



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,  $\text{CF}_3^+$  or  $\text{Br}^+$  will be discussed. Compounds identified while monitoring the  $\text{Br}^+$  ion include  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CF}_2\text{Br}_2$ ,  $\text{CF}_2\text{BrCF}_2\text{Br}$ , and  $\text{CF}_2\text{BrCl}$ . Those identified while monitoring the  $\text{CF}_3^+$  ion are  $\text{CF}_4$ ,  $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_3\text{CF}_2\text{Cl}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{CFH}_2$ . 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  $\text{CF}_3\text{H}$  and  $\text{CF}_2\text{Br}_2$  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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A thesis submitted in partial fulfillment  
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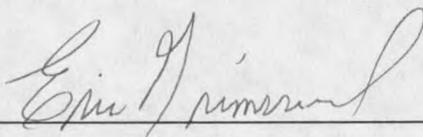
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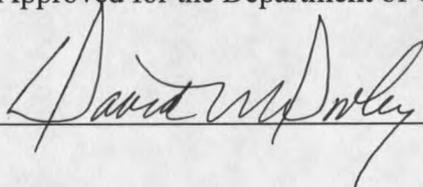
Eric P. Grimsrud



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David M. Dooley



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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,  $\text{CF}_3^+$  or  $\text{Br}^+$  will be discussed. Compounds identified while monitoring the  $\text{Br}^+$  ion include  $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CF}_2\text{Br}_2$ ,  $\text{CF}_2\text{BrCF}_2\text{Br}$ , and  $\text{CF}_2\text{BrCl}$ . Those identified while monitoring the  $\text{CF}_3^+$  ion are  $\text{CF}_4$ ,  $\text{CF}_3\text{H}$ ,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_3\text{CF}_2\text{Cl}$ ,  $\text{CF}_3\text{Br}$ , and  $\text{CF}_3\text{CFH}_2$ . 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  $\text{CF}_3\text{H}$  and  $\text{CF}_2\text{Br}_2$  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  $\text{CFCl}_3$  (CFC-11), a man-made compound used as a refrigerant. In 1975, Grimsrud and Rasmussen detected and

