Thermal Decomposition Products Testing With 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one (C_6 F-ketone) During Fire Extinguishing

by

Benjamin D. Ditch

A Thesis
Submitted to the Faculty
of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Degree of Master of Science
in
Fire Protection Engineering

December 2002

Approved:

Professor Jonathan Barnett, Major Advisor Fire Protection Engineering Department	Professor Robert Zalosh, Reader Fire Protection Engineering Department
Dr. Scott Thomas, Advisor 3M Company	Professor David Lucht, Head of Department Fire Protection Engineering Department

Thermal Decomposition Products Testing With 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one (C_6 F-ketone) During Fire Extinguishing

by

Benjamin D. Ditch

A Thesis
Submitted to the Faculty
of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Degree of Master of Science
in
Fire Protection Engineering

December 2002

Approved:

Professor Jonathan Barnett, Major Advisor
Fire Protection Engineering Department

Robert Zalosh

Professor Robert Zalosh, Reader
Fire Protection Engineering Department

Dr. Scott Thomas, Advisor
3M Company

Professor David Lucht, Head of Department
Fire Protection Engineering Department

Abstract

The thermal decomposition products (TDP) generated during fire suppression with 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one were studied using wet chemistry and FTIR. Small-scale testing was conducted in a 1.28-m^3 (45-ft^3) enclosure. The effects of fire size, agent discharge time, and agent concentration on TDP are reported. A comparison of the two methods is presented. In terms of magnitude and generation trends, the TDPs were found to be comparable to other in-kind halon alternatives.

Acknowledgements

This thesis would not have been possible without the assistance and knowledge of several people. Foremost, I would like to thank Scott Thomas for advising this project and providing invaluable insight for the completion of this thesis. I am grateful to Professor Barnett and Paul Rivers for providing the opportunity and backing for this project. Further the efforts of the 3M Specialty Material Division for assisting in the technical issues encountered during the testing of the new product. Finally, I would like to thank my family who have always extended a supporting hand whenever it was needed and Kristen for her infinite patience and encouragement through the final stages of my educational endeavor.

Executive Summary

Since introduced into commercial use during the 1960's, halons have been the agents of choice for protecting hazards in local applications where any fire could present a risk to human life or high value property [1]. High efficiency and low residue led to halon systems protecting a wide variety of applications. The low toxicity of halon 1301 (CF_3Br), at use concentrations, makes use where human exposure may occur, such as aircrafts, particularly beneficial. Other localized applications include industrial, commercial, marine, defense, and aviation. The relatively high boiling point of halon 1211 (CF_2ClBr), compared to other halons, is beneficial for streaming applications. Other halons, such as 1011 ($CClBr$), 2402 ($C_2F_4Br_2$), and 1202 (CF_2Br) were much less commonly used [1].

The fire extinguishing performance of halon is due to the presence of bromine. Unfortunately, bromine and chlorine have been linked to the catalytic destruction of stratospheric ozone. This has led to global regulations on the production, sale, and use of halons. A complete phase-out of halon production has already occurred, while the phase-out on use can happen as early as 2003 in some countries [2].

With the phase out deadlines rapidly approaching the need for a sustainable halon alternative is increasing. The fire protection industry has put forth considerable effort in finding an alternative with the right combination of performance, environmental characteristics, and safety. A deficiency in any one of these characteristics may lead to an unsustainable technology (i.e. one with environmental characteristics that may be restricted under future regulations). Some important considerations of performance are the mass ratio to halon, compatibility with existing systems, and extinguishing concentration [3]. The mass ratio to halon refers to the quantity of the alternative required to achieve the same fire extinguishing effectiveness as halon. Extinguishing performance refers to an agent's ability to extinguish fires at use concentrations. Environmental characteristics include the ozone depletion potential (ODP), the global warming potential (GWP), and atmospheric lifetime (ALT) [3,4,1].

Human safety is the most important consideration when dealing with any fire protection product. Therefore, the toxicity of a halocarbon is an important characteristic especially when protecting occupied spaces. There are two toxicological aspects to consider. One is the toxicity of the agent itself. The other is the toxicity of the thermal decomposition products (TDP) generated when an agent is used under fire conditions [3]. The TDPs are those compounds produced due to an agent's exposure to a fire.

The 3M Company has investigated a new chemical class of compounds of which one molecule, C_6 F-ketone or 1,1,1,2,2,4,5,5,5 nonafluoro-4-trifluoromethyl pentan-3-one, has shown potential for use in both local and streaming applications. The physical properties of C_6 F-ketone allow applications in both streaming and localized flooding [5,6].

The TDPs of C_6 F-ketone have not been previously investigated. With the exception of thermally inert agents like carbon dioxide and nitrogen, halons and organic halocarbon alternatives thermally decompose upon exposure to a fire. The TDPs of most concern are hydrogen halides (HX) and carbonyl halides (COX_2) [7]. Concerns over the effects of exposure to acid gases have lead to several studies on the effects of the concentrations of these exposure levels [8,9,10,11]. Studies have shown that acid-gas production by in-kind halocarbons is between 2 and 10 times greater than that of halon 1301. It has also been shown that the three key factors resulting in thermal decomposition production are the fire size-to-volume ratio, the agent volumetric concentration, and the discharge time [12].

The purpose of this study is to investigate the TDPs of C_6 F-ketone. Testing conducted in a 1.28-m^3 (45-ft^3) enclosure included class-B fires and class-A fires. The three variables in the test matrix were fire size, agent discharge time, and agent concentration. Two methods for analyzing TDP generation were used: an indirect wet chemistry technique utilizing an ion-selective electrode (ISE) and a direct technique utilizing Fourier-Transform Infrared Spectroscopy (FTIR).

Results from the testing have shown, in terms of TDP, that C_6 F-ketone is directly comparable to other commercially available halon alternatives. The maximum TDP concentrations are consistent with those for other agents. Also the main factors effecting TDP generation (fire size, discharge time, agent concentration) were consistent with previous results for in-kind agents. The wet chemistry technique used for this testing was found to be inappropriate for analysis of C_6 F-ketone. In contrast FTIR analysis proved to be a very useful tool for determining TDP.

Table of Contents

Table of Figures

List of Tables

Nomenclature

Symbols

^{o}C - Celsius

amu – atomic mass unit

cm - centimeter

dia - diameter

ft^{3} - cubic feet

gal - gallon

g·mol - gram·moles

hrs - hours

in - inch

kPa - kiloPascal

kW - kilowatt

l - liter

lb - pound

lpm - liters per minute

m - meter

m.w. - molecular weight

m^{3} - cubic meter

µg - micrograms

min - minute

ml - milliliter

mV - millivolt

nm - nanometer

ppm - parts per million [for liquid mass or gas volume basis]

psi - pound per square inch

s - second

V - Volts

v/v – volume / volume

Abbreviations

1990 CAAA - 1990 Clean Air Act Amendment

ALT - Atmospheric Lifetime

CLS - Classic Least Squares

COX_2 - Carbonyl Halide

DTL - Dangerous Toxic Load

EPA - Environmental Protection Agency

EU - European Union

FTIR - Fourier Transform Infrared Spectroscopy

GC/MS - Gas Chromatography / Mass Spectroscopy

GWP - Global Warming Potential

HCFC - Hydrochlorofluorocarbon

HFC - Hydrofluorocarbon

HFP - Hexafluoropropylene

HX - Hydrogen Halide

IC - Ion Chromatography

ISE - Ion Selective Electrode

IPCC – Intergovernmental Panel on Climate Change

LOAEL - Lowest Observable Adverse Effect Level

MCT - Mercury Cadmium Telluride

MDL - Minimum Detection Limit

MIT - Massachusetts Institute of Technology

MS - Mass Spectroscopy

MSDS - Material Safety Data Sheet

NIR/TDL - Near-Infrared Tunable Diode Laser

NOAEL - No Observable Adverse Effect Level

ODP - Ozone Depletion Potential

ODS - Ozone Depleting Substance

OH - Hydroxyl Radical

PFC - Perfluorocarbon

PTFE - Polytetrafluoroethylene

RT-ISE - Real-time Ion Selective Electrode

SNAP - Significant New Alternatives Policy

TDL - Theoretical Detection Limit

TDL - Tunable Diode Laser

TDP - Thermal Decomposition Products

UN - United Nations

VCOP - Voluntary Code Of Practice

WMO - World Meteorology Organization

1.0 Background

1.1 Introduction

Nations around the world have acknowledged the need to protect the earth's ozone layer. The signing of the Vienna Convention, in 1985, marked the first international agreement to protect the ozone layer. Currently the production and consumption of certain classes of ozone depleting substances (ODSs) are controlled by the Montreal Protocol and its amendments and adjustments. Major changes occurred in 1990 (London Amendment), 1992 (Copenhagen Amendments), 1995 (Vienna Adjustments), and 1997 (Montreal Amendments). Ratified by the U.S. in 1988, the Montreal Protocol called for the phase out of all halon manufacturing by January of 1994 in developed countries. However, no phase-out date has been set for distribution [13,14].

The European Union (EU) regulation, EC No 2037/2000, goes beyond the requirements of the Montreal Protocol. Included is a ban on the sale and use of halons after December 31, 2002 (except for critical uses) with mandatory decommissioning of non-critical systems required by December 31, 2003. Critical uses include, for halon 1301, protection of certain military equipment and compartments occupied by personnel, national security issues, and installations in the Channel Tunnel. The new regulations make compulsory the recovery and disposal of halons for fire protection equipment [2].

In the US, the sale of any ODS is controlled by the Environmental Protection Agency (EPA) under the Significant New Alternatives Policy (SNAP) [15]. The authority to enforce EPA regulations is based on the directives and mandates in the 1990 Clean Air

Act Amendment (1990 CAAA) [13]. The SNAP program requires that all replacement agents must be approved for each application considered. Therefore testing is needed to determine the performance, environmental characteristics, and safety of the agent. This legislation has no authority outside of the US.

Many researchers have investigated the halocarbon class of compounds, including hydrofluorocarbon (HFC), hydrochlorofluorcarbon (HCFC), and perfluorocarbon (PFC) for a suitable alternative [3]. Poor environmental or toxicological characteristics may prevent these agents from becoming long-term sustainable solutions. Reasons for this include a voluntary code of practice (VCOP) instituted by the industry, which constrains the use of HFCs and PFCs [16]. Further, pending the ratification of the 1997 Kyoto Protocol to the United Nations (UN) Framework, agents with a high potential for climate change may be facing further regulations. Potential for climate change is largely dependent on a material’s GWP and ALT [17]. This is particularly important for agents such as HFC-227ea and HFC-236fa, which have high GWPs. More importantly, in the US, the 1990 CAAA Sec. 612 [18] instructs the EPA to issue regulations making it unlawful to replace Class I (halons, CFCs, and others) and II (HCFCs) substances with a certain substitute if other available alternatives would reduce the overall risk to health and environment [13].

Halon fire extinguishing agents are low boiling point halocarbons. The term ‘halocarbon’ refers to chemical compounds that contain carbon and one or more of the halogen elements (fluorine, chlorine, bromine, and iodine) [19]. It has been found that halogen elements, when introduced into a fire can act as a fire suppressant. Bromine is particularly effective at chemically suppressing fires by disrupting the free radical reaction crucial to fire development. However, due to the presence of bromine and chlorine in their chemical structure, halons have been implicated in the catalytic destruction of the stratospheric ozone layer [1,20]. This effect was first discussed by Molina and Rowland in the mid-1970's [20] and has since been the subject of several papers [21,22].

Table 1 - Halon Alternative Chemical Classes [*23, *24, 19]

HCFC	Hydrochlorofluorocarbons
PFC	Perfluorocarbons
HFC	Hydrofluorocarbons
FIC	Fluoroiodocarbons

*Additional information on halocarbon nomenclature

Considerable research into finding an alternative to halons has led to the creation of several new chemical classes, Table 1. Many of the resulting chemical compounds are used as halon alternatives under certain conditions, Table 2. Several studies have presented an overview of halon alternative development [25,26,27,28,29,30]. Unfortunately all of these alternatives have some trade off of performance, environmental characteristics, or safety.

Table 2 – Historic Halon Alternatives [19, 31]

Fluorocarbon Number	Chemical	Formula	Trade Name
1211	Bromochlorodifluoromethane	CF_2ClBr	Halon 1211
1301	Bromotrifluoromethane	CF_3Br	Halon 1301
HCFC-124	Chlorotetrafluoroethane	$CHClFCF_3$	FE-124[a]
HCFC Blend A	Additive plus		NAF S-III[b]
HCFC-123	Dichlorotrifluoroethane	$CHCl_2CF_3$	
HCFC-125	Chlorodifluoromethane	$CHClF_2$	
HFCF-124	Chlorotetrafluoroethane	$CHClFCF_3$	
HFC-23	Trifluoromethane	CHF_3	FE-13[a]
HFC-125	Pentafluoroethane	CHF_2CF_3	FE-25[a]
HFC-227ea	Heptafluoropropane	CF_3CHFCF_3	FM-200[c]
HFC-236fa	1,1,1,3,3,3-Hexafluoropropane	$CF_3CH_2CF_3$	FE-36[a]
FC-218	Perfluoropropane	$CF_3CF_2CF_3$	CEA-308[d]
FC-3-1-10	Perfluorobutane	$CF_3CF_2CF_2CF_3$	CEA-410[d]
FC-5-1-14	Tetradecafluorohexane	C_6F_{14}	CEA-614[d]
FIC-13I1	Trifluoroiodomethane	CF_3I	Triodide[e]

[a]Dupont [b]NAFG [c]Great Lakes Chemical Company [d]3M [e]Pacific Scientific

For the purpose of this paper any compound used in place of halon is referred to as a "halon alternative". This includes halocarbon agents that are chemically similar to the present halons, which are often called halon "replacements." This designation does not include "chemical alternatives", which often indicate materials such as carbon dioxide, argon, water, or other materials that are chemically distinct from halons [19].

