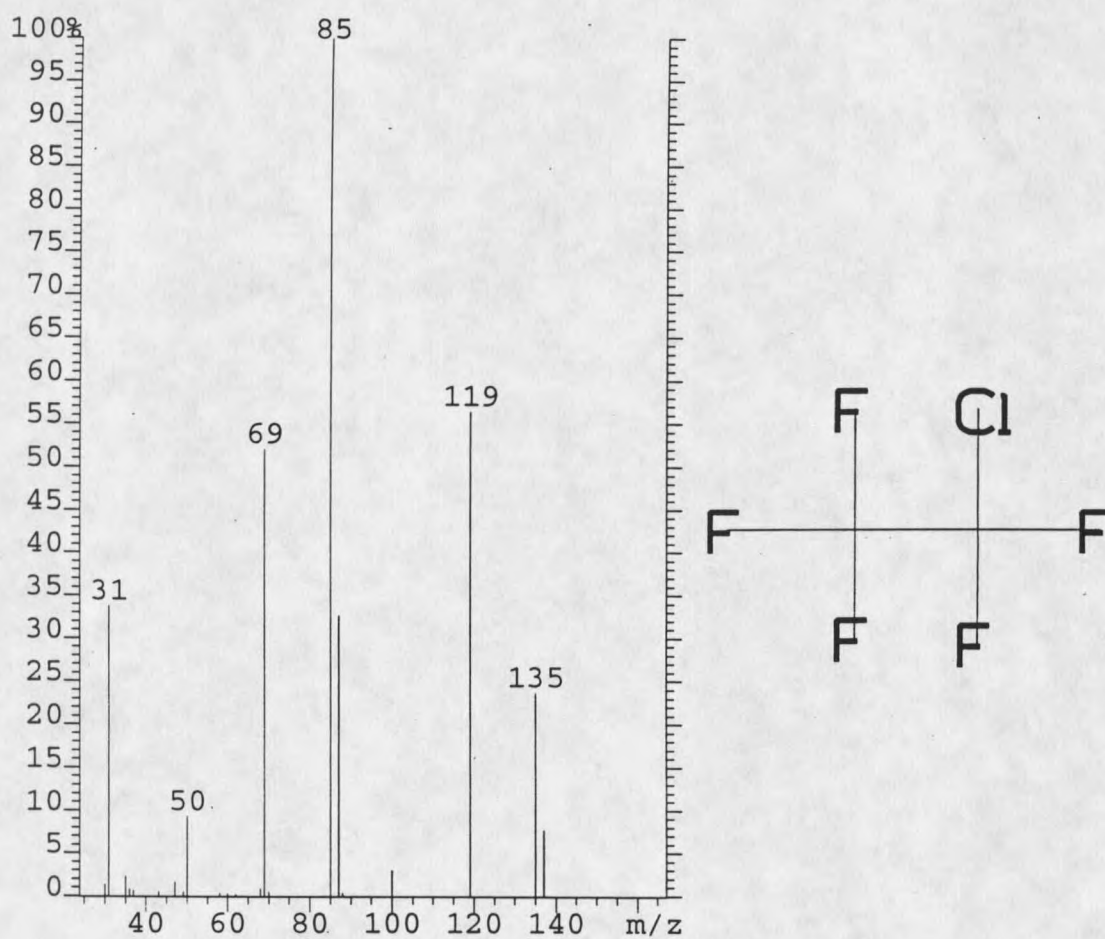


Figure 33. EI mass spectrum of $\text{CF}_3\text{CF}_2\text{Cl}$.

