



In situ conversion of methyl bromide to methyl iodide : a new technique for the measurement of atmospheric methyl bromide by GC-ECD
by Richard Allen Hughes

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:

Measurements of methyl bromide in the atmosphere have been complicated by the uncertain stability of methyl bromide in containers traditionally used for capture and storage of air samples. In addition, with atmospheric concentrations of methyl bromide at 10 pptv, current detection techniques require pre-concentration of large sample volumes. A method that provides a fast and simple measurement of methyl bromide in small air samples without pre-concentration would prove useful in many field applications. In this thesis, a technique is described which allows for the measurement of atmospheric concentrations of methyl bromide in 45-mL air samples. This is accomplished by in situ conversion of methyl bromide to the highly electron capture active methyl iodide with subsequent detection by electron capture detector. Conversion is accomplished by exposure of the methyl bromide to zinc iodide, which is contained in a heated in line column. Signal to noise ratios of better than 150:1 have been observed and reproducibility is +/-10% based on the data collected thus far. This technique should prove useful for the automated determination of methyl bromide in field applications.

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TECHNIQUE FOR THE MEASUREMENT OF ATMOSPHERIC METHYL
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by

Richard Allen Hughes

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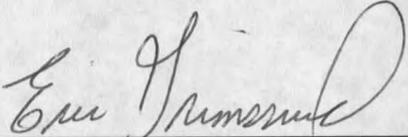
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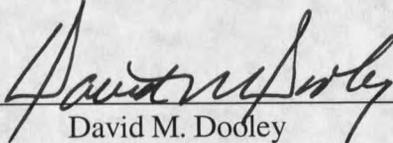
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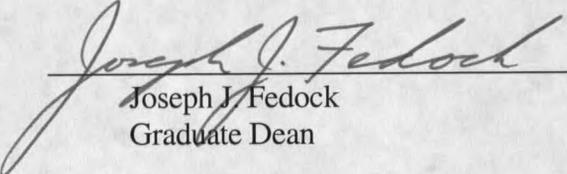
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... but we rejoice in our sufferings, because we know that suffering produces perseverance;
perseverance, character; and character, hope...

Romans 5:3-4 (NIV)

To Tammy

Because without her great abilities as a wife, a mother and a friend, I would not have made it this far. She has been my inspiration!

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ABSTRACT

Measurements of methyl bromide in the atmosphere have been complicated by the uncertain stability of methyl bromide in containers traditionally used for capture and storage of air samples. In addition, with atmospheric concentrations of methyl bromide at 10 pptv, current detection techniques require pre-concentration of large sample volumes. A method that provides a fast and simple measurement of methyl bromide in small air samples without pre-concentration would prove useful in many field applications. In this thesis, a technique is described which allows for the measurement of atmospheric concentrations of methyl bromide in 45-mL air samples. This is accomplished by in situ conversion of methyl bromide to the highly electron capture active methyl iodide with subsequent detection by electron capture detector. Conversion is accomplished by exposure of the methyl bromide to zinc iodide, which is contained in a heated in line column. Signal to noise ratios of better than 150:1 have been observed and reproducibility is +/-10% based on the data collected thus far. This technique should prove useful for the automated determination of methyl bromide in field applications.

INTRODUCTION

Current Understanding of Stratospheric Ozone

The earth is protected from much of the sun's UV-B radiation (290 nm-320 nm) and UV-C radiation (175 nm-290 nm) by a layer of ozone (O_3) in the stratosphere, which strongly absorbs in the 230 to 290nm region^{1,2}. This is critical to life on earth since short wavelength UV of less than 290 nm can damage DNA². Ozone is ubiquitous in the atmosphere, but its concentration reaches a maximum in the stratosphere between 19 and 23 km above the surface of the earth³.

A two-step process in the upper stratosphere naturally generates a majority of ozone². First, molecular oxygen is photodissociated by the sun's UV radiation (<230 nm).



This is then followed by a reaction of atomic oxygen with a molecule of oxygen to form ozone. There is a third body involved in the reaction, M, which absorbs the energy produced by this reaction. M is usually a molecule of nitrogen, oxygen or an aerosol particle.



These reactions are most prevalent near the equator due to the intensity of the sun.

Currents in the atmosphere distribute the ozone with the general motion being toward the poles.

Once formed, the ozone absorbs UV radiation, 230 to 290nm, which results in its destruction.

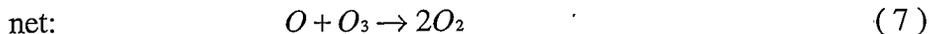


Ozone can be further destroyed by reaction with atomic oxygen to give two oxygen molecules.



This series of reactions was long thought to be the sole regulation mechanism for natural ozone and is often referred to as the Chapman mechanism⁴. However, it proved to be inadequate for explaining the steady state concentration of ozone in the stratosphere, which is lower than the mechanism suggests. It should be noted here that the stratosphere warms with altitude due in most part to the exothermicity of reaction (2) and (4).

There must, therefore, be other sinks of ozone to account for the extra loss not accounted for in the Chapman mechanism. Natural sinks for stratospheric ozone are, in fact, numerous. Only when these sinks are taken into account, does the mechanistic theory of equilibrium for this system explain the observed concentration. The major chemical pathways for destruction of ozone are a result of the catalytic interaction shown below².



where $X = H, OH, NO, Cl$ or Br . The source of these radicals in a pristine stratosphere is from $H_2O, N_2O, CH_3Cl, CH_3Br$ and other naturally occurring halocarbons¹. These radicals are formed as a result of reactions with light, atomic oxygen or other radicals. The reactive species HO_x, NO_x, ClO_x and BrO_x , where $x = 1$ or 2 , produced in reaction (5) become the path through which each radical participates in the catalytic destruction of ozone. Note that the net effect of this cycle is the same as in (4) above.

