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TROPODEGRADABLE BROMOCARBON EXTINGUISHANTS

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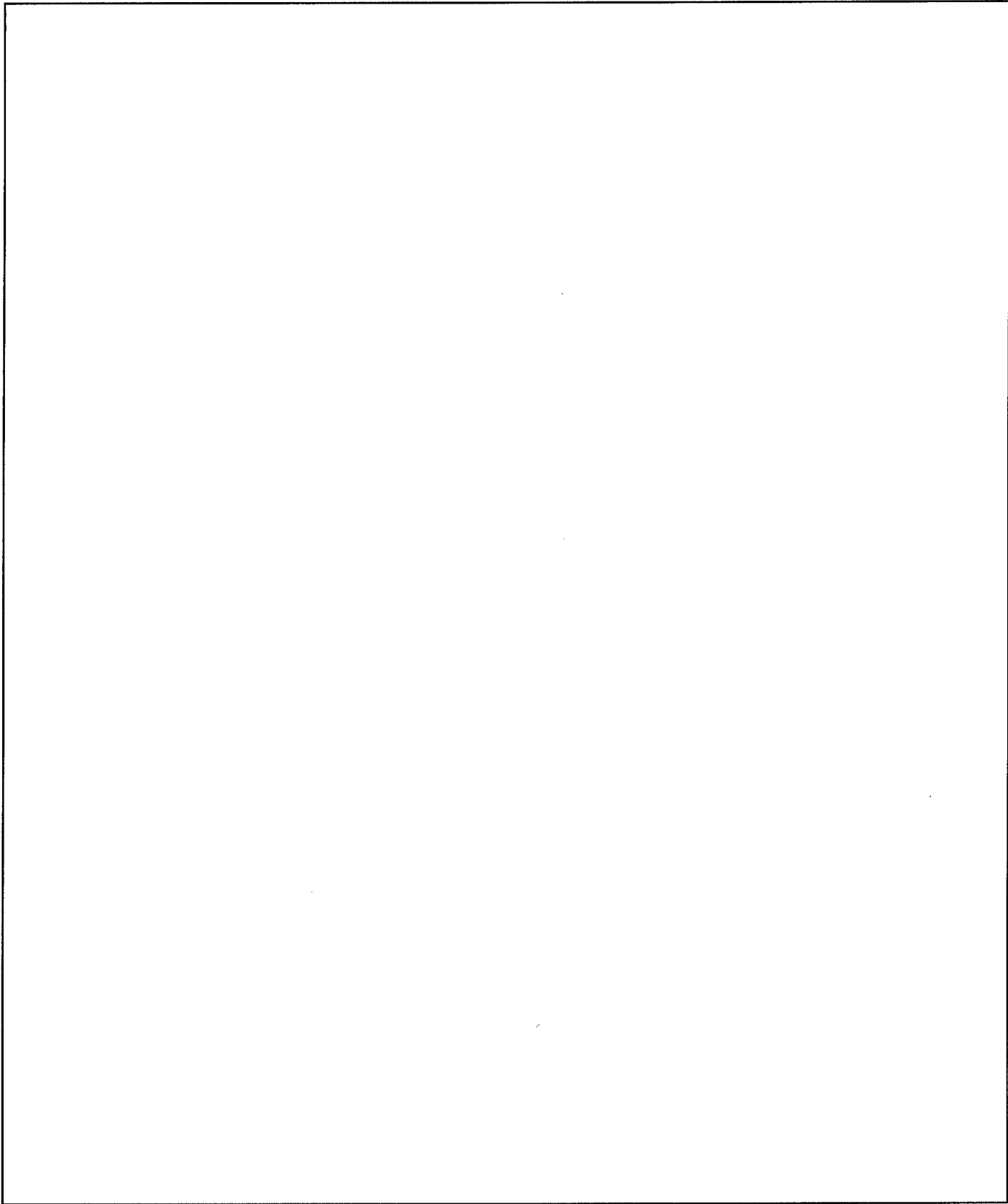
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13. ABSTRACT (Maximum 200 words) Current commercially available Halon 1301 replacement compounds (other than CF3I) lack the fire suppression effectiveness of halon primarily because they do not contain bromine in their molecular structure. Bromine is thought to catalyze radical recombination reactions which deprive the combustion process of the •OH and •H radical species which promote the combustion of fuel molecules in the gas phase. This project was conceived to develop new fire suppressants incorporating bromine by basing the compounds on chemical families with expected or demonstrated short atmospheric lifetimes. These compounds are said to be tropodegradable bromocarbons. The targeted chemical families in order of importance were partially fluorinated alkenes, ethers, and amines. The alkenes have now been shown to have very short lifetimes on the order of days. This project identified several low boiling brominated and partially fluorinated alkenes, ethers, and amines with potential of meeting the toxicity, fire suppression, and environmental criteria currently identified under the EPA's SNAP program for halon replacements. Several of these tropodegradable compounds were subsequently acquired and their cup-burner flame suppression performance evaluated with promising results. Several of the bromofluoro alkenes have now also been evaluated in an acute inhalation toxicity test which yielded extremely promising results for this chemical family. This is an interim report covering the first phase of an ongoing effort.				
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PREFACE

This report was prepared by the Center for Global Environmental Technologies (CGET) at the New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico, for the Department of Defense Strategic Environmental Research and Development Program Next Generation Fire Suppression Program under Contract DASW01-00-P3345. The corresponding University of New Mexico Contract Number is 8-33350.

The Start Date was March 1, 1998, and the End Date was September 30, 1999. The NGP Contracting Officer's Technical Representative is Dr. Ronald Sheinson and the NMERI Principal Investigator is Dr. J. Douglas Mather and the Co-Principal Investigator is Dr. Robert E. Tapscott.

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EXECUTIVE SUMMARY

The objective of the Tropodegradable Bromocarbon Extinguishants project is to identify new chemical compounds with the potential to replace Halon 1301 in total flood fire extinguishment and explosion inertion applications.

Development of replacement chemicals for existing halons is mandated by international treaty, based on the now widely accepted link between atmospheric bromine levels and stratospheric ozone depletion.

Under the Montreal Protocol, an international treaty enacted in 1987 and amended in 1990, 1992, and 1995, the production of halon fire and explosion protection agents was phased out in the United States and other industrialized nations at the end of 1993. One of these agents, Halon 1301, is used throughout the US DoD in total flood applications. To date, no environmentally acceptable substitute equivalent to Halon 1301 in toxicity, effectiveness, and dimensionality has been identified. Most of the replacements now being commercialized or proposed for commercialization are saturated fluorine-containing halocarbons: hydrofluorocarbons (HFC), hydrochlorofluorocarbons (HCFC), and perfluorocarbons (PFC or FC) and fluoroiodocarbons (FIC). Except for CF_3I these replacement chemicals are less effective than Halon 1301 in most scenarios and/or have one or more adverse global environmental impacts (ozone depletion, global warming, long atmospheric lifetime). It is unlikely that new, exceptionally effective, and environmentally acceptable halon replacements will be identified among the normal saturated fluorine-containing halocarbons. Earlier DoD funded projects determined that brominated halocarbons with chemical features leading to very short atmospheric lifetimes ("tropodegradable" bromocarbons) are very promising compounds for evaluation as halon replacements. This projects goal was to identify, acquire and characterize the flame extinguishment performance of tropodegradable bromocarbons with the potential of meeting all toxicity, environmental, and performance requirements of a Halon 1301 replacement.

The history of halon replacement development reflects concurrent progress in fire science and basic environmental and atmospheric research areas. Halon development history has the

appearance of a sequential process involving research-based agent discovery, environmental research resulting in tighter acceptance and selection criteria followed by rejection of developed alternatives, and a resumption of applied research focused on fire suppression agents. At this point environmental property requirements and to a lesser extent toxicological performance targets for halon replacements have become more clearly refined and reliably serve as guides in compound selection and evaluation.

The targeted compounds in this project all contain bromine and are fluorinated to render them non-flammable. Their expected short atmospheric lifetimes translate directly into very low ozone depletion and global warming potentials. The chemical families of interest include the bromofluoro alkenes, ethers, and amines.

In this project, bromofluoroalkenes were the primary focus of compound selection, acquisition and testing efforts due to their promising toxicity, flame suppression, short atmospheric lifetime, and acceptable physical properties. The bromofluoro-alkene chemical family is probably the most studied of all candidate families. Should the remaining chemical families advance to the same level of study they may also prove to be just or more promising as sources of halon replacements.

Data from the RTECS database as well as acute inhalation toxicity and subsequent AMES test data for several of the bromofluoro alkenes of interest here is very promising. Flame extinguishment testing of several bromofluoro alkenes have yielded cup-burner values comparable to those of halon 1301 and 1211. Finally, synthetic methods, in some cases, are expected to enable relatively low cost manufacture of selected bromofluoroalkenes and give hope to the potential for low cost industrial preparation of others.

This project continued previous efforts to identify tropodegradable bromofluoro organic compounds with optimal boiling point and flame extinguishment properties. Through collaboration with the Advanced Agent Working Group (AAWG) and a U.S. Air Force Halon 1211 replacement project eight bromofluoro-alkenes were evaluated for acute inhalation toxicity resulting in the identification of five promising compounds.

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LIST OF ABBREVIATIONS

AAWG	Advanced Agent Working Group
ALC	Approximate Lethal Concentration
AD ₅₀	Dose that is anesthetic to 50 percent of an animal test population
CAS	Chemical Abstracts Service (American Chemical Society)
CCOD	CGET Chemical Options Database
CGET	Center for Global Environmental Technologies
CS _{NOAEL}	cardiac sensitization - no observable adverse effect level
DoD	Department of Defense
DTIC	Defense Technical Information Center
EPA	U.S. Environmental Protection Agency
FC	(per)fluorocarbon
FEC	flame extinguishment concentration
FIC	fluoroiodocarbon
GWP	Global Warming Potential
HCFC	hydrochlorofluorocarbon
HCFPPE	hydrochlorofluoropolyether
HFC	hydrofluorocarbon
HFE	hydrofluoroether
HFPE	hydrofluoropolyether
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LC _{LO}	lowest concentration causing death
LC ₅₀	concentration required to cause death in 50 percent of an animal test population
LD ₅₀	dose required to cause death in 50 percent of an animal test population
LOAEL	Lowest Observable Adverse Effect Level
MEDLARS	Medical Literature Analysis and Retrieval System
MSDS	Material Safety Data Sheet
NIOSH	National Institute for Occupational Safety and Health
NGP	Next Generation Program

LIST OF ABBREVIATIONS (concluded)

NOAEL	No Observed Adverse Effect Level
ODP	Ozone Depletion Potential
PFC	perfluorocarbon
QSAR	Quantitative Structure-Activity Relationship
QSPR	Quantitative Structure-Property Relationship
RTECS	Registry of Toxic Effects of Chemical Substances
SERDP	Strategic Environmental Research and Development Program
SNAP	Significant New Alternatives Policy
TSCA	Toxic Substance Control Act
USAF	United States Air Force
UV	ultraviolet
WPAFB	Wright-Patterson Air Force Base

LIST OF UNITS AND SYMBOLS

A	constant in vapor pressure equation
B	coefficient in vapor pressure equation
g	gram
H	hour
K	Kelvin
lb	pound
M	minute
mL	milliliter
p	pressure
ppm	parts per million
s	second
T	temperature
vol.%	percent by volume
wt.%	percent by weight
•	denotes a free radical, e.g., •OH, the hydroxyl free radical

SECTION I. PROJECT SUMMARY

A. BACKGROUND

Under the Montreal Protocol the production of the fire and explosion protection agents Halon 1301, Halon 1211, and Halon 2402 was phased out in the U.S. at the end of 1993.* To date, no environmentally acceptable halon substitute comparable to the existing halons in toxicity, effectiveness, and dimensionality has been identified.

Halocarbons as replacements for halons have been well studied, and exceptionally effective, halon replacements have not been identified among the normal saturated halocarbons (excluding iodides and other halocarbons with chemical features leading to short atmospheric lifetimes).† The hydrochlorofluorocarbons (HCFC), perfluorocarbons (PFC or FC), and hydrofluorocarbons (HFC) are all less effective than the present halons in most scenarios. Moreover, all of these have some adverse global environmental impact (ozone depletion, global warming, and/or long atmospheric lifetime). PFCs and HCFCs are already subject to some restrictions, and such restrictions may eventually extend to HFCs.

There is, therefore, reason to look at compounds other than the normal saturated halocarbons. Nonhalocarbon candidates and halocarbons with chemical features leading to very short atmospheric lifetimes ("tropodegradable" halocarbons) are known as "advanced agents" have been assessed in detail [1, 2]. These compounds represent an opportunity to retain bromine in the chemical structure of the fire suppressant without risking significant impact on stratospheric ozone levels.

Prior to this project very few tropodegradable bromocarbons had been acquired and evaluated for cup-burner performance. Those compounds for which data existed, Table 1, provided limited evidence of the potential of this group of chemicals to be halon replacements.