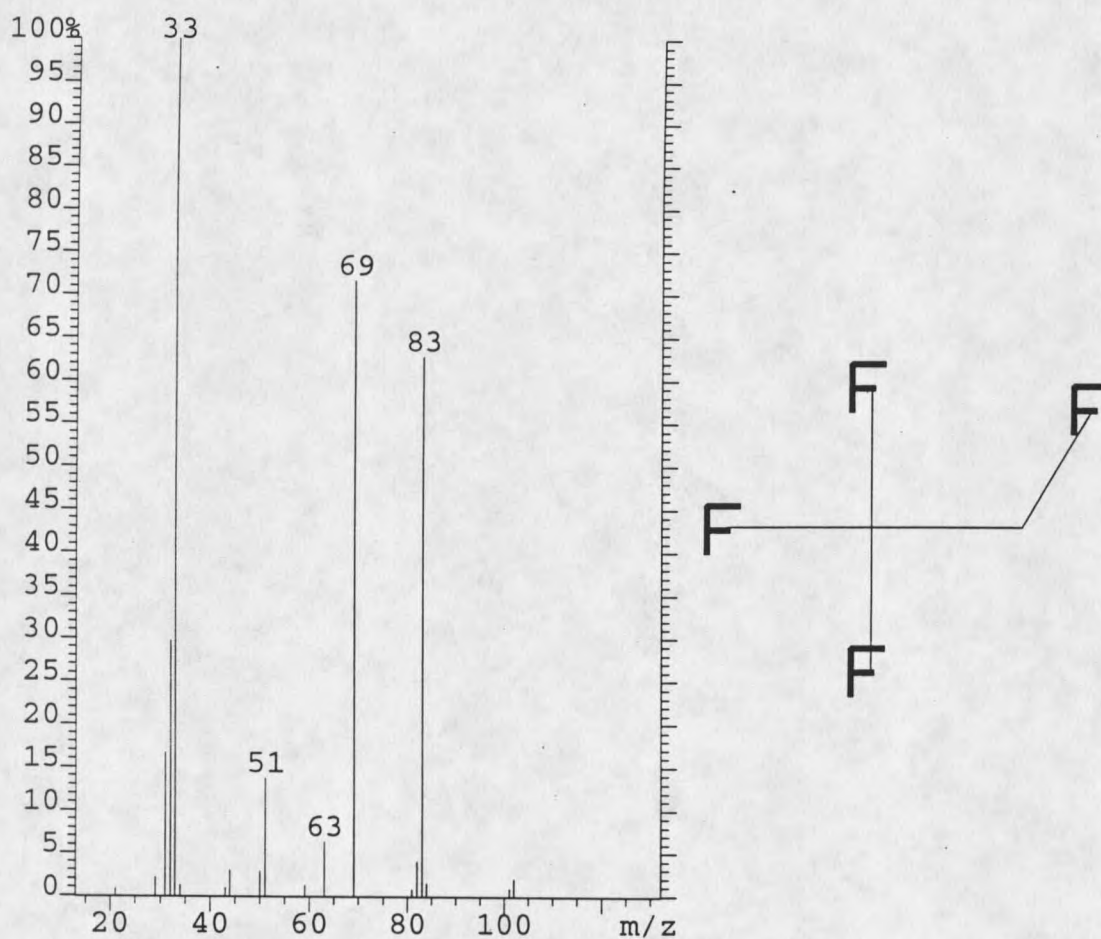


Figure 34. EI mass spectrum of CF_3CFH_2 .

