TROPODEGRADABLE HALOCARBONS AND
MAIN GROUP ELEMENT COMPOUNDS

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INTRODUCTION

Although it is not certain that a "drop-in" chemical substitute (as opposed to a new technology) for halons that can be used in normally occupied areas will ever be identified. there are two promising paths to such an agent. The first is to target bromocarbons with very short atmospheric lifetimes. We refer to these materials as "Tropodegradable Halocarbons." The second path is to develop non-halocarbons—chemicals that are unlike the classic halocarbon agents used in the past (halons) and those halocarbons now being commercialized (HFCs, HCFCs, and perfluorocarbons). We refer to these non-halocarbon materials as "Compounds of Main Group Elements." Herein we discuss projects sponsored by the Department of Defense Strategic Environmental Research and Development Program (SERDP) under the Next-Generation Fire Suppression Technology Program (NGP) to explore these two paths. The initiation of this work was discussed at the Halon Options Technical Working Conference 1998 [1].

TROPODEGRADABLE HALOCARBONS

Overview

One approach to halon substitutes is to keep bromine in the molecule, but add features that decrease the tropospheric lifetime. The resultant compounds are said to be "tropodegradable," a term used by Dr. Jon Nimitz. A very short tropospheric lifetime can solve two problems at once. First, if the lifetime is sufficiently short, ozone depletion can be negligible, even when bromine is present. Second, a short lifetime means a low global warming potential. Research work has established the potential of tropodegradable bromocarbons as fire suppressants: however, insufficient flame extinguishment experiments have been carried out to relate performance and (for some compounds) flammability to structure. This project was established, in part, to address the need for laboratory-scale fire extinguishment information for tropodegradable compounds.

Four primary processes exist for the removal of organic molecules from the troposphere: (1) reaction with atmospheric hydroxyl free radicals: (2) photolysis: (3) physical removal: and (4) reaction with tropospheric ozone [2]. Hydroxyl free radicals, which are found in low concentrations throughout the atmosphere, are nature's way of cleaning the troposphere. These highly reactive species react with many atmospheric contaminants converting them to chemicals that are rapidly eliminated. The reaction is slow for most halocarbon contaminants: however, chemical features can speed up the reaction with hydroxyl free radicals. Photolysis is nothing more than decomposition by sunlight. Only a few types of chemicals undergo significant photolysis. Rainout is the most common physical removal process. Finally, tropospheric ozone can react with a few molecules to remove them from the atmosphere. Though chemically identical, tropospheric ozone and stratospheric ozone play entirely different roles in the atmosphere. Stratospheric ozone is welcome since it protects the earth from ultraviolet radiation. Tropospheric ozone. on the other hand, is an environmentally harmful contaminant. Removal by reaction with tropospheric ozone is actually the reaction of one contaminant with another. Various substituents can be added to molecules to enhance each of the tropospheric removal processes mentioned here.

Tropodegradable compounds that we consider the most promising are bromine-containing fluoroethers, fluoroalkyl amines, and fluoroalkenes. This paper provides some information on the ethers and the amines: however, the alkenes are emphasized.

Bromofluoroalkenes contain carbon-carbon double bonds. These materials react rapidly with both hydroxyl free radicals and tropospheric ozone. The atmospheric lifetimes are about one day. in some cases less. This compares with atmospheric lifetimes of 65 years for Halon 1301 and 20 years for Halon 1211. The commercialized halon replacements have even longer atmospheric lifetimes (except for CF_3I).

Some of these materials look remarkable good. Some examples of extinguishment concentrations determined by cup burner with n-heptane fuel are shown below (Table 1). These concentrations are all lower than most of the commercialized halocarbon replacements (one exception being CF_3I), and are comparable to the extinguishing concentration of approximately 3 vol.% for Halon 1301.

TABLE 1. EXAMPLES OF EXTINGUISHMENT CONCENTRATES.

Agent	*n*-Heptane Extinguishment Concentration, vol.%
$CH_2{=}CHCBrF_2$	4.50
$CH_2{=}CBrCF_3$	2.55
$CH_2{=}CHCF_2CBrF_2$	3.50

Under sponsorship of the US Air Force and the Advanced Agent Working Group (AAWG), toxicity evaluations have recently been carried out on eight bromofluoroalkenes. Ten (10) rats were exposed for 30 min at 5 vol.%. The results are shown in Table 2.