Recent work by the 3M Company has investigated fluorinated ketones as halon alternatives. A fluorinated ketone is one class of carbonyl that may result when a hydrocarbon acquires one or more oxygen atoms [32]. In general, little information on the physical properties of fluorinated ketones is available. The majority of the work revolves around their synthesis [32,33]. It should be noted that there is a distinct difference between hydrocarbon ketones and fluorinated ketones. For example, hydrocarbon ketones, such as acetone, are commonly flammable.

1.2 C_6 F-ketone Properties

C_6 F-ketone, a fire protection fluid designated as a halon alternative, was developed by the 3M Company under the commercial name 3M™ Novec™ 1230 Fire Protection Fluid. A boiling point of 49°C (120.4 °F) allows uses in streaming applications such as small portable fire extinguishers and larger wheeled units. However, due to a low heat of vaporization, in local applications using fixed systems and small quantities, complete vaporization can occur during discharge [5]. Table 3 contains physical properties for C_6 F-ketone.

Table 3 - C_6 F-ketone Physical Properties [5]

Properties	**Units**
Chemical formula	$CF_3CF_2C(O)CF(CF_3)_2$
Molecular weight	316.04
Boiling point @ 101 kPa	49.0°C (120.4°F)
Freezing point (pour point)	-108°C (-162.4°F)
Density, saturated liquid @ 25°C	1.60 g/ml (99.9 lbm/ft^3)
Density, gas 101 kPa @ 25°C	0.0184 g/ml (1.15 lbm/ft^3)
Specific volume, 101 kPa @ 25°C	0.0543 m^3 /kg (0.870 ft^3 /lb)
Heat of vaporization @ b.p.	41.4 BTU/lb (96.4 kJ/kg)
Liquid viscosity @ 25/0°C	0.41/0.56 centistokes
Solubility of water in $C_6F_{12}O$ @ 25°C	<0.001 % by wt.
Vapor pressure @ 25.0°C	40 kPa (5.87 psia)
Dielectric strength (rel. to N_2 @ 25°C)	2.3

Comparable to other commercially available halon alternatives, C_6 F-ketone is electrically non-conductive, inert, and stable in storage containers [5]. Also, a freezing point of –108°C (-226°F) allows use in extremely cold climates. A comparison of C_6 F-ketone properties with some other commercially available agents as well as halon 1211 and 1301 can be found in Table 4. Note C_6 F-ketone remains liquid over most expected use temperatures.

Table 4 - Properties Comparison [5, 7, 35, 36, 37]

Agents	Molecular Weight	Boiling Point @ 101 kPa	Freezing Point	Heat of Vaporization at b.p.	Viscosity, liquid at 25°C
Units	g/mol	°C	°C	kJ/kg	centipoise
C_6 F-ketone	316.04[e]	49.2[e]	-108[e]	88.0[e]	0.524
Halon 1211	165.38[d]	-3.4[d]	-160.5[d]	32.0 cal/g[d]	0.34[d]
Halon 1301	149[a]	-57.8[a]	-168.0[b]	118.8[b]	0.159[b]
HCFC-124	136.50[e]	-12.1[e]	-198.9[e]	163.1[e]	0.305[e]
HCFC Blend A	92.90[e]	-38.3[e]	<-107.2[e]	225.6[e]	0.21[e]
HFC-23	70.01[a,e]	-82.1[a,e]	-155.2[e]	238.8[e]	0.083[e]
HFC-125	120.00[a,e]	-48.5[a,e]	-102.8[e]	164.8[e]	0.143[e]
HFC-227ea	170.03[a,e]	-16.4[a,e]	-131[e]	132.6[e]	0.184[e]
HFC-236fa	152.00[e]	-1.4[e]	-103[e]	160.1[e]	0.306[e]
FC-218	188.00[e]	-37.0[e]	-183.0[e]	104.8[e]	0.297[e]
FC-3-1-10	238.03[a,e]	-2.0[a,e]	-128.2[e]	96.3[e]	0.324[e]
FC-5-1-14	338.0[c]	56.0[c]	-90.0[c]	88.4[c]	NA
FIC-13I1	195.91[e]	-22.5[e]	-110[e]	112.4[e]	0.196[e]

[a]7 [b]36 [c]35 [d]37 [e]5

1.3 Halon Alternative Properties Comparison

Comparisons on the extinguishing effectiveness of halon alternatives are commonly based on the minimum extinguishing concentration for n-heptane using the cup burner, in accordance with NFPA 2001, *Standard for Clean Extinguishing Agent Fire Extinguishing Systems Ed.2000* [31]. It should be noted that heptane does not necessarily represent the worst-case scenario for all agents. Table 5 lists a comparison of performance data for several halon alternatives.

Table 5 – n-heptane Cup Burner Performance Comparison [3, 5, 7, 31, 35, 38]

Agents	Minimum cup-burner, heptane fuel [% v/v]	Maximum mass ratio to halon 1211
C_6 F-ketone	4.0-4.9[e]	2.91
Halon 1211	3.22[f]	1.00
Halon 1301	5[e] (3.1[c]) 2.9[f]	0.81
HCFC-124	8.5[e] (6.4-8.2[a]) 6.6[d] (6.7[f])	2.18
HCFC Blend A	11.9[e] (9.9-11.6[a]) 9.9[d]	2.08
HFC-23	16[e] (12-13[a]) 12[c] (12.9[d]) 12.6[f]	2.10
HFC-125	10.9[e] (8.1-9.4[a]) 9.1[c] (8.7[d]) 9.41[f]	2.46
HFC-227ea	7[e] (5.8-6.6[a]) 6.6[c] (6.5[d]) 6.3[f]	2.24
HFC-236fa	6.3[e] 6.4 (5.6-6.5[a]) 6.3[d] (5.6[f])	1.86
FC-218	8.8[e] (6.1-7.3[a]) 6.5[d]	3.11
FC-3-1-10	6.0[e] (4.1-5.9[a]) 5.2[c] (5.5[d]) 5.0[f]	2.68
FC-5-1-14	4.0[b] (4.42[f])	2.81
FIC-13I1	3.6[e] (3.0-3.2[a]) 3.2[d]	1.32

[a]3 [b]35 [c]7 [d]31 [e]5 [f]38

1.4 Environmental Considerations

Three environmental characteristics of particular interest in assessing halon replacements are, ALT, GWP, and ODP. The environmental toxicity profiles for several commercially available halocarbons are listed in Table 6.

As the name implies, atmospheric lifetime refers to a compound's persistence in the atmosphere. In general hydrocarbon ketones have a short ALT due to reactivity with the tropospheric hydroxyl (OH) radicals. This, however, does not hold true for fluorinated ketones. In fact, C_6 F-ketone is non-reactive with the OH radical. Also unlike other hydrocarbon ketones, it is also not water-soluble so rainout is not possible. Studies have indicated that the extremely low ALT, on the order of 5 days, is due to the rate of photolysis. A study conducted at the Massachusetts Institute of Technology (MIT) measuring the UV cross-section for C_6 F-ketone found the maximum wavelength of absorbance at 306 nm. Due to this absorbance above 300 nm, significant photolysis occurs in the lower atmosphere [5,39,41]. This is because higher wavelengths have lower energy, and can therefore be found lower in the atmosphere [20]. The long ALTs of fully fluorinated compounds (such as PFCs) are due to the molecules stability. Note that compounds with short atmospheric lifetimes generally have lower GWPs and ODPs.

The GWP is an index that provides a relative measure of the possible warming impact due to a compound that acts as a greenhouse gas in the atmosphere. The GWP of a compound, as defined by the Intergovernmental Panel on Climate Change (IPCC), is the amount of warming potential a compound has compared with CO_2, over a 100-year time interval. The commonly accepted ITH interval of 100 years represents a compromise between short-term effects (20 years) and longer-term effects (500 years or longer) [17]. Using a measured IR cross-section and the method of Pinnock *et al.* [40] the instantaneous radiative forcing for C_6 F-ketone is calculated to be 0.50 $Wm^{-2}ppbv^{-1}$. This radiative forcing and a 5-day atmospheric lifetime result in a GWP of one for C_6 F-ketone [39].

The ODP is a measure of the ability of a chemical to deplete stratospheric ozone. The ODP is defined by the World Meteorology Organization (WMO) as the total steady-state ozone destruction potential for a compound relative to CFC-11 [32]. The lack of chlorine or bromine in the chemical structure results in a zero ODP. Also, like other fluorochemicals, C_6 F-ketone is expected to degrade to fluorinated alkyl radicals. These degradation products have been shown to have no impact on the stratospheric ozone [39].

Table 6 - Environmental Characteristics Comparison [5, 17, 19, 31, 35, 36]

Agent	ALT	Radiative Forcing	GWP (100 year *i*th)	ODP	% Water Solubility
Units	Years	Wm^{-2}ppbv^{-1}	CO$_2$ = 1	CFC-11 = 1	ppm @ 21°C
C$_6$ F-ketone	0.014[b]	0.50[b]	1[b]	0[b]	<0.001% by wt.[b]
CFC-11	NA	0.25[a]	4600[a]	NA	NA
Halon 1211	11[b] / 20[c]	0.30[a]	1300[a,b]	4[b] / 5.1[c]	NA[f]
Halon 1301	12[c]	0.32[a]	6900[a]	12[c]	0.0095% by wt.[f]
HCFC-124	6.1[c]	0.22[a]	620[a] / 470[c]	0.03[c]	700 @ 25°C[d]
HCFC Blend A	12[c]	NA	1450[c]	0.044[c]	0.12% by wt.[d]
HFC-23	264[c]	0.20[a]	14800[a] / 11700[c]	0[c]	500 @ 10°C[d]
HFC-125	32.6[c]	0.23[a]	3800[a] / 2800[c]	0[c]	700 @ 25°C[d]
HFC-227ea	36.5[b,c]	0.30[a]	3800[a,b] / 2900[c]	0[b,c]	0.06% by wt.[d]
HFC-236fa	226[b] / 209[c]	0.28[a]	9400[a] / 6300[c]	0[c]	740 @ 20°C[d]
FC-218	2600[c]	NA	7000[c]	0[c]	<0.005% by wt.[d]
FC-3-1-10	2600[c]	0.33[a]	8600[a] / 7000[c]	0[c]	0.001% by wt.[d]
FC-5-1-14	3200[b]	0.49[a]	9000[a]	0[b]	Nil[e]
FIC-13I1	0.005[a] / <0.005[c]	0.23[a]	<1[a,c]	0.0001[a,c]	1.0062% by wt.[f]

[a]17 [b]5 [c]19 [d]31 [e]35 [f]36

1.5 Safety

Toxicity testing of C$_6$ F-ketone has shown it to be safe when expected end use conditions are considered. The effective toxicity exposure limit, as determined by the LC$_{50}$ 4-hour acute inhalation test, is greater than 100,000 ppm (>10% v/v). The No Observable Adverse Effect Level (NOAEL) is also 100,000 ppm (10% v/v). Since no testing at higher concentrations has been conducted, the Lowest Observable Adverse Effect Level has been set at greater than 100,000 ppm. (>10% v/v) [5]. Comparative properties can be seen in Table 7. Note that C$_6$ F-ketone is acceptable for use in occupied areas [15].

Table 7 - Toxicity Comparison [3, 5, 19]

Agent	Physical State	LC_{50} 4-hour acute inhalation (UNO)	NOAEL	LOAEL	Use in occupied areas
Units	**@ 25°C**	**% v/v**	**% v/v**	**% v/v**	**---**
C_6 F-ketone	Liquid	>10.0[b]	10.0[b]	>10.0[b]	Yes[b]
Halon 1211	Gas	20.0[b] (15 min)	0.5[a] / 1.0[b]	1.0[a] / 2.0[b]	No[b]
Halon 1301	Gas	>80.0[b]	5.0[a,bb]	7.5[a,b]	Yes[b]
HCFC-124	Gas	36[c]	1.0[a,c]	2.5[a,c]	Yes[b]
HCFC Blend A	Gas	64[c]	10.0[a,c]	>10.0[a,c]	Yes[b]
HFC-23	Gas	65[c]	30.0[a,c]	>50.0[a]	Yes[b] (restricted)
HFC-125	Gas	70[c]	7.5[a,c]	10.0[a,c]	Yes[b] (restricted)
HFC-227ea	Gas	>80.0[b]	9.0[a,b,c]	10.5[a,b,c]	Yes[b]
HFC-236fa	Gas	13.5[c]	10.0[a,c]	15.0[a,c]	Yes[b]
FC-218	Gas	NA	30.0[a,c]	40.0[a,c]	Yes[b]
FC-3-1-10	Gas	80[c]	40.0[a,c]	>40.0[a,c]	Yes[b]
FC-5-1-14	Liquid	>30.0[b] (@ sat)	17.0[b]	>17.0[b]	Yes[b]
FIC-13I1	Gas	~16.0[b] / 27.4[c]	0.2[a,b,c]	0.4[a,b,c]	No[b]

[a] 19 [b] 5 [c] 3

1.6 TDP Testing

1.6.1 Effects of TDP

It is difficult to compare agent toxicity since safety concerns are not limited to the properties of the agent itself. Another important safety aspect is the toxicity of the thermal decomposition products resulting when halon alternatives are exposed to a fire. Halocarbon agents decompose during exposure to fire. The products of decomposition are relative to the chemical structure of the agent. The TDPs associated with highly fluorinated agents, such as C_6 F-ketone are hydrogen fluoride (HF) and carbonyl fluoride (COF_2). Note that COF_2 is hydrolyzed rapidly by water to give carbon dioxide (CO_2) and HF.