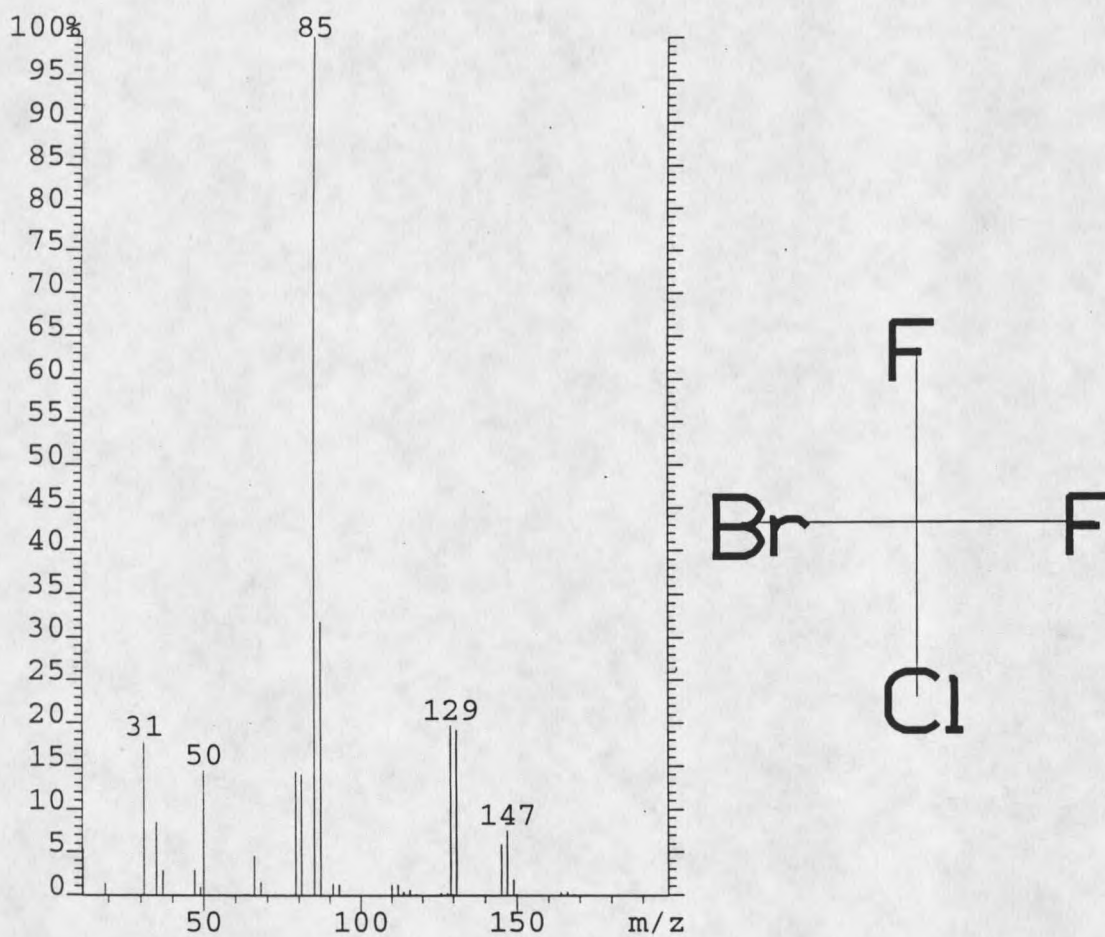


Figure 35. EI mass spectrum of CF_2ClBr .