Compounds 873 and 903 appeared to be the most innocuous in this test. Both compounds induced a degree of anesthesia during exposure, and animals awoke following the exposure without any apparent toxicity or lung impairment. Post-exposure sleeping time was slightly greater for Compound 903 compared with 873.

Although not lethal under these conditions. Compound 707 had apparent nervous system effects as evidenced by tremors during exposure and abnormal muscular contractions postmortem. Exposure to Compound 707 did not result in any lung impairment, and respiration was normal during the exposure. Compound 1116 was also nonlethal, but animals did not achieve a normal clinical appearance after exposure, and some lung toxicity was associated with exposure.

TABLE 2. TOXICOLOGICAL RESULTS FOR EXPOSURE.

CCOD ID	Formula	Number of Rat Deaths	Lung Tissue Observations
873	$CH_2=CBrCF_3$	0	All rat tissues normal
707	$CHBr=CHCF_3$	0	All rat tissues normal
872	$CH_2=CHCBrF_2$	7	At necropsy lungs were mottled
903	$CH_2=CHCF_2CBrF_2$	0	All rat tissues normal
1116	$CH_2=CBrCF_2CF_3$	0	At necropsy lungs were mottled
1360	$CH_2=CBr(OCF_3)CFCF_3$	10	At necropsy lungs were mottled
1358	$CH_2=CBrCF_2CF_2CF_3$	1 (post exposure)	At necropsy lungs were mottled
1359	$CH_2=CBrCFC(CF_3)_2$	10	At necropsy lungs were mottled

Compound Selection and Acquisition

Approximately 70 tropodegradable bromofluoro-alkenes, -amines and -ethers with potential as Halon 1301 replacements have been identified. These organobromine compounds are estimated to have acceptably low Ozone Depletion Potential (ODP) and Global Warming Potential (GWP).

Twenty-five (25) alkenes representing highly fluorinated with a single vinyl bromine or bromine substitution on saturated carbons well removed from the double bond were identified. Some of the alkenes initially considered have fluorine and bromine substitution on unsaturated carbons. While compounds with this substitution pattern may exhibit higher cup-burner values and possibly increased toxicity, actual testing is required to determine their potential as halon replacements.

The eight bromofluoroalkenes listed in Table 2 and the two additional bromofluoroalkenes, 1-bromo-3,3,3-trifluoro-2-trifluoromethyl propene $(CF_3)_2C=CHBr$ and 1-bromo-2,2,3,3,3-pentafluorobutene ($CF_3CF_2CH=CHBr$), more recently acquired all have no substitution by fluorine on the carbon-carbon double bond. Cup-burner flame extinguishment values for all of the alkenes are expected to be less than *5%* and atmospheric lifetimes may well be on the order of a few days.

A list of 24 bromofluoroamines was developed based on estimates of flame extinguishment. physical properties, toxicity and environmental performance. From this a list of 8 promising candidate compounds was identified and targeted for synthesis.

Amine synthesis is perhaps the most difficult challenge. A facile method based on the preparation of perfluoro-2-azapropene with subsequent bromination to form bromobis(trifluoromethyl)-amine enables preparation of a series of compounds has been identified and is being attempted, (Reaction 1). By substituting a variety of fluoroethenes (e.g., $CHF=CH_2$, $CF_2=CH_2$, $CHF=CHF$, $CF_2=CHF$) for the ethylene in Reaction 1, a series of new tropodegradable compounds can be obtained.

$$(CF_3)_2NBr + CH_2=CH_2 \rightarrow (CF_3)_2NCH_2\text{-}CH_2Br \qquad (1)$$

A list of 20 bromofluoroethers was developed based on estimates of their flame extinguishment, physical properties. toxicity and environmental performance. Work on the synthesis of bromofluoroamines is currently in progress under the direction of Dr. Jean'ne Shrceve of the University of Idaho **(USA).** Efforts to synthesize bromofluoroethers are currently underway in the NMERI laboratory

Summary

This research has demonstrated the potential of tropodegradable bromofluoroalkenes to replace Halon 1301 (as well as Halon 1211). Efforts to characterize further the toxicity and fire suppression performance of selected compounds are in the planning stage. Based on the results observed to date. continued research, focused on the acquisition and testing of new tropodegradable bromofluoroalkenes, is warranted.

