ENVIRONMENTALLY ACCEPTABLE FLAME EXTINGUISHANTS

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INTRODUCTION

Research geared to the identification and testing of environmentally friendly extinguishants – specifically compounds with low boiling points suitable for use in cold environments - is sponsored by the National Institute of Standards and Technology and the Next Generation Fire Suppression Technology Program.

Low temperature conditions are a characteristic of aircraft in-flight at higher altitudes. Fire suppression agents with lower boiling points are expected to disperse more rapidly and uniformly than higher boiling agents.

A broad review of chemical families identified many with potential to meet the restrictive list of requirements for a suitable halon replacement. This subsequent chemical selection effort builds on several prior projects and guidance from in depth assessment of a wide range of chemical families [1, 2., 3, 4, 5, 6]

Chemical families examined as potential sources of halon 1301 alternatives covered a broad range of elements, chemical functionalities. Information relating to environmental persistence, toxicity, flame suppression, reactivity and a number of other factors were considered. The resulting list of chemical families presented as being worthy of continued or initial consideration ranged from brominated carbon based compounds to metal containing compounds.

The current focus on low boiling compounds eliminated many of theses down-selected chemical families. The remaining chemical families were reexamined and the higher boiling members eliminated from further consideration. Additional chemical families with structural properties indicating shorter atmospheric lifetime were identified and subsequently added to the list of potential low boiling chemical families to be considered, Table 1.

Table 1. Current Down Select of Chemical Families

Bromofluoro alkenes
Bromofluoroethers
Bromofluoroalkylamines
Fluoroalkylamines
Bromofluoro Oxiranes
Bromofluoro & Fluoro Nitriles
Bromofluoro vinylethers

BRIEF OVERVIEW OF THE CHEMICAL FAMILIES UNDER CONSIDERATION

The bromofluoroalkenes continue to receive considerable attention. The amount of toxicity, atmospheric lifetime, and flame extinguishment data for members of this family dwarfs that accumulated for the remaining families. The relatively higher availability of the alkenes offers continued hope that optimal low toxicity compounds may eventually be identified once a concerted toxicity testing program is initiated. The chemical acquisition focus is on the tetrafluorinated bromopropenes and on one difluorinated bromoethylene.

Bromofluoroethers are more challenging synthetically than the aforementioned alkenes. The favorable toxicities of some brominated fluoro ethers (i.e., roflurane) suggest that the overall family might well yield some of the lowest toxicity halon replacement candidates. With the emphasis on low boiling points only the simplest two and three carbon ethers are under consideration. Efforts to develop synthetic approaches to the 2 carbon ethers are still being pursued.

Bromofluoropropene oxides represent a new addition to the chemical families to be considered. The low boiling point of the parent propene oxide and potential for reactivity with OH radical and therefore possible shorter atmospheric lifetime warranted a closer look at this family to obtain baseline data on flame suppression and boiling points.

Bromofluoronitriles and fluoronitriles also represent new chemical families for consideration. Representative compounds for both of these families are relatively easily to acquire and test. The low boiling point of the bromofluoronitrile CF2BrCN and the extremely low boiling point of the fluoronitile analogue CF3CN offered hope of identifying compounds with the potential to address the needs of low temperature extinguishment applications such as those encountered in aircraft.

Bromofluorovinyl ethers are a family of compounds whose potential as flame suppressants was untested. The presence of an ether linkage and a site of unsaturation had suggested possibly poor flame extinguishment performance.

Brominated fluoroamines have long been sought for testing. The expected low toxicity of the fluoroalkyl amines makes the brominated analogue to this family of great interest. Past work has only resulted in the testing of three compounds from this family. Recently a possible source for additional compounds and critical intermediates with the potential to lead to a wide number of low molecular weight and possibly low boiling point bromofluoroamines has been identified. This has led to renewed efforts in this area of chemical acquisition and testing.

N-Brominated fluoroalkyl amines and imines are of interest as well. These compounds may well exhibit short atmospheric lifetimes through hydrolysis of the Br-N and imine bonds. Boiling point information suggests the likelihood of several of these compounds boiling in the range of 10 to 25 °C.