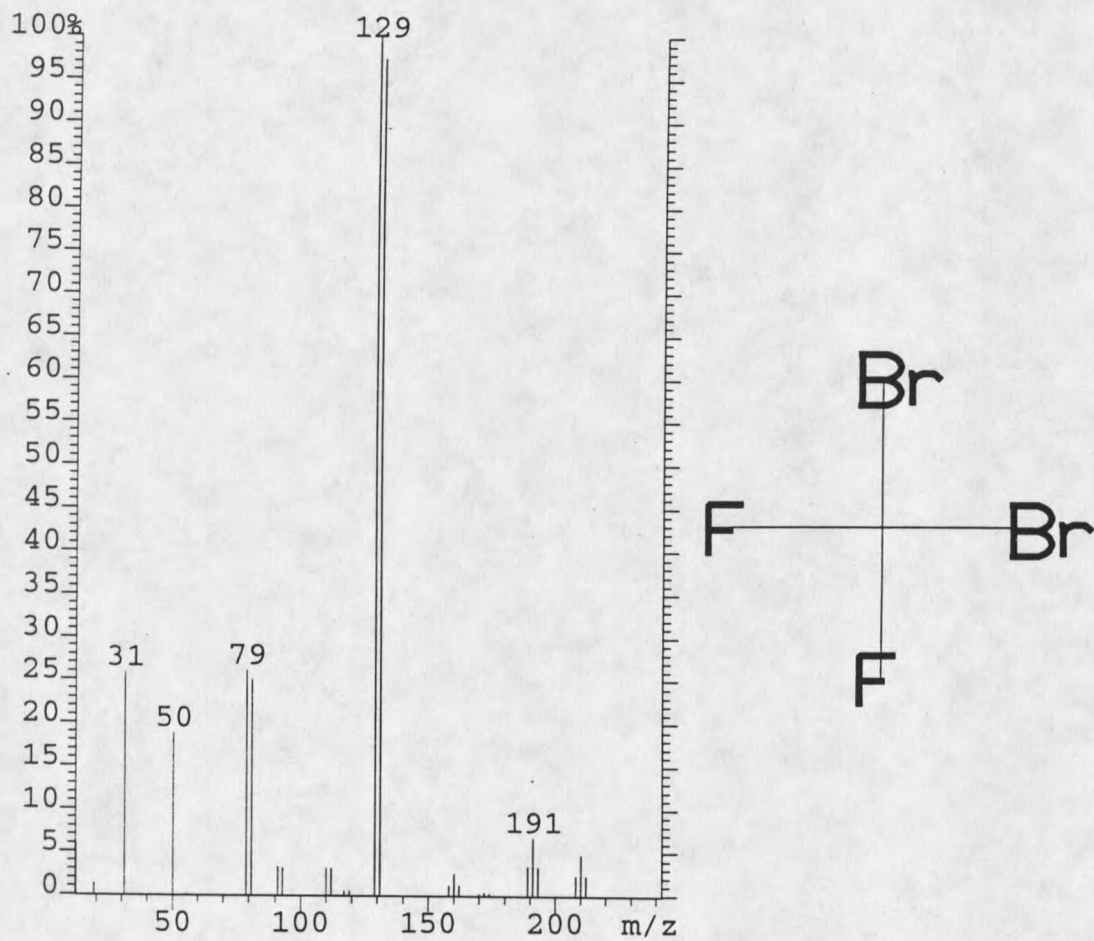


Figure 36. EI mass spectrum of CF_2Br_2 .