The toxicological effects of HF exposure have been well documented [10,11,9,8,31,42]. Studies from Meldrum and from the Robens Institute provide analyses indicating levels at which HF exposure can be dangerous. Meldrum concluded that the dangerous toxic load (DTL), for various animals, is 12000 ppm-minutes. In other words the DTL for a 30-minute HF exposure is 400 ppm [8]. The Robens Institute study found that the highest tolerable HF concentration, for human subjects, was 120 ppm for a 1-minute exposure [9].

1.6.2 Comparison of Results

Laboratory testing has shown the TDP concentrations of halocarbon agents to be between 2 and 10 times greater than for halon 1301, see Figure 1 [12, 6]. Fire sizes are normalized to allow the comparison of TDP irrespective of test compartment size. Lines are drawn in Figure 1 for comparison purposes only. The lower HF concentrations produced by halon 1301 can be attributed to the low concentrations required for extinguishment coupled with fewer fluorine atoms, at a given mole concentration, carried into the flame [43].

The key factors leading to TDP generation have been identified as agent concentration, fire size, and extinguishment time. The extinguishment time is directly linked to agent concentration and discharge time. Increased agent concentration reduces the quantity of hazardous gases produced, regardless of fire size. However, a point of diminishing returns can be reached after which additional agent will have negligible effect on TDP generation [44]. See Figure 2.

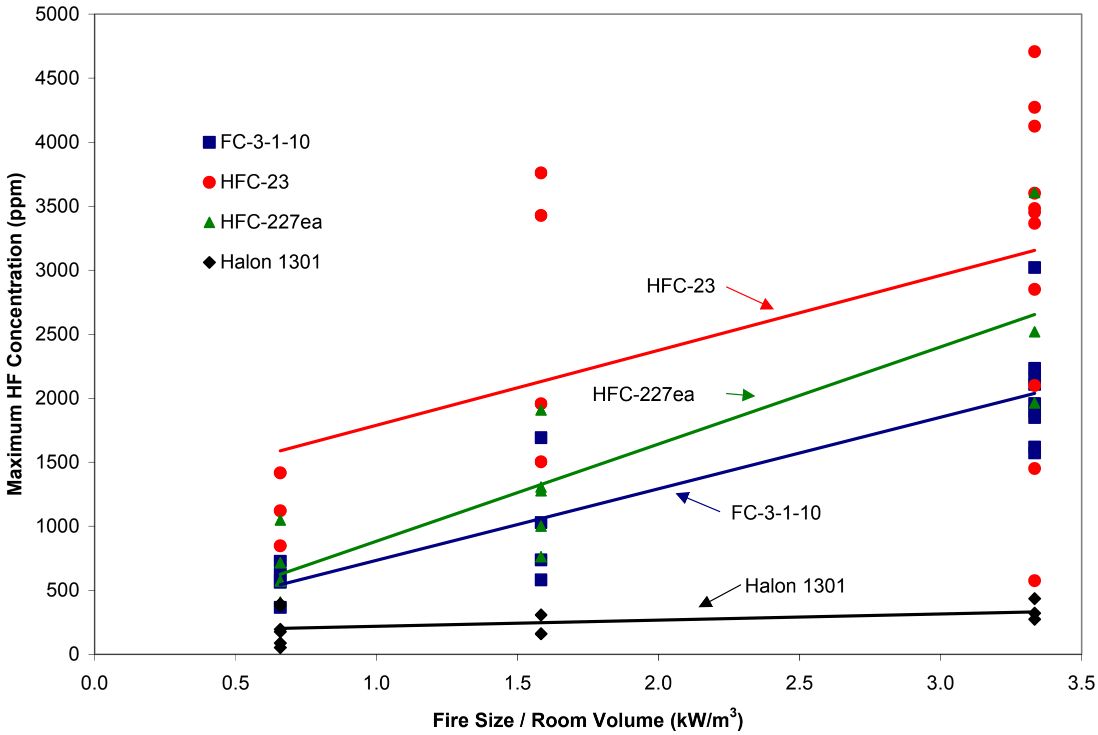


Figure 1, Maximum HF Production vs. Normalized Fire Size [12]. Discharge times range to a maximum of 16 seconds.

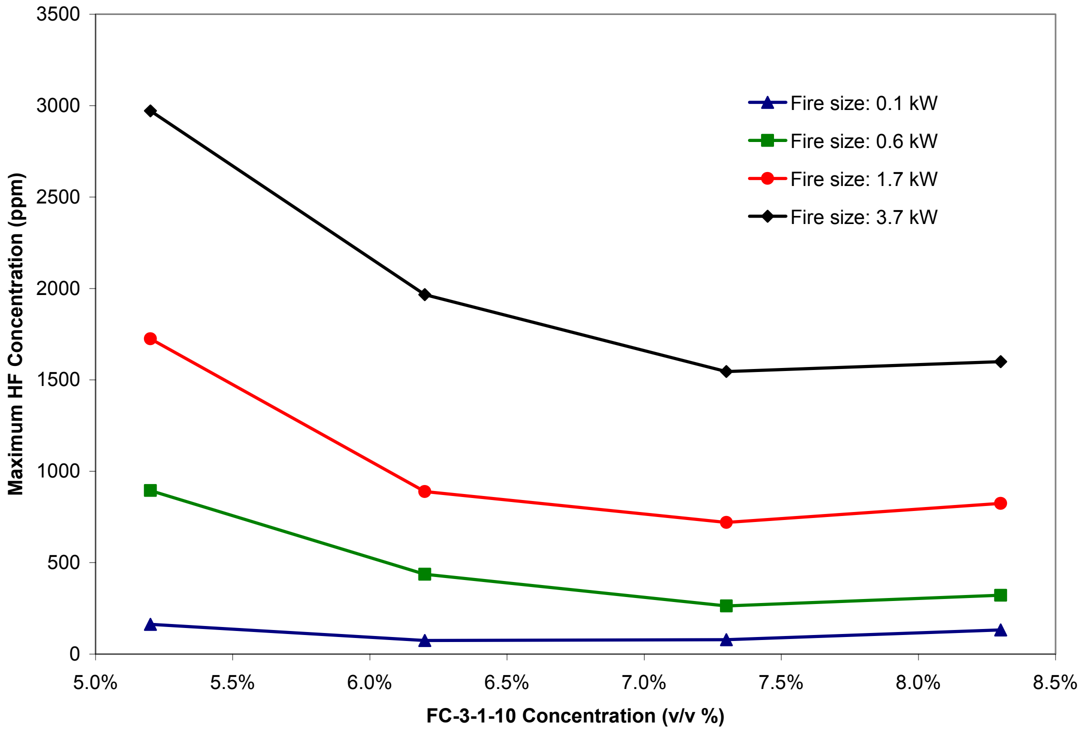


Figure 2, Effect of FC-3-1-10 Concentration on HF Generated at Various Fire Sizes in a 1.28 m^3 Enclosure [44].

As seen in Figure 3, TDP generation monotonically increases with fire size. The data are linearly regressed for comparison purposes. Note the y-intercept of the linear regression line is approximately 400 ppm HF. This means that theoretically, if the discharge time were zero, acid gas would still be produced. Regardless of the discharge time, the agent needs to be exposed to fire before extinguishment, yielding TDPs [45].

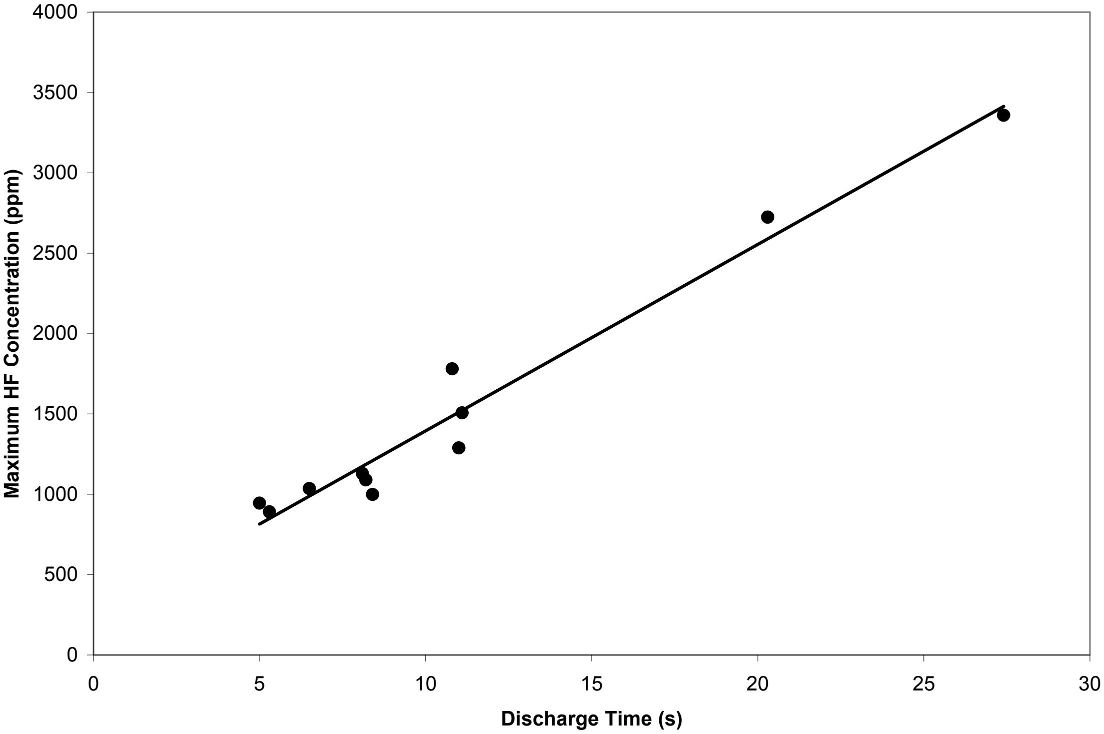


Figure 3, Effect of Discharge Time on HF Generation [45]. FC-3-1-10 at 6.5% v/v and a 1.7 kW fire.

1.6.3 Methods of Analysis

Two primary methods have been used to experimentally measure TDP generation; a wet chemistry technique utilizing an ion-specific electrode (ISE) and Fourier-transform infrared spectroscopy (FTIR) [46,47]. Wet chemistry is an indirect method of analysis. This is because all hydrolysable fluorine present in a grab sample from the test enclosure is measured by an ISE and then converted to a concentration of HF. FTIR is a direct method of analysis. Air in the test enclosure is measured in real-time for HF and COF_2 concentrations. Both methods have proven useful for testing under various testing conditions. Table 8 presents a historic list of local application halon alternative testing, which monitored TDP generation. Note that FTIR analysis has been more widely used than ISE analysis. Additional studies have presented an overview of TDP testing [48,49], while others have sought to determine an empirical method of predicting TDP concentrations [43,50,51,52].

Table 8 - Historic TDP Testing [6,7,44,45,51,53,54,55,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77]

Reported by	Year	TDP Analysis Method	Agents Tested	Test Scale
Sheinson[76]	1981	ISE	Halon 1301	Full (645 m^3)
Sheinson[72]	1991	N/A	HFC-23, FE-25, HFC-227ea, FC-3-1-10, HBFC-22B1, HFC-227ea, FM-100/200 (1:5), Halon 1301, Halon 1211, Sulfur Hexafluoride	Intermediate (56 m3)
Ferreira[45]	1992	ISE	FC-3-1-10	Lab (1.28 m^3)
Filipczak[53]	1993	MS	Flame only, CO_2, Halon 1301, Halon 1211, HBFC-22B1, HFC-23, HFC-123, FC-3-1-10, FC-5-1-14	Lab[*]
DiNenno[7]	1993	FTIR	HFC-23, FE-25, HFC-227ea, FC-2-1-8, FC-3-1-10	Lab (1.2 m^3)
Moore[69] Dierdorf[70]	1993	FTIR	Halon 1301, HFC-23, HFC-227ea, FC-3-1-10, HCFC Blend A	Intermediate (18.3 m^3)
Dierdorf[70]	1993	FTIR	Halon 1301, FC-3-1-10, HFC-227ea, HFC-23	Lab (0.17 m^3)
			Halon 1301, HFC-227ea, FC-3-1-10, HCFC Blend A	Intermediate (18.3 m^3)
Sheinson[58,61,68,73,75]	1993 1994	IC	HFC-23, HFC-227ea, FC-3-1-10, Halon 1301	Intermediate (56 m^3)
Hansen[66,71]	1994	FTIR	FC-3-1-10, HFC-23, HFC-227ea, HCFC Blend A	Full (560 m^3)
Brockway[44]	1994	ISE	FC-3-1-10, HFC-227ea, HFC-23	Lab (1.28 m^3)
Sheinson[65,74]	1994 1995	FTIR	HFC-23, HFC-227ea, Halon 1301	Full (843 m^3)
Linteris[51]	1995	ISE	Halon 1301, HFC-227ea, HFC-125, FC-218	Lab (Open air)
Driscoll[55]	1996	ISE	FC-3-1-10	Lab (1.28 m^3)
Su[62] Kim[67]	1996	FTIR	HFC-227ea, HCFC Blend A	Full (121 m^3)
Chattaway[64]	1996	FTIR	Halon 1301, HFC-23, HFC-125, HFC-134a, HFC-227ea, HFC-236fa, FC-3-1-10, FIC-13I1	Lab (0.2 m^3)

Table 8 [continued] - Historic TDP Testing [6,7,44,45,51,53,54,55,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73,74,75,76,77]

Reported by	Year	TDP Analysis Method	Agents Tested	Test Scale
Modiano[63]	1996	FTIR	Halon 1301, HFC-227ea	Open Air
Su[59]	1997	FTIR ISE GC/MS**	HCFC Blend A	Full (121 m^3)
Hoke[60]	1997	FTIR NIR-TDL RT-ISE	Halon 1301, HFC-227ea	Scale Not stated
McNesby[86, 63]	1997	MIR-TDL NIR-TDL TFIR	Halon 1301, HFC-227ea, FC-3-1-10, HFC-236fa, HFC-125, HFC-23	Full (Open air) Lab (Flame)
Miser54	1999	FTIR, TDL**** RT-ISE****	Halon 1301, HFC-227ea, HFC-236fa, FC-218	Scale Not stated
Ditch[6]	2001	FTIR	C_6 F-ketone	Lab (1.28 m^3)

IC- Ion Chromatography	GC/MS – Gas Chromatography, Mass Spectroscopy
ISE- Ion Selective Electrode	NIR-TDL- Near-Infrared Tunable Diode Laser
MS- Mass spectrometer	TDL- Tunable Diode Laser
FTIR- Fourier Transform Infrared Spectroscopy	RT-ISE- Real-Time Ion Selective Electrode

*Agents introduced to a methane flame (250 watt) below extinguishment concentration to generate steady-state conditions
**Used for analysis of agent components ***Agents pyrolyzed at elevated temperatures ****Used for comparative purposes

Previous test data on COF_2 generation is limited due to complications in the analysis. COF_2 is known to rapidly hydrolyze into HF in the presence of water [50]. Further, the fluoride specific electrode only detects the fluoride ion concentration of a solution. There is an implicit assumption that anything that generates F^- has toxicity on the order of HF. In other words, all F^- found is assumed to be HF. Also, due to a lack of reference and sample calibration data, most FTIR analysis of COF_2 is qualitative [7,3].