These catalytic cycles are broken when the reactive compounds react with each other or other species to produce "reservoir" species, which act to control the rate of ozone destruction and to remove the radicals from the catalytic cycle and potentially the atmosphere. Reservoir species are more stable and are less likely to participate in ozone depleting reactions. Some of the major reactions that produce these species are:



Nitrogen analogs provide the bulk of the chain termination reactions. These nitrogen species are present in comparatively high concentrations, 10 ppb to 200 ppb, and in effect provide a supply of reactants with which the radicals can react.⁵ Many of these reactions also have fast reaction rates making their formation even more probable. In fact, at any one time only a few percent of the chlorine species exist in their active, ozone depleting, form. However, bromine compounds do not form reservoir species as readily and over 50% of inorganic bromine in the stratosphere resides in its active, BrO_x , form.⁵ The formation of reservoir species due to nitrogen compounds as well as the lack

of bromine containing reservoir species will become critical to understanding the unique chemistry that takes place in the stratosphere at the geographic poles, which will be discussed shortly.

The "Ozone Hole"

The material presented above represents the basic chemistry of ozone in the pristine stratosphere. In 1957, Dobson and others began taking routine measurements of total column ozone in the atmosphere over Antarctica.⁶ Total column ozone is measured by a spectrophotometer in Dobson units, which represents the vertical thickness in cm of ozone (reported as times 1000) in the atmosphere reduced to a layer of pure gas at 0°C and 760 mm Hg.⁶ Over the next two decades, periodic measurements of total column ozone made at various locations on the continent of Antarctica indicated that average ozone levels were 350 Dobson units with seasonal variations of +/- 75 units¹.

In the early 1970's, Roland and Molina⁷ put forth a theory about the potential of man-made halogenated compounds to effect the natural balance of ozone in the stratosphere. The source of these halogenated compounds was proposed to be from chlorofluorocarbons (Freons) and bromofluorocarbons (Halons). The specific chemistry involved will be discussed below. Prior to this point very little research had been conducted on the trace gas make up of the atmosphere and more specifically the stratosphere. There has since been, and continues to be, extensive study of atmospheric dynamics and chemistry at all altitudes.

Then in the early 1980s, it became very apparent that the levels of total column ozone were changing drastically over Antarctica each spring (September, October)⁸. By the middle 1980s, observations noted that total column ozone over the South Pole would decrease by as much as 50 % each spring. Other experiments measuring the vertical profile of ozone indicated that summer ozone concentrations reach a maximum at approximately 20 km and that the spring time decrease was mostly a result of an extreme loss of ozone at this altitude.^{9,10,11}

The extreme thinning of the ozone layer over Antarctica each spring has become known as the "ozone hole". Physically, the ozone hole is defined as the area where ozone levels drop to 220 DU or less¹². Depletion of 90% of the total column ozone has been recorded in portions of the hole and 100% depletion has been observed at altitudes from 14 to 19 km. The spring ozone hole has been observed regularly over the *entire* continent of Antarctica since the early 1980s. What is often overlooked is that Antarctica is quite large, approximately 13 million square kilometers (the U.S. has 9.3 million square kilometers). Data from 1992 and 1993 show the hole to encompass an area of over 24 million square kilometers.¹³ Calculations have indicated that springtime ozone loss over Antarctica represents a loss of up to 3% of the global ozone in a one to two month period.¹⁴ Measurements have indicated negative decadal trends in ozone over all areas of the globe with the exception of the tropics.^{5,15}

Ozone loss over the Arctic has been observed in the spring as well.^{16,17} Although the depletion is not as extensive, concern has been high due to the additive effects of another ozone sink and the relative proximity of the Arctic to major population centers

as compared to the Antarctic. Questions have been raised concerning the potential effects of significant stratospheric ozone depletion over metropolitan areas even if for short periods. Spring ozone loss within the Arctic vortex has been measured since the middle 1970s. In the early 80s measurements indicated that maximum total column ozone loss was 5 to 8%, which is within the expected annual variability.³ By the mid 90s that level had only changed slightly and, unlike its Antarctic counterpart, was still within expected annual variability.

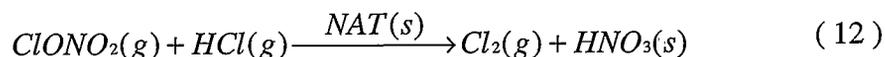
As a result of the theories on the effects of halocarbons on ozone and subsequent confirmation through the formation of the spring time ozone hole and the measurements of decadal declines in ozone, Roland and Molina along with Crutzen, for his work on understanding atmospheric nitrogen chemistry, were awarded the 1995 Nobel Prize in Chemistry. Since this recognition, these theories have been widely accepted in the scientific communities, although some disagreement remains.¹⁸

Ozone Depletion Chemistry

The conditions that allow such severe ozone depletion to take place are unique to the geographic Polar Regions, although the severity in Antarctica is unrivaled. Discussion here will focus on the chemistry in the stratosphere over Antarctica with some discussion of the differences seen in the Arctic.