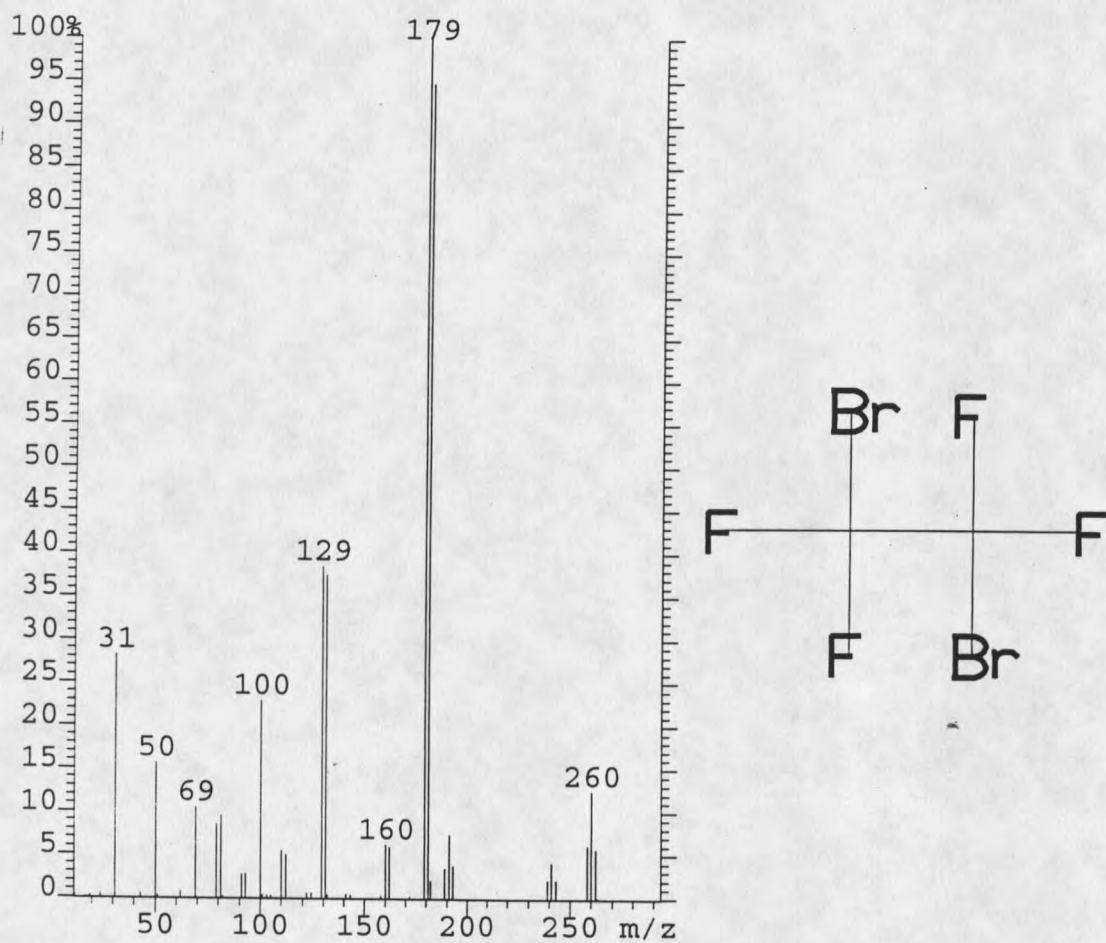


Figure 37. EI mass spectrum of $\text{CF}_2\text{BrCF}_2\text{Br}$.