Several comparison studies have been performed for the two analysis techniques [59,60]. One such study by Hoke demonstrated a linear response of FTIR and a method employing an ISE [78]. It should be noted that the method of preparing a sample for analysis with an ISE varies between labs [45,78,44,59,60]. However, all ion detection with an ISE follows the same chemical principles.

A study conducted by Su [59] collected samples for ISE analysis during testing by flowing gas through a glass bubbler. The glass bubbler had a collection vial filled with a sodium hydroxide solution. The resulting solution was analyzed for fluoride ion concentration [59]. Another study by Hoke continuously flows sample gas into an aqueous trapping solution with an impinger. The trapping solution is then pumped through a fluoride electrode flow cell where an ISE is used to measure fluoride ion [60]. The method used by Ferreira trapped sample gas in a gas-sampling bulb lined with crystallized sodium hydroxide. A vacuum was created in the bulb allowing gas to be drawn in when a stopcock was opened. The bulbs were flushed with de-ionized water and the aqueous solutions were prepared for analysis with an ISE [45].

A comparison of the 3M wet chemistry technique and FTIR can be seen in Figure 4. The longer discharge times for the Brockway testing results in a higher HF concentration, especially at larger fire sizes. This effect is less noticeable at the smaller fire sizes, where HF concentrations show better consistency [12,44]. However, all data shown falls within a 95% confidence interval.

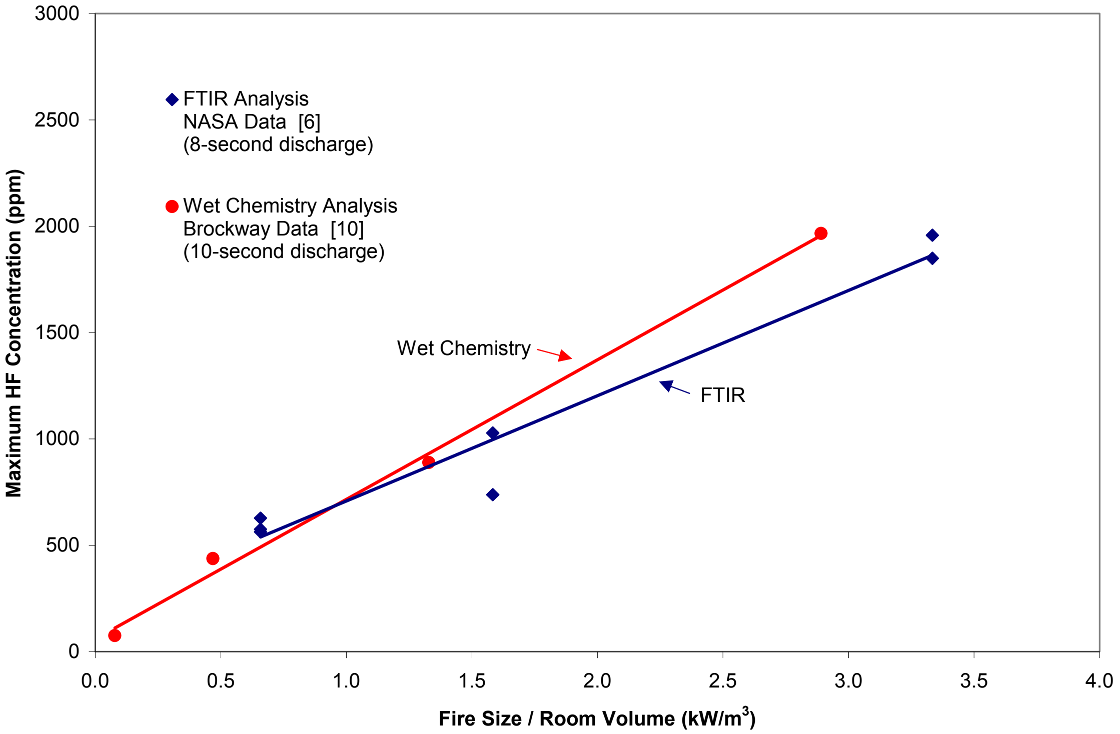


Figure 4, Comparison of FTIR and Wet Chemistry Analysis [12,44]. FC-3-1-10 at 6.2%-6.5% v/v concentration, nominally the heptane cup burner extinguishing value plus 20%.

2.0 General test apparatus

2.1 Test enclosure

Testing was conducted in a 0.91x0.91x1.7-m^3 (3x3x5-ft^3) enclosure; constructed of 1.3-cm (0.5-in) thick polycarbonate walls, reinforced with a 5-cm (2-in) angle iron frame, see Figure 5. The enclosure provides a 1.28-m^3 (45-ft^3) total floodable volume. Two sealable doors, on opposing walls, allow access to the enclosure once it is sealed. The doors are equipped with four compression latches and a rubber gasket to ensure an airtight seal. Sampling ports, thermocouples, ventilation ports, and agent piping are located on the other two walls. Ventilation is accomplished by an air inlet valve located near the bottom of the enclosure and an outlet valve located on the opposite wall and near the enclosure top. Both of these valves are controlled by solenoids. Three additional openings allow for 0.64-cm-dia (¼-in) Swagelok™ bulkhead fittings, which can be used for gas sampling. Fires are located 7.5-cm (3-in.) above the enclosure floor on a riser. Surrounding the fire is a metal baffle that measures 38x38x20.3–cm^3 (15x15x8-in^3), which is used to reduce turbulence around the fire and eliminate a possible fire “blow-out”. A complete schematic of the box is seen in Figure 5.

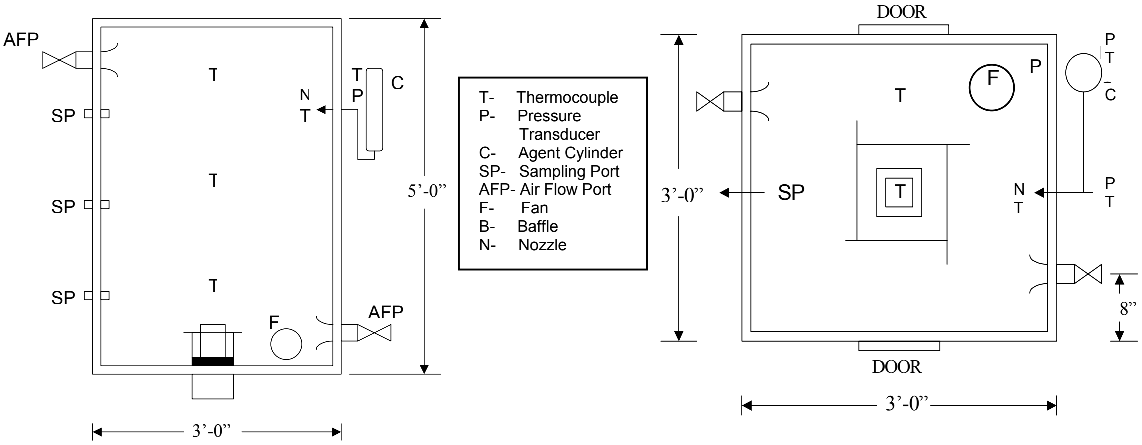


Figure 5a, Side View
Side View

Figure 5b, Top View
Top View

Figure 5, Schematic of Test Enclosure

2.2 Instrumentation

The box is equipped with 5 Omega™ Type-K stainless-steel thermocouples. A thermocouple tree, consisting of three thermocouples evenly spaced in the vertical direction, is orientated directly over the fire. The two other thermocouples are used to measure temperatures around the nozzle during discharge, one is located in the discharge stream 2.5 cm (1 in) from the nozzle and the other is located inside the piping immediately before the nozzle.

Two Omega™ PX-102 sealed gauge pressure transducers with a working range of 0 to 344 kPa (0 to 500 psi) measure pressure in the cylinder and at the nozzle. Data are collected by an Omega™ DaqBook 100 with one Omega™ DBK 19 card for pressure transducer data and one Omega™ DBK 13 card for thermocouple data. The data collection system is run by an IBM™ ThinkPad™ T21 utilizing LabTech Notebook™ v 10.02 software.

2.3 Discharge Apparatus

Agent is stored in a 3.8-l (1-gal.) Whitey™ stainless-steel cylinder fitted with a valve at the base. The cylinder is connected to the discharge nozzle by a simple piping network of 0.64-cm-dia (¼ in) pipe bolted to the exterior of the box, with a ball valve for discharge. The discharge nozzle is located on a sidewall, centrally in the horizontal direction, on the upper quarter point in the vertical direction.

2.4 Agent Concentration Calculations

Two agent concentrations were chosen: initial cup burner and initial cup burner + 20%. In accordance with NFPA 2001 [31], the volumetric agent concentration was determined as the initial cup-burner extinguishing concentration for heptane, as established by a recognized testing lab. An increased agent concentration was based on the initial heptane extinguishing cup-burner value plus a 20% safety factor. Agent mass required to produce the desired agent concentrations in the box were calculated as follows:

[Eq. 1]

$$W = \frac{V}{s}\left(\frac{C}{100 - C}\right)$$

where, W is the agent mass kg, V is the enclosure volume in m^3, C is the agent design concentration (volume percent), and s is the agent specific vapor volume (l/kg) at 101 kPa (1 atm) and ambient temperature [31]. Note that the agent specific vapor volume is based on ideal gas law calculations.

2.5 Discharge Time

Discharge times of 3 s, 9 s, and 25+ s were chosen to compare with previous testing [12,44,45,55]. The discharge time is controlled by the flow rate (orifice size) of the discharge nozzle. Initial testing was conducted to determine which nozzles were needed to produce the desired discharge time, the results of those tests are presented in Table 9.

Table 9 - Nozzle Discharge Times

Agent Concentration	Agent Discharge Time		
	3 Seconds	9 Seconds	25+ Seconds
Initial Cup Burner (4.9% v/v)	Spraying Systems; TP8020	Spraying Systems; TP8005	Spraying Systems; TP8001
Initial Cup Burner + 20% (5.9% v/v)	Spraying Systems; TP8020	Spraying Systems; TP8006	Bete Company; NF0300

The computer data acquisition allowed for the experimental determination of the discharge time for each test [54]. A typical pressure history is shown in Figure 6. The beginning of discharge was manually chosen at the midpoint of the initial nozzle pressure spike. The end of discharge was manually chosen at the point of inflection on the nozzle temperature increase. This corresponds with the 95% agent discharge (from cylinder) required by NFPA 2001 [31].

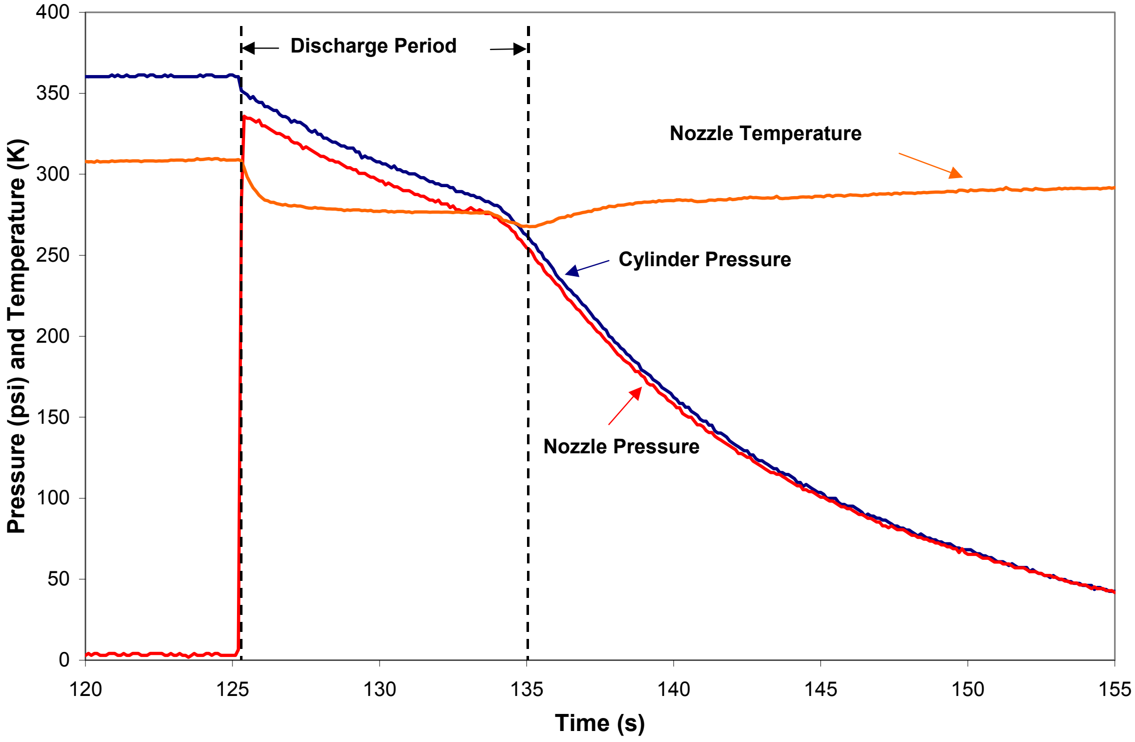


Figure 6, Typical Pressure History for Agent Discharge.