COMPOUND SELECTION, ACQUISITION AND TESTING

Bromofluoroalkenes: The emphasis in compound selection is on low boiling points and short atmospheric lifetime. Unfortunately, the uncertainty in atmospheric lifetime and boiling point estimates for unknown compounds is large however and practical limitations of compound availability from contract synthesis sources often leave few real

choices. The choices made though do help to establish boiling point and structure information and confirm or not the acceptability of flame extinguishment performance. As unacceptably high extinguishment values are disqualifying the information gathered is of immediate use in the further selection of compounds within that family.

Past acquisition and testing of alkenes took a broad look at a range of compounds including propenes, butanes, pentenes and branched compounds. Toxicity testing of several initially available compounds indicated considerable promise, Tables 2 – 5 Of the alkenes studied the boiling points of the propenes were the only ones low enough to justify continued consideration. The present focused acquisition efforts are primarily of tetrafluorinated and remaining pentafluorinated bromopropenes.

The atmospheric lifetime evaluations of alkenes confirm short lifetimes. Calculated Log K_{OW} values for the 35 possible penta-, tetra- and trifluorinated bromofluoropropenes ranged from 1.4 to 2.5. Using experimental K_{OW} values of 1.84 for Halon 1301 and 2.3 for Halothane (CF3CHBrCl) as guides, a list of compounds whose low calculated values predicted a possibly equivalent or higher LOAEL was prepared and promising compounds selected for acquisition. Of particular interest are the bromotetrafluoropropenes listed as these compounds are generally of lower boiling point and may well have higher LOAEL values.

A sample of $CHF_2CBr=CF_2$ was acquired. T_b was estimated to be about 30 °C. The cup burner extinguishment value was 3.3 vol. %, as expected for a bromine-containing compound with only one hydrogen atom.

Table 2. Acute inhalation toxicity tropodegradable bromofluoroalkenes

Compound	Formula	Deaths*
1-Bromo-3,3,3-trifluoropropene	$CF_3CH=CHBr$	0
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr=CH_2$	0
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH=CH_2$	0
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr=CH_2$	0
2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$CF_3CF_2CF_2CBr=CH_2$	0

*30-minute exposure at 5% v/v air concentration

Table 3. Ames mutagenicity test results

Compound	Formula	Ames Test Result
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr=CH_2$	Negative
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH=CH_2$	Negative
2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr=CH_2$	Negative

Table 4. Chromosomal aberration test results

Compound	Formula	Test Result
2-Bromo-3,3,3-trifluoropropene	$CF_3CBr=CH2$	Negative
4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH=CH_2$	Negative

Table 5. Cardiac sensitization data for bromofluoropropenes

Compound Name	Formula	NOAEL	LOAEL
2-Bromo-3,3,3-trifluoropropene	$CH_2=CBrCF_3$	0.5 vol. %	1.0 vol.%

A very large number of potential penta tetra and tri fluorinated propene candidates exist. Compound acquisition and testing efforts have provided data for only a fraction of these, Table 6.

Table 6. Penta, tetra and tri fluorinated propenes

Formula	Chemical Name
$CF_2=CBrCF_3$	2-bromo-1,1,3,3,3-pentafluropopene
$CFBr=CFCF_3$	1-bromo-1,2,3,3,3-pentafluropopene, (E) (Z)
$CF_2=CHCF_2Br$	3-bromo-1,1,3,3-tetrafluropopene
$CFH=CBrCF_3$	2-bromo-1,3,3,3-tetrafluropopene, (E) (Z)
$CHBr=CFCF_3$	1-bromo-2,3,3,3-tetrafluropopene, (E) (Z)
$CH_2=CBrCF_3$	2-bromo-3,3,3-trifluropopene
$CFH=CHCBrF_2$	3-bromo-1,3,3-trifluropopene, (E) (Z)
$CHBr=CHCF_3$	2-bromo-3,3,3-trifluropopene, (E) (Z)
$CFBr=CFCF_2H$	1-bromo-1,2,3,3-tetrafluropopene, (E) (Z)
$CFBr=CHCF_3$	1-bromo-1,3,3,3-tetrafluropopene, (E) (Z)
$CHF=CFCF_2Br$	3-bromo-1,2,3,3-tetrafluropopene, (E) (Z)
$CF_2=CFCFHBr$	3-bromo-1,1,2,3-tetrafluropopene
$CF_2=CBrCF_2H$	2-bromo-1,1,3,3-tetrafluropopene
$CF_2=CBrCFH_2$	2-bromo-1,1,3-trifluropopene
$CFH=CBrCF_2H$	2-bromo-1,3,3-trifluropopene, (E) (Z)
$CF_2=CFCBrH_2$	3-bromo-1,1,2-trifluropopene
$CFH=CFCFBrH$	3-bromo-1,2,3-trifluropopene, (E) (Z)
$CF_2=CHCFBrH$	3-bromo-1,1,3-trifluropopene
$CH_2=CFCF_2Br$	3-bromo-2,3,3-trifluropopene
$CF_2=CFCF_2Br$	3-bromo-1,1,2,3,3-pentafluropopene
$CHBr=CFCHF_2$	1-bromo-2,3,3-trifluropopene, (E) (Z)
$CFBr=CFCFH_2$	1-bromo-1,2,3-trifluropopene, (E) (Z)
$CBrF=CHCHF_2$	1-bromo-1,3,3-trifluropopene, (E) (Z)