COMPOUNDS OF MAIN GROUP ELEMENTS

Overview

Most studies to date on chemical substitutes for halons have focused on halocarbons. Some limited past work, however. has looked at chemicals containing silicon, phosphorus. and nitrogen, i.e., materials based on chemical elements other than carbon [3]. The present project expands that past work to ensure that no promising non-halocarbon candidate substitutes are overlooked.

The term "main group elements" denotes elements other than transition metals. This project, however, excludes the main group of families — halocarbons, amines, ethers, and silicon compounds that have been examined extensively elsewhere. One class of non-halocarbon agents has long been used for fire and explosion protection—dry powder agents such as potassium bicarbonate and monoammonium phosphate. The present project. however, is restricted to liquids or gases.

With one major exception. the results of the search have been disappointing. Few materials with potentially acceptable physical (primarily, volatility) and toxicological properties have been identified. The lowest molecular weight materials (i.e., the materials with the highest volatilities) often have hydrogen or halogen atoms directly attached to noncarbon atoms. The former (containing hydrogen) are often flammable, and the latter (containing halogens) are usually toxic (owing to hydrolysis). Both often have low stabilities. The major exception is that fluoroalkyl phosphorus compounds, though having a relatively low volatility, continue to hold significant promise.

In the remainder of this paper, two areas of major interest in this study are examined: volatility (evaporation) and phosphorus compounds.

Evaporation

Compounds that are not solids at room temperature are targeted under the present project. Most of the compounds identified as having potential extinguishment capabilities are liquids with relatively high boiling points. **A** major criterion for such liquids is an ability to evaporate and fill a space to a required concentration within the time required for extinguishment. Thus, evaporation properties must be taken into account during compound review and selection. Areas to be considered are evaporation equilibrium and evaporation rate. Only the first are looked at herein.

The question of whether a given compound can achieve the required extinguishment concentration upon discharge, given sufficient time for evaporation to occur, 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 Equation 1 (Clausius-Clapeyron equation), where R is the ideal gas constant and ΔH_{vap} is the heat of vaporization. This equation is based on the assumption that (1) ΔH_{vap} is temperature independent and (2) the vapor is an ideal gas. The ratio of $\Delta H_{vap}/T_b$, where T_b is the boiling point temperature, is equal to the molar entropy of vaporization ΔS_{vap} at the boiling point. For closely related compounds, ΔS_{vap} at the boiling point is nearly constant with a value of t_c, Trouton's constant (Equation 2). 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.

$$\log_{10}(p_2/p_1) = (\Delta H_{vap}(T_2-T_1)/2.302585RT_2T_1) \qquad [1]$$

$$\Delta H_{vap}/T_b = \Delta S_{vap} \approx t_c \qquad [2]$$

The two equations can be combined to simplify the estimation. Thus, for a boiling point T_b in **K** at a pressure P_b (Equation 3), where Trouton's constant t_c in units of J/K-mol is a variable to be determined for a particular family of compounds, is obtained.

$$p_2 = P_b 10^{**}(0.05221065)t_c[1-(T_b/T_2)] \qquad [3]$$

For example, if t_c is taken to be equal to 88 J/K-mol, which holds for many compounds, one can estimate that the vapor pressure at 25 °C for a compound with a boiling point of $T_b = 50$ °C at 760 torr is 313 torr. From vapor pressure values, one can calculate the maximum concentration possible. For one atmosphere total pressure, the maximum volume fractions are $p_2/760$ for p_2 in torr. Of particular interest is the maximum allowable boiling point (T_b) that can achieve a given concentration (C) for various ambient temperatures, T_2. Equation 4 gives the calculation for boiling points at $P_b = 760$ torr, where temperatures are in **K** and t_c is in J/K-mol. Table 3 gives the estimated maximum boiling point that can achieve concentrations from 1 to 20 vol.% for a Trouton constant of 88 J/K-mol. The data are plotted in Figure 1 (some data have been omitted to simplify the figure).

$$T_b = [1-(\mathrm{Log}(760C/100P_b)/0.05221065t_c)]T_2 = [1-(\mathrm{Log}(C/100)/0.05221065t_c)]T_2 \qquad [4]$$

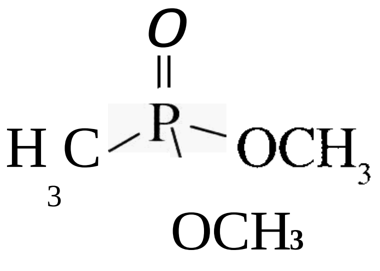
TABLE 3. ESTIMATED MAXIMUM BOILING POINT FOR GIVEN CONCENTRATION.