*Only Halon 1211 and Halon 1301 have had significant use in the U.S. The primary use of Halon 2402 has been in the former Soviet Union and in a few eastern European countries.

†Appendix A contains a glossary of chemical, toxicological, and other terms.

Table 1. Tropodegradable Compound Cup-Burner Values

Compound name	Compound formula	^a Cup-Burner, %
1-bromo-3,3,3-trifluoropropene	CHBr=CHCF ₃	4.5
3-bromo-3,3-difluoropropene	CH ₂ =CHCBrF ₂	^b 4.5
2-bromo-3,3,3-trifluoropropene	CH ₂ =CBrCF ₃	2.6
4-bromo-3,3,4,4-tetrafluorobutene	CH ₂ =CHCF ₂ CBrF ₂	3.5
4-bromo-3-chloro-3,4,4-trifluorobutene	CH ₂ =CHCClFCBrF ₂	4.5
1-bromo-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene	C ₆ BrF ₄ CF ₃	4.3
3-bromo-1,1,1-trifluoro-2-propanol	CF ₃ CHOHCH ₂ Br	4.1
3,3-dibromo-1,1,1-trifluoro-2-propanol	CF ₃ CHOHCHBr ₂	4.9

^a*n*-heptane fuel using the NMERI Cup-Burner and mixing of separate air/agent flows.

^bA value of 8.5% was reported earlier based on insufficient compound.

Short atmospheric lifetimes of tropodegradable result from one or more of the following: (1) reaction with atmospheric hydroxyl free radicals; (2) photolysis; (3) reaction with tropospheric ozone; and (4) physical removal (rain-out) [2]. A number of tropodegradable or potentially tropodegradable halocarbons (e.g., alkenes, aromatics, polar-substituted halocarbons) have been identified as promising candidates for both Halon 1301 and Halon 1301 replacement.

For the compounds of interest here, the atmospheric hydroxyl free radicals (\bullet OH) abstract a hydrogen atom and/or add to an unsaturated molecule to give polar products. It has been found that the activation energy for hydrogen atom abstraction decreases (as expected) with decreasing dissociation energy of the C-H bond. Replacement of either a fluorine atom or a hydrogen atom by an oxygen or nitrogen atom alpha to a CH group decreases the bond dissociation energy and increases the reaction rate. Beta substitution generally has a much lower substituent effect on bond dissociation energies. We have calculated (in agreement with some experimental data) that rate constants for reaction with hydroxyl free radicals increase by a factor of approximately 200 for addition of an ether linkage adjacent to a hydrogen atom. This gives atmospheric lifetimes as short as 0.3 years for some hydrofluoroethers (HFEs). Replacement of a fluorine with a bromine will reduce the atmospheric lifetime by about a factor of 10. Thus brominated HFEs should have atmospheric lifetimes as short as 11 days. Experimental

characterization of OH radical addition to alkene double bonds indicate the trans-2-butene derivatives are likely to have the highest rates of OH addition to the double bond.

Unfortunately, no reliable data exist for amines containing fluorine substitution. The atmospheric environmental parameters of some HFAs have been reported [3]. The reported lifetime for $(CF_3)_2NCH_3$ of 0.28 years is of particular interest since replacement of one of the fluorine atoms by bromine is likely to reduce this to about 0.028 years due to enhanced photolysis[4]. A very small amount of data indicates that for bromine-containing compounds, each 10 years increase in atmospheric lifetime increases the ODP by approximately 2. Thus, for an atmospheric lifetime of 0.028, $(CBrF_2)(CF_3)NCH_3$ would have an ODP of 0.006.

Addition of $\bullet OH$ free radicals to unsaturated chemicals is a highly effective removal process. For alkenes, the hydroxyl radical adds to give a highly energetic product radical. The energetic product can then either revert back to products, or it can be stabilized by collision with another molecule which can carry off the excess energy. The reverse reaction is probably not important below 100°C. Hydroxyl free radicals can also add to a triple bond and to aromatics.

In general, halocarbons require one of the groups carbonyl, conjugated double bonds, double bond conjugated to aromatic, polynuclear aromatic, nitro aromatic, or bromine/iodine to be present for there to be significant absorption and photodissociation in the troposphere. All of the proposed compounds contain bromine; otherwise, only carbonyls are of major interest in the proposed research as far as photolysis is concerned.

The only chemicals exhibiting rapid reaction with tropospheric ozone are the alkenes. Removal by tropospheric ozone is expected to be significant for these compounds. The mechanisms of these reactions are not well understood, and the potential for reaction of highly fluorinated alkenes with tropospheric ozone is uncertain. For a globally averaged tropospheric ozone concentration of $[O_3] = 5.0 \times 10^{11}$ molecules/cm³ and using a maximum repeated rate constant of 2×10^{-16} cm³/molecule-s reported in the literature, one calculates a first-order reaction rate constant of $k_1 = (k_{O_3})[O_3] = 1 \times 10^{-4}$. This allows a calculation for alkenes for the atmospheric lifetime of $t_{1/e} = 1/k_1 = 10^4$ seconds or less than one day. Thus, removal by tropospheric ozone could be significant for alkenes. Generally, estimates of the atmospheric

lifetime of alkenes focus entirely on the hydroxyl radical reaction rate constant and ignore the ozonolysis reaction.

Table 2 lists the various removal mechanisms and the families that are likely to have significantly decreased tropospheric lifetimes due to each mechanism.

Table 2. Tropospheric Removal Mechanisms

Primary removal mechanism	Example families
Photodegradation	Iodides, Carbonyls, Bromides
Reaction with Hydroxyl	Alkenes, Aromatics, Hydrogen-Containing Amines, Hydrogen-Containing Ethers, Carbonyls
Physical Removal	Ketones, Alcohols, Esters
Reaction with Tropospheric Ozone	Alkenes

The successful development of a halon replacement is predicated on the identification of all critical parameters needed for eventual SNAP approval as well as those parameters central to the intended fire and explosion inertion and suppression application(s). The compound selection criteria employed in this project reflect current toxicity and environmental concerns and overall were the result of an evolving understanding of desired halon replacement properties.

This project identified and acquired several tropodegradable compounds (primarily alkenes) estimated to satisfy the requirements of a Halon 1301 replacement. The compound properties reviewed or estimated included toxicity, boiling point, fire extinguishment performance, and tropospheric lifetime.

Commercial chemical companies and institutes of chemical science in Russia and the US were provided with lists of the compounds of interest and quotes for synthesis were requested. Commercially available and synthesizable compounds were obtained and evaluated. Extinguishment tests run on the acquired compounds employed the NMERI cup-burner.

B. PROJECT TASKS

In order to advance the study of tropodegradable bromocarbon extinguishants as possible Halon 1301 replacements three tasks were identified and undertaken. The development of lists of potential tropodegradable bromocarbons preceded this effort as has the identification of chemical syntheses and some commercial sources of compounds. Earlier studies compiled toxicity information, atmospheric lifetime estimates, and preliminary lists of potential compounds of interest [1, 2]. Despite these assets few tropodegradable compounds had actually been acquired and had their flame extinguishment properties evaluated. The lack of actual flame extinguishment data (and toxicity test data) greatly slowed earlier efforts in the area of halon replacement research.

Three basic tasks identified to advance research in this area are identified briefly below.

Task 1. Compound selection.

Of critical importance in the selection of candidate compounds is an adequate understanding of chemical compositional and structural factors contributing to compound toxicity and extinguishment capability. Target compounds were evaluated and promising candidates identified. The compound properties reviewed or estimated included toxicity, boiling point, fire extinguishment performance, and tropospheric lifetime. Toxicity estimates are based on toxicity literature, toxicology databases and anesthesiology reports. Promising tropodegradable compounds were selected based on either known or predicted properties and subsequently procured or synthesized. Toxicity and anesthesiology literature review coupled with results from Quantitative Structure-Activity Relationships (QSAR) and Quantitative Structure-Property Relationships (QSPR) computational evaluations of chemical properties were employed to identify tropodegradable compounds with promise as Halon 1301 replacements. In all cases, the compounds selected are predicted to have low tropospheric lifetimes (on the order of days), low toxicities (LC_{50} comparable to that of Halon 1301), fire extinguishing concentrations as measured by the cup-burner method of no more than 5 vol.% in air, and boiling points generally below 50°C.

Table 3 lists initial targeted performance criteria for Halon 1301 replacement candidate compound physical, environmental, and toxicological properties. These criteria, are similar to those employed in the selection of streaming agent replacements.*

Table 3. Targeted Halon 1301 Replacement Criteria

Attribute	Guideline
Boiling Point	Dependent on application temperature (<50°C)
LC ₅₀ (4-hour)	> 50,000 ppm (5.0%)
Cup-Burner Ext. Concentration	< 5.0%
Ozone Depletion Potential	< 0.02 ^a
Global Warming Potential	< 5,000 ^b
Atmospheric Lifetime	<< 0.1 years
Cardiac Sensitization – No Adverse Effect Level	> 2 times the cup-burner value

^aWith respect to CFC-11

^bWith respect to CO₂

Task 2. Acquisition - Synthesis and Characterization

A survey of commercial and academic sources of chemical synthesis expertise was performed and lists of selected bromofluoro-alkenes, bromofluoro-ethers, and bromofluoro-amines were sent to all potential sources of synthetic support. Synthetic pathways to the compounds of interest were in some cases identified and tested in order to support the synthesis efforts being made by suppliers [2].

Task 3. Cup-Burner Testing

Extinguishment performance of selected tropodegradable bromocarbons was conducted using the NMERI Standard Cup-Burner. Use of this cup burner significantly reduces the cost of compounds and provides a reliable means of quickly screening compounds to determine flame

*Juan A. Vitali, Applied Research Assoc., personal correspondence to J. Douglas Mather, NMERI, February 1997.

extinguishment performance. NMERI Cup-burner test methods developed in earlier halon replacement efforts require approximately 50g of the test compound and give significantly less scatter than an apparatus similar to the ISO burner.* Subsequent modifications to the standard method were developed in the course of this research effort. The modified method involves introducing premixed agent/air mixtures into the flame zone. This permits flame extinguishment characterization of with as little as 2 to 5 grams of a chemical depending on molecular weight and actual cup-burner flame extinguishment performance. Observed flame extinguishment concentration values were employed in the ongoing review and compound selection process.

C. TECHNICAL PROBLEMS

The acquisition of chemicals, most of whom have never been synthesized, is very costly and very time consuming. In order to minimize per compound costs a modification to cup-burner test methods was developed as indicated in Task 3. This modification makes it possible to obtain an upper-bound value for the cup-burner extinguishment using as little as 2 grams of a test compound instead of the typical 50 gram requirement. This modification does not affect the utility of the resulting cup-burner value and in fact provides greater stability and accuracy in air concentration measurements and actual test conditions. This modification will be described in greater detail in Section 4, Detailed Description of the Project.

D. GENERAL METHODOLOGY

Alkene halocarbons are among the chemical groups identified as being tropodegradable and having low atmospheric lifetimes. The relative ease of syntheses and the low atmospheric lifetimes of bromofluoro-alkenes result in their being considered a very promising source of Halon 1301 replacement candidates. Alkenes react rapidly with tropospheric •OH radicals through addition to the double bond, a reaction that proceeds faster than H atom abstraction. In addition, the alkene double bond readily undergoes reaction with tropospheric O₃ in a process referred to as "ozonolysis." Both OH and ozonolysis reaction products are expected to be

*Testing in our laboratory comparing cup burners of various sizes and types have shown this.

rapidly removed from the troposphere by rainout. This project focused most of its efforts on the identification, acquisition, and testing of bromofluoro-alkenes.

Tropodegradable compounds, with an emphasis on bromofluoro-alkenes, were evaluated and a list of potential replacements was developed. Promising tropodegradable compounds were selected based on either known or predicted properties and subsequently procured or synthesized. The compound properties reviewed or estimated included toxicity, boiling point, fire extinguishment performance, and atmospheric lifetime. Toxicity estimates were attempted using QSPR/ QSAR, toxicity literature, and anesthesiology reports. Toxicity, cup-burner performance, and atmospheric lifetime estimates were made on these and similar compounds.

Synthetic routes for the compounds of interest were investigated, starting materials were determined, and several compounds were synthesized. Commercial chemical companies and institutes of chemical science in Russia were provided with lists of the compounds of interest and quotes for synthesis were requested. Extinguishment tests run on the selected compounds utilized the NMERI Standard Cup-burner.

E. TECHNICAL RESULTS

Tropodegradable bromofluoro-alkenes were evaluated in fire suppression tests during the program. The results of laboratory cup-burner tests with the tropodegradable bromofluoro-alkene, 2-bromo-3,3,3-trifluoropropene ($\text{CH}_2=\text{CBrCF}_3$) demonstrated fire extinguishment performance close to that of Halon 1301, Table 4 and Table 5.

Extinguishment test results and (limited) toxicity information show the potential of tropodegradable bromofluoro-alkenes as Halon 1301 replacements. Future work should continue to focus on these compounds.