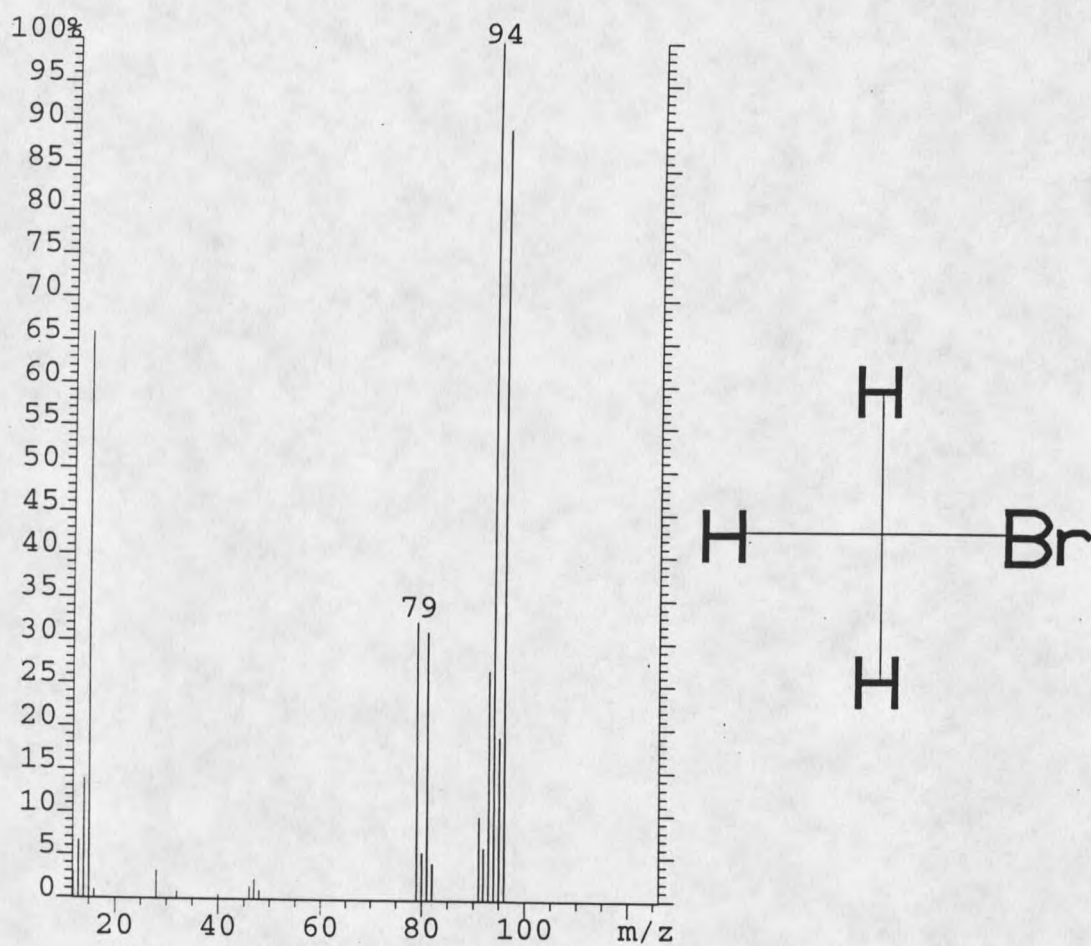


Figure 38. EI mass spectrum of CH_3Br .