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

This analysis shows that one 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.

Phosphorus Compounds

Compounds of phosphorus have been of particular interest [4]. Phosphorus compounds appear to provide **a** chemical fire extinguishment mechanism, just like the bromine-containing halons, and some appear to be highly effective. Much work has been performed on dimethyl methyl phosphonate (DMMP) and related compounds by Professor Elizabeth Fisher and her co-workers at Cornell [5,6]. Though DMMP shows very promising flame suppression characteristics. this compound and most ***of*** the related compounds studied to date have some serious drawbacks. First, the material **is** flammable (it is actually possible. though not practical, to extinguish flames with **a** flammable material). Second, most compounds studied to date have low vapor pressures and are not very volatile.



DMMP

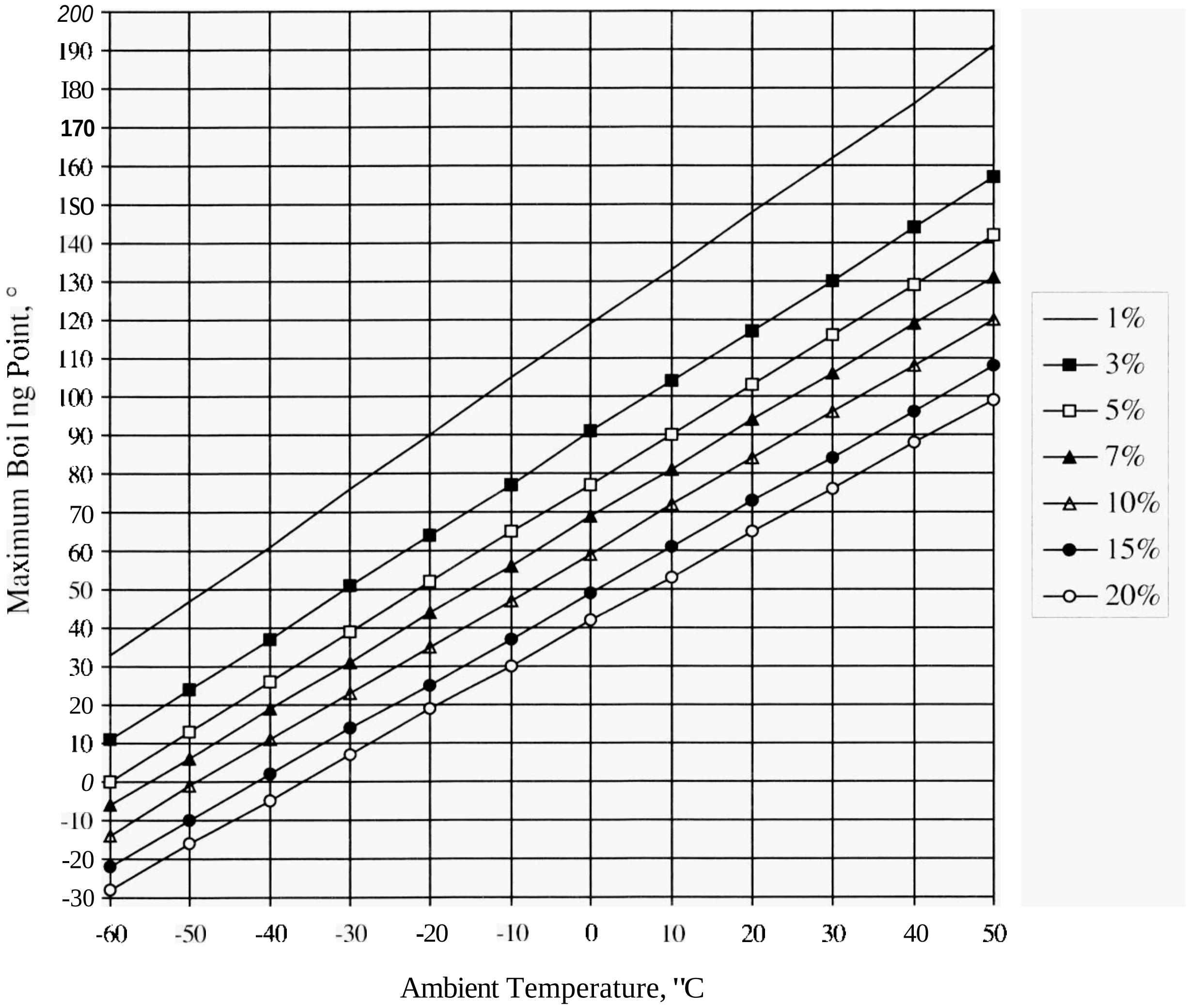
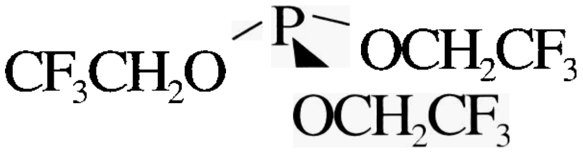