Table 4. Tropodegradable Brominated Halocarbon Cup-burner Values

CCOD ID	Compound, Formula	Boiling point (°C)	Cup-burner (%)
707	1-Bromo-3,3,3-trifluoropropene, $\text{CF}_3\text{CH}=\text{CHBr}$	40	3.5*
872	3-Bromo-3,3-difluoropropene, $\text{CBrF}_2\text{CH}=\text{CH}_2$	42	4.5
873	2-Bromo-3,3,3-trifluoropropene, $\text{CF}_3\text{CBr}=\text{CH}_2$	34	2.6
903	4-Bromo-3,3,4,4-tetrafluorobutene, $\text{CF}_2\text{BrCF}_2\text{CH}=\text{CH}_2$	54	3.5
1116	2-Bromo-3,3,4,4,4-pentafluorobutene, $\text{CF}_3\text{CF}_2\text{CBr}=\text{CH}_2$	56	3.8*
1358	2-Bromo-3,3,4,4,5,5-heptafluoropentene, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CBr}=\text{CH}_2$	78	3.7*
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene, $\text{CF}_3\text{CF}(\text{CF}_3)\text{CBr}=\text{CH}_2$	78	3.3*
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene, $\text{CF}_3\text{CF}(\text{OCF}_3)\text{CBr}=\text{CH}_2$	75	3.8*
1391	1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene, $(\text{CF}_3)_2\text{C}=\text{CHBr}$	63	2.6*
1413	1-Bromo-4,4,4,3,3-pentafluorobutene, $\text{CF}_3\text{CF}_2\text{CH}=\text{CHBr}$	58	3.1*

*Testing performed using premixed agent/air mixtures all others involved mixing of separate air/agent flows

Table 5. Tropodegradable Bromofluoro-Amines

CCOD ID**	Compound, Formula	Boiling point °C	Cup-burner (%)
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, $N(CF_3)_2(CHF CF_2 Br)$	72	2.4*
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, $N(CF_3)_2(CF_2 CFH Br)$	72	
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, $N(CF_3)_2(CH_2 CF_2 Br)$	80	2.4

Testing performed using premixed agent/air mixtures

* Results of a 60/40 blend of CCOD's 1392 and 1393

** NMERI Chemical Compound Options Database ID

F. IMPORTANT FINDINGS

The findings to date continue to be promising. Cup-burner extinguishment data and limited toxicity data both are encouraging and several of the bromofluoro-alkenes and the bromofluoro-amines demonstrated flame extinguishment performance comparable to Halon 1301. By far, bromofluoro-alkenes are the easiest group of compounds to acquire while bromofluoro-amines are the most difficult and expensive.

G. SIGNIFICANT HARDWARE DEVELOPMENT

The NMERI Cup-burner as originally designed employed a gravimetric method for dispensing liquid agents into the cup-burner base where an air stream aided by heating evaporated the agent as quickly as it is added. This method required approximately 50 to 100 grams of test agent depending on the agents density and extinguishment properties. This method was revised to employ premixed agent air mixtures of air and agent which decreased the amount of material required and hence the cost of performing this test. The agent/air mixture is contained in a 10L Tedlar gas sample bag which is itself housed within an airtight rigid container. The container is penetrated by a sample line which connects to the Tedlar bag and a second line which simply penetrates into the air space between the bag and the inner wall of the rigid container. Detailed drawings are provided in Section III.

H. SPECIAL COMMENTS

Very few commercial or academic laboratories are willing to entertain the challenge of synthesizing unknown compounds. Environmental regulations have eliminated a lot of the small molecule starting materials required to attempt synthesis of compounds of interest and have also significantly driven-up the cost of acquiring chemicals. Consolidation of the commercial fluorochemical synthesis companies has greatly reduced the number of sources of synthetic expertise. All of these factors greatly limit the number of compounds that can be obtained and tested.

I. IMPLICATIONS FOR FURTHER RESEARCH

In this project, bromofluoroalkenes were the primary focus of compound selection, acquisition and testing efforts due to their promising toxicity, flame suppression, short atmospheric lifetime, and acceptable physical properties. Data from the RTECS database as well as acute inhalation toxicity and subsequent AMES test data for several of the bromofluoro alkenes of interest here is very promising.

This project has resulted in the identification and acquisition of a number of tropodegradable bromofluoro-alkenes and bromofluoro-amines with expected low atmospheric lifetimes and demonstrated flame extinguishment performance. Their expected short atmospheric lifetimes translate directly into very low ozone depletion and global warming potentials. Some of these compounds were evaluated in acute inhalation toxicity exposures at 5% (vol./vol.) for 30 minutes, Table 6[5]. The results of this test were very promising as three of the bromofluoro-alkenes evidenced no mortality and no changes in lung tissue appearance or weight.

Flame extinguishment testing of several bromofluoro alkenes have yielded cup-burner values comparable to those of halon 1301 and 1211. Finally, synthetic methods, in some cases, are expected to enable relatively low cost manufacture of selected bromofluoroalkenes and give hope to the potential for low cost industrial preparation of others.

Table 6. Acute Inhalation Data for Tropodegradable Alkenes

CCO D ID	Compound	Formula	Mortality	Lung Tissue Condition
873	2-Bromo-3,3,3-trifluoropropene	$\text{CH}_2=\text{CBrCF}_3$	0	Normal
707	1-Bromo-3,3,3-trifluoropropene	$\text{CHBr}=\text{CHCF}_3$	0	Normal
872	3-Bromo-3,3-difluoropropene	$\text{CH}_2=\text{CHCBrF}_2$	7	Mottled
903	4-Bromo-3,3,4,4-tetrafluorobutene	$\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$	0	Normal
1116	2-Bromo-3,3,4,4,4-pentafluorobutene	$\text{CH}_2=\text{CBrCF}_2\text{CF}_3$	0	Mottled
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	$\text{CH}_2=\text{CBr}(\text{OCF}_3)\text{CFCF}_3$	10	Mottled
1358	2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$\text{CH}_2=\text{CBrCF}_2\text{CF}_2\text{CF}_3$	1 (post exposure)	Mottled
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	$\text{CH}_2=\text{CBrCFC}(\text{CF}_3)_2$	10	Marked mottling

It is recommended that future work continue the acquisition of these compounds, with an emphasis on those with low boiling points, in quantities sufficient to allow flame extinguishment performance characterization. Toxicity screening studies leading to the selection of several compounds judged to have a high probability of meeting all SNAP requirements should be followed by manufacturing evaluations to select the least costly chemical(s) for the final phase of toxicity testing and development.

SECTION II.
BIBLIOGRAPHY

A. PAPERS PRESENTED

Tapscott, R.E., and Mather, J.D., "Research on Main Group Element Compounds and Tropodegradable Halocarbons as Halon Substitutes," *Proceedings, Fire Suppression and Detection Research Application Symposium*, Orlando, National Fire Protection Research Foundation, 1999.

Mather, J.D., and Tapscott, R.E., "Tropodegradable Halocarbons and Main Group Element Compounds," *Proceedings of the 1999 Halon Options Technical Working Conference*, Albuquerque, 1999.

Tapscott, R.E and Mather, J.D., "Tropodegradable Fluorocarbon Replacements for Ozone Depleting and Global Warming Chemicals, International Conference on Fluorine Chemistry '99, Tokyo, 1999.

SECTION III PROJECT DESCRIPTION

A. COMPOUND SELECTION

Three tasks were identified in order to accomplish the objectives of this project. These are: (1) to identify and select for acquisition promising tropodegradable fluorinated organobromine compounds; (2) acquire or synthesize identified compounds; and (3) to test the flame extinguishment capability of the acquired compounds. All targeted compounds in this effort were estimated to have acceptably low toxicity, ODP, and GWP for use as total flooding agents.

The goal of the selection process is to identify compounds meeting the fundamental requirement of adequate to excellent flame extinguishment performance that also comply with standards of environmental performance in the areas of ozone depletion and global warming potential. Additionally, these compounds also needed to meet physical property requirements (boiling point, fill-density for drop in applications) related to the range of applications and delivery systems, and their toxicity must be judged as not presenting undue hazard under the circumstances of use and handling i.e. normally occupied vs. unoccupied spaces. To this core of requirements could be added the eventual requirement that the finalist in this process of development must be manufacturable at a cost that is acceptable by the user. This project is focused only on the primary elements of the halon replacement selection process, those being estimated acceptable environmental, flame extinguishment performance, toxicity, and physical properties as the first step in the identification of a tropodegradable chemical as a Halon 1301 replacement.

Chemical families presented in an early list of tropodegradable compounds, reviewed by the AAWG, all contained functionalities which limit atmospheric lifetime through reaction with atmospheric $\bullet\text{OH}$ or O_3 and or render the compound naturally prone to rainout, Table 7.

Table 7. List of 26 Halon 1301 Replacement Candidates

Formula	Name
Alkenes	
CH ₂ =CHCF ₂ Br	3-bromo-3,3-difluoropropene
CF ₂ BrCH=CHCF ₃	<i>cis</i> - and <i>trans</i> -1-bromo-1,1,4,4,4-pentafluoro-2-butene
CF ₂ BrCF ₂ CH=CH ₂	4-bromo-3,3,4,4-tetrafluorobutene
CF ₂ BrC(CF ₃)=CH ₂	3-bromo-3,3-difluoro-2-(trifluoromethyl)propene
Alcohols	
CF ₂ BrCH ₂ OH	2-bromo-2,2-difluoroethanol
CF ₃ CFBrCH ₂ OH	2-bromo-2,3,3,3-tetrafluoropropanol
CF ₂ BrCF ₂ CH ₂ OH	3-bromo-2,2,3,3-tetrafluoropropanol
CF ₃ CHOHCH ₂ Br	3-bromo-1,1,1-trifluoro-2-propanol
Ethers	
CF ₂ H-O-CFHBr	(bromofluoromethyl)(difluoromethyl)ether
CF ₂ Br-O-CH ₃	(bromodifluoromethyl)(methyl)ether
CF ₂ BrCH ₂ -O-CF ₃	(2-bromo-2,2-difluoroethyl)(trifluoromethyl)ether
CF ₂ BrCF ₂ -O-CH ₃	(2-bromo-1,1,2,2-tetrafluoroethyl)(methyl)ether
-CH ₂ CF ₂ CBrFCH ₂ -O-	3-bromo-2,2,3-trifluorooxolane
Amines	
(CBrF ₂)(CHF ₂) ₂ N	bis(difluoromethyl)(bromodifluoromethyl)amine
(CBrF ₂)(CF ₃)(CH ₃)N	(bromodifluoromethyl)(trifluoromethyl)(methyl)amine
(CF ₃) ₂ (CH ₂ CBrF ₂)N	bis(trifluoromethyl)(2-bromo-2,2-difluoroethyl)amine
(CBrF ₂)(CF ₃) ₂ N	bis(trifluoromethyl)(bromodifluoromethyl)amine
Carbonyl Compounds	
CBrF ₂ CH ₂ C(O)H	3-bromo-3,3-difluoropropanal
CH ₃ C(O)CH ₂ CF ₂ Br	4-bromo-4,4-difluoro-2-butanone
CBrF ₂ CH ₂ C(O)OCH ₃	methyl 3-bromo-3,3-difluoropropionate
CBrF ₂ CH ₂ C(O)OCF ₃	trifluoromethyl 3-bromo-3,3-difluoropropionate
Aromatics	
C ₆ F ₅ Br	bromopentafluorobenzene
C ₆ F ₅ CBrF ₂	(bromodifluoromethyl)pentafluorobenzene
C ₆ BrF ₄ CF ₃	2-bromoheptafluorotoluene
	3-bromoheptafluorotoluene
	4-bromoheptafluorotoluene

The AAWG review of these chemical families yielded the recommendation that several be dropped from further consideration, primarily for toxicity and or physical property reasons.

The compound groups selected for study in this project were in order of decreasing promise the bromofluoro-alkenes, the bromofluoro-ethers, and bromofluoro-amines. Each of these groups is discussed in the balance of this section with respect to estimates of flame extinguishment, toxicity, atmospheric lifetime, and relevant physical properties.

1. Alkene toxicity information reviewed

Some general (but not universal) toxicity trends shown in Table 8 have been used to provide a relative toxicity ranking for the candidate compounds and compound groups (alkenes, ethers, cyclics etc.)*

Table 8. General Toxicity and Cardiac Sensitization Rules

<u>Toxicity Ranking Criteria</u>
Aromatics are more toxic than aliphatics.
Asymmetric molecules are more toxic than symmetric.
Straight (carbon) chains are more toxic than branched.
Ethers are more toxic than alkanes.
Short chain ethers are more toxic than long chain ethers.
Vinyl ethers are more toxic than saturated ethers.
Polyoxy ethers are more toxic than mono ethers.

<u>Cardiac Sensitization Ranking Criteria</u>
Halogen presence is more potent than hydrogen.
Bromine presence is more potent than fluorine presence.

*Allen Vinegar, ManTech Environmental Technology Inc., Dayton, Ohio, personal correspondence to Robert E. Tapscott, New Mexico Engineering Research Institute, The University of New Mexico, Albuquerque, New Mexico, May 1997.