measured  $\text{CF}_2\text{Cl}_2$  (CFC-12) and  $\text{CH}_3\text{Cl}$  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 <sub>2</sub> Cl <sub>2</sub>	CFC-12		120	0.9
CFCl <sub>3</sub>	CFC-11		60	1
C <sub>4</sub> F <sub>10</sub>			2600 (15)	0
CF <sub>4</sub>	CFC-14	80 (16)	>50,000 (15)	0
C <sub>2</sub> F <sub>6</sub>	CFC-116	3 (16)	>10,000 (15)	0
c-C <sub>4</sub> F <sub>8</sub>			3200 (15)	0
(CF <sub>3</sub> ) <sub>2</sub> C-C <sub>4</sub> F <sub>6</sub>			2900 (15)	0
C <sub>5</sub> F <sub>12</sub>			4100 (15)	0
C <sub>6</sub> F <sub>14</sub>			3100 (15)	0
C <sub>2</sub> F <sub>5</sub> Cl	CFC-115	4 (17)	1700 (15)	0.4
C <sub>2</sub> F <sub>4</sub> Cl <sub>2</sub>	CFC-114	5 (17)	300 (15)	0.7
CF <sub>3</sub> Cl	CFC-13	10 (16)	640 (15)	
SF <sub>6</sub>		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 Name</u>	<u>Tropospheric Concentration</u> <u>(pptv)</u>	<u>Atmospheric Lifetime</u> <u>(years)</u>	<u>Ozone Depleting Potential</u>
CHFC <sub>2</sub> Cl <sub>2</sub>	HCFC-21	0.1-2.5 (20)	2-3 (6)	
CHF <sub>2</sub> Cl	HCFC-22	80 (17)	15 (21)	0.053 (21)
CH <sub>3</sub> CF <sub>2</sub> Cl	HCFC-142b		21 (21)	0.059 (21)
CH <sub>3</sub> CFCl <sub>2</sub>	HCFC-141b		8 (21)	0.081 (21)
CF <sub>3</sub> CHCl <sub>2</sub>	HCFC-123		2 (21)	0.016 (21)
CF <sub>3</sub> CHClF	HCFC-124		8 (21)	0.019 (21)
CF <sub>3</sub> CHF <sub>2</sub>	HFC-125		35 (21)	0 (21)
CF <sub>3</sub> CH <sub>2</sub> F	HFC-134a		21 (21)	0 (21)
CF <sub>3</sub> CH <sub>3</sub>	HFC-143a		50 (21)	0 (21)
CHF <sub>2</sub> CH <sub>3</sub>	HFC-152a		2 (21)	0 (21)
CF <sub>3</sub> H	HFC-23			0
C <sub>3</sub> HCl <sub>2</sub> F <sub>2</sub>	HCFC-225ca			
C <sub>3</sub> HCl <sub>2</sub> F <sub>2</sub>	HCFC-225cb			
C <sub>2</sub> HF <sub>3</sub> 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 <sub>3</sub> Br		11 (29)	1.7 (6)	0.1-0.6 (6)
CH <sub>2</sub> BrCH <sub>2</sub> Br		1-37 (29)		
CHBr <sub>3</sub>		2-46 (29)		
CH <sub>2</sub> Br <sub>2</sub>		3-60 (29)		
CF <sub>3</sub> Br	H-1301	2 (30)	72-107 (6)	8-16 (6)
CF <sub>2</sub> Br <sub>2</sub>	H-1202		1.5 (6)	0.3 (6)
CF <sub>2</sub> ClBr	H-1211	2 (30)	12-18 (6)	2.2-3.5 (6)
CF <sub>2</sub> BrCF <sub>2</sub> Br	H-2402	0.5-1.0 (30)	23-28 (6)	5-6 (6)
CHF <sub>2</sub> Br	H-1201		7 (6)	0.4-1.8 (6)
CH <sub>2</sub> BrCl		2.5 (31)		
CH <sub>3</sub> I		1.04 (32)	4 days (32)	
CH <sub>2</sub> ClI				
CH <sub>2</sub> I <sub>2</sub>		0.46 (32)		
C <sub>2</sub> H <sub>5</sub> I		2 (32)		
CF <sub>3</sub> I				
CH <sub>2</sub> 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  $\text{CF}_3\text{Br}$  (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<sup>a</sup></u>	<u><math>\Delta m^b</math></u>
<sup>12</sup> C	12.0000	0
<sup>13</sup> C	13	+0.00335
<sup>1</sup> H	1.01	+0.00783
<sup>19</sup> F	19	0
<sup>35</sup> Cl	34.97	-0.03
<sup>37</sup> Cl	36.97	-0.03
<sup>79</sup> Br	78.92	-0.08
<sup>81</sup> Br	80.91	-0.08
<sup>14</sup> N	14	0
<sup>16</sup> O	15.99	-0.01
<sup>32</sup> S	31.97	-0.03

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

<sup>b</sup> 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,  $\text{CF}_3^+$  or  $\text{Br}^+$ , 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,  $\text{CF}_3\text{H}$  and  $\text{CF}_2\text{Br}_2$  have not been previously detected in background air. A possible source of  $\text{CF}_3\text{H}$  is suggested from the analyses of air samples obtained from a fume hood of an aluminum smelter. A source for the compound  $\text{CF}_2\text{Br}_2$  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).