Many of these higher boiling compounds might still be useable as extinguishants, Table 7, in the more intermediate temperature ranges of interest.

Table 7. Maximum Boiling Point and Ambient Temperature Relationship

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
10	-14	-1	11	23	35	47	59	72	84	96	108	120
15	-22	-10	2	14	25	37	49	61	73	84	96	108
20	-28	-16	-5	7	19	30	42	53	65	76	88	99

Example: To achieve a 5 vol. % concentration at -20 °C, the calculated maximum boiling point is 52 °C.

Finally, the intriguing observation that 1-chloro-1,2-difluoroethylene, bp -5 °C, has no flash point and that its structural isomer 1-chloro-2,2-difluoroethylene, bp -18 °C, is flammable has led to interest in the acquisition and testing of the brominated analogue of 1-chloro-1,2-difluoroethylene. Initial literature searches for 1-bromo-1,2-difluoroethylene yielded no information and no indication that it had ever been prepared. Subsequently, efforts to develop a synthesis have been successful and the compound is now on order.

Bromofluoroalkylethers: These compounds are expected to have relatively low toxicity and good flame extinguishment properties but unless they prove sufficiently polar they will require some degree of hydrogenation to achieve a short atmospheric lifetime and minimize ODP impact. Two of the simplest brominated ethers are $CBrH_2$-O-CF_3 (39 ºC) and $CBrF_2$-O-CF_3, (boiling point estimated between -30 °C and -8 °C). The tetrafluorinated C_2 bromoethers CBrHF-O-CF_3 (bromofluoromethyl trifluoromethyl ether) and $CBrF_2$-O-CHF_2 (bromodifluoromethyl difluoromethyl ether) are predicted to boil in the range 5 °C to 15 ºC and are still being sought for testing.

The bromofluoro ethers $CF_2HCFBrOCF_3$ and $CFBrHCFHOCF_3$ were successfully sourced and acquired. Boiling point values are estimated as 42 °C and 37 °C, respectively. Cup-burner values are below 4.5 volume % for both compounds.

Bromofluorovinyl ethers: A sample of the bromofluorovinyl ether $CF_2BrCF_2OCF=CF_2$ (boiling point aprox 55 °C) was acquired and a cup-burner value 4.5 vol. % determined. Other compounds will be acquired only if they have lower boiling points. Changes in the bromination site might help.

Bromofluoropropene oxides: A sample of this compound was acquired, with boiling point estimated to be 20 °C. The measured cup burner value was a marginal 4.9 vol. %. A low atmospheric lifetime was expected.

Fluoro nitriles: The commercially available compound CF_3CN, was of great interest due to its boiling point -64 °C. As no data on the effects of a CN group on cupburner flame extinguishment existed a sample was obtained and the cup burner value determined to be 9.0 vol. %. Thus, there is no chemical activity from the CN group. The compound is no better than HFC-125.