As winter develops in the Southern Hemisphere, a phenomenon known as the polar vortex forms as a result of strong westerly winds. The vortex causes a major portion of the Southern Hemisphere's stratosphere to become isolated from the rest of

the global stratosphere. The vortex is generally centered over the South Pole and can encompass latitudes to 50°S. Due to the lack of sunlight and the isolation of the air within the vortex from warmer, higher latitude air, temperatures within the vortex drop to below -80°C during the winter. At this low temperature, clouds of nitric acid trihydrate (NAT), sulfuric acid tetrahydrate (SAT) and water begin to form in the Antarctic stratosphere. These clouds, known as polar stratospheric clouds, remove the reactive nitrogen (NO_x) species from the atmosphere by direct physical adsorption. With this nitrogen unavailable, ClO and BrO concentrations can then rise to as high as 2 ppb and 20 ppt, respectively, due to their inability to form reservoir species. As discussed above, nitrogen compounds in the stratosphere are critical to the formation of these reservoir species and to the balance of ozone concentration in the stratosphere. Reactive nitrogen species are further removed from the atmosphere through heterogeneous reactions of remaining reservoir species on these cloud surfaces.



Sedimentation of these cloud particles is thought to worsen the problem because it essentially denitrifies the stratosphere. If sunlight were available, the NAT could photochemically produce NO_x's, however, sedimentation minimizes this turn around and allows the reactive chlorine to remain active. This buildup of active chlorine and bromine in the stratosphere takes place throughout the winter. When the spring sun returns to the polar region, the UV light quickly initiates reactions between this excess

reactive chlorine and bromine and ozone as shown in (5), (6) and (7). Ozone is destroyed at a rate of 2-4% per day during the height of the ozone depleting process.^{14,19}

As spring progresses, three factors control the end of the spring ozone hole. First, there is a depletion of available reactants due to the extreme loss of ozone. Second, as the stratosphere warms the PSCs sublime and reactive nitrogen becomes available by the photolysis of HNO_3 . The reservoir species then begin to form and break the chain reactions. As mentioned above there has been evidence of sedimentation of the NAT which minimized this pathway. Third, the vortex begins to break up, which allows mid-latitude air to once again mix with the polar air and replenish the ozone in the polar stratosphere and bring in a supply of reactive nitrogen compounds to reestablish the equilibrium.

The Arctic wintertime chemistry is similar except for two major factors. First, the winter time vortex is weaker and not as clearly defined.¹⁶ Second, the temperatures in the Arctic stratosphere do not get as low as they do in the Antarctic. The limited vortex allows for more mixing with mid-latitude air and therefore the isolated ozone loss is not observed. At these higher temperatures, PSCs do not form as readily and therefore heterogeneous chemistry plays a much more limited role. The warmer temperatures also support the existence of the reservoir species, which also limits the loss of ozone

Atmospheric Bromine

Up to this point three main factors concerning ozone have been covered. First, it has been shown that a few basic reactions drive the overall steady-state system, which

acts to regulate the amount of ozone in the stratosphere. Second, it was shown that under certain conditions severe perturbation of the ozone equilibrium could be seen. Third, it was suggested that bromine is at least a participant in the chemistry of stratospheric ozone. There are, however, many indications bromine actually plays a *major* role in the perturbation of atmospheric ozone levels that have been observed for the past 20 to 25 years.^{20,21,22} A brief overview, emphasizing the ozone/bromine related interactions, will show, in fact, that bromine plays a critical role in the ozone cycle and especially in the ozone depletion phenomenon. It is important to highlight what might otherwise be perceived as an insignificant contribution to the make-up of the atmosphere.

Sources of Bromine in the Atmosphere

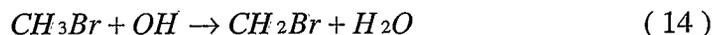
Vertical profiles indicate that there is little change in the concentration from ground level to the tropopause of the most common alkyl bromides in the atmosphere. Most recent measurements show that the total organic bromine at the tropical tropopause (~12km) has been measured to be 17.4 +/- 0.9 ppt.²³ Of this, methyl bromide, which has both natural and anthropogenic sources, accounts for 54%. The specific sources of methyl bromide will be discussed in a later section. Most of the remainder of the organic bromine comes from Halons (38%), which are used as fire suppressants and are of entirely anthropogenic origin, dibromomethane (6%), bromochloromethane and dichlorobromomethane (0.8% combined) all are produced from natural sources. This low concentration of bromine-related compounds pales in comparison to the 3.5 ppb of chlorine containing species.²⁴ As will be demonstrated shortly, however, bromine not

only plays a critical role in the equilibrium of ozone in the atmosphere as discussed above but also the perturbation of atmospheric ozone.

Troposphere

Once released into the troposphere, the halocarbons mix rapidly and become relatively evenly distributed. In the troposphere, for those compounds with a C-H bond, the most common path of chemical destruction is reaction with the hydroxyl radical.²⁵

Using methyl bromide as an example:



After formation of the radical, it subsequently reacts with a variety of other species, such as O₂, to produce water-soluble products, which then are rained out of the troposphere. Fully halogenated chemicals such as the Halons do not react with the hydroxyl radical, as shown in (14), and reach the stratosphere unchanged.⁵

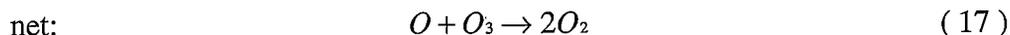
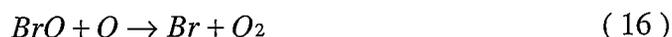
Stratosphere

Once in the stratosphere, organic bromine is photolyzed or reacts with OH or O to produce free bromine. This bromine then reacts with a variety of species (OH, O, O₂, O₃, ClO, NO and NO₂) to produce a variety of inorganic bromides such as BrO, HOBr, HBr, BrCl and BrONO₂.⁵

The formation of the reservoir species BrONO₂, BrCl HOBr and HBr is much less favored than those of its chlorinated counterparts. As such, only about one-half of the inorganic bromine resides in these forms. The remainder of the bromine stays in the reactive forms, Br and BrO.^{26,27} Also, the brominated reservoir species are much more

photochemically active, which allows them to be converted to reactive bromine much more quickly than their chlorine counterparts.