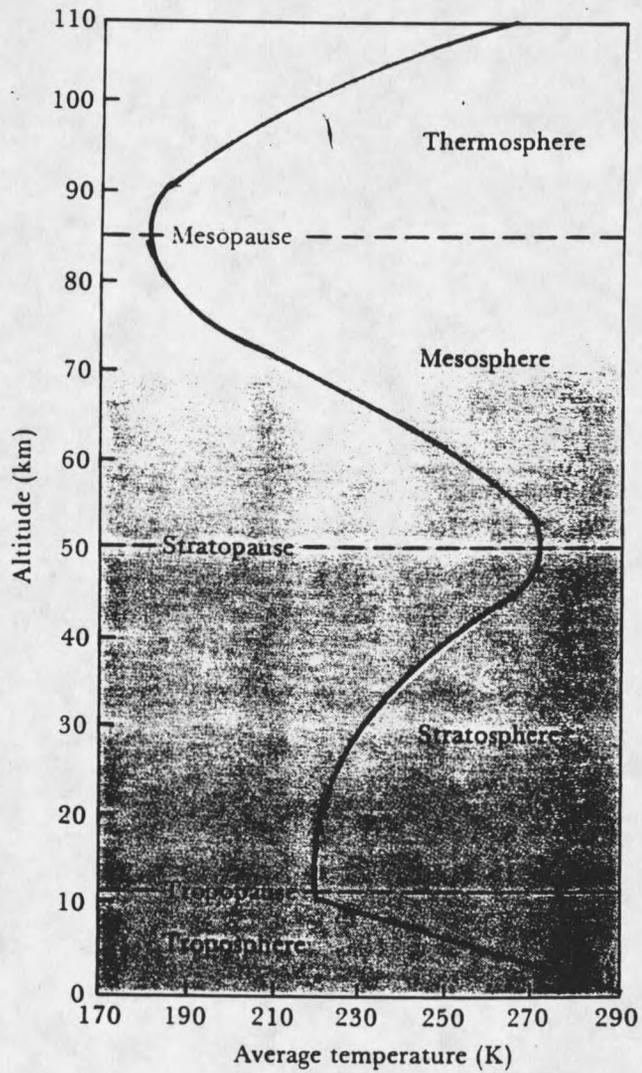
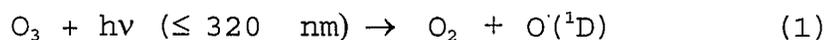
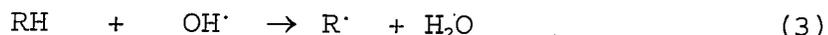


Figure 1. Physical description of the atmosphere.

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).



$$\downarrow \text{M}$$


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  $\text{HO}_2$  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  $\text{CF}_3\text{Cl}$  (CFC-13) is 640 years,

compared to that of  $\text{CHF}_2\text{Cl}$  (HCFC-22) at 15 years (see Tables 1 and 2).

### Stratosphere

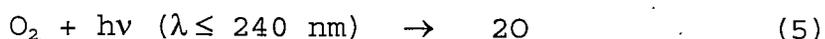
The stratosphere extends from the tropopause at about eleven kilometers to the stratopause at about 50 km. Mixing in the stratosphere takes place horizontally with chemical species diffusing up through the stratosphere very slowly. It can take 50 to 60 years for a compound to reach the upper stratosphere.

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,

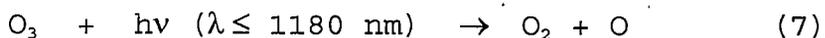
atmospheric scientists use statistical methods to reveal the long-term global thinning of ozone believed to be caused by halogen-catalyzed reactions with ozone.

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.