Bromofluoro nitriles: The commercially available compound $CBrF_2CN$, was of great interest due in part to its low boiling point of 3 °C and the presence of bromine in the structure. Cup-burner extinguishment testing indicates a value less than 4.0 vol. %. This compound should have a short atmospheric lifetime due to OH reactivity. The rumored existence of unpublished toxicity test data indicating CF_2BrCN was highly toxic has currently halted further consideration of this compound. Attempts to identify the source of this toxicity data and verify the findings have so far been unsuccessful.

Bromofluoroalkyl amines, n-bromo-fluoroalkyl amines and imines: Discussion of these chemical families has been combined for the purpose of achieving a more efficient presentation of the efforts to identify synthetic approaches, identify sources and ultimately obtain and test representative chemicals. To aid in following this discussion a table follows which lists these families and provides an typical or generic example of each.

Table 7. Bromofluoro amines and imines

Chemical familiy	Example(s)
Bromofluoroalkyl amines	(CF3)(CF2Br)NH, (CF2Br)NH2,
n-bromo-fluoroalkyl amines	(CF3)2NBr
n-bromo-fluoroalkyl imines	CF2=NBr

Attempts to source two compounds that due to their low boiling points are of particular interest have made significant progress. Published syntheses for (CF3)2NBr, boiling point 22 C, and CF2=NBr, boiling point 14.7 C indicated that preparation of these compounds is feasible in relatively high yield [7, 8, 9] . The synthesis of both compounds is underway. Should this effort be successful the availability of the useful intermediate, perfluoro-2-azapropene, could provide access to a variety of possibly low boiling n-bromofluoroalkylamines and bromofluoroalkyl amines such as those listed in Table 7.

The Preparation of N-Bromo bis(trifluoromethyl) amine, (CF3)2NBr, (Eq. 1 – 3)

$$CF3NO + CF2=CF2 \rightarrow CF3\text{-}N=CF2 \qquad \text{Eq. 1}$$

$$CF3\text{-}N=CF2 + HgF2 \rightarrow (CF3)2N\text{-}Hg\text{-}N(CF3)2 \qquad \text{Eq. 2}$$

$$(CF3)2N\text{-}Hg\text{-}N(CF3)2 + Br2 \rightarrow (CF3)2NBr \qquad \text{Eq. 3}$$

and preparation of N-Bromodifluoromethanimine, CF2=NBr, are both describe as being fairly straight forward, (Eq. 4,5).

$$FCN + KF + CsF \rightarrow CF2=N\text{-}\ K+ \qquad \text{Eq. 4}$$

$$CF2=N\text{-}\ K+ + Br2 \rightarrow CF2=NBr \qquad \text{Eq. 5}$$

FUTURE CARDIAC SENSITIZATION SCREENING OPTIONS

There are simply no current options for screening compounds for the purpose of identifying the most promising or least cardiac sensitizing compounds for continued testing. The only choice for developers of halogenated and or fluorinated fire extinguishants has been to perform the tremendously expensive formal dog exposure testing. This approach has exhausted available funds (and interest) rapidly.

Only limited research targeting the development of cardiac sensitization screening methods for compounds is in progress. It seems these efforts are still only in their infancy. Methods based on in-vitro cell cultures do offer hope of an eventual solution to the screening problem as well as some hope of valuable insight into the cellular and biochemical mechanism(s) involved in the cardiac arrhythmia observed.

As described earlier an alternative method with the potential for more immediate use in compound selection and testing is the use of hydrophobic hydrophilic partition coefficients. In particular Reverse Phase High Pressure Liquid Chromatography (RP-HPLC) based determination appears to have potential to serve as a means of evaluating the relative tendencies of a series of compounds to induce arrhythmia. Correctly ordering compounds would be in itself a tremendous boost to the selection process. Relationships between partition coefficients and cardiac events and arrhythmia has received some

attention in the past though experimental data is limited. Anesthesia agent and chlorofluorocarbon effects on cardiac muscle studies in some cases provide some reason to consider a physiochemical mechanism [10, 11, 12, 13, 14., 15]

Partition coefficients are a measurement of lipophilicity and substances having high negative partition coefficient values dissolve better in fats and oils than in water. This enhances their ability to enter lipid membranes in the body and enhances their potential for interaction with ion channel performance and cell membrane processes of absorption.

Cardiac arrhythmia induced by clinical anesthetics, Table 9 appear to follow a trend . More precise Log(KOW) experimental method applied to evaluating the link between compounds with known LOAEL values and their experimental Log(KOW) values is desirable.