Due to a lack of available data on extinguishment time, the agent exposure time to the fire is measured by the discharge time. The extinguishment time for all tests in this study can be found in Appendix A2.1, for wet chemistry, and B3.1, for FTIR.

2.6 Fire Size

The four different fires sizes used in this study were chosen to compare with previous work conducted with Class B fires[12,45]. A cone calorimeter was used to determine the heat release rates of the four square pans, which measure (w,h), 2x3.8 cm (0.75x1.5 in), 4.5x3.8 cm (1.75x1.5 in), 7x3.8cm (2.75x1.5in), and 9.5x3.8 cm (3.75x1.5 in). The corresponding heat release rates for these pans when filled with heptane are, 0.1 kW, 0.6

kW, 1.7 kW, and 3.7 kW, respectively. For each test, the pans were filled to the top with fresh heptane immediately before the test to prevent agent build-up in the fuel.

The Class A fire sizes represented the peak heat release rate as determined by a recognized testing lab. These fuel packages were chosen to directly compare with previous test data for other in-kind halocarbon agents [45].

2.7 Experimental Design

The test matrix for Class B fires can be seen in Table 10. There are 24 individual scenarios for testing, each requiring 3 tests, for a total of 90 tests. The test matrix for Class A fires can be seen in Table 11. There are 8 individual scenarios for testing, each requiring 3 tests.

Table 10 - Class B Test Matrix*.

Agent Concentration	**Fire Size**	**Discharge Time (s)**		
		3	**9**	**25+**
4.9%	**0.1**	3	3	3
	0.6	3	3	3
	1.7	3	3	3
	3.7	3	3	3
5.9%	**0.1**	3	3	3
	0.6	3	3	3
	1.7	3	3	3
	3.7	3	3	3

*Non-bold numbers represent number of tests scheduled per scenario.

Table 11 - Class A Test Matrix*.

Fuel Type	**Agent Concentration**	
	4.9%	**5.9%**
Wood	3	3
Cotton	3	3
Polyethylene	3	3

*Non-bold numbers represent number of tests scheduled per scenario.

3.0 Wet Chemistry Methodology

3.1 General Theory

The wet chemistry technique described by Ferreira [45], Brockway [44], and Driscoll [55] was utilized to measure total hydrolysable fluoride. This method utilizes an ion selective electrode to detect the presence of fluoride ion in a liquid sample. Typically, fluoride ion levels are converted to an equivalent concentration of hydrogen fluoride for reporting. Since an ISE only detects the presence of an ion, not the source, HF levels reported represent a maximum concentration. The only other fluoride containing compound expected is carbonyl fluoride. The following section contains the experimental setup, procedure, and calculations used for wet chemistry analysis.

3.2 General Test and Analysis Procedure

1) Gas sampling bulb preparation
2) Box test procedure
    i. Fire ignition and pre-burn
    ii. Agent discharge
    iii. Gas sample grabbed

3) 24-hour neutralization in bulb
4) Sample prepared for ISE analysis
5) ISE calibration and samples

3.2.1 Gas Sampling Bulb Preparation

In preparation for a test, the 250-ml polypropylene gas sampling bulbs are thoroughly cleaned and prepared. The bulbs are first partially filled with concentrated hydrochloric acid (HCl), shaken rigorously for 2 minutes, and rinsed thoroughly with de-ionized water. Regular tap water cannot be used because it can contain, among other things, a high fluorine content, which would increase the concentration found in the bulb. The bulbs are then flushed with acetone and blown dry with nitrogen. One milliliter of 1.25 M sodium hydroxide (NaOH) in methanol is added to the bulb and the bulbs are dried in an oven at 110^{o}C for approximately 4 hrs, with the stopcock open and the septum cap removed. To reduce pooling of the solution, the bulbs are rotated at five-minute increments for the first 20 minutes and at 15-minute increments for the remainder of the drying process.

3.2.2 Box Test Procedure

Immediately before each test begins the calibrated heptane pan is filled to the top with fresh heptane. The test begins when the fuel is ignited, at which time the access door is sealed. The 60-s pre-burn occurs with both the box inlet and outlet valves open, minimizing combustion product buildup and oxygen depletion. The valves are then closed, and 5 s later the agent is discharged. After extinguishment, the fan inside the enclosure is turned on to thoroughly mix the enclosure volume. Thirty seconds later, the gas samples are drawn into the evacuated sampling bulbs; making sure the characteristic "swooshing" sound of air being drawn into the bulbs is heard.

3.2.3 24-Hour Neutralization in Bulbs

Following the withdrawal of a sample, the gas-sampling bulbs are allowed to sit for a minimum of twenty-four hours, with the stopcocks closed, to ensure the complete neutralization of acid gases gained during the sampling procedure.

3.2.4 Sample Prepared for ISE Analysis

The resulting salt compounds (acid gas + NaOH) are flushed from the bulbs by injecting 5-ml of de-ionized water through the septum. The bulbs are then placed in a slow-speed shaker for 30 min, rotated once at 15 min, and drained into a 50-ml graduated polypropylene centrifuge tube. This procedure is repeated twice more, using 5-ml of de-ionized water each time so that a total of 15 ml of de-ionized water is used. For the two subsequent drainings the bulbs are shaken vigorously by hand.

Next, 100 μl methyl red indicator is added to the sample, producing a yellow color, and titrated with 69-72% perchloric acid until the sample turns light pink. This indicates the solution is approximately neutral. The sample is then made up to 20 ml with de-ionized water.

The samples are prepared for analysis with the fluorine-specific electrode by mixing 500 µl of sample (as prepared above) and 500 µl Total Ionic Strength Adjustor Buffer (TISAB) into a 14-ml round bottom polystyrene test tube. The TISAB ensures the pH of solution is maintained between 5 and 6, the range where the fluorine-specific electrode has the highest response. This is due to the governing chemical reaction;

[Eq. 2] $HF \leftrightarrow H^{+} + F^{-}$

Where the F^{-} on the right-hand-side of the reaction is detectable by the electrode.

3.2.5 ISE Calibrations and Samples

Fluoride standards (1 ppm F^{-}, 10 ppm F^{-}, 100 ppm F^{-}) are prepared to calibrate the fluoride-specific electrode. 500-µl standards are then added with 500 µl of TISAB buffer solution into separate 14-ml round bottom polystyrene test tubes.

The samples and the standards, in the test tubes, are initially scanned with the fluoride-specific electrode for 1 minute each. The voltage (mV) readings are recorded and the samples and standards are placed in ascending order of the expected fluorine levels. Final measurements are taken by increasing the fluoride-specific electrode scan time to 2 minutes.

The voltage readings are converted into a fluoride concentration (ppm F^{-}) using the calibrated standards. For the standards, concentration (ppm F^{-}) is plotted against voltage (mV) on a semi-log chart producing a near-linear response, see Appendix A1.1. The voltage readings for the samples are then interpolated to determine the F^- concentration. Assuming that all hydrolysable fluoride detected is from hydrofluoric acid, the sample fluoride concentration is then converted to a HF concentration, for comparison purposes.

3.3 Discussion

The wet chemistry technique provides an easily accessible and relatively inexpensive method of analysis. A researcher needs only a basic knowledge of chemistry and no expensive analytical equipment. TDP analysis utilizing an ion specific electrode has historically been a common method of analysis, however there are several limitations.

1. The wet chemistry method is very time consuming. There are multiple time consuming steps, including the preparation of gas-sampling bulbs before a test, the neutralization time, and scanning the resulting sample solution with the ISE.
2. There is considerable room for experimental error in the procedure, including proper preparation of gas-sampling bulbs, especially creating and maintaining a consistent vacuum before sampling. Also, results are dependent on solutions mixed correctly and without contamination.
3. The fluorine-specific electrode is only capable of detecting the presence of fluoride ion in a solution. The two decomposition products of a halocarbon are HF and COF_2, and it is known that COF_2 readily hydrolyzes in water (to form HF), therefore it is assumed that all F^- detected is from HF. This assumption can lead to a possible over-estimation of actual HF concentrations present.

4. It is not possible to take real-time data. The concentrations determined represent the F^- concentration present at the point [in time] of collection. This makes determining the peak/average F^- concentrations impossible.

4.0 FTIR Methodology

Thermal decomposition products were analyzed using Fourier Transform Infrared Spectroscopy. FTIR allows the direct analysis of multiple compounds present in a gaseous sample [56]. The following section contains the experimental setup and procedure for FTIR analysis. FTIR setup and measurement system, including sample abstraction and analysis, was contracted out to American Engineering Testing, Inc, [57].

4.1 Equipment

Two MIDAC I-2000 Series spectrometers were used for this field test. Each spectrometer was configured with a Zinc-Selinide beam splitter and a mercury cadmium telluride (MCT) detector. A 1-cm, unheated stainless-steel gas cell utilizing ethylene as a diluent was used to acquire C_6 F-ketone concentration data. TDP concentrations, which are orders-of-magnitude less than C_6 F-ketone concentrations, were acquired using an undiluted 10-cm, unheated, stainless steel gas cell. The spectrometers had an ultimate resolution of 0.5 cm^{-1} with triangular apodization. Sample gas extraction was accomplished with 110V gas sampling pumps. Portable computers were used for data acquisition.

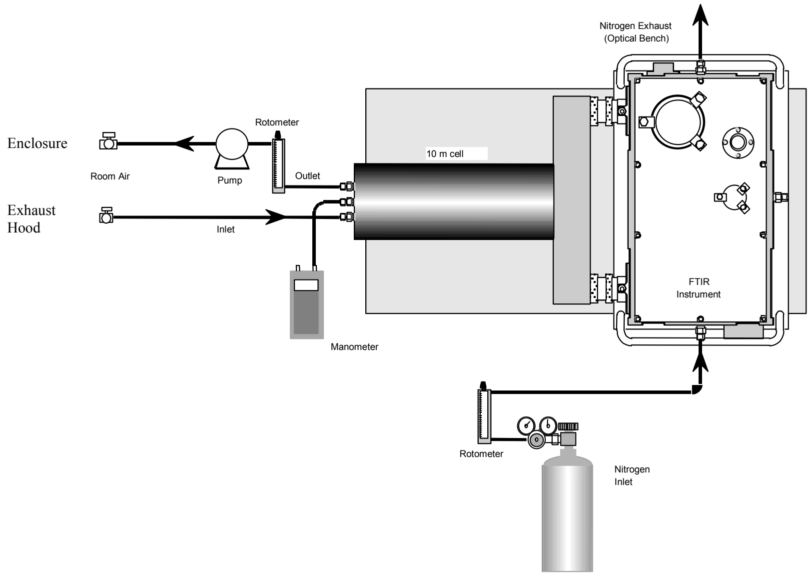


Figure 7, Extractive FTIR System Schematic

4.2 Sampling

The extractive gas sampling system used for the enclosure testing consisted of approximately 2-m (6.6-ft) of 0.64-cm (¼-in) diameter polytetrafluoroethylene (PTFE) tubing leading into the gas cells. Each spectrometer and its sampling system were operated independently. TDP samples were drawn from the box through a 2-m long, 0.64-cm diameter PTFE sampling line into the spectrometers by the gas sampling pumps. Samples were continuously pumped through the sample line and the gas cells at a flow rate of 1 and 2 lpm (0.26 and 0.53 gpm) for the 1-cm and 10-cm gas cells, respectively. Flows were verified on site using a Dry Cal™ flow meter. High soot deposits in the test enclosure required dynamic dilution of sample gas with 20,010-ppmv ethylene cylinder gas in the 1-cm infrared gas cell. Three, 2.5-min spectra were taken for every test. Sampling began at agent discharge. The maximum HF concentration was determined by taking the greatest of the 3 spectra, which was commonly the middle spectrum.

4.3 Test Procedure

Immediately before each test begins the calibrated heptane pan is filled to the top with fresh heptane. The test begins when the fuel is ignited, at which time the access door is sealed and the FTIR sampling starts. The 60-s pre-burn occurs with both the box inlet and outlet valves open, minimizing combustion product buildup and oxygen depletion. The valves are then closed, and 5 seconds later the agent is discharged. After extinguishment, the fan inside the enclosure is turned on to thoroughly mix the enclosure volume. The box remains sealed during the FTIR analysis cycle.

4.4 Data Collection

For the determination of TDP concentrations the AutoQuant Version 3.01 method was used. This employs a classic least squares (CLS) fit algorithm for automatic spectral analysis. The CLS methods used for analyte quantitation are included in Appendix A3.