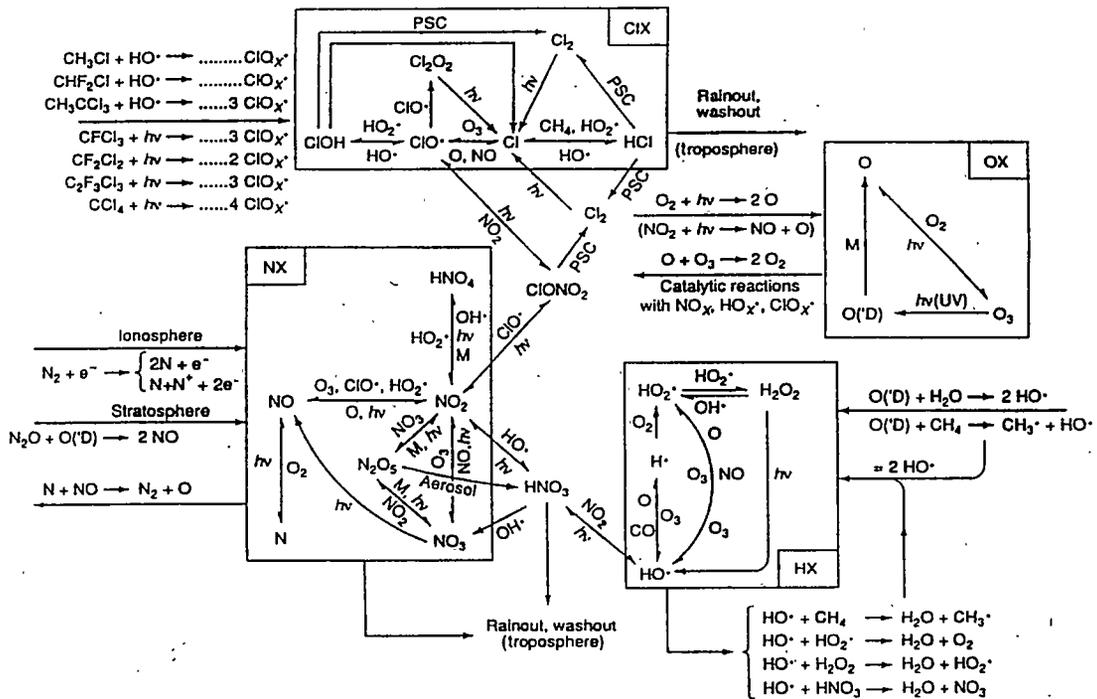
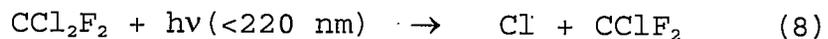


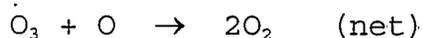
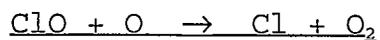
Figure 2. Schematic presenting the chemical interactions in the stratosphere.

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?

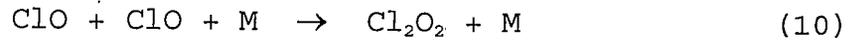
Once CFC's and Halons rise above the bulk of the ozone layer, which lies between 15 and 30 km altitude depending on latitude, they are photolyzed by ultraviolet light producing halogen atoms. For Example (8):



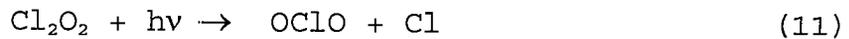
The atomic chlorine, bromine, or iodine can then participate in catalytic cycles which destroy ozone. For example, chlorine atoms will react with ozone as follows:



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

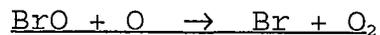


to produce  $\text{Cl}_2\text{O}_2$ , which if radiated by UV light (Eq. 11)



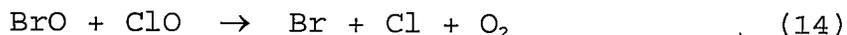
regenerates chlorine atoms (Eq. 12). A more comprehensive explanation of chlorine's role in the stratosphere can be seen in the schematic shown in Figure 2.

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.

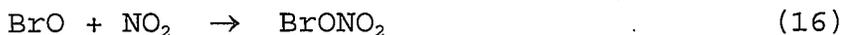
First, the fast synergistic reaction between the much more abundant ClO radical and the BrO radical (Eq. 14) producing atomic chlorine and bromine.



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 NO<sub>2</sub> to form the stable product ClONO<sub>2</sub> (Eq. 15).

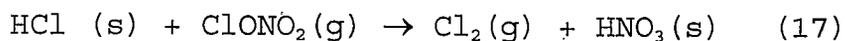


Chloronitrate is stable in the stratosphere except in special cases where heterogeneous chemical reactions occur (35). The reaction between BrO and NO<sub>2</sub> produces bromonitrate (Eq. 16), but BrONO<sub>2</sub> is not nearly as stable as chloronitrate and the equilibrium lies to the left (Eq. 16) with the reactive species BrO being an abundant species of bromine in the stratosphere (36,37).