Approximate Lethal Concentration (ALC) data Table 9 [6] indicate that for halogenated ethenes, toxicity increases with increasing halogen substitution and that chlorine substitution gives a higher toxicity than does fluorine substitution. Note that for alkanes, toxicity is observed to first increase and then decrease with increasing fluorine substitution. For example, perfluoroalkanes and non-fluorinated alkanes are generally less toxic than the hydrofluoroalkanes.

Table 9. ALC Values for Halogenated Amines.

Compound name	Compound formula	^a ALC, ppm
Fluoroethene	CH ₂ =CHF	>800,000
1,1-Difluoroethene	CH ₂ =CF ₂	>128,000
Tetrafluoroethene	CF ₂ =CF ₂	40,000
Chlorotrifluoroethene	CF ₂ =CClF	4,000
1,1-Dichloro-2,2-difluoroethene	CF ₂ =CCl ₂	1,000

^aOne exposure of 4 to 19 hours.

A compilation of the inhalation toxicity of all halogenated compounds listed in the Registry of Toxic Effects of Chemical Substances (RTECS) database was reviewed.* This information was accessed through the Chemical Abstracts STN service. LC₅₀ and LC_{LO} data for selected halogenated compounds, tropodegradable alkenes, and ethers were compiled from this information and are presented in Table 10 and Table 11.

*Lawrence R. Grzyll, Mainstream Engineering Corporation, Rockledge, Florida, personal correspondence to J. Douglas Mather, New Mexico Engineering Research Institute, The University of New Mexico, Albuquerque, New Mexico, April 1997.

Table 10. Selected Inhalation LC₅₀ Toxicity Information.

CAS No.	Compound name	Species	Duration ^a	LC ₅₀ , ppm
20591-32-6	2-Bromo-1,1,1,4,4,4-hexafluoro-2-butene	Mouse	1H	5,000
11111-49-2	Dichlorohexafluorobutene	Rat	4H	16
	"	Mouse	4H	26
	"	Dog	4H	182
2418-21-5	<i>trans</i> -2,3-Dichloro-1,1,1,4,4,4-hexafluoro-2-butene	Mouse	1H	61
706-79-6	1,2-Dichlorohexafluorocyclopentene	Mouse	2H	210
677-21-4	3,3,3-Trifluoropropene	Mouse	2H	430,676
434-64-0	Octafluorotoluene	Rat	1H	1141
392-56-3	Hexafluorobenzene	Mouse	2H	12,487
382-21-8	Perfluoroisobutylene	Rat	6H	0.50
382-10-5	3,3,3,4,4,4-Hexafluoroisobutylene	Rat	4H	1,425
360-58-7	Ethylheptafluoroisobutenyl ether	Mouse	NR	4,976
344-07-0	Chloropentafluorobenzene	Rat	4H	>59
303-04-8	2,3-Dichlorohexafluoro-2-butene	Rat	4H	16
	"	Mouse	4H	26
	"	Dog	4H	182
116-15-4	Hexafluoropropene	Rat	4H	1825
	"	Mouse	4H	750
116-14-3	Perfluoroethene	Rat	4H	40,000
	"	Mouse	4H	34,963
392-56-3	Perfluorobenzene	Mouse	2H	12,500
336-19-6	1,2-Dichloro octafluorocyclohexene	Mouse	2H	76
79-35-6	1,1-Dichloro-2,2-difluoroethylene	Rat	4H	93
11111-49-2	Dichlorohexafluorobutene	Rat	4H	16
79-38-9	Chlorotrifluoroethylene	Rat	4H	1,000

Table 11. Selected RTECS Alkene LC_{LO} Inhalation Toxicity Information.

CAS No.	Compound name	Species	Duration ^a	LC _{LO} , ppm
2356-01-6	1-(2',2',2'-Trifluoroethoxy)nonafluoro cyclohexene	Mouse	15M	19,000
1759-60-0	Monomethoxyheptafluorocyclopentene	Mouse	NR	12,000
2418-22-6	<i>cis</i> -2,3-Dichlorohexafluoro-2-butene	Mouse	1H	179
697-11-0	Hexafluorocyclobutene	Mouse	NR	50,000
647-53-0	Monomethylnonafluorocyclohexene	Mouse	NR	8,000
598-73-2	Bromotrifluoroethene	Rat	4H	279
434-64-0	Perfluorotoluene	Mouse	10M	5,000
360-89-4	Octafluoro-2-butene	Mouse	4H	6,100
355-75-9	Decafluorocyclohexene	Mouse	NR	8,000
79-47-0	3-Chloropentafluoro-3-propene	Rat	NR	27
2418-22-6	2,3-Dichlorohexafluoro-2-butene	Mouse	1H	179

^a H = hours, M = minutes. NR indicates duration not reported.

Experimental data for three bromofluoro-alkenes and fluoro-alkenes highlight the potential for these lower molecular weight compounds to meet toxicity requirements for a Halon 1301 replacement. Toxicity information for these three compounds is presented below.

3,3,3-Trifluoropropene has been reported to have a 2-hour mouse LC₅₀ of 430,676 ppm, Table 10. This is a rather impressive and hopeful result. A number of mono-brominated structural isomers can be easily envisioned based on this molecule.

More extensive information is available on 4-Bromo-3,3,4,4-tetrafluorobutene. This compound has been reported [7] to have a 4-hour ALC in rats greater than 19,300 ppm. The compound is not mutagenic in Ames bacterial assay, with and without metabolic activation, in strains TA 1537, TA 1538, and TA 98, and it is not clastogenic in Chinese Hamster Ovary (CHO) cell assay with and without metabolic activation. In a 2-week sub chronic study, male rats were exposed to concentrations of 0, 1000 or 10,000 ppm, 6 hours/day, 5 days/week for 2 weeks. Clinical observations during exposure included a decreased response to sound and loss of coordination in rats exposed to 10,000 ppm. Rats in this group had significantly lower body

weights than controls during the exposure period but showed a normal rate of weight gain during recovery period. Rats exposed to 1000 ppm showed a normal rate of weight gain throughout the study. Pathological examination showed no compound-related macroscopic or microscopic changes in any of the rats. The mean relative liver weight of rats exposed to 10,000 ppm was significantly higher upon comparison with controls after Exposure 10 but was in the normal range after 14 days recovery. Mean absolute spleen weights for rats in both test groups were significantly lower than those of controls after 14 days recovery. In the absence of any microscopic changes, the relevance of these organ weight changes is questionable. Clinical chemistry measurements showed that rats exposed to 1,000 ppm excreted more fluoride than controls following exposure while rats exposed to 10,000 ppm showed an increase in both concentration and in the total amount of urine excreted.

2-Bromo-3,3,3-trifluoropropene, $\text{CH}_2=\text{CBrCF}_3$, has been reported to be an "excellent anesthetic with a rapid, uneventful recovery" in exposures of dogs [8]. It is impossible to determine the anesthetic potency of this chemical since the concentrations used were not reported; however, since anesthesia was attained and no adverse effects were observed, this material appeared to have a low acute inhalation toxicity (this conclusion was later confirmed in testing). 2-Bromo-3,3,3-trifluoropropene is one of two bromine adducts of 3,3,3-trifluoropropene whose low inhalation toxicity, Table 10, is discussed above. Based on these results the mono-brominated trifluoro- and possibly tetrafluoro- three carbon alkenes appear to be a promising area for consideration as halon replacement candidates. There is no evidence that the mono-bromo tetrafluoro- and pentafluoro-butenes should not also be considered promising.

3-Bromo-3,3-difluoropropene's rat ALC is 10,000 ppm all four animals in this test died in the last hour of the 4-hour exposure. It is expected that compounds in which the bromine is alpha to the double bond will be more likely to form allyl cations (Reference 9). These cations could contribute to toxicity.

2. Amine Toxicity Information Reviewed

The acute inhalation toxicity of some fluorinated alkyl amines are give in Table 12.* In addition to these, the LC_{LO} for mouse inhalation has been reported as 500 mg/m³ for 2,2,2-trifluoroethylamine ((CF₃CH₂)NH₂, CAS No. = 753-90-2, SAX No. = TKA500) with a SAX Hazard Rating (HR) of 2, [10].

TABLE 12. ACUTE INHALATION TOXICITY OF HFAs.

Compound	LC ₅₀ , mg/L	Conditions
(CF ₃) ₂ NCH ₃	>20	3-Hour rat
(CF ₃) ₂ NCF ₂ CF ₂ H	>20	3-Hour rat
(CF ₃) ₂ NCFHCF ₃	>20	3-Hour rat
(CF ₃) ₂ NCH ₂ CF ₃	>20	3-Hour rat
(CF ₃) ₂ NCH ₂ CF ₂ H	>20	4-Hour rat
(CF ₃) ₂ NCH ₂ CH ₃	>20	4-Hour rat

3. Ether Toxicity Information Reviewed

Ethers have relatively low toxicities due to the low reactivity of the C–O–C functional group arising from the high strength of the C–O bond. Volatile ethers can affect the CNS, however, flammability and the formation of explosive peroxides tend to be more serious problems than toxicity. Table 13, Table 14,† and Table 15 indicate that most of the HFES exhibit relatively low toxicities and are not mutagenetic.

*Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

†Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

TABLE 13. TOXICITY OF ETHERS

Formula	^a Hazard rating	^b Toxicity comments
CF ₂ HOCF ₂ H	c	No toxicity data available.
CF ₂ HOCHF ₃	c	No toxicity data available.
CF ₂ HOCF ₂ CHFCI	2	Used as an anesthetic under names enflurane and enthrane. Mildly toxic by inhalation, ingestion, and subcutaneous routes.
CF ₃ CHClOCHF ₂	c	Used as an anesthetic under name isoflurane.
C ₄ F ₉ C ₄ F ₇ O	c	Used as blood substitute.
CF ₂ BrOCF ₂ Br	c	No toxicity data available.
CF ₂ BrOCF ₃	c	No toxicity data available.
CF ₂ BrOCF ₂ CHFCI	c	No toxicity data available. The non-brominated version is an anesthetic known as enflurane.
C ₅ F ₈ O	c	No toxicity data available. The perfluorobutyl substituted compound is used as a blood substitute, and the toxicity of this compound may be acceptable.
C ₄ F ₇ BrO	c	No toxicity data available.

^a[10], ^b[11], ^cNot available.

TABLE 14. TOXICITY OF HFEs.

Compound	^{a,b} Acute oral LD ₅₀ , mg/kg	Acute inhalation LC ₅₀ , mg/L	^{a,c} Mutagenicity, Ames test	Skin irritation, rabbit
CH ₃ OCH ₂ CH ₂ F	<30	0.5-2.0 mg/L	Negative	Not available
CH ₃ OCF ₂ CHF ₂	>300	>20	Negative	Non-irritant
CHF ₂ OCF ₂ CH ₂ F	>300	>20	Negative	Non-irritant
CH ₃ OCF ₂ CF ₂ CF ₃	>300	>20	Negative	Non-irritant
CHF ₂ OCH ₂ CF ₂ CF ₃	>300	>20	Negative	Non-irritant
CH ₃ OCH(CF ₃) ₂	>300	>20	Negative	Non-irritant
CH ₃ CH ₂ OCF ₂ CHF ₂	>300	>20	Negative	Slight irritant
CF ₃ CH ₂ OCF ₂ CHF ₂	>300	>20	Negative	Non-irritant

^a Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December, 1995.

^bRat, 2 doses. The authors of the paper cited consider an LD₅₀ < 30mg/kg to be toxic.

^cRat, 4-hour. The authors of the paper cited consider an LC₅₀ of 0.5-2.0 mg/L to be toxic.

TABLE 15. HFE TOXICITY EVALUATION.

Compound	Toxicity evaluation
CH ₃ OCF(CF ₃) ₂	Acute inhalation, 3% for 4 hours: no observable effects Subacute inhalation, 6 hr/day for 7 days: NOAEL >2.0g/m ³
CH ₃ OCF ₂ CF ₃	Acute inhalation, 3% for 4 hours: no observable effects Inhalation test, 28 days: NOAEL >20.0 g/m ³ Ames test: Negative Chromosome aberration: Negative
CH ₃ OCF ₂ CF ₂ CF ₃	Acute inhalation, 3% for 4 hours: no observable effects Acute oral: LD ₅₀ > 2 g/kg Ames test: Negative Subacute inhalation: 6 hr/day for 7 days: NOAEL 7.0 g/m ³

4. Atmospheric lifetime estimates for alkenes

Estimates of atmospheric lifetime were developed and reported in an earlier publication a synopsis of which is presented in this subsection [1]. Comparison of these estimates reveals a striking differences between the three favored candidate families.

TABLE 16. ATMOSPHERIC LIFETIMES AND ODP VALUES FOR COMMON HCFCs AND CFCs.