Figure 1. Estimated maximum boiling points that can achieve given concentrations as a function of ambient temperature (simplified), calculated for t_c = 88 J/K-mol.

One way to address both of these problems is to work with phosphorus compounds containing a fluoroalkyl group–substituents with fluorine replacing part or all of the hydrogen atoms. The presence of fluorine decreases or eliminates flammability and increases volatility. For example, tris(2,2,2-trifluoroethyl)phosphite (TFEP) has a lower boiling point than DMMP and is non-flammable. Moreover, the material is an excellent fire suppressant. We have determined that the concentration required to extinguish an n-heptane flame is 1.78 ± 0.04 vol.%. This can be compared with the concentration of approximately 3.2 vol.% for Halon 1301.



$P(OCH_2CF_3)_3$

TFEP

Heat extraction experiments also indicate an excellent extinguishing ability for TFEP (Figure 2). In these experiments, the heat extracted by a burner top from **a** premixed methane flame is measured as a function of added TFEP. **As** the flame approaches extinguishment, less and less heat is extracted. **A** distinct (and, as yet, unexplained) break occurs in the curve. To the left of the break, the fitted straight line has **a** slope of -107 cal/cc CH_4. Extrapolation to a zero heat output gives **a** predicted extinguishment concentration of 0.008 mole fraction TFEP (0.8 vol.%). To the right of the break the fitted straight line has a slope of -50 cal/cc CH_4 and gives an extrapolated extinguishment mole fraction of 0.015 (1.5 vol.%).

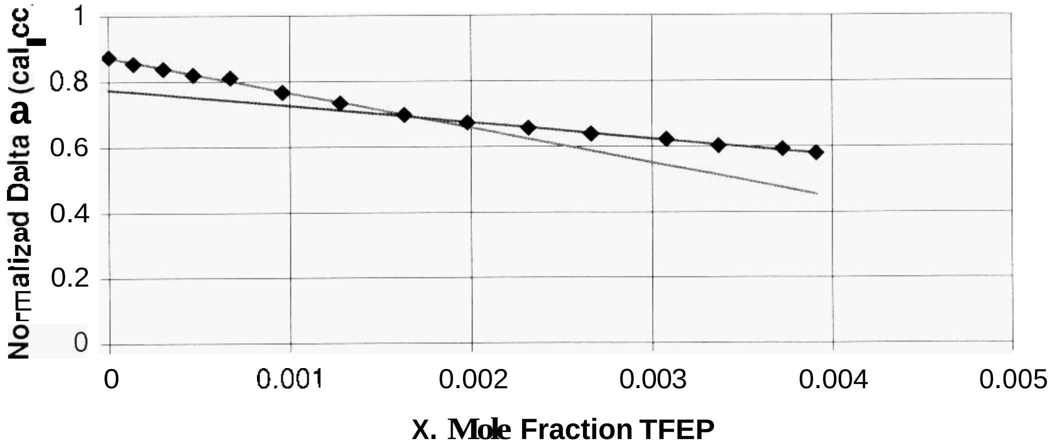
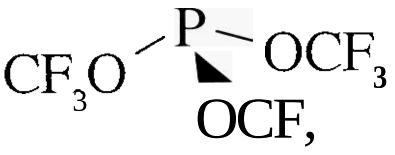


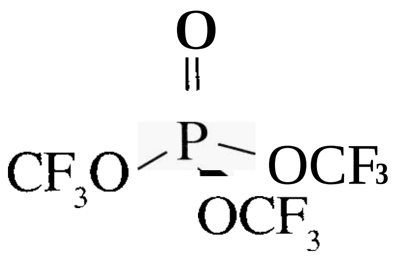
Figure 2. Heat absorption curves for methane flame with TFEP.