The FTIR instruments were set so that apodized (triangle) data were collected from 4500 to 650 cm^{-1} with 64 co-added scans at 0.5 cm^{-1} resolution (gain 1). Reference spectra for ethylene and applicable target compounds were developed or acquired by the 3M Company. Background spectra were generated on the test instrument using compressed cylinders of high purity dry nitrogen or ambient room air.

Theoretical Detection Limits (TDLs) were calculated using target compound response factors determined from quantitative infrared spectra from 3M Company library data. Peak-to-peak noise levels were determined from representative sample spectra generated on the instrument used in the testing. Three times the peak-to-peak noise levels determined for the sample spectra at selected infrared regions were used to generate TDLs for all target compounds.

4.5 Quality Control

To determine the cell path length, the certified concentration of ethylene was temporarily entered into the AutoQuant 3.01 software for the instrument path length in the method. The method then returned the instrument path length rather than the ethylene concentration. An extractive FTIR cell path length of 10.3 cm for 10-cm cell and 1.3 cm for 1-cm cell was used for quantitative analysis. The path length determination is based on an average of numerous spectra. This data is presented in Appendix A3.

Ethylene overflow measurements were conducted to ensure the integrity of the sampling system. The measurement was made by flowing a constant concentration of ethylene through the spike/dilution line at a flow rate at least double the flow rate of the sampling system. Recovery results agreed to within 5% of the ethylene cylinder concentration.

4.6 Discussion

Fourier transform infrared spectroscopy is a powerful method for gas sample analysis. Since this is a direct analysis method samples can be simultaneously analyzed for multiple compounds. Also, data is taken in real-time, so maximum and average compound concentrations can be determined. However, there are several limitations that should be considered.

1. The FTIR technique is limited by spectral properties, which are fundamental problems that must be managed because they cannot be changed. For example, chemical spectra can overlap in the same frequencies causing qualitative analysis to become difficult [59].
2. The HF spectrum does not exhibit a linear increase at high concentrations (major peak does not increase linearly at high concentrations).
3. High soot levels require the use of dilution lines into the FTIR cells, which make concentration analysis more difficult
4. Expensive equipment is required as well as skilled technicians to run the equipment and analyze data.

5.0 Wet Chemistry Results and Discussion

5.1 Wet Chemistry Method Validation using FC-3-1-10

Initial FC-3-1-10 testing was conducted to verify the wet chemistry analysis method and new operator. For comparison, three previous studies using FC-3-1-10 were chosen: Ferreira 1991 [45], Brockway 1994 [44], and Driscoll 1996 [55]. Each utilized a similar analysis method as the one in this report. The agent concentration was chosen as the heptane cup burner extinguishment value [31] plus a 20% safety factor. Variations in agent concentrations reflect the range in reported cup burner extinguishment values. The differences in cup burner apparatus between labs as well as proposals for a standard cup burner have been the topics of several studies [31, 79,80,81].

Table 12 - FC-3-1-10 Comparison Data (Fire Size: 3.7 kW) **[44,45,55]**

Researcher	Agent Concentration (v/v %)	Discharge Time (s)	TDP Generation (ppm HF)
Ferreira[45]	6.5	8.2	3540
	6.5	8.4	2723
Brockway[44]	6.2	10	1548
	6.2	11	1994
	6.2	9	2357
Driscoll[55]	6.3	10	3198
	6.3	6.5	2462
Ditch	6.3	7	3207

TDP concentrations are consistent with the reported values from Ferreira and Driscoll, Table 12. A wide range of TDP values are reported by each operator, up to 800 ppm, even though testing conditions remain constant. This is common to the wet chemistry technique and results in a low confidence level for individual test values. Due to the wide variation in reported results, all tests fall within a 95% confidence interval. This variation is evident in the Brockway data, which is up to 60% lower than all other reported values. More testing of a particular scenario is required to better determine the experimental error. Note that the discharge time is dependent on the definition of end of discharge (audible, pressure trace). This accounts for the variations in reported discharge times between operators, even though the test setup was consistent for all operators.

5.2 C_6 F-ketone Results

Once the method was verified using FC-3-1-10, testing was conducted with C_6 F-ketone. A volumetric concentration of 4.2% was used. This is an arbitrary value chosen because the cup burner extinguishing concentration for heptane [31] had not yet been determined. For this series, the agent concentration and discharge time were constant, while the fire size was varied, Figure 8.

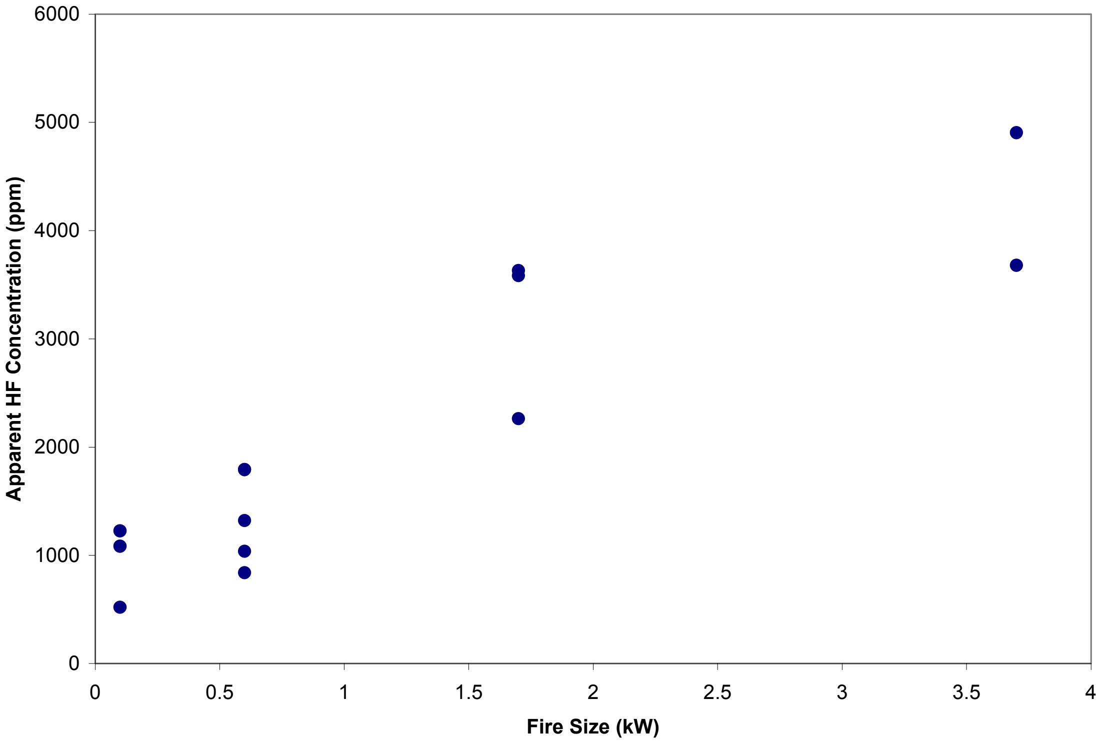


Figure 8, Effect of Fire Size on Apparent HF Production for C_6 F-ketone. Agent concentration at 4.2% v/v and a 7-s discharge.

The functional form of TDP generation for C_6 F-ketone is consistent with those found with other in-kind agents. That is, TDP generation is a monotonically increasing function of fire size with large variation at a given fire size. The concentrations found were, however, higher than expected. If the data were linearly regressed, the y-intercept would be approximately 1000 ppm HF. This effect has been previously reported by Ferreira [45], however, the concentrations were an order-of-magnitude lower using FC-3-1-10.

5.3 Neutralization Time Study

Subsequently, tests were run to determine if TDPs were produced during the analysis process by introducing a concentration of C_6 F-ketone into the gas sampling bulbs, this simulates an enclosure test run with no fire. From the results of Table 13, it is apparent that a considerable amount of F^- is produced during the neutralization time. Even the minimum neutralization time of 30-min produced over 800-ppm HF. The minimum neutralization time is determined by the shortest amount of time required to complete the sample analysis. Fluoride ion concentrations are converted to HF concentrations for comparative purposes. It can also be seen that a point-of-diminishing returns is reached at approximately 4 hrs, after which a negligible amount of F^- is generated.

Table 13 - Effect of Neutralization Time on HF Production. C_6 F-ketone at 4.2% v/v and a 7-second discharge.

Neutralization Time (hr)	Maximum HF Production (ppm v/v)	Average* HF Production (ppm v/v)
0.5	934	816
1	1037	852
2	1094	852
4	1386	1185
20	1273	1250
64	1792	1261

*Represents the average of up to 3 tests

5.4 Hydrolysis Experiments

Further testing was conducted to verify that the levels of HF detected are a result of C_6 F-ketone interaction with the wet chemistry analysis technique. For this, two experiments were conducted. One to verify that no HF was produced by the wet chemistry technique without C_6 F-ketone interaction and the other to measure the inorganic fluoride concentrations inherent in C_6 F-ketone.

For the first experiment, gas-sampling bulbs were prepared as normal, then analyzed, using the wet chemistry technique described in this paper, without any exposure to test conditions. This test was repeated twice and each time less than 1 ppm F^- was detected. This implies the wet chemistry technique, without the presence of C_6 F-ketone, does not generate F^-.

For the second experiment, C_6 F-ketone was treated with silica gel to remove any inorganic fluoride present (inorganic fluoride will readily react with silica gel and be removed from the liquid). This material was then compared to untreated material as reference. To measure the inorganic fluoride concentrations, the material was extracted at a 1:1 ratio with high-purified water at an interval extraction time. TISAB II reagent was added to the water phase, to control pH, before scanning samples with a fluoride ISE. Note that this method is markedly different than the wet chemistry technique describe in this paper. In particular no strong base is required, the importance of which will be discussed later [82].

The results of this experiment showed a minimal amount of inorganic fluoride was detected in both samples, Table 14. However, the fact that both samples contained almost identical concentrations implies no free fluoride ion is present in C_6 F-ketone. Rather the fluoride detected was generated during the ISE analysis. Note that samples reached 2-ppm fluoride ion quickly before leveling off at 3 ppm [82].

Table 14 - Inorganic Fluoride Concentrations [82]

Extraction Time (min)	Sample 1 w/SiGel (ppm F^-)*	Sample 2 (ppm F^-)*
10	1.66	1.71
20	2.04	2.03
60	2.41	2.45
90	2.63	2.65
120	2.77	2.78

*Concentration in blank solutions (i.e. not volumetric)

Independent testing has shown that the presence of a strong base during hydrolysis can significantly increases the production of F^- [82].

The hydrolysis of C_6 F-ketone observed when conducting the wet chemistry analysis is not anticipated to be an issue in real world fire extinguishing scenarios. Hydrolysis is not known in the gaseous phase, so hydrolysis during discharge will not occur. Hydrolysis in an aqueous pool within a protected space would be severely limited by the solubility of C_6 F-ketone in water (10 ppm). In addition, decomposition products from hydrolysis would remain in the aqueous phase and not pose an inhalation threat. However, when protecting highly reactive materials care should be taken to understand the reaction potential with the agent.

5.5 Discussion

Due to the complications listed above, the wet chemistry technique was determined impractical for C_6 F-ketone TDP analysis. It may be possible to determine a baseline amount TDP generated during the analysis, however, more comprehensive knowledge of the hydrolysis mechanism of C_6 F-ketone in both water and the presence of a strong base would be required. Also, the analysis method including neutralization time required for sufficient absorption of acid gases are time consuming and subject to considerable error.

6.0 FTIR Results and Discussion

6.1 FTIR Method Validation

It is important to distinguish the difference between the HF concentrations reported using different analysis methods. Analysis using wet chemistry reports the ‘maximum HF concentration’ due to the inability of the ISE to distinguish between the sources of fluoride ions. Analysis using FTIR reports the actual HF and COF_2 concentrations.
To compare wet chemistry results with those found using FTIR, it is necessary to convert FTIR results into an equivalent HF concentration. COF_2 is the only other significant contributor to hydrolysable fluoride in the wet chemistry method. Due to the known hydrolysis, COF_2 values are doubled and added to HF values (i.e. Equivalent HF = HF + $2COF_2$), see Eq. 24.

[Eq. 3] $$COF_2 + H_2O \rightarrow CO_2 + 2HF$$

To verify the FTIR analysis method, initial testing was conducted using FC-3-1-10. For comparison, two previous studies using FC-3-1-10 were chosen: Ferreira 1991 [45] and Brockway 1994 [44]. Both use a similar test method (i.e. test procedure, fuel, fire size, discharge time, enclosure size), however, the samples were analyzed using wet chemistry. The agent concentration was chosen as the heptane cup burner extinguishment value [31] plus a 20% safety factor. Variations in agent concentrations reflect the range in reported cup burner extinguishment values. A constant discharge time, nominally 9 seconds, was used for all tests while the fire size was varied. This discharge time was chosen because the industry standard for clean extinguishing systems is 10±1 seconds.

Table 15 - Comparison of FC-3-1-10 TDP Literature and This Study [45, 44]

	Equivalent HF Concentrations [ppm]		
Fire Size [kW]	Ferreira[45],* (6.5% v/v)	Brockway[44],* (6.2% v/)	Ditch** (6.5%v/v)
0.1	98, 90	48, 76, 100	82
0.6	275, 336	428, 445	320, 520
1.7	999, 1071, 1128, 1089	945, 832	1000, 970
3.7	3540, 2723	1548, 1994, 2357	1860, 2210, 2220

*Total F^- found using ISE converted to HF

**Equivalent HF concentration (HF + COF_2) found using FTIR

TDP concentrations are consistent with Ferreira and Brockway, Table 15. Ferreira and Brockway report a wide range of TDP values, up to 800 ppm absolute, even though testing conditions remain constant. This is common when using the wet chemistry method. Note that the range in results found using FTIR is at least 50% smaller.