Halocarbon number	IUPAC name	Formula	Lifetime, years	ODP
HCFC-141b	1,1-dichloro-1-fluoroethane	CH ₃ CCl ₂ F	9.4	0.1
HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane	CHClF ₂ CF ₃	5.9	0.03
HCFC-123	2,2-dichloro-1,1,1-trifluoroethane	CHCl ₂ CF ₃	1.4	0.014
HCFC-225ca	3,3-dichloro-1,1,1,2,2-pentafluoropropane	CF ₃ CF ₂ CHCl ₂	2.5	0.02
HCFC-225cb	1,3-dichloro-1,1,2,2,3-pentafluoropropane	CClF ₂ CF ₂ CHClF	6.6	0.02
HCFC-22	chlorodifluoromethane	CHClF ₂	13.3	0.04
HCFC-142b	1-chloro-1,1-difluoroethane	CH ₃ CClF ₂	19.5	0.05
CFC-11	trichlorofluoromethane	CCl ₃ F	50	1
CFC-12	dichlorodifluoromethane	CCl ₂ F ₂	102	0.82
CFC-13	chlorotrifluoromethane	CClF ₃	640	1
CFC-113	1,1,2-trichloro-1,2,2-trifluoroethane	CCl ₂ FC ₂ ClF ₂	85	0.9
CFC-114	1,2-dichloro-1,1,2,2-tetrafluoroethane	CClF ₂ CClF ₂	300	0.85
CFC-115	chloropentafluoroethane	CClF ₂ CF ₃	1700	0.4

The reaction rates of haloalkenes with hydroxyl radicals range from approximately 10^{-13} to 10^{-11} cm³/molecule-s compared with approximately 10^{-15} to 10^{-12} cm³/molecule-s for saturated

halocarbons 12.* On an average, the reactions are about 100 times faster for alkenes than for alkanes, and the atmospheric lifetimes are reduced accordingly. Thus, based on an atmospheric lifetime on the order of 10 years for a typical HCFC, Table 16, one would predict atmospheric lifetimes of approximately 1/10 year (about 1 month) for a typical haloalkene.

Estimates of reaction rate constants and atmospheric lifetimes using the method of Wuebbles and Connell several things should be noted [13]. This has been done for several alkenes, Table 17. First, the addition of fluorine atoms at the double bond increases the atmospheric lifetime. Second, lifetime decreases when alkyl groups are placed at the double bond. Finally, photodecomposition due to the presence of bromine and, to a lesser extent, the reaction of compounds containing hydrogen with tropospheric hydroxyl free radicals will lower the lifetimes. These approximations indicate that lifetimes for compounds of interest will range from 3 months down to less than a day.

Removal by reaction with tropospheric ozone is also possible for alkenes. A number of halogenated alkenes have atmospheric lifetimes that range from less than 1 day to about 7 days as a result of the reaction with tropospheric ozone [14]. The reaction is faster when alkyl groups (but not totally fluorinated alkyl groups) are substituted at the double bond.

Taking all of this into account, haloalkenes (more importantly, fluoroalkenes) are expected to have tropospheric lifetimes on the order of days due to reaction with hydroxyl free radicals and ozone, and this is likely to be even lower with bromine substitution [15].

*These rate constants are for 298 K (0 °C). This is a little higher than the actual average for tropospheric temperature; however, it is difficult to find reported or estimated rate constants at 265 K, the temperature that is closer to the average. Unless reported otherwise, assume that all rate constants in this report are for 298 K or approximately this temperature.

Table 17. Estimated hydrogen atom abstraction rate constants and alkene atmospheric lifetimes

Compound	$K[\bullet\text{OH}], \text{s}^{-1}$	Lifetime, days
$\text{CF}_2=\text{CFBr}$	1.3×10^{-7}	90
$\text{CF}_2=\text{CFCF}_2\text{Br}$	5.8×10^{-7}	19
cis- $\text{CF}_3\text{CF}=\text{CFCF}_2\text{Br}$	2.2×10^{-6}	5.4
trans- $\text{CF}_3\text{CF}=\text{CFCF}_2\text{Br}$	2.5×10^{-6}	4.6
$(\text{CF}_3)_2\text{C}=\text{CFCF}_2\text{Br}$	4.8×10^{-6}	2.4
$(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)\text{CF}_2\text{Br}$	1.5×10^{-5}	0.8
$\text{CH}_2=\text{CFBr}$	3.6×10^{-7}	32
$(\text{CF}_3)_2\text{C}=\text{CHCF}_2\text{Br}$	8×10^{-6}	1.4

For the initial acquisition effort selection of candidate bromofluoro-alkenes, for acquisition and cup-burner evaluation, employed the following general guidance. Compounds were limited to three, four and five carbon alkene structures. Fluorination of each structure was limited to the non-vinylic positions. Selected molecules were partially fluorinated such that the number of fluorine's exceeds the number of hydrogens to ensure non-flammability. Bromination sites avoided the allylic position. These guidelines ensured that only non-flammable compounds would be acquired and eliminated the higher boiling alkenes from consideration. They also avoided the possibility of toxicity associated with the allylic bromination site, and avoided, for the time being, the possibility of flammability due to fluorination of vinylic sites. Examples of the compounds considered are presented in Table 18.

Table 18. Partial List of Tropodegradable Alkenes

IUPAC name	Compound formula
1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene	$(\text{CF}_3)_2\text{C}=\text{CHBr}$
1-Bromo-2-trifluoromethyl-1,3,3,3-tetrafluoropropene	$(\text{CF}_3)_2\text{C}=\text{CFBr}$
1-Bromo-3,3,3-trifluoropropene	$\text{CF}_3\text{CH}=\text{CHBr}$
2-Bromo-3,3,3-trifluoropropene	$\text{CF}_3\text{CBr}=\text{CH}_2$
2-Bromo-1,3,3-trifluoropropene	$\text{CF}_2\text{HCB}r=\text{CHF}$
1-Bromo-2,3,3-trifluoropropene	$\text{CF}_2\text{HCF}=\text{CHBr}$
1-Bromo-1,3,3-trifluoropropene	$\text{CF}_2\text{HCH}=\text{CFBr}$
2-Bromo-1,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CBr}=\text{CHF}$
1-Bromo-2,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CF}=\text{CHBr}$
1-Bromo-1,3,3,3-tetrafluoropropene	$\text{CF}_3\text{CH}=\text{CFBr}$
2-Bromo-3,3,4,4-tetrafluorobutene	$\text{CF}_2\text{HCF}_2\text{CBr}=\text{CH}_2$
1-Bromo-3,3,4,4-tetrafluorobutene	$\text{CF}_2\text{HCF}_2\text{CH}=\text{CHBr}$
4-Bromo-3,3,4,4-tetrafluorobutene	$\text{CF}_2\text{BrCF}_2\text{CH}=\text{CH}_2$
4-Bromo-2,3,3,4,4-pentafluorobutene	$\text{CF}_2\text{BrCF}_2\text{CF}=\text{CH}_2$
4-Bromo-1,3,3,4,4-pentafluorobutene	$\text{CF}_2\text{BrCF}_2\text{CH}=\text{CHF}$
2-Bromo-3,3,4,4,4-pentafluorobutene	$\text{CF}_3\text{CF}_2\text{CBr}=\text{CH}_2$
1-Bromo-3,3,4,4,4-pentafluorobutene	$\text{CF}_3\text{CF}_2\text{CH}=\text{CHBr}$
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CBr}=\text{CH}_2$
1-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}=\text{CHBr}$
5-Bromo-3,3,4,4,5,5-hexafluoropentene	$\text{CF}_2\text{BrCF}_2\text{CF}_2\text{CH}=\text{CH}_2$
2-Bromo-3,3,4,4-tetrafluorobutene	$\text{CF}_2\text{HCF}_2\text{CBr}=\text{CH}_2$

5. Atmospheric lifetime estimates for ethers

Estimates of atmospheric lifetime were developed and reported in an earlier publication a synopsis of which is presented in this subsection [1]. The atmospheric lifetimes of PFEs are very long, and there is little evidence that the presence of an oxygen atom (which would give a small increase in polarity) causes a significant decrease in atmospheric lifetime. On the other hand, the

addition of hydrogen atoms makes hydrogen atom abstraction possible by hydroxyl free radicals. Moreover, the presence of an ether linkage increases the reaction rate. Insertion of an ether group alpha to the position from which hydrogen abstraction occurs should increase the rate constant. Moving a CF₃ group out of this position also increases the rate constant 16. Indeed, data for a number of ethers show rate constants approximately 10² larger than similar hydrocarbons [12].

Lifetimes reported for HFEs vary widely. For example, pentafluorodimethyl ether, CHF₂OCF₃ (HFE-125) and bis(difluoromethyl)ether, CHF₂OCHF₂ (HFE-134) are reported to have atmospheric lifetimes of 82 years and 8 years [17]. The value for HFE-125 is particularly long. On the other hand, a recent report lists HFEs with atmospheric lifetimes as low as 0.3 years.*† As expected, the atmospheric lifetimes decrease as the number of hydrogen atoms increase[1]. The presence of the oxygen atom makes the α-carbons hydrogens C-H bond weaker suggesting that for the same number of hydrogens those compounds with the largest number on α-carbons will have the lowest atmospheric lifetimes. Table 19 lists a number of ethers, those with the largest number hydrogens and greatest percentage on α-carbons are predicted to have the shortest atmospheric lifetimes.

*Misaki, S., and Sekiya, A., "Development of a New Refrigerant," presented at the International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii, 17-22 December 1995.

†Grenvell, M. W., Klin, F. W., Ows, J. G., and Yanome, H., "New Fluorinated Solvent Alternatives," Precision Cleaning '95, Rosemont, Illinois, 15-17 May 1995.

TABLE 19. Tropodegradable Ethers

IUPAC name	Compound formula	Mol. Wt.	Hydrogens α /Total
1-Bromo-2-trifluoromethoxy-1,1-difluoroethane	$\text{CF}_3\text{-O-CH}_2\text{CF}_2\text{Br}$	228.9	2/2
1-Bromo-2-trifluoromethoxy-1,1,2,2-tetrafluoroethane	$\text{CF}_2\text{H-O-CFHCF}_2\text{Br}$	228.9	2/2
1-Bromo-2-fluoromethoxy-1,1,2,2-tetrafluoroethane	$\text{CH}_2\text{F-O-CF}_2\text{CF}_2\text{Br}$	228.9	2/2
1-Bromo-2-(1,2,2,2-tetrafluoroethoxy)-1,1,2-trifluoroethane	$\text{CF}_3\text{CFH-O-CFHCF}_2\text{Br}$	278.9	2/2
1-Bromo-2-perfluoroethoxy-1,1-difluoroethane	$\text{CF}_3\text{CF}_2\text{-O-CH}_2\text{CF}_2\text{Br}$	278.9	2/2
1-Bromo-2-(2,2,2-trifluoroethoxy)-1,1,2,2-tetrafluoroethane	$\text{CF}_3\text{CH}_2\text{-O-CF}_2\text{CF}_2\text{Br}$	278.9	2/2
1-Bromo-2-(2,2-difluoroethoxy)-1,1,2,2-tetrafluoroethane	$\text{CF}_2\text{HCH}_2\text{-O-CF}_2\text{CF}_2\text{Br}$	260.9	2/3
1-Bromo-2-(2-fluoroethoxy)-1,1,2,2-tetrafluoroethane	$\text{CH}_2\text{FCH}_2\text{-O-CF}_2\text{CF}_2\text{Br}$	242.9	2/4
1-Bromo-2-fluoromethoxy-1,2-difluoroethane	$\text{CH}_2\text{F-O-CFHCFHBr}$	192.9	3/4
1-Bromo-2-(2,2,2-trifluoroethoxy)-1,1,2-trifluoroethane	$\text{CF}_3\text{CH}_2\text{-O-CFHCF}_2\text{Br}$	260.96	3/3
1-Bromo-2-difluoromethoxy-1,1-difluoroethane	$\text{CF}_2\text{H-O-CH}_2\text{CF}_2\text{Br}$	210.95	3/3
1-Bromo-2-fluoromethoxy-1,1,2-trifluoroethane	$\text{CH}_2\text{F-O-CFHCF}_2\text{Br}$	210.95	3/3
1-Bromo-2-methoxy-1,1,2,2-tetrafluoroethane	$\text{CH}_3\text{-O-CF}_2\text{CF}_2\text{Br}$	210.95	3/3
1-Bromo-2-(2,2-difluoroethoxy)-1,1,2-trifluoroethane	$\text{CF}_2\text{HCH}_2\text{-O-CHF}_2\text{CF}_2\text{Br}$	242.97	3/4
1-Bromo-2-(2,2-difluoroethoxy)-1,1-difluoroethane	$\text{CF}_2\text{HCH}_2\text{-O-CH}_2\text{CF}_2\text{Br}$	224.98	3/5
1-Bromo-2-(2,2,2-trifluoroethoxy)-1,1-difluoroethane	$\text{CF}_3\text{CH}_2\text{-O-CH}_2\text{CF}_2\text{Br}$	242.97	4/4

Table 19 (continued). Tropodegradable Ethers

IUPAC name	Compound formula	Mol. Wt.	Hydrogens α /Total
1-Bromo-2-methoxy-1,1,2-trifluoroethane	CH ₃ -O-CFHCF ₂ Br	192.96	4/4
1-Bromo-2-fluoromethoxy-1,1-difluoroethane	CH ₂ F-O-CH ₂ CF ₂ Br	192.96	4/4
1-Bromo-2-(2,2,2-trifluoroethoxy)-1,1-difluoroethane	CF ₃ CH ₂ -O-CH ₂ CF ₂ Br	242.97	4/4
1-Bromo-2-(2,2-difluoroethoxy)-1,1-difluoroethane	CF ₂ HCH ₂ -O-CH ₂ CF ₂ Br	224.98	4/5

6. Atmospheric lifetime estimates for amines

Estimates of atmospheric lifetime were developed and reported in an earlier publication a synopsis of which is presented in this subsection [1]. When hydrogen atoms are present on both an amine alkyl group and on the nitrogen, C-H abstraction tends to occur in preference to or in competition with N-H abstraction. The presence of a nitrogen atom decreases the C-H bond strength. Thus, the bond energies for C-H in CH₄, CH₃NH₂, (CH₃)₂NH, and (CH₃)₃N are, respectively, 435, 391, 364, and 352 kJ/mol (104, 93.3, 87, and 84 kcal/mol) [18]). As would be expected from these data, a nitrogen atom alpha to a C-H bond significantly increases the reaction rate constant for hydrogen abstraction by hydroxyl free radicals. This can be seen in the comparison of rate constants between amines and structurally similar hydrocarbons [1]. For this limited set of data, the amine rate constants are 23 to 65 times large than the hydrocarbon rate constants. The calculated atmospheric lifetimes $t_{1/e}$ for mono-, di- and tri-methyl amines are less than 1 day based on their reactions with tropospheric hydroxyl free radicals only [1].