Figure **3** plots the heat abstraction for a fixed concentration of TFEP in a premixed methane flame as a function of the fuel/air ratio Φ. For a stoichiometric flame. Φ is 1.00. Higher values of Φ indicate a fuel-rich flame: lower values, a fuel lean flame. The plot **is** symmetric. which indicates that the TFEP is not acting as a fuel in the flame.



TFMP

There is one major problem with TFEP. Though the volatility is improved. it is still not nearly what one would like. For that reason, the synthesis of fluoroalkyl phosphorus compounds with lower molecular weights should be undertaken. For example, tris(trifluoromethyl)phosphite (TFMP), which should have a relatively high volatility, is particularly promising. **A** major problem exists — TFMP has never been made! Though this appears to be a severe drawback. there is no reason to believe that it cannot be made. The very closely related compound, tris(trifluoromethyl)phosphate has. in fact, been prepared, though, as yet, it is untested, and has a boiling point of 52 °C [7]. This boiling point is **a** little high; however, there is good reason to believe that it could be acceptable. The unknown compound TFMP is expected to have a lower boiling point.



Tris(trifluoromethyl)phosphate

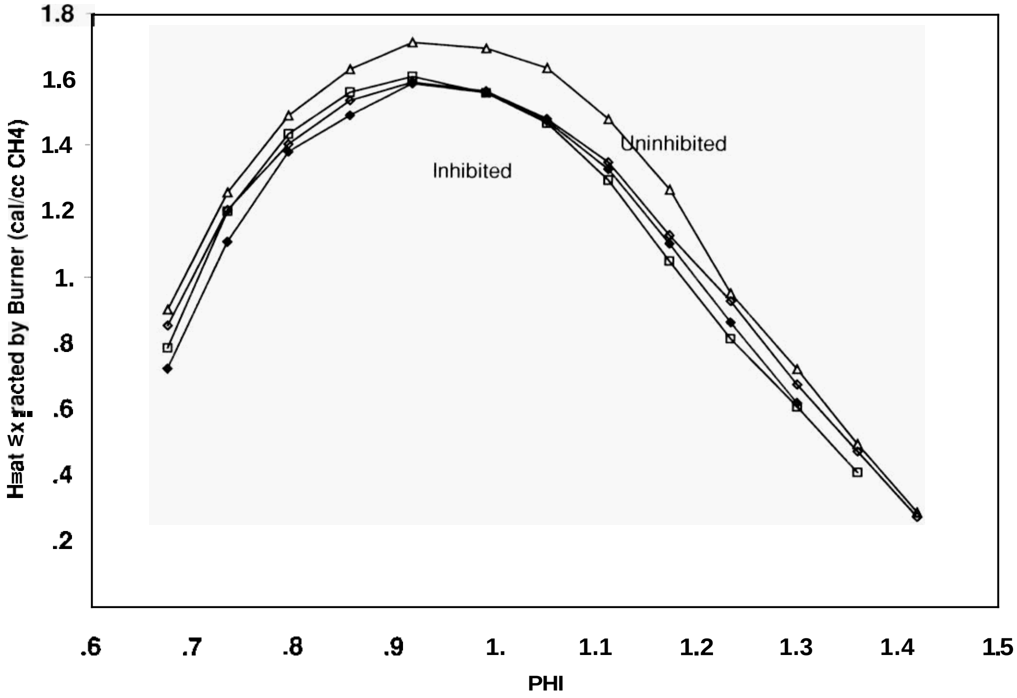


Figure 3. Heat extraction from methane flame with TFEP versus fuel/air ratio (Φ).

The work to date indicates that, of all of the non-halocarbon and non-metal compounds, phosphorus-containing derivatives hold the most promise as halon substitutes. Little is still known about toxicity, and this is always of major concern. Also, the volatility and discharge properties may not be ideal. We have been working on ways to increase discharge rates, and it may be possible to use these materials as aerosols or as blends with appropriate carriers.

ACKNOWLEDGMENTS

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