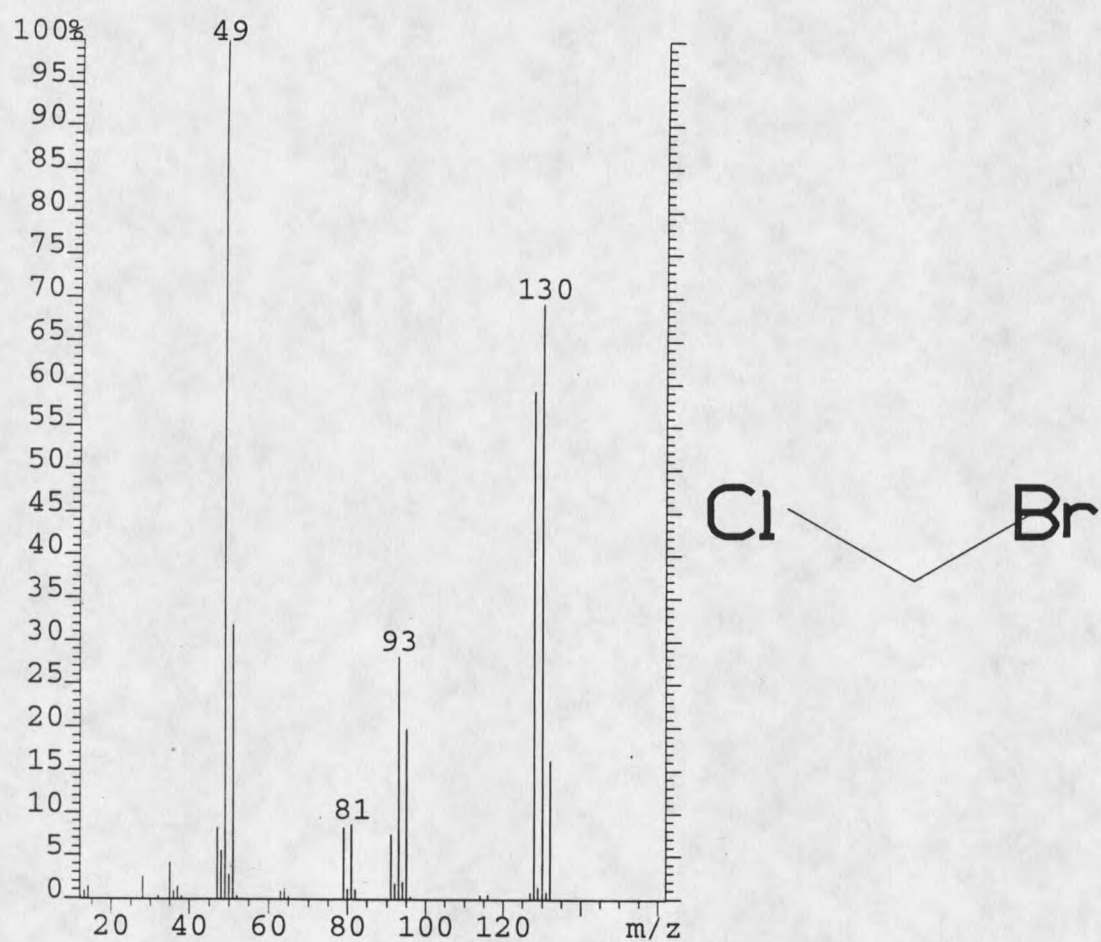


Figure 39. EI mass spectrum of CH_2ClBr .

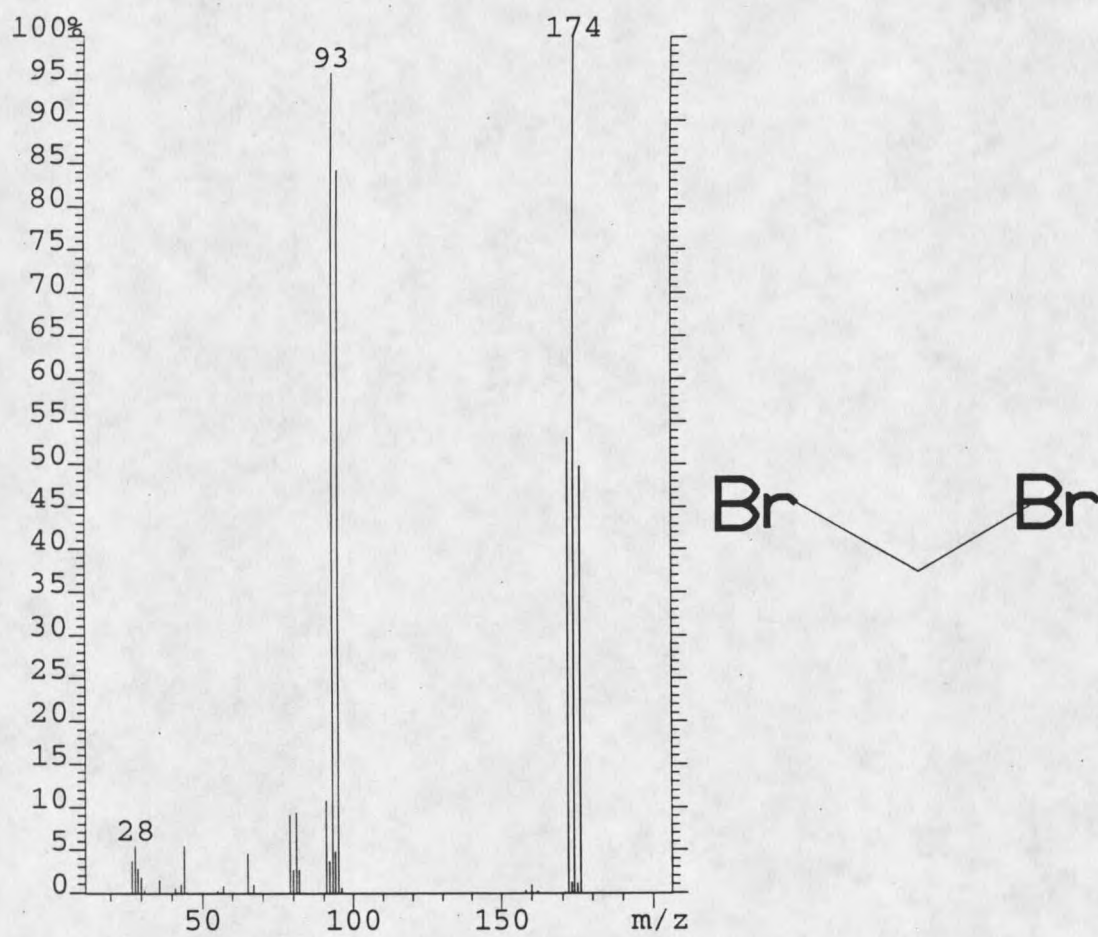


Figure 40. EI mass spectrum of CH_2Br_2 .