Limiting consideration to three, Table 20, and four, Table 21, carbon amines for the present potential candidates for acquisition can be readily identified and compared. Atmospheric life time is predicted to decrease for compounds further down each list. Potential toxicity due to the presence of brominated α -carbons is a concern in the selection process but data which would provide concrete guidance is lacking.

TABLE 20. THREE CARBON TROPODEGRADABLE AMINES—NR₁R₂R₃

Formula	R ₁	R ₂	R ₃	Hydrogens α/Total	Mol. Wt.
NC3F7HBr	CF ₃	CF ₃	CFHBr	1/1	263.9
NC3F7HBr	CF ₃	CF ₂ H	CF ₂ Br	1/1	263.9
NC3F6H2Br	CF ₃	CF ₂ H	CFHBr	2/2	245.9
NC3F6H2Br	CF ₃	CF ₃	CH ₂ Br	2/2	245.9
NC3F6H2Br	CF ₃	CF ₂ H	CFHBr	2/2	245.9
NC3F6H2Br	CF ₂ H	CF ₂ H	CF ₂ Br	2/2	245.9
NC3F6H2Br	CF ₃	CF ₃	CH ₂ Br	2/2	245.9
NC3F5H3Br	CF ₃	CF ₂ H	CH ₂ Br	3/3	227.9
NC3F5H3Br	CF ₃	CF ₂ H	CH ₂ Br	3/3	227.9
NC3F5H3Br	CF ₂ H	CF ₂ H	CFHBr	3/3	227.9
NC3F4H4Br	CF ₂ H	CF ₂ H	CH ₂ Br	4/4	209.9

TABLE 21. FOUR CARBON TROPODEGRADABLE AMINES—NR₁R₂R₃

Formula	R ₁	R ₂	R ₃	Hydrogens α/Total	Mol. Wt.
NC4F9HBr	CF ₃	CF ₃	CFHCF ₂ Br	1/1	313.9
NC4F9HBr	CF ₃	CF ₂ H	CF ₂ CF ₂ Br	1/1	313.9
NC4F8H2Br	CF ₃	CF ₃	CFHCFHBr	1/2	295.9
NC4F8H2Br	CF ₃	CF ₂ H	CFHCF ₂ Br	2/2	295.9
NC4F8H2Br	CF ₂ H	CF ₂ H	CF ₂ CF ₂ Br	2/2	295.9
NC4F8H2Br	CF ₃	CF ₃	CH ₂ CF ₂ Br	2/2	295.9
NC4F7H3Br	CF ₃	CF ₂ H	CFHCFHBr	2/3	277.9
NC4F7H3Br	CF ₃	CF ₂ H	CFHCFHBr	2/3	277.9
NC4F6H4Br	CF ₃	CF ₃	CH ₂ CH ₂ Br	2/4	259.9
NC4F7H3Br	CF ₃	CF ₂ H	CH ₂ CF ₂ Br	3/3	277.9
NC4F7H3Br	CF ₂ H	CF ₂ H	CFHCF ₂ Br	3/3	277.9
NC4F6H4Br	CF ₂ H	CF ₂ H	CFHCFHBr	3/4	259.9
NC4F5H5Br	CF ₃	CF ₂ H	CH ₂ CH ₂ Br	3/5	241.9
NC4F4H6Br	CF ₂ H	CF ₂ H	CH ₂ CH ₂ Br	3/6	223.9
NC4F6H4Br	CF ₂ H	CF ₂ H	CH ₂ CF ₂ Br	4/4	259.9

α-Hydrogens are attached to those carbons directly bonded to amine nitrogens (i.e., H-C-N).

7. Physical property estimates – boiling point effects

A major criterion for any liquid to perform as a total flood agent is an ability to evaporate and fill a space to a required concentration within the time required for extinguishment

under the ambient conditions. Thus, evaporation properties must be taken into account during compound review and selection in addition to a full understanding of the temperature range for application. Areas that must be considered are evaporation equilibrium and evaporation rate. An estimate of the effects of the boiling point on evaporation equilibrium and application temperature was partially undertaken under this project and a related project "Main Group Compounds as Extinguishants" also funded under the NGP program. This presentation can be found in full in the associated final project report for the NGP project "Main Group Compounds as Extinguishants" only the results are presented here.

The question of whether a given compound can achieve the required extinguishment concentration is easily answered since only thermodynamics are involved. The logarithm of the ratio of the vapor pressure (p) at two different temperatures T_2 and T_1 can be estimated from the Clausius-Clapeyron equation. For closely related compounds, ΔS_{vap} at the boiling point is nearly constant with a value of t_c , Trouton's constant. Thus, by selecting T_1 as the boiling point (T_b) at, for example, 1 atmosphere pressure (i.e., $p_1 = 760$ Torr), one can estimate the vapor pressure at some other temperature and develop an approximate vapor pressure/temperature curve if t_c is known. Table 22 gives the estimated maximum boiling point T_b that can achieve concentrations from 1 vol.% to 20 vol.% for a Trouton constant of 88 J/K-mol, (1).

$$T_b = [1 - (\text{Log}(C/100)/0.05221065t_c)]T_2 \quad (1)$$

This analysis shows that a compound with a boiling point of over 100 °C can likely achieve a concentration of 5 vol.% at normal room temperature (25 °C). Whether such a compound can achieve such a concentration in a reasonable amount of time is, however, a quite separate question. The shaded region represents the lower end of the compound boiling points of those compounds acquired and tested in the course of this project and the projected application temperature limitations.

TABLE 22. ESTIMATED MAXIMUM BOILING POINT THAT CAN ACHIEVE A GIVEN CONCENTRATION.

Conc. %	Ambient Temperature, °C											
	-60	-50	-40	-30	-20	-10	0	10	20	30	40	50
1	33	47	61	76	90	105	119	133	148	162	176	191
2	19	33	46	60	74	87	101	115	128	142	156	169
3	11	24	37	51	64	77	91	104	117	130	144	157
4	5	18	31	44	57	70	83	96	109	122	135	148
5	0	13	26	39	52	65	77	90	103	116	129	142
6	-3	9	22	35	47	60	73	85	98	111	123	136
7	-6	6	19	31	44	56	69	81	94	106	119	131
8	-9	3	16	28	40	53	65	78	90	102	115	127
9	-11	1	13	25	38	50	62	74	87	99	111	124
10	-14	-1	11	23	35	47	59	72	84	96	108	120
11	-16	-3	9	21	33	45	57	69	81	93	105	117
12	-17	-5	7	19	31	43	55	67	79	91	103	115
13	-19	-7	5	17	29	41	53	65	77	88	100	112
14	-20	-9	3	15	27	39	51	63	74	86	98	110
15	-22	-10	2	14	25	37	49	61	73	84	96	108
16	-23	-11	0	12	24	36	47	59	71	83	94	106
17	-24	-13	-1	11	22	34	46	57	69	81	92	104
18	-25	-14	-2	9	21	33	44	56	68	79	91	102
19	-27	-15	-3	8	20	31	43	54	66	78	89	101
20	-28	-16	-5	7	19	30	42	53	65	76	88	99

B. COMPOUND SYNTHESIS AND ACQUISITION

Synthetic efforts were directed to providing experimental quantities of the tropodegradable compounds from the bromofluoro-alkene, bromofluoro-amine, and bromofluoro-ethers. While synthesis approaches were readily identifiable actual laboratory synthesis efforts were inevitably constrained by the availability of required starting materials.

Commercial chemical sources frequently required up to six months to synthesize and deliver chemicals project.

In preparation for the planned compound synthesis effort, an extensive survey of database sources for information on existing bromofluoro-alkenes and methods for their synthesis was performed. The information obtained was carefully summarized and is presented in the following sections grouped according to the basic functionality of the molecular structure.

1. Bromofluoro-alkenes

An extensive literature search revealed that several bromofluoro-alkenes have been prepared by dehydrohalogenation of the appropriate partially fluorinated dibromopropanes with a base (e.g., Reaction 1) (Reference 19). Depending on the difficulty in preparing the starting materials, this is a fairly straightforward reaction. Other preparations following the same scheme (References 20, through 22) and an improved procedure to prepare the precursors (Reference 23) have been reported. Many of the precursors are classified as Class 1 Ozone depleters and as such have all but disappeared from commercial catalogues.



A preparation has been reported for the dibrominated compound 2,3-dibromo-3,3-difluoropropene [20]). Fluorination of this compound gives 2-bromo-3,3,3-trifluoropropene [20]. 3-Bromo-1,1-difluoropropene has been obtained in small amounts by reaction of hexafluorocyclopropane with vinyl bromide [24]). The preparation of 1-bromo-3,3,3-trifluoropropene by dehydrohalogenation of $\text{CBrF}_2\text{CH}_2\text{CBrF}_2$ has been reported [21]. A number of (mostly) higher molecular weight alkenes, some with multiple bromine atoms and some containing chlorine, have been reported [25], [26]. 1-Bromo-1,1,2,2-tetrafluoro-3-pentene, boiling point 97 °C and 1-bromo-1,1,2,2-tetrafluoro-4-methyl-3-pentene, boiling point 116 °C have been prepared by dehydrohalogenation of 1,1,2,2-tetrafluoro-1,4-dibromopentane and 1,1,2,2-tetrafluoro-1,4-dibromo-4-methylpentane, respectively [27 and 28].

Dehydrohalogenation reactions of brominated fluorinated alkanes involve the formation of an alkene by removal of HF or HBr from an incompletely halogenated alkane. The dehydrohalogenation reaction typically requires heating of the incompletely halogenated

compound in the presence of potassium hydroxide. The reactions can be selective, yielding a single alkene product in high purity.

Additional methods applicable to the synthesis of bromofluoro-alkenes include the Wittig reaction. This synthetic approach employs substituted methylenetriphenylphosphoranes, $(C_6H_5)_3P=CR_1R_2$, where $R_{1,2} = H, F, CF_3$, etc. Methylenetriphenylphosphoranes are reactive when combined with carbonyl containing compounds. The reaction results in replacement of the carbonyl oxygen ($C=O$) of the carbonyl compound with the methylene (CR_1R_2) group from the methylenetriphenylphosphoranes and yields an alkene product one carbon longer than the original carbonyl compound.

The Wittig reaction has been demonstrated for numerous fluorine-containing carbonyl compounds and can provide high yields of product compounds. Triphenylphosphorane starting materials are not expensive, and the reaction conditions are not extreme. Compounds can be isolated and purified by standard methods.

2. Bromofluoro-ethers

The hydrobromofluoro-ether (HBFE) 1-bromo-1,1,2,2-tetrafluoro-6-ethoxyhexane, boiling point $67\text{ }^\circ\text{C}$ has been isolated during dehydrohalogenation of $CBrF_2CF_2CH_2CH_2CH_2CH_2Br$ with KOH in ethanol [25]. 1-Bromo-1,2,2-trifluoro-3-methoxypropane, boiling point $125\text{ }^\circ\text{C}$ has been prepared in a multi-step synthesis.