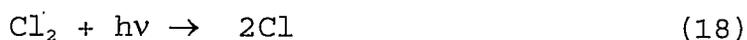


The Antarctic Ozone Hole

The Antarctic ozone hole is due to a special case in stratospheric chemistry where the generally nonreactive forms of chlorine ( $\text{ClONO}_2$  and  $\text{HCl}$ ) 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  $-77^\circ\text{C}$  and sufficient amounts of  $\text{HNO}_3$  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  $\text{NO}_2$  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- $\alpha$  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  $\text{CF}_3\text{CFH}_2$  (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

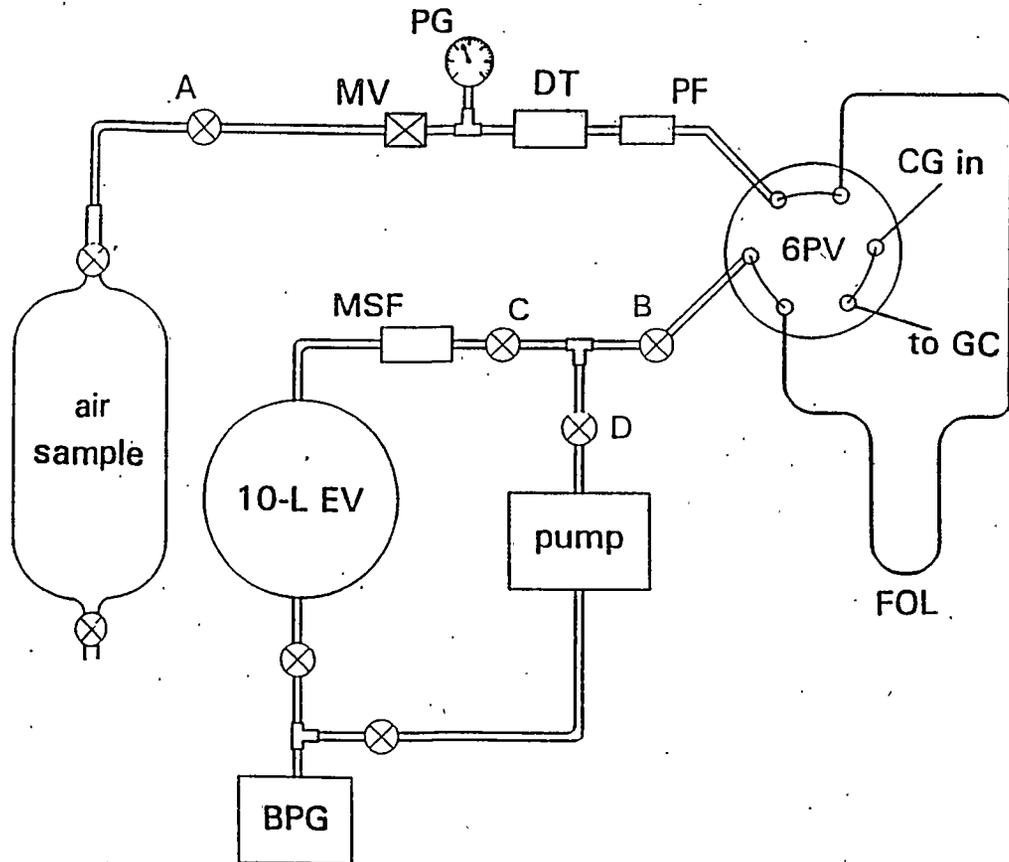
Air samples were introduced into the GC-HRMS by the sampling system represented in Figure 3. Sample sizes of up to  $1000$  atm-cm<sup>3</sup> of whole air can be concentrated with the typical sample size being  $340$  atm-cm<sup>3</sup>. After the connection of a flask containing an air sample, the 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  $CF_3Cl$ ,  $CF_3Br$ ,  $C_2F_5Cl$ , and  $CF_3CFH_2$ . The initial GC temperature was held at  $30^\circ C$  for 2 minutes, then the oven was ramped up at  $25^\circ C$  per minute to  $220^\circ C$  and held for 12 minutes. Temperature program 2, used

for  $\text{CF}_4$  and  $\text{CF}_3\text{H}$ , was the same except for an initial temperature of  $-10^\circ\text{C}$ .