Once formed, these inorganic bromides can react through a variety of pathways with ozone. Wofsy and Watson first recognized the role of bromine in stratospheric chemistry in 1975²¹ but their ideas were largely treated as a minor contender until 1980 when Yung²² expanded on their proposals. He showed that stratospheric bromine could play a major role in ozone depletion in two ways. First, he reiterated that bromide analogs themselves are effective ozone sinks through similar reactions as shown above.



Second, he noted that the bromine analogs could react with ClO, NO₂ and HO₂ synergistically to remove ozone even more effectively. Yung indicated that the cycle shown below is one of the most important due to its regeneration of the chlorine and bromine radical.



This regeneration process enables the bromine and chlorine to participate in more reactions with ozone than they might otherwise. It is this synergistic effect that makes this path so critical. Prior to this understanding, models of ozone depletion were not adequate to explain the losses being seen. When the bromine chemistry as discussed by Yung was taken into account, a significant increase in model accuracy was observed

when compared with field data. As a result of this understanding, it is now believed that bromine may be responsible, either directly or indirectly, for approximately 25% of the ozone loss in the stratosphere.^{3,5} However, during the unique conditions that bring about the ozone hole, bromine may be responsible for as much as 50% of the depletion of ozone. Utilizing the kinetics of the known bromine and chlorine containing reactions, it has been shown that bromine is 50 to 100 times more efficient than chlorine on a per atom basis at destroying ozone.²⁸

As mentioned above the sources of bromine in the atmosphere are both anthropogenic and natural. Because the Halons, which have not been made since 1993, are not reactive in the troposphere their life times are exceedingly long.²⁹ Even if emission from current feed stock were to cease today, their presence would be evident for many decades. However, methyl bromide, responsible for 54% of the organic bromine in the atmosphere, readily reacts in the troposphere. There are predictions that the elimination of anthropogenic sources of methyl bromide could have profound impact on the ozone hole in a very short time due to its reactivity in the troposphere and short tropospheric lifetime.²⁵

Methyl Bromide

Methyl bromide is unique among the brominated compounds that are prevalent in the atmosphere because it has both natural and anthropogenic origins. However, studies on the sources of methyl bromide are limited and there has been no definitive agreement regarding the output from all of the sources or even what the all of the sources are. This

section will focus on what is known about the sources of methyl bromide in an attempt to provide a clear understanding as to the implications regarding the depletion of ozone and as to the potential implications and applications of this project.

Anthropogenic Methyl Bromide

In the middle 1930s, methyl bromide was determined to be an excellent anti-fungal agent for horticulture produce.²⁵ Over the next thirty years, it was discovered that methyl bromide was also useful for structural fumigation and pest/disease fumigation in soil. The popularity of methyl bromide grew due to its effectiveness and its ability to replace several pesticides and herbicides. The effectiveness of methyl bromide has been unsurpassed by any single chemical or treatment process for control of pests and fungus. Unlike many other treatments, no observed pest tolerance toward methyl bromide has ever been detected. As a volatile gas, it is quick to dissipate after application. The only potential hazards to the consumer are consumption of inorganic bromides that were created as a product of the methylation process or by direct exposure to methyl bromide as a result of application processes. Consumption of inorganic bromides has been determined to be inconsequential. However, illness and death have been reported as a result of direct exposure to methyl bromide. Farm workers and residents living near fields where methyl bromide is applied are the most likely candidates for exposure. Since methyl bromide is a gas and because of the nature of the fumigation process, it has been estimated that up to 60% of the methyl bromide applied is released into the atmosphere and as such the potential for human exposure is high.³⁰ This figure is highly

variable as it is dependent on soil conditions, application technique, recovery technique and in situ destruction.

Atmospheric methyl bromide of anthropogenic origin has three main sources. These include industrial use and production, leaded gasoline and bio-mass burning. Industrial production is relatively well quantified in developed countries but production in undeveloped countries is difficult to monitor and of that which is produced, the determination of the amount released into the atmosphere is highly speculative. Today, worldwide industrial production of methyl bromide is approximately 76,000 tons annually. Of this amount, more than 70% is applied annually in the U.S. for agricultural soil fumigation, 24% is used for fumigation of structures, durables and perishables and 3% is used as chemical feedstock. Most recent numbers estimate that of this amount 41,000 tons are released annually. While recent developments in plastics may enable farmers to release less methyl bromide into the atmosphere, mechanical constraints dictate that loss to the atmosphere will never be eliminated.³⁰

Another anthropogenic source of methyl bromide comes as a result of a byproduct of the combustion of dibromoethane in leaded gasoline. Best estimates for methyl bromide's contribution to the atmosphere as a result of this process is 2500 tons annually +/- 100%. This value is highly speculative because of a lack of data regarding its use worldwide. Again, the measurements are poor and but levels should be dropping with fewer and fewer autos using leaded gasoline.³¹

Biomass burning is known to produce methyl bromide but quantitation of this effect has been difficult.^{32,33} Most methyl bromide from this source is thought to result

from the large fires in South America, Indonesia and other tropical zones where forests are burned to clear areas for agriculture. It has been estimated that natural fires account for less than 10% of the biomass that is burned annually.⁵ Best estimates indicate that fires contribute 25,000 tons of methyl bromide to the atmosphere annually. This value represents fires from both natural and anthropogenic causes.