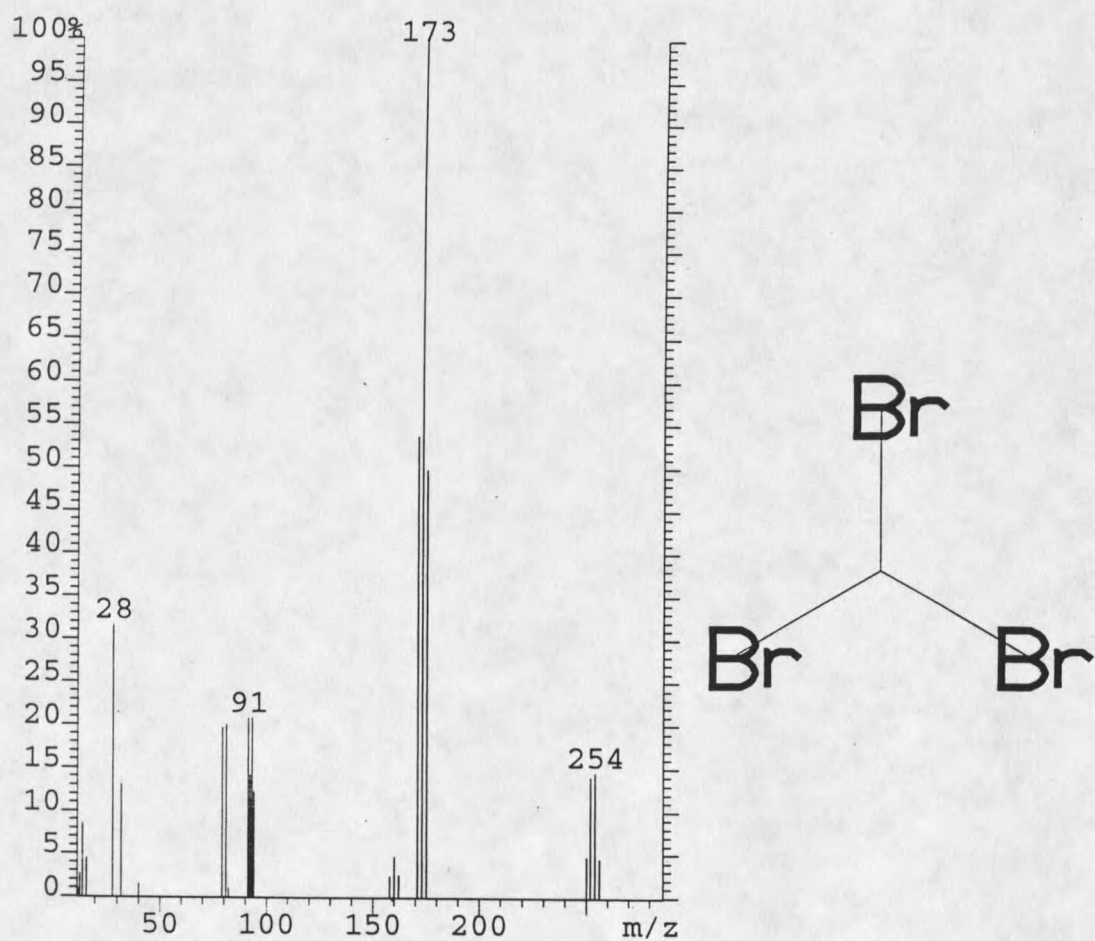


Figure 41. EI mass spectrum of CHBr_3 .

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