It can be convenient to graph the average TDP values by an operator, see Figure 9. This more clearly shows TDP concentrations are consistent with Brockway for all fire sizes, while Ferreira reports higher concentrations at the 3.7 kW fire size. Due to the agreement of the majority of the data, the FTIR analysis method is deemed consistent.

Note, at the smaller fire sizes the concentration of COF_2 fell below the minimum detection limit (MDL), 26 ppm, for the FTIR system. In these instances, a value of 0 ppm was chosen for comparison. For actual system design, a value equal to the MDL of the system should be used. That would represent a more conservative value important when safety is the major concern.

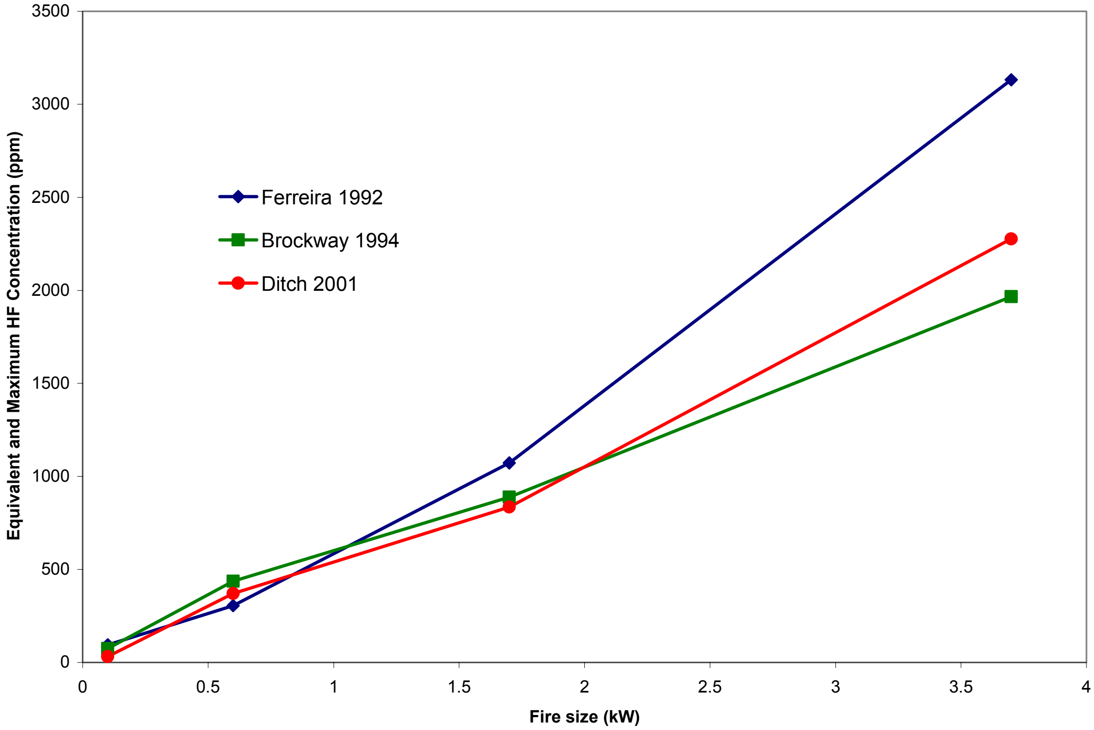


Figure 9, Operator Comparison Data. FC-3-1-10 at cup burner plus 20% and a 9-second discharge [45, 44].

6.2 C_6 F-ketone Results

TDP concentrations measured using FTIR for testing conducted with C_6 F-ketone are shown in Figures 10 through 14. The values are reported as equivalent HF concentrations. TDP generation is a monotonically increasing function of fire size. As seen in Figure 10, an increase in the discharge time yields increased TDP. Decreasing the discharge time from 9 seconds to 3 seconds results in up to a 47% reduction in TDP. A larger decrease from 25 seconds to 3 seconds results in up to a 67% reduction in TDP. The standard deviation for these tests is less than 200 ppm, which is significantly lower than results found using wet chemistry.

C_6 F-ketone is also useful in extinguishing class A fires, Figure 11. The equivalent HF production from class A fires is lower than for class B fires. This is consistent with previous work and shows that heptane was a good choice for a "worst-case" scenario for HF production [12]. Note that TDP generation with class A fuels is also a monotonically increasing function of fire size.

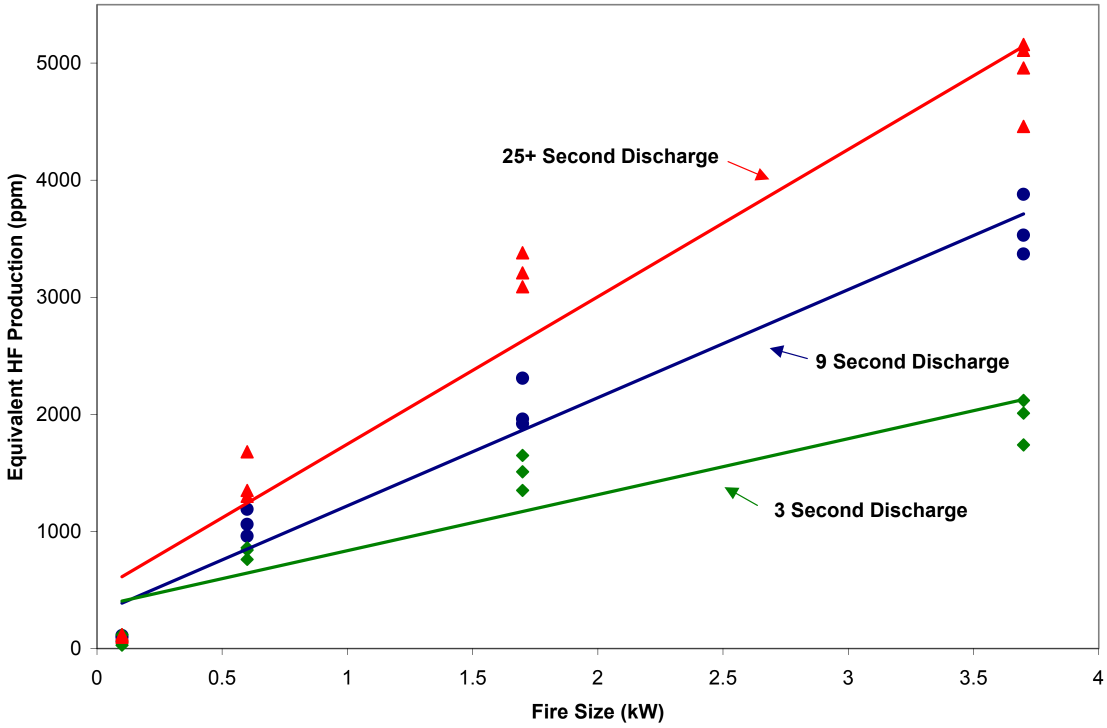


Figure 10, C_6 F-ketone Equivalent HF Production vs. Fire Size. C_6 F-ketone at 5.9% v/v.

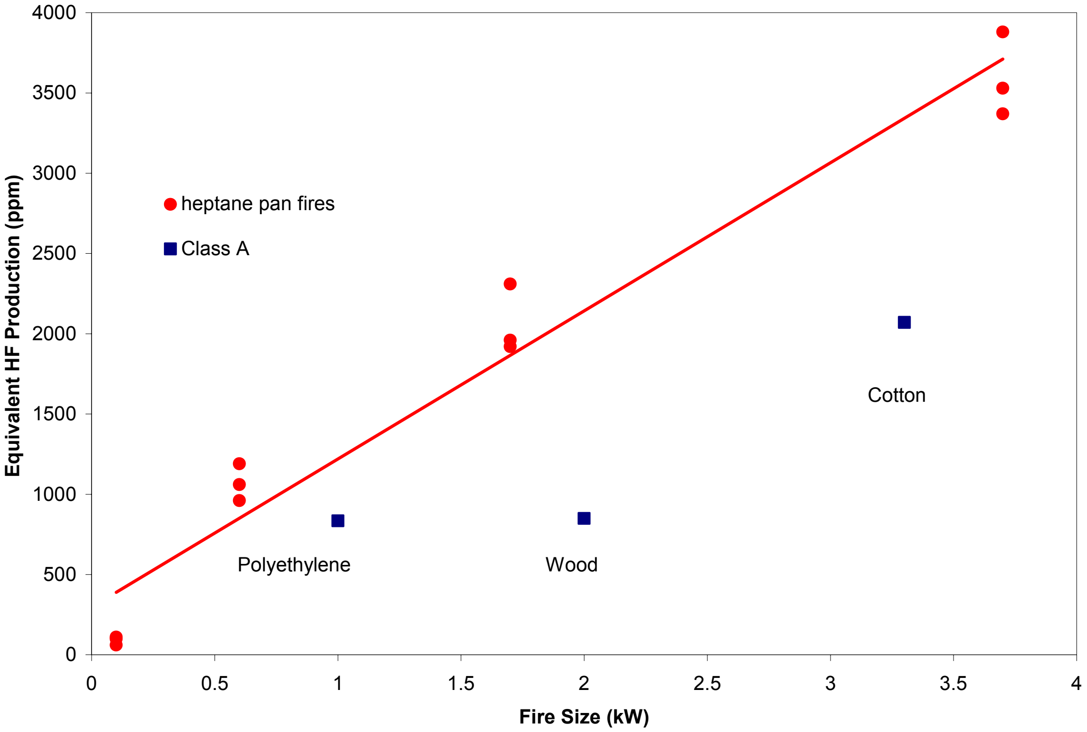


Figure 11, HF Production from Class A and Class B Fires [6]. C_6 F-ketone at 5.9% and a 9-second discharge.

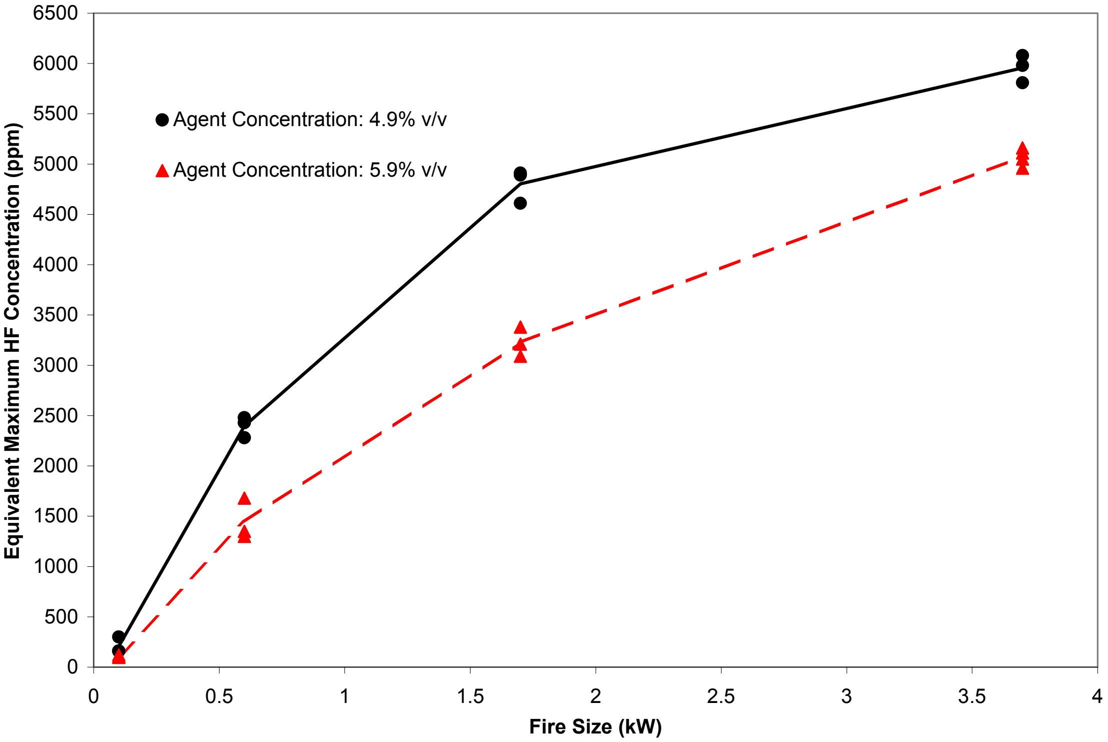


Figure 12, Effect of Agent Concentration on TDP Generation. C_6 F-ketone with a 25+ second discharge.