Natural Methyl Bromide

The ocean is known to be both a source and a sink of methyl bromide. Recent measurements indicate that the ocean produces 56,000 tons/y of methyl bromide. However, the ocean also consumes about 77,000 tons/y of methyl bromide, mostly through hydrolysis. This data then indicates that the ocean is a net sink of 21,000 tons/y of methyl bromide.^{15, 34, 35} Again, quantitating such a value is difficult and associated uncertainties can have large implications with regard to the global budget of methyl bromide. All of these values depend on the validity of the rates for loss, which are also under constant scrutiny.

Soil has recently been realized as a viable sink for methyl bromide.^{36, 37} Calculations have indicated that the average annual loss to soil is on the order of 42,000 tons/y. The mechanism by which this loss takes place is proposed to be a result of biological oxidation. Proof of this is limited and the mechanisms up to this point are only speculative. Due to the wide variability of soil types and transport mechanisms, quantitating this sink has obvious hurdles to overcome.

Global Budget of Methyl Bromide

The currently accepted concentration of methyl bromide in the troposphere is 10 ppt +/- 1 ppt.¹⁵ Using this number the global burden, the amount in the atmosphere at any one time, is calculated to be 150,000 tons.³⁸ This causes a dilemma since the above numbers indicate that sources are only 60% of sinks. This would naturally lead to the conclusion that the concentration of methyl bromide in the atmosphere should either be declining or non-existent, which is not the case. Uncertainties in the sources and sinks as well as the non-uniformity of these sources and sinks make reconciling a global budget difficult. Most of the values presented above for natural sources and sinks have variability of at least 100%. Numbers for anthropogenic sources range in variability from 50% to 100%. Nevertheless, it has still been shown that methyl bromide has a significant anthropogenic element.

Consequences of Anthropogenic Methyl Bromide

Bromine, as mentioned, is responsible for 30 to 50% of the ozone depletion seen at the poles each spring both directly and indirectly. Also discussed is the fact that methyl bromide accounts for 55% of tropospheric bromine and is responsible for an equal portion of the stratospheric inorganic bromine. Since approximately 50% of methyl bromide is of anthropogenic origin, anthropogenic methyl bromide may be responsible for 8 - 12% of the Antarctic ozone hole. Research has shown that elimination of anthropogenic sources of methyl bromide could be equivalent to moving the phase out date of CFCs up 3 years.²⁵ Only through a better understanding of the

methyl bromide budget and sources will better estimates of the overall effects of methyl bromide be determined.

Current Methods of Detecting Methyl Bromide

The most common techniques used for the detection of halogenated compounds, and more specifically of concern here, methyl bromide, in air are the GC/ECD, the oxygen doped GC/ECD and GC/MS.^{23, 24, 37, 39, 40} All of these techniques are widely used and accepted in the field of atmospheric chemistry.

In order to detect atmospheric levels of methyl bromide it is often necessary to preconcentrate large volumes of sample with subsequent separation and detection by the GC/ECD or by GC/MS techniques mentioned above. Pre-concentration of samples is accomplished by the cryogenic focusing or adsorptive trapping of large sample volumes in a pre-column prior to chromatographic separation. Sample volumes are typically 0.5 to 2 L. Cryogenic methods rely on liquefied permanent gas temperatures to freeze out the constituents of a sample. After the desired volume is captured, the pre-column is heated, allowing the sample to enter the chromatographic column. Adsorbent trapping relies on the sample chemically adsorbing to a substrate packed into a pre-column. As before, once the desired volume of sample is trapped, the column is heated and the sample is desorbed and allowed to enter the chromatographic column. Detection by ECD can also be enhanced by using the oxygen-doped technique.⁴¹ Here, a known amount of oxygen is allowed to enter the ECD. The characteristics of the ECD chemistry are changed and signal enhancement is observed for selected compounds.

All of the methods mentioned have drawbacks when used for the determination of atmospheric methyl bromide on a routine basis. Cryofocusing samples requires the use of relatively large volumes of liquefied gases. This tends to be impractical in field applications. Cryofocusing might also require the collection of samples in the field for later analysis, which could lead to sample degradation, small sample numbers per location and elevated costs. Adsorbent traps rely on the chemical interaction of the species of interest and the adsorbent. If trapping is too efficient the compound of interest may be irreversibly trapped on the column. If the trapping is not efficient, the compound of interest might be unretained and lost out of the trap effluent. The Oxygen-doped ECD has limited versatility and tends to negatively effect the signal-to-noise ratio for response to methyl bromide. Methods, such as mass spectrometry, that do have good sensitivity are typically not field portable and as with cryofocusing discussed above, this then requires that the sample of interest be collected in a container and transported to the lab. Although sample containers exist that have been shown to not appreciably effect sample integrity, it becomes prohibitively expensive to collect a large number of samples.

STATEMENT OF PROBLEM

Motivation for Continued Investigation of Atmospheric Methyl Bromide

From the background that has been given on the basic chemistry of the atmosphere, it is clear that methyl bromide is a major contributor to processes involving atmospheric ozone. As seen above, the catalytic and synergistic effects of bromine on the destruction of ozone can be profound. Several groups and organizations have stated that the global levels of methyl bromide are still not completely characterized and that the sources and sinks as well as the source and sink mechanisms are not well understood.^{5,15,25,40} Determination of such values would allow for better estimates of atmospheric lifetime, ozone depletion potentials and overall atmospheric makeup.²⁵ Current techniques for the detection of methyl bromide rely on collecting samples in a container for later testing, thereby potentially affecting sample integrity, or pre-concentrating large sample volumes, which then requires equipment that may not be practical in many field settings. Investigation of the ability to increase the detectability of methyl bromide in small volume whole air samples is the primary goal of this thesis. A technique that relies on standard GC instrumentation but eliminates the need for pre-concentration would be of great interest to the atmospheric science community.