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  $25 \text{ cm sec}^{-1}$  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  $\text{CF}_3\text{Br}$  ( $\text{CF}_3\text{Br}$  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  $220^\circ\text{C}$ . The temperature was maintained at  $220^\circ\text{C}$  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 N<sub>2</sub> 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  $90^\circ$  off the axis of the ion beam. A stainless-steel conversion dynode (where positive ions are converted to electrons) is also located at  $90^\circ$  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  $\Delta m$  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.

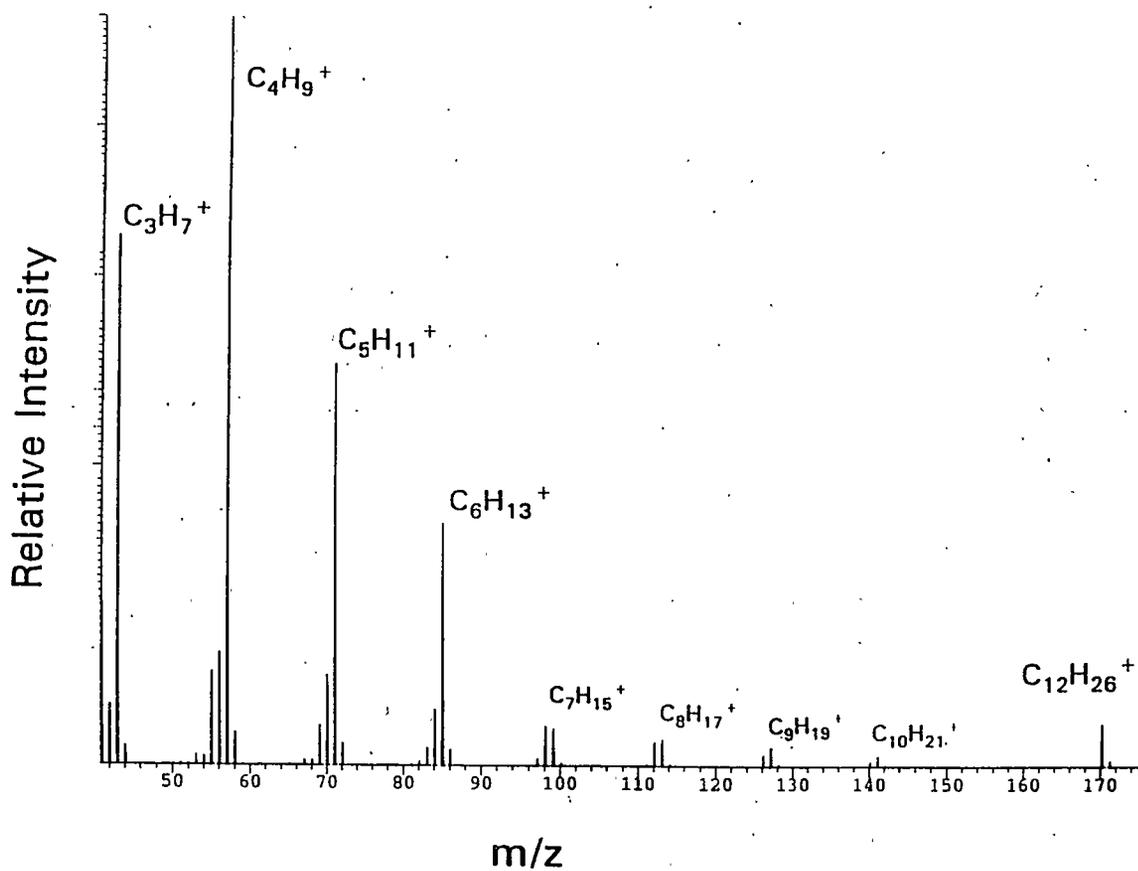


Figure 4. Electron impact mass spectrum of the mass calibration gas, n-dodecane.

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.

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









































































































































