Reactions of alkenes with CF_3OF and CF_3OCl has allowed preparation of HBFEs and a hydrobromochlorofluoroether (HBCFE) (Reference 29). 2-Bromo-1,1,2-trifluoro-1-(trifluoromethoxy)ethane and 2-bromo-1,1,1-trifluoro-2-(trifluoromethoxy)ethane are provided by reaction of $CF_2=CHBr$ with CF_3OF . The two regioisomers (CF_3-O-CF_2CHBrF and $CF_3CHBr-O-CF_3$) are difficult to separate. Reaction of $CH_2=CHBr$ with CF_3OF gives 1-bromo-1-fluoro-2-(trifluoromethoxy)ethane. 2-Bromo-2-chloro-1,1-difluoro-1-(trifluoromethoxy)ethane is prepared by reaction of $CF_2=CHBr$ with CF_3OCl . The IR (in some cases of a mixture) and ^{19}F NMR spectra are reported for all of these compounds.

A number of hydrobromofluoro-ethers have been prepared by addition of alcohols (alkoxides) to bromofluoroethenes [30 and 31]. The preparation of 2-bromo-1,1,2-trifluoro-1-

ethoxyethane by this same route has been reported elsewhere [32]. 1-Bromo-1,1,2,2-tetrafluoro-2-methoxyethane has been prepared by reaction of CXF_2CBrF_2 ($X = \text{halogen}$) with methoxide ion [33].

Reaction of formaldehyde and HF with 2-bromo-1,1-difluoroethene ($CF_2=CHBr$) gives 2-bromo-1,1,1-trifluoro-3-(2-bromo-3,3,3-trifluoropropoxy)propane, boiling point 167°C) and bis(2-bromo-3,3,3-trifluoropropoxy)methane. Reaction of chloro-1,2-bis(trifluoromethoxy)ethene with bromine has been used to prepare 1,2-dibromo-chloro-1,2-bis(trifluoromethoxy)ethane, boiling point 94 to 95°C .

3. Bromofluoro-amines

A number of fluorinated amines have been prepared by reactions of alkenes with bromobis(trifluoromethyl)amine ($NBr(CF_3)_2$) (Table 23) [34]. N,N-Bis(trifluoromethyl)bromodifluoromethanamine, boiling point 35.6°C has been prepared by ultraviolet (UV)-induced decarbonylation of N,N-dimethylaminodifluoroacetyl bromide ($(CH_3)_2NCF_2C(O)Br$) [35] and by reaction of (difluoromethylene)(trifluoromethyl)amine ($F_3C-N=CF_2$) with bromodifluoromethyltriphenyl-phosphonium bromide ($(C_6H_5)_3(CF_2Br)P^+ Br^-$) [36]. The latter synthesis also gives N,N-bis(trifluoromethyl)difluoromethanamine, boiling point 7.8°C .

Table 23. Amines Prepared by Bromobis-(trifluoromethyl)amine Addition to Alkenes.

CCOD ID	Compound name	Compound formula	^a Boiling point, °C
919	N,N-bis(trifluoromethyl)-1-bromo-1,1,2,2-tetrafluoroethan-2-amine	$N(CF_3)_2(CF_2CF_2Br)$	60.9
1053	N,N-bis(trifluoromethyl)-2-bromo-2,2-difluoroethanamine	$N(CF_3)_2(CH_2CBrF_2)$	79.9
1200	2-bromo-1,2-difluoro-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2CHFCHBrF$	76.4
1202	2-bromo-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2(CH_2CH_2Br)$	85.6
1203	2-bromo-1,2,2-trifluoro-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2(CHFCF_2Br)$	62.4
1204	2-bromo-1,1,2-trifluoro-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2(CF_2CHFBr)$	74
1207	2-bromo-2-chloro-1,1,2-trifluoro-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2(CF_2CFCIBr)$	93.5
1208	2-bromo-1,2-dichloro-1,2-difluoro-N,N-bis(trifluoromethyl)ethanamine	$N(CF_3)_2(CFCICFCIBr)$	125.6
1209	2-bromo-1,1,2,3,3,3-hexafluoro-N,N-bis(trifluoromethyl)propanamine	$N(CF_3)_2(CF_2CFBrCF_3)$	82.2

^aAt one atmosphere.

C. SYNTHESSES PERFORMED OR ATTEMPTED

1. 2-Bromo-3,3,3-trifluoropropene, $CH_2=CBrCF_3$

The synthesis of 2-bromo-3,3,3-trifluoropropene ($CH_2=CBrCF_3$) was successful. Commercially available and relatively inexpensive 3,3,3-trifluoropropene ($CF_3CH=CH_2$) was brominated to produce the intermediate compound 1,2-dibromo-3,3,3-trifluoropropane ($CF_3CHBrCH_2Br$), which was subsequently dehydrohalogenated yielding the final product 2-bromo-3,3,3-trifluoropropene. Bromination of 3,3,3-trifluoropropene was performed photochemically in the presence of carbon tetrachloride and under reflux conditions to yield 1,2-dibromo-3,3,3-trifluoropropane. This compound was subsequently dehydrohalogenated using

dry potassium hydroxide and reflux conditions. The product 2-bromo-3,3,3-trifluoropropene was isolated quantitatively following distillation.

2. 1-Bromo-2-trifluoromethyl propene, $((CF_3)_2C=CHBr)$

Wittig reaction has been used for a long time as a generally useful method for the synthesis of alkenes from carbonyl compounds under mild conditions. Considering the commercial availability of starting material hexafluoroacetone $(CF_3)_2C=O$, it is a reasonable way to use Wittig reaction to synthesize 1-Bromo-2-trifluoromethyl propene (I). This reaction route consists of two steps. The first step is the synthesis of Bromomethyltriphenylphosphonium Bromide. The second step involves generating the corresponding ylide and carrying out the Wittig reaction to generate the alkene. Though this effort did result in 1-bromo-2-trifluoromethyl propene being identified by gas chromatography/mass spectroscopy a commercial source ultimately was located and the material acquired for testing.

3. Fluorobromoalkyl-amines

Several potential commercial sources for the synthesis the starting material, $(CF_3)_2NBr$, which would be used in subsequent synthesis of several of the bromofluoro-amines of interest were contacted. This starting material is reported to readily undergo insertion reactions with a variety of alkenes yielding compounds of the general structure $(CF_3)_2NC_2H_xF_yBr$. The approach was abandoned following repeated unsuccessful attempts to obtain this starting material. Bromofluoroalkyl-amines were eventually acquired by an alternate synthetic method, Section III, D.

D. COMMERCIAL AND ACADEMIC SOURCES

To take advantage of a broad range of synthetic specialists and facilitate the acquisition of compounds for test and evaluation inquiries were addressed to the former Soviet Union; Sigma Aldrich; Fluorochem Limited; PCR, Inc.; Oakwood Products, Inc.; Lancaster Synthesis; SynQuest Laboratories, Inc.; Durham Organics; Dr. Ed Kiskowski (Flura Corp.); P&M-1, LTD; Dr. Bill Banister (University of Massachusetts, Lowell); Dr. Jon Kremsky (Prime Organics); Dr.

Jean'ne Shreeve, University of Idaho; Dr. William Allcock (University of Tenn.); and Dr. Lorrain Deck (Univ. of New Mexico).

1. Compounds acquired

The ten bromofluoro-alkenes and bromofluoro-amines acquired are listed in Table 24 and Table 25. Boiling points ranged from 40°C for 1-bromo-3,3,3-trifluoropropene to a high of 80°C for bis(trifluoromethyl)-2-bromo-2-fluoroethylamine.

Table 24. Brominated Tropodegradable Alkenes Acquired

CCOD ID	Compound, Formula	Boiling point (°C)
707	1-Bromo-3,3,3-trifluoropropene, $\text{CF}_3\text{CH}=\text{CHBr}$	40
1116	2-Bromo-3,3,4,4,4-pentafluorobutene, $\text{CF}_3\text{CF}_2\text{CBr}=\text{CH}_2$	56
1358	2-Bromo-3,3,4,4,5,5,5-heptafluoropentene, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CBr}=\text{CH}_2$	78
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene, $\text{CF}_3\text{CF}(\text{CF}_3)\text{CBr}=\text{CH}_2$	78
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene, $\text{CF}_3\text{CF}(\text{OCF}_3)\text{CBr}=\text{CH}_2$	75
1391	1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene, $(\text{CF}_3)_2\text{C}=\text{CHBr}$	63
1413	1-Bromo-4,4,4,3,3-pentafluorobutene, $\text{CF}_3\text{CF}_2\text{CH}=\text{CHBr}$	58

*Testing performed using premixed agent/air mixtures

Table 25. Tropodegradable Bromofluoro-amines Acquired

CCOD ID**	Compound, Formula	Boiling point °C
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, $N(CF_3)_2(CHFCF_2Br)$	72*
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, $N(CF_3)_2(CF_2CFHBr)$	72*
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, $N(CF_3)_2(CH_2CF_2Br)$	80

* As a 60/40 mixture of 1392 and 1393

** NMERI Chemical Compound Options Database ID

The source of each of the compounds acquired is listed in Table 26.

Table 26. Compound Suppliers

CCOD ID	Compound, Formula	Source
707	1-Bromo-3,3,3-trifluoropropene, $CF_3CH=CHBr$	SynQuest Laboratories
1116	2-Bromo-3,3,4,4,4-pentafluorobutene, $CF_3CF_2CBr=CH_2$	P&M-1, Ltd
1358	2-Bromo-3,3,4,4,5,5,5-heptafluoropentene, $CF_3CF_2CF_2CBr=CH_2$	P&M-1, Ltd
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene, $CF_3CF(CF_3)CBr=CH_2$	P&M-1, Ltd
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene, $CF_3CF(OCF_3)CBr=CH_2$	P&M-1, Ltd
1391	1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene, $(CF_3)_2C=CHBr$	SynQuest Laboratories
1413	1-Bromo-4,4,4,3,3-pentafluorobutene, $CF_3CF_2CH=CHBr$	P&M-1, Ltd
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, $N(CF_3)_2(CHFCF_2Br)$	Univ. of Idaho
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, $N(CF_3)_2(CF_2CFHBr)$	Univ. of Idaho
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, $N(CF_3)_2(CH_2CF_2Br)$	Univ. of Idaho

E. CUP-BURNER TESTING

While the basic cup-burner design employed at NMERI to characterize the flame extinguishments of test compounds has not changed the manner in which samples are introduced has undergone improvement. Illustrated below is the approach employed in gathering data prior to this project, Figure 1. The method introduces liquid or gaseous agents from a pressurized storage vessel situated on a computer interfaced standard balance into the air stream entering the base of the cup-burner. The base of the cup-burner is heated to ensure complete evaporation of liquids. Agent/air concentrations are automatically calculated based on input on weight loss rates and total air flow.

While this method works well in principal occasionally the flow of gaseous as well as highly volatile liquid agents is not smooth due to evaporation in the needle valve assembly and the capillary tubing employed. Higher boiling liquid agents can also present a flow rate calculation problem when they fail to instantly evaporate o introduction into the base of the cup-burner. Both of these problems can vary in severity depending on the precise conditions of the test. To eliminate errors and allow a more precise comparison of the flame extinguishments performance of agents tested the agent introduction method was modified.

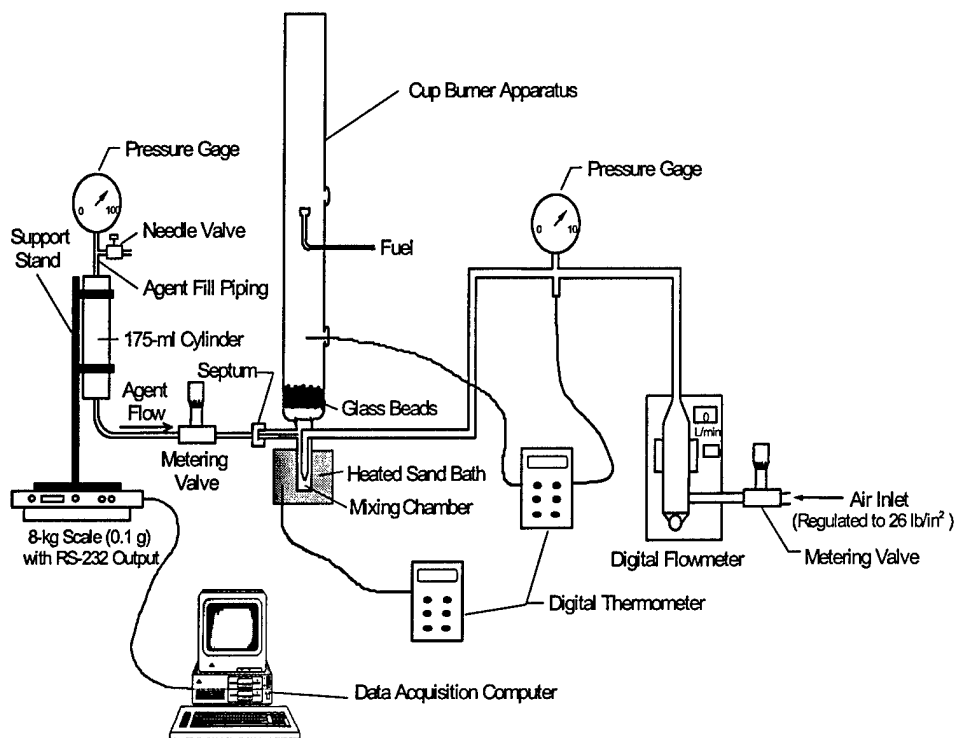


Figure 1. NMERI cup-burner utilizing mass loss flow rate characterization

Illustrated below are the changes and improvements made to the agent introduction method, Figure 2. The principal change is the use of a pre-mixed and pre-analyzed agent/air reservoir. This change ensures uniformity in agent/air concentrations during flame extinguishment testing as well as sufficient sample for analytical determination of the agent concentration. In the current configuration a 10L Tedlar bag is employed. This allows several extinguishment determinations to be made from the same sample. The technique employed starts with an air concentration of approximately 5% (vol./vol.). Flame extinguishment for the compounds studied is very rapid ($\ll 5$ sec.) at this level. Following each successful extinguishment the bag of agent and air is diluted, mixed and retested. This process is repeated until the agent/air mixture no longer extinguishes the flame.