Watson and co-workers⁴² investigated a technique involving the in situ conversion of methyl chloride to methyl iodide, which is EC active, by exposure of the methyl chloride to a heated in-line sodium iodide column in order to enhance the detectability of

methyl chloride by electron capture detection. The first goal of this thesis is to investigate the potential conversion of methyl bromide to methyl iodide using a similar sodium iodide column along with electron capture detection. The second objective is to determine if this conversion reaction is restricted to sodium iodide or are other metal iodide salts also capable of facilitating the conversion of methyl bromide to methyl iodide. Third, can the conversion be made efficient enough without detrimentally affecting the ECD and yet still be able to enhance the response of methyl bromide? The fourth objective is to determine what effect the conversion column may have on the more abundant chlorocarbons that will be present in real air. Lastly, using the information from the first four steps, real air samples will be tested to determine if the improved detection of atmospheric concentrations of methyl bromide can be realized.

EXPERIMENTAL

In Situ Conversion of Methyl Bromide to Methyl Iodide

Instrument Design

A schematic of the instrument is shown in Figure 1. The base chromatograph was a Varian 3700. Standard grade nitrogen was used as the carrier gas at a flow rate of 35 ml/min except as noted in the section below detailing other system setups and optimization. Oxygen and water were removed from the carrier gas nitrogen by in-line Oxy-trap(Alltech) and Drierite / 5Å molecular sieve filters. Samples were introduced into the carrier gas stream via a 6-port valve, V1, (Carle Instruments, OK) fitted with a sample loop. The 2-ml sample loop was constructed of 3-mm o.d. stainless tubing. Two, three-meter 10% SF-96 on Chromasorb-W columns constructed of 3-mm o.d. stainless steel tubing were used for chromatographic separation. The chromatographic columns were used at ambient temperature. The first column provided initial separation of the sample prior to the metal iodide conversion column. The second column provided post conversion column separation of products and reactants that resulted from reactions within the metal iodide conversion column. The conversion column could be switched into or out of the flow path between the two chromatographic columns by a second 6-port valve, V2.(Valco Instruments). This valve allowed the effluent from the first chromatographic column to bypass, BP mode, the conversion column or be directed onto the conversion column, TC mode. A separate nitrogen source is used to maintain

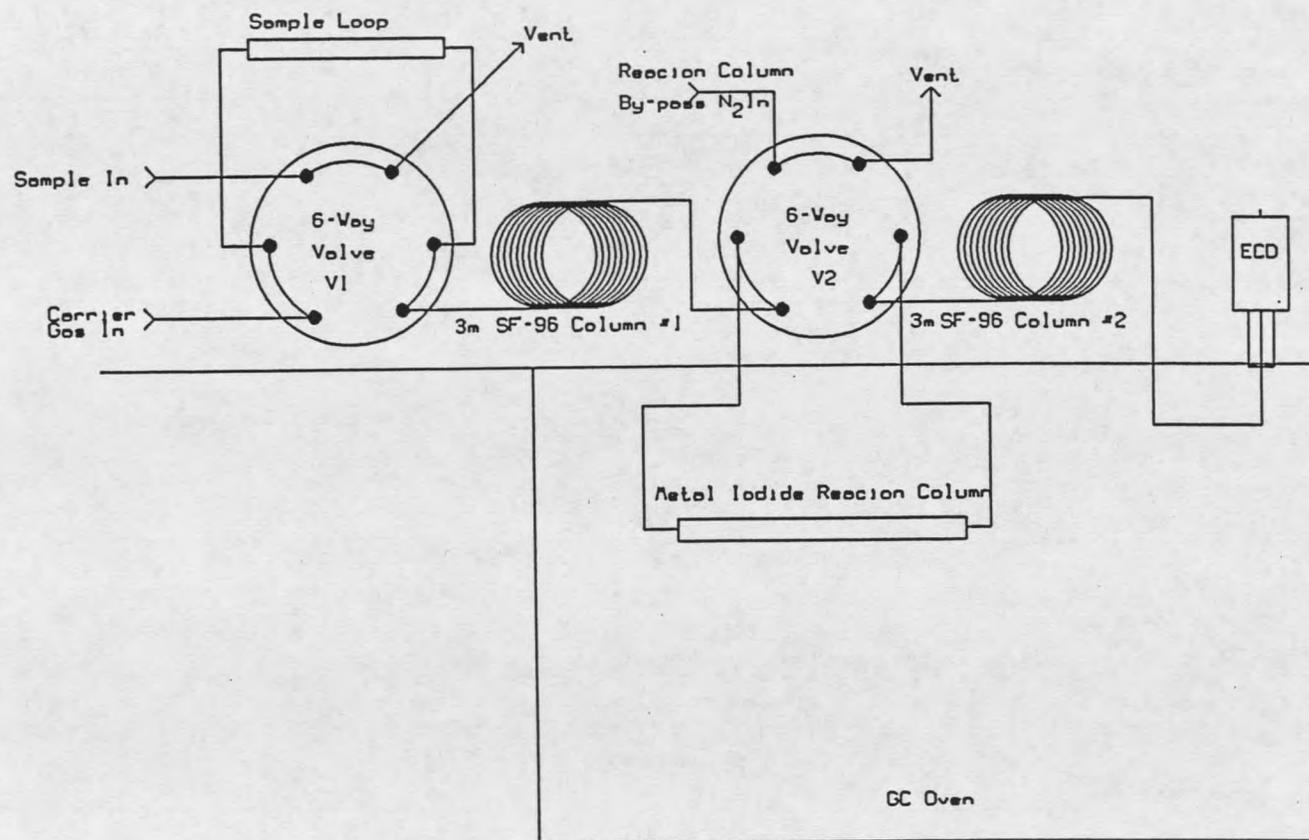


Figure 1. Schematic of instrument used to investigate the in situ conversion of methyl bromide to methyl iodide using a variety of metal iodide salts.

nitrogen flow through the conversion column when the option of bypassing the reaction column is utilized. The temperature of the conversion column was controlled by use of the Varian 3700 oven and associated controls. Effluent from the chromatographic columns was directed into an electron capture detector. The detector was operated at 250°C.