Table 9. Anesthesia Compounds – Partitioning and Arrhythmia Properties

Property	Halothane	Enflurane	Isoflurane	Desflurane	Sevoflurane
Formula	$CF_3CHBrCl$	CF_3-O-CF_2CHFCl	CF_3-O-$CHCl$-CF_3	CHF_2-O-CHF-CF_3	CH_2F-O-$CH(CF_3)_2$
Blood-gas Ratio [a]	2.5	1.9	1.4	0.42	0.6
Oil-water Ratio [b]	220	120	170	19	55
Arrhythmia [c]	+++	+	+	~	~
MAC [d]	0.74 %	1.68 %	1.15 %	6.3 %	2.0 %

[a] Ratio - (blood anesthesia agent concentration)/(air concentration).

[b] The "oil" phase is commonly, but not exclusively, octanol.

[c] The symbols "+++," "+," and "~" reflect, in order, a decreasing tendency of the anesthetic to induce PVC's in human patients during anesthesia. "~" indicates only a slight tendency.

[d] Minimum Alveolar (air) Concentration (MAC) is a measure of the anesthetic potency of the compound, *i.e.*, the air concentration where 50 % of patients don't have a motor response to a pain stimulus.

Reverse Phase High Pressure Liquid Chromatography (RP-HPLC) based determination appears to have potential to serve as a means of evaluating the relative tendencies of a series of compounds to induce arrhythmia. The chromatographic method yield high precision data for retention time – data that is reproducible within 0.1 second on a consistent basis.

The great chemical separation power of the capillary gas chromatography method is illustrated in Figure 1. A single RP-HPLC analysis of a broad series of compounds is expected to cost between $5,000 and $10,000 to set up and execute. The results could well point reliably to compounds with the lower tendencies to induce cardiac arrhythmia. Formal dog exposure cardiac testing would still be a necessity but the need to test many compounds could well be greatly reduced.

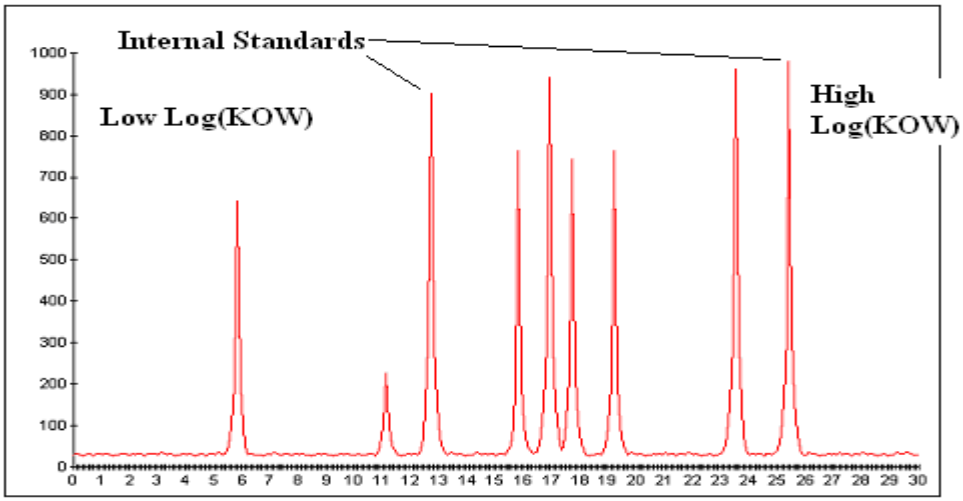

Figure 1. Illustration of RP-HPLC characterization of chromatographic retention times for use in estimating Log(KOW) values (x-axis is time).[16]

SUMMARY

With efforts concentrated on identifying and obtaining the lowest boiling tropodegradable bromocarbons for application to aircraft fire suppression work to further develop the higher boiling compound applications has diminished. Of the many compounds identified it will require toxicity testing to identify those with potential for use in occupied areas. Cardiac sensitization screening and testing remains the greatest hurdle to progress.

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16 The reader is directed to the following internet site for additional examples and discussion of the application of RP-HPLC to comparison of compound retention times www.limathon.com/