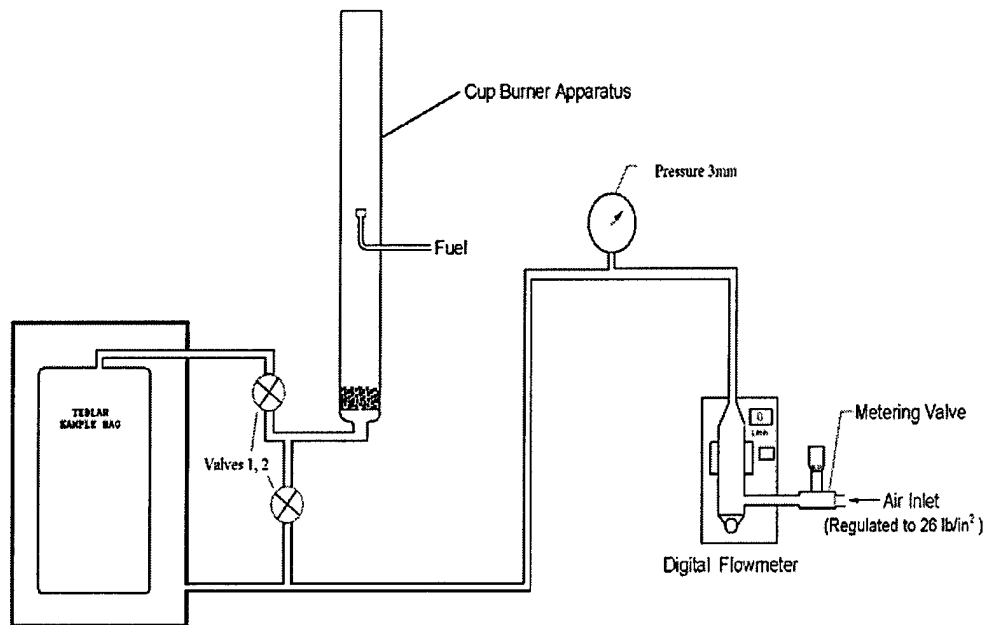


Figure 2. NMERI cup-burner with premixed agent/air source.

The twelve tropodegradable compounds acquired in this project were tested for their flame extinguishment performance using this technique. The extinguishment concentrations (% vol./vol.) observed are listed in Table 27 and Table 28. All agent air concentration data were determined by capillary gas chromatography employing three point calibration curves bracketing the air concentration ranges tested. Calibration standards were prepared from the neat liquid agent and room air as 0.5L or 1.0L samples. Compound purity, barometric pressure and ambient temperature corrections were employed in the preparation of all standards.

Table 27. Cup-burner Flame Extinguishment and Application Temperature Limits

Compound	Formula	Boiling point (°C)	Cup-burner (%)	Lowest temp for 5% conc.
1-Bromo-3,3,3-trifluoropropene	CF ₃ CH=CHBr	40	(3.5)	-30 °C
3-Bromo-3,3-difluoropropene	CBrF ₂ CH=CH ₂	42	4.5	-30 °C
2-Bromo-3,3,3-trifluoropropene	CF ₃ CBr=CH ₂	34	2.6	-35 °C
4-Bromo-3,3,4,4-tetrafluorobutene	CF ₂ BrCF ₂ CH=CH ₂	54	3.5	-15 °C
2-Bromo-3,3,4,4,4-pentafluorobutene	CF ₃ CF ₂ CBr=CH ₂	56	(3.8)	-15 °C
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	CF ₃ CF ₂ CF ₂ CBr=CH ₂	78	(3.7)	-10 °C
2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	CF ₃ CF(CF ₃)CBr=CH ₂	78	(3.3)	-10 °C
2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	CF ₃ CF(OCF ₃)CBr=CH ₂	75	(3.8)	-10 °C
1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene	(CF ₃) ₂ C=CHBr	63	(2.6)	-15 °C
1-Bromo-4,4,4,3,3-pentafluorobutene	CF ₃ CF ₂ CH=CHBr	58	(3.1)	-15 °C

Table 28. NMERI Cup-Burner Flame Extinguishment and Application Temperature Limits

CCOD ID**	Compound, Formula	Boiling point °C	Cup-burner (%)	Lowest temp for 5% conc.
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine, N(CF ₃) ₂ (CHF ₂ CF ₂ Br)	72	2.4*	-10
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine, N(CF ₃) ₂ (CF ₂ CFHBr)	72	2.4*	-10
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine, N(CF ₃) ₂ (CH ₂ CF ₂ Br)	80	2.4	-10

* Results of a 60/40 blend of CCOD's 1392 and 1393

** NMERI Chemical Compound Options Database ID

SECTION IV.
TECHNICAL PROBLEMS

The acquisition of chemicals, most of whom have never been synthesized, is very costly and very time consuming. In order to minimize per compound costs a modification to cup-burner test methods was developed and indicated in Task 3. This modification makes it possible to obtain an upper-bound value for the cup-burner extinguishment using as little as 2 grams of a test compound, in some cases, instead of 50 grams. This modification does not affect the utility of the resulting cup-burner value and in fact provides greater accuracy in air concentration measurements and actual test conditions. This modification was described earlier in greater detail in Section 4, Detailed Description of the Project.

SECTION V. RECOMMENDATIONS

This project has further developed the list of tropodegradable bromocarbons for which flame extinguishment performance is known. Recent data on the inhalation toxicity the bromofluoro-alkenes underscores the potential of these compounds. The boiling points of the current bromofluoro-alkenes which range down to 34 and in some cases as low as 25 °C may permit their use at application temperatures as low as -40°C depending on actual evaporation rates and low temperature fire suppression requirements.

The identification of compounds with lower boiling points is highly likely and would potentially enhance the low temperature performance of this class of compounds in fire suppression applications. There remain several bromofluoro-alkene structures with the potential to have lower boiling points than that of 2-bromo-3,3,3-trifluoropropene. The acquisition and cup-burner testing of these compounds should be a priority.

Limited toxicity testing is essential to progress in the area of compound selection. As has been stated in this report on several occasions actual toxicity test data on the bromofluoro-alkenes, ethers, and amines of interest is very limited. Cost effective sources of testing have been identified and should be considered for future projects.

SECTION VI. CONCLUSION

The objective of the project is to develop new chemical compounds to replace Halon 1301 for total flood fire extinguishment applications. Potential halon replacements must be highly efficient fire suppressants, have low environmental and toxicological impacts, have the same performance characteristics as Halon 1301, and be compatible with existing fire extinguishing equipment and aircraft materials. This research program includes syntheses of new compounds; laboratory analyses of fire suppression characteristics; analyses of environmental and toxicity parameters. This project builds on several previous DoD funded projects [37 and 38].

Past research work on tropodegradable bromocarbons had limited funding from the U.S. Air Force (USAF) and U.S. Navy (USN). Cup-burner flame extinguishment testing presented here and in previous reports as well as the recent acute inhalation toxicity testing data continue to underscore the potential of tropodegradable bromocarbons as to perform as Halon 1301 replacements [2, 39]. This research project greatly expanded the list of tropodegradable bromocarbons whose flame extinguishment has been characterized and also provided estimations of compound environmental characteristics, evaluations of acute inhalation toxicity, physical properties, and boiling point limitations affecting agent air concentrations.

In this project, bromofluoroalkenes were the primary focus of compound selection, acquisition and testing efforts due to their promising toxicity, flame suppression, short atmospheric lifetime, and acceptable physical properties. Data from the RTECS database as well as acute inhalation toxicity and subsequent AMES test data for several of the bromofluoro alkenes of interest here is very promising. Flame extinguishment testing of several bromofluoro alkenes have yielded cup-burner values comparable to those of halon 1301 and 1211. Finally, synthetic methods, in some cases, are expected to enable relatively low cost manufacture of selected bromofluoroalkenes and give hope to the potential for low cost industrial preparation of others.

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APPENDIX A

GLOSSARY

Acute Toxicity—The effect of a single high-level exposure, as would occur during accidental release.

Alcohol—Compounds containing one or more hydroxyl (-OH) groups attached to a nonaromatic hydrocarbon. Examples are methanol (CH₃OH), ethanol (C₂H₅OH), and ethylene glycol [C₂H₂(OH)₂].

Alkene—Also designated “olefin.” A compound containing doubly bonded carbon atoms (excluding aromatic compounds) as in ethene (H₂C=CH₂) and propene (H₂C=CHCH₃).

Alkoxy—A group of the type -OR, where R is an aliphatic hydrocarbon radical or a substituted aliphatic radical. Examples are methoxy (-OCH₃) and ethoxy (-OC₂H₅).

Alkyl—An aliphatic substituent. Examples are methyl (-CH₃), ethyl (-CH₂CH₃ or -C₂H₅), *n*-propyl (-CH₂CH₂CH₃ or -C₃H₇), *i*-propyl (-CH(CH₃)₂), *n*-butyl (-CH₂CH₂CH₂CH₃ or -C₄H₉), *t*-butyl (-C(CH₃)₃).

Ames Assay—A preliminary test for mutagenicity on bacteria - designed primarily as a rapid screen for possible carcinogens. Both false positives and false negatives are common, so the test is never used on its own.

Aromatic—Cyclic molecules or fused cyclic molecules containing formally alternating single and double bonds with delocalized π electrons. The most common simple aromatic compound is benzene.

Carcinogenic or Carcinogenicity—A term applied to substances causing cancer.

Cardiac—Having to do with the heart.

Cardiac Sensitization—An effect in which the heart is rendered more sensitive to the action of adrenaline and similar drugs. This can result in sudden heart failure.

Ether—Compound containing the group C-O-C as in dimethyl ether, CH₃-O-CH₃.

Genotoxicity—The ability of a material to cause damage to genes or chromosomes. Genotoxicity studies provide an early screen for possible cancer-inducing activity.

Haloalkane—Saturated halocarbons containing only carbon, halogen, and, in some cases, hydrogen atoms.

Haloalkoxy—A group of the type -OR, where R is an aliphatic hydrocarbon group or a substituted aliphatic group containing one or more halogen atoms. Examples are chloromethoxy (-OCH₂Cl) and 2-bromoethoxy (-CH₂CH₂Br).

Haloalkyl—An aliphatic substituent containing one or more halogen atoms. Examples are tribromomethyl (-CBr₃) and 2-chloroethyl (-CH₂CH₂Cl).

Halocarbon—A compound of carbon and one or more halogen atoms with or without hydrogen.

Halogenated—Containing halogen atoms or having halogen atoms added to the structure.

Hydrochlorofluorocarbon—An aliphatic compound containing only hydrogen, chlorine, fluorine, and carbon. An example is HCFC-123, CHCl₂CF₃.

Hydrofluorocarbon—An aliphatic compound containing only hydrogen, fluorine, and carbon. An example is HFC-134a, CH₂FCF₃.

In vitro—Studies or methods using cultured cells or organisms.

In vivo—Studies or methods which involve the use of whole animals.

LC₅₀—Lethal concentration 50%; a measure of acute toxicity. The concentration of a substance in air expected to kill half of a group of test animals exposed for a specified period.

LD₅₀—Lethal dosage 50%; a measure of acute toxicity. The dose of a substance expected to kill half of a group of test animals exposed for a specified period.

LOAEL—Lowest Observed Adverse Effect Level. The minimum dose or concentration at which a sign of harm is observed.

Mouse Micronucleus Assay—An *in vivo* test for clastogens using a mouse.

NOAEL—No Observed Adverse Effect Level. The maximum dose or concentration at which no signs of harm are observed.

Perfluorocarbon—An aliphatic compound containing only fluorine and carbon. An example is FC-218 (sometimes called PFC-218), CF₃CF₂CF₃.

Quantitative Structure-Analysis Relationships—Correlations between a biological activity and physical, chemical, and structural composition of a compound. QSARs are used to determine the toxicity of an unknown substance based on the measured toxicity of similar chemicals.

Tropodegradable—An adjective applied to compounds that are rapidly removed from the earth's troposphere by such mechanisms as photolysis, reaction with hydroxyl free radical, rainout, and physical removal.