Metal Iodide Conversion Columns

Conversion columns were constructed of 6-mm o.d. copper or stainless steel tubing packed with a mixture of Chromasorb-W and metal iodide salt. A list of the metal iodide salts tested is given in Table 1. All chemicals were used as received.

Table 1. Metal iodide salts used to facilitate the conversion of alkyl bromides to alkyl halides.

AgI ₂	CsI	MnI ₂	RbI
BaI ₂	CuI	NaI	SnI ₂
BiI ₃	KI	NH ₄ I	SnI ₄
CaI ₂	LiI	NiI ₂	SrI ₂
CdI ₂	MgI ₂	PbI ₂	ZnI ₂
CoI ₂			

Conversion columns were prepared according to the following procedure. The metal iodide salt was ground to a fine powder using a mortar and pestle and then combined with an equal volume of Chromasorb-W in a graduated cylinder. The piece of tubing was plugged on one end with a small piece of glass wool. The mixture was then poured, with the aid of a funnel, into the other end of the tube with light tapping of the tube on the bench to ensure even filling and to minimize air pockets. The tube was filled to within 6 mm of the end of the tube. Typically, 1.5 – 2.0 g of the mixture was put into

each 15-cm length of 6-mm o.d. tubing. A glass wool plug was used to fill the rest of the tube. Ends of the column were fitted with Swagelok fittings to allow installation on to the instrument. All stages of column preparation were done in a fume hood except when using compounds with extreme air sensitivity. These columns were prepared in a nitrogen filled glove bag. Methodology for preparing conversion column materials, as described by Ooman,⁴⁶ where the metal iodide is dissolved in a solvent and mixed with the support followed by removal of the solvent under vacuum was attempted but results were poor. After each column was prepared, it was baked out at 250 °C for 24 to 72 hours under a flow of 30 ml/min nitrogen. After bakeout, the column was either installed or capped for future use. After installation the column was heated to 150°C and allowed to equilibrate for at least two hours.

Metal Iodide/Phase Transfer Catalyst Conversion Columns

These columns contained a mixture of phase transfer catalyst (PTC), metal iodide salt and support media. Support media was either Chromasorb-W (Alltech or Supelco) or silica gel. Table 2 shows the PTCs used in this study. Methodology for the preparation of the contents of PTC columns was followed as described in the literature.⁴³ This basically involved adding the three components mentioned above to a mixture of water/methanol (7/3) with stirring. After 10 minutes of stirring the water/methanol mixture was removed under aspirator vacuum using a rotary evaporator. The mixture was then baked in a 110°C oven overnight and subsequently stored in an airtight

Table 2. Phase transfer catalyst and metal iodide salt mixtures used to promote low temperature conversion of alkyl bromides to alkyl iodides.

Phase Transfer Catalyst	Metal Iodide Salt	Mixture in gram ratios of Support : Phase Transfer Catalyst : Metal Iodide Salt
Tetrabutylammonium Iodide	Potassium Iodide	Silica Gel:PTC:KI 5.58:0.48:3.94
Tetrabutylammonium Iodide	Zinc Iodide	Silica gel:PTC:ZnI ₂ 5.58:0.48:3.94
Tetrabutylammonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 2.65:0.48:3.94
Tetraethylammonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 3.6:0.50:6.24 Dry prep
Tetraethylammonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 4.0:0.50:6.24 Wet prep
Tetraethylphosphonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 4.0:0.50:5.82
Tetraphenylphosphonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 2.0:0.50:3.42
Tetrabutylammonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 2.67:0.48:3.96 Wet prep
Tetrabutylammonium Iodide	Lead Iodide	ChromasorbW:PTC:PbI ₂ 3.25:0.50:6.24
Tetrabutylphosphonium Iodide	Zinc Iodide	ChromasorbW:PTC:ZnI ₂ 4.15:0.50:2.72 Wet prep

container until needed. The columns themselves were then constructed as described previously.

Sample Makeup

Compounds used in this study were purchased from a variety of commercial vendors. All of the compounds purchased were used as received. Samples of each compound to be tested were made by standard dilution into airtight glass carboys, which were maintained at above-ambient pressure. Carboy volumes were either 20 L or 4.5 L.

Nitrogen was used as the diluent gas and was checked for the presence of electron capturing impurities prior to sample preparation. Initial dilution was performed by injecting a small aliquot of either a neat liquid (0.5 to 100 μ l) or gas (0.5 to 5 ml) into a carboy that was subsequently pressurized to between 1 and 10 psi, depending on the desired concentration. Subsequent dilution was performed by transferring a sample from this initial carboy using a 10 ml gas tight syringe for sample transfer and a second carboy, which was subsequently pressurized to between 1 and 10psi. On occasion this second carboy was used to make a third carboy of even lower concentration. However, final dilutions and sample transfer were usually accomplished using a 100-ml or a 250-ml gas-tight syringe equipped with a Hamilton HV Plug Valve.

Evaluation of Conversion Column Efficiency

After construction, conditioning and installation of a metal-iodide conversion column, samples of methyl bromide or methyl chloride were introduced into the system via the sampling loop. Each metal iodide listed in Table 1 was evaluated for its efficiency of converting 1-ppm methyl bromide and 1-ppm methyl chloride to methyl iodide. The reaction column temperature was varied from 50°C to 150°C in 25°C increments for each metal iodide salt. After adjusting the column temperature, the system was allowed to equilibrate for 1 hour. A strip-chart recorder was used to monitor the output signal of the ECD. This procedure was repeated for each metal iodide. Each salt was evaluated for conversion efficiency by monitoring the peak height of the product methyl iodide.

Investigation of the Conversion Products of Selected Halogenated Organic Compounds

Instrument Design and Conversion Evaluation

For these experiments an identical instrument to that described above except was used except that a FID detector was utilized. The flow rates of air and hydrogen were 300 and 30 ml/min, respectively, for the FID. The detector was operated at 250°C.

Table 3 provides a list of compounds that were analyzed for their possible transformation to an alkyl iodide product using a zinc iodide conversion column and the conditions under which they were tested. All of these chemicals were used as received and prepared in carboys as previously described. Samples from carboys were introduced into the system via the sampling loop. Selected compounds were tested at concentrations ranging from 0.1 ppb to 100 ppm although most were only tested at 10 ppm. Most compounds were tested at two conversion column temperatures, typically 50°C and 150°C. Different concentration and temperature regimes were used when unique results prompted further investigation, as will be discussed below. A computer with a data acquisition card was used to monitor the output signal of the FID. The extent of conversion was determined by monitoring the peak areas of products produced. Because the response of the FID is approximately equal for compounds of equal carbon chain length and similar substitution pattern, peak areas were based on the following formula:

$$\% \text{conversion} = \frac{(\text{peak area for compound of interest})}{(\text{sum of peak areas for all products})} \times 100$$

Table 3. Thirty five alkyl halides that were tested for conversion to alkyl iodides with conversion column temperatures and concentration of alkyl halide tested.

Compound	Concentrations of Alkyl Halide Tested	Conversion Column Temperatures
Brominated Compounds		
CH ₃ Br	100 ppm to 100 ppt	30°C to 200°C
CH ₂ Br ₂	10 ppm	50°C, 100°C, 200°C
C ₂ H ₅ Br	0.1 ppm to 10 ppm	50°C to 150°C
1,2 – dibromoethane	10 ppm	50°C, 100°C, 150°C
n – bromopropane	0.1 ppm to 10 ppm	50°C to 150°C in 25°C inc.
2 – bromopropane	0.1 ppm to 10 ppm	50°C to 150°C in 25°C inc.
1,2 – dibromopropane	0.3 ppm to 10 ppm	100°C and 150°C
1,3 – dibromopropane	10 ppm	50°C, 80°C, 100°C, 105°C, 150°C
2,2 – dibromopropane	1 ppm and 10 ppm	30°C, 50°C, 100°C, 150°C, 180°C
2 – bromobutane	10 ppm	50°C, 100°C, 150°C
iso – butylbromide	0.3 ppm to 10 ppm	50°C, 80°C, 150°C
t – butylbromide	10 ppm	50°C, 80°C, 150°C
Chlorinated Compounds		
CH ₃ Cl	0.3 ppm to 100 ppm	30°C to 200°C
CHCl ₃	10 ppm	50°C and 150°C
CCl ₄	10 ppm	50°C, 100°C, 150°C
C ₂ H ₅ Cl	10 ppm	50°C and 150°C
C ₂ H ₃ Cl	10 ppm	50°C and 150°C
1,1 – dichloroethane	10 ppm	150°C
1,1,1 – trichloroethane	10 ppm	50°C and 150°C
1 – chloropropane	10 ppm	50°C, 100°C, 150°C
2 – chloropropane	0.3 ppm to 100 ppm	50°C and 150°C
2 – chlorobutane	10 ppm	50°C, 100°C, 150°C
t – butylchloride	10 ppm	50°C, 100°C, 150°C
Bromo-chloro Compounds		
CCl ₃ Br	10 ppm	150°C
CHClBr ₂	10 ppm	150°C
C ₂ H ₄ ClBr	10 ppm	150°C
Bromofluoro, chlorofluoro and bromochlorofluoro Compounds		
CF ₃ Br	10 ppm	150°C
CF ₂ Br ₂	10 ppm	150°C
CFBr ₃	?	?
CHFBr ₂	10 ppm	150°C
CF ₂ Cl ₂	10 ppm	50°C and 150°C
CFCl ₃	10 ppm and 110 ppm	50°C and 150°C
CF ₂ ClBr	10 ppm	150°C
CFClBr ₂	10 ppm	150°C

Determination of Methyl Bromide in Whole Air

Instrument Design

For these experiments an instrument similar to that initially described above was used except for the changes noted below. A schematic of this instrument is shown in Figure 2. Samples were introduced through a 6-way valve fitted with a sample loop. The sample loop size was varied and the details will be covered in the results and discussion. The carrier gas was dried beyond that described above and all samples were dried by use of an inline water trap. This trap was located between the outlet of valve V1 and the inlet of the main chromatography column and was constructed of 10 cm of 6-mm o.d. (5.33-mm i.d.) stainless steel tubing packed with ground magnesium perchlorate (Fisher Scientific). Initial chromatography was performed on a 30-m long by 0.53-mm i.d. mega-bore J&W Scientific GS-Q capillary column. The oven of the Varian 3700 and its associated controls were used to control the temperature of this column. This column was chosen over the SF-96 column due to its ability to separate oxygen from the remaining components of whole air. Post conversion column chromatography was achieved using a 1-m by 3-mm o.d 10% SF-96 on Chromasorb-W column. The temperature of the conversion column was controlled by wrapping the column with a heat tape. The heat tape was controlled by a variac and the temperature was monitored by thermometer. The temperature was kept stable by wrapping the heated column with fiberglass insulation.