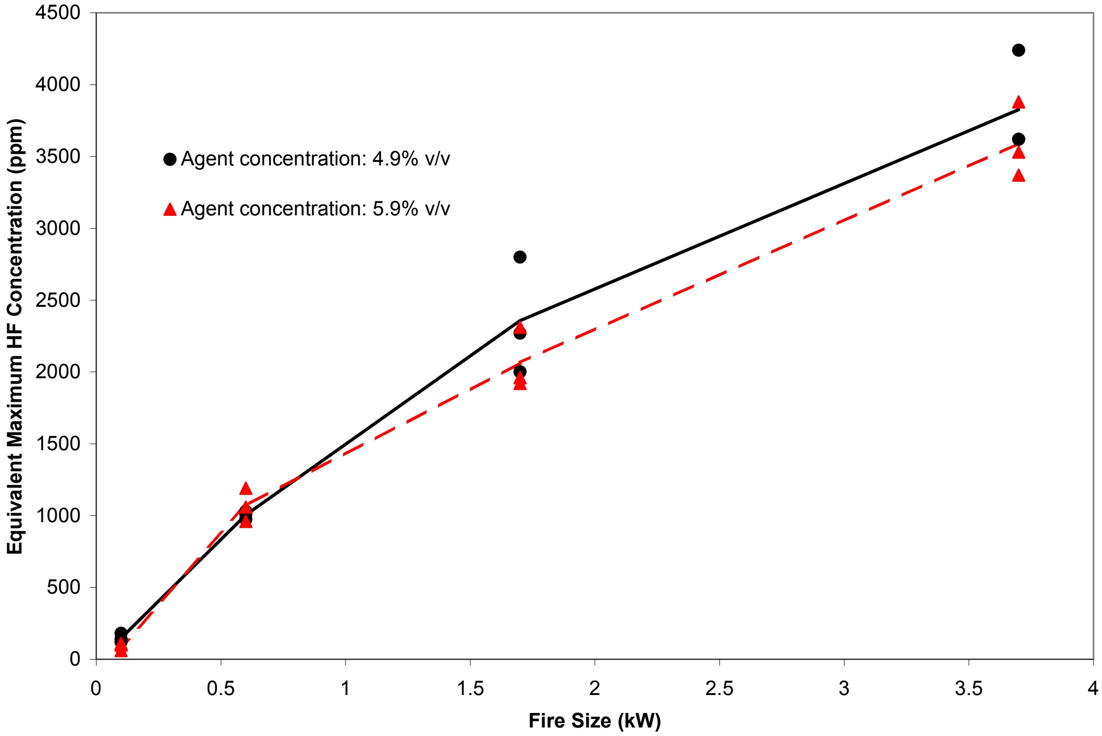


Figure 13, Effect of Agent Concentration on TDP Generation. C_6 F-ketone with a 9 second discharge.

Figure 12 shows the effects of added agent concentration on TDP. As expected an increase in concentration corresponds to a decrease in TDP. However, when shorter discharge times are considered the effect of agent concentration has less effect, see Figure 13. This suggests that the heptane cup burner value used for this testing is too high. Typically, increasing the minimum cup burner value by 20% v/v yields a 50% reduction in TDP [44]. Note that TDP appears to level off as the fire size increases. This effect, previously reported by Linteris, may be attributed to kinetic limitations on the rate of inhibitor consumption [51].

It is also important to investigate the concentrations of the other main constituent to TDP. As expected, carbonyl fluoride generation is significantly lower than hydrogen fluoride generation [51]. The results in Table 16 show COF_2 generation is approximately 3-4 times less than HF generation at 4.9% (v/v) C_6 F-ketone with a 9-second discharge. Note COF_2 concentrations for a 0.1 kW fire are below the 50-ppm MDL of the FTIR. It is not possible to compare this with other halon alternatives due to a lack of available data. No other significant concentrations were identified during the FTIR analysis.

Table 16 - Average HF and COF_2 Concentrations (C_6 F-ketone at 4.9% and a 9-second Discharge)

Fire Size (kW)	HF (ppm)	COF_2 (ppm)	Ratio $HF:COF_2$
3.7	2847	980	2.9:1
1.7	1817	540	3.4:1
0.6	810	194	4.2:1
0.1	147	<50*	NA

*Values are below minimum detection limit of FTIR

6.3 TDP Comparison

Figure 14 shows a comparison of the equivalent HF production for various agents resulting from exposure to a fire. The high HF concentration exhibited by HFC-227ea at the lowest fire size results from the inability to extinguish the fire. In terms of thermal decomposition, C_6 F-ketone is directly comparable to other commercially agents [78] under the test conditions considered. Note that commercially available halon alternatives generally produce between 2 and 10 times more HF than halon 1301 [12].

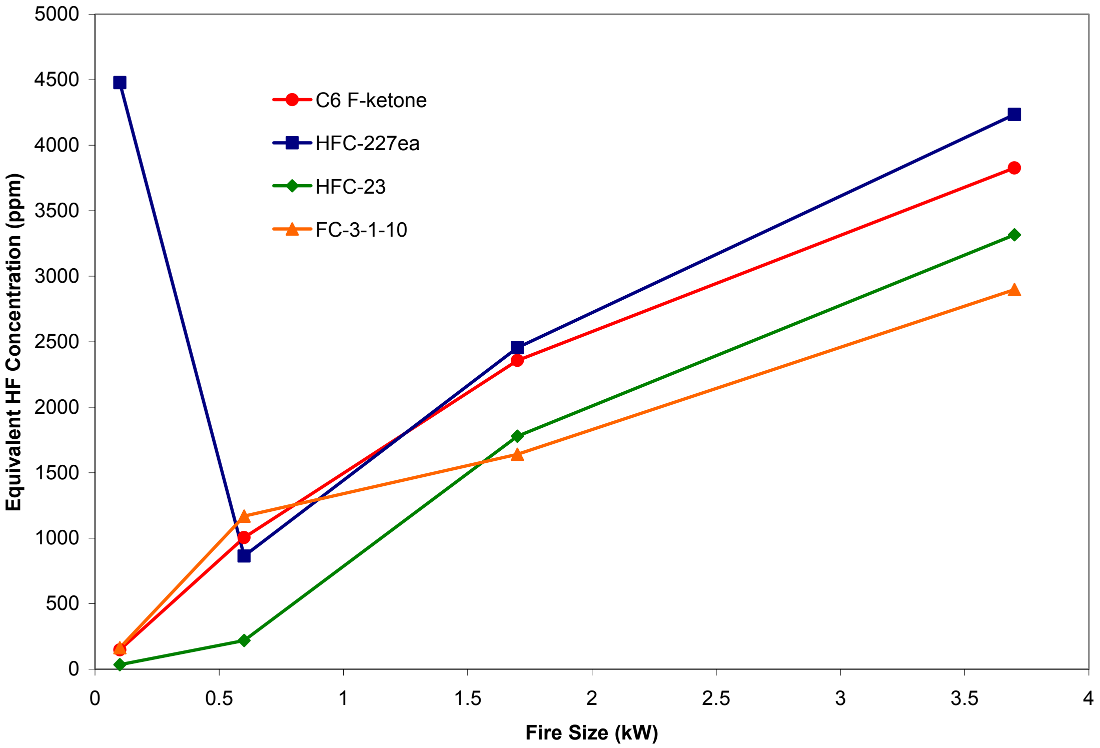


Figure 14, Equivalent HF Production vs. Fire Size [44]. Agent concentrations at heptane cup burner and a discharge time of 9-10 seconds.

6.4 Effective System Design

The tests in this report are representative of fire conditions in real hazard scenarios. For example, the maximum fire size tested is 3.7 kW, similar to the typical fire size for a circuit board, which is on the order of 3 to 5 kW, according to industry experts [48]. Also, for systems in the telecommunication industry, detection at a fire size of 1 kW is often desired [31] and easily achieved [83].

Figure 15 can be used as a tool such that the TDP can actually be predicted for a given room size. A system is then engineered to limit TDP below hazardous levels through effective design. For example, to maintain HF concentrations in a 1000 ft^3 room (typical closet), fire detection should occur before 3.7 kW.

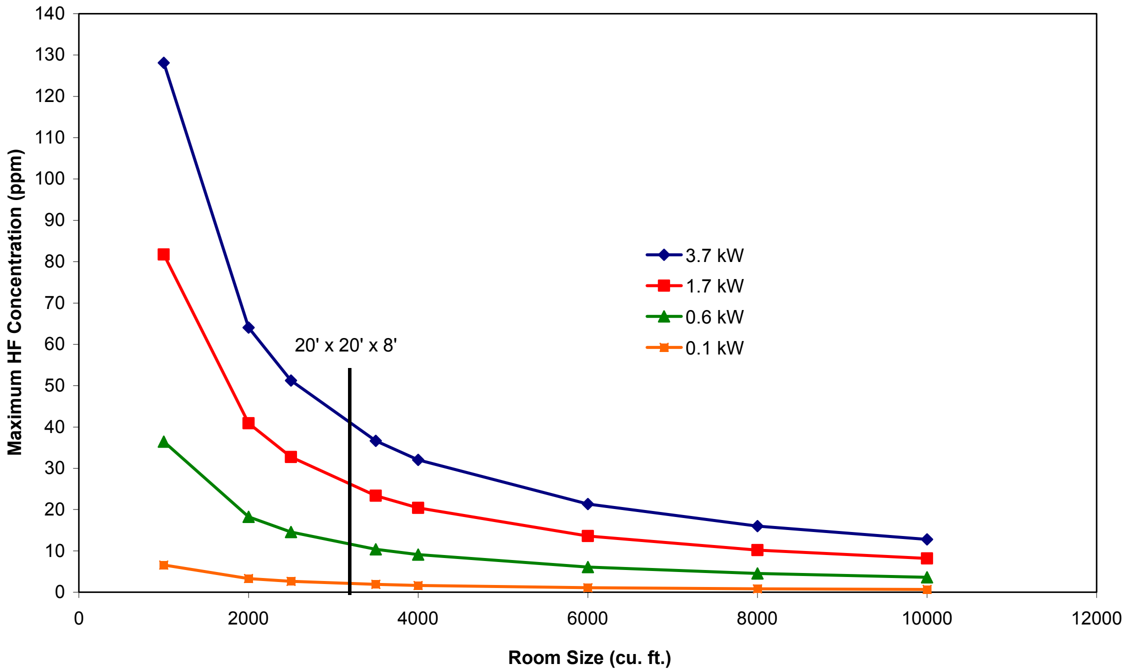


Figure 15, Effect of Room Size on HF Production [6]. C_6 F-ketone at 4.9% v/v.

The severity of a fire size is relative to the size of the enclosure. Increasing the size of a fire while also increasing the size of the enclosure may not lead to higher concentrations of HF during extinguishing. However, increasing the fire size while maintaining the enclosure size has been shown to increase the HF production. Therefore, it is anticipated that larger fire sizes (one order of magnitude larger in the same enclosure) than those used in this study would have led to higher HF production. The fire size-to-room volume ratio for this study was chosen to directly compare to previous testing with other in-kind halocarbon agents [44,45,55]. Peatross and Forssell point out that in many large fire scenarios (i.e. over 1 MW), the high temperatures and combustion products (i.e. CO) outweigh any concerns over HF exposure [84].

7.0 Conclusions

There are two primary methods of determining TDP, wet chemistry utilizing an ISE and FTIR. Several studies have been conducted to verify these two methods produce comparable results. C_6 F-ketone has been found to partially hydrolyze and liberate fluoride ion under the highly alkaline condition used in the wet chemistry technique. Other important drawbacks include, the inability to take real-time data (making the determination of maximum and average concentrations impossible), the time involved in analysis, large variations in results, and an inability to distinguish between HF and other possible fluoride ion sources. FTIR has proven to be very useful for TDP analysis of all halon alternatives. Especially for C_6 F-ketone, since none of the hydrolysis problems encountered with the wet chemistry analysis method are experienced.

FTIR has several advantages over wet chemistry. Foremost, FTIR is a direct method of analysis. Gas is extracted into the IR cell and spectrally analyzed (via infrared light absorption) for specific compounds. Data is taken in real-time and capable for multiple compounds simultaneously. This also allows for the determination of both maximum and average TDP concentrations.

Test results have shown, in terms of TDP magnitude and functional form, C_6 F-ketone is directly comparable to other commercially available halon alternatives. The equivalent HF concentrations found are consistent with those for other in-kind halocarbon agents. The discharge time and agent concentration have a direct effect on the fire extinguishment time. Also, TDP is a monotonically increasing function of fire size.

TDP analysis included both HF and COF_2 concentrations. COF_2 concentrations were found to be between approximately seven times less than HF concentrations for C_6 F-ketone. No other TDPs were identified using FTIR analysis. Other TDPs were either undetectable using FTIR or present in concentrations insufficient for detection.

Analysis of the results suggests that the assumed cup burner extinguishing concentration for heptane used for this study, 4.9% v/v, may not be the actual minimum extinguishing value. Typically the addition of a 20% v/v safety factor onto the minimum cup burner concentration decreases the TDP produced by 50%. However, this effect was not seen in the FTIR results for C_6 F-ketone using discharge times less than 25+ seconds. It is common to find wide disparity in the cup burner extinguishing concentrations between laboratories, especially when applying a high boiling liquid into an apparatus designed for gaseous agents.

8.0 Future Work

Small scale testing provides a means to compare performance of agents. However, large-scale testing is still necessary to validate small-scale results. Large-scale testing introduces variables that cannot be accounted for with small-scale testing, such as air currents, effects of humidity, or variation in agent volatization at the nozzle.

Further development of a standard cup burner apparatus, for all extinguishants, would yield more consistent results between laboratories. Also, due to the unique chemical characteristics of C_6 F-ketone, additional development of a more effective cup burner apparatus for easily vaporized liquids is desirable.

Since the cup burner minimum heptane extinguishing concentration is suspect of over-estimation, additional work should be done to validate the initial heptane extinguishment concentration for C_6 F-ketone (4.9% v/v). If a new concentration were found to be significantly different (±0.1% v/v) then testing with the new cup burner value would be appropriate. The TDP concentrations for C_6 F-ketone did not exhibit the customary 50% reduction by increasing the concentration (v/v) from cup burner to cup burner plus 20% (v/v).

Further testing with increased agent concentrations can also be conducted to determine the point-of-diminishing returns (POD). The POD refers the maximum agent concentration after which further increases yield negligible reductions in TDP concentrations. Previous testing has found the POD at agent concentration in excess of 140% of the minimum n-heptane cupburner extinguishing concentration [44].

For the purposes of statistical analysis, an increased number of tests should be run per scenario. In general, a minimum of 5 data points is required for meaningful statistical analysis. This would give greater insight into the inherent variations in the test procedure (discharge time, extinguishment time) as well as factors effecting TDP.

Testing with an optimized nozzle would be valuable. A nozzle that more efficiently vaporizes C_6 F-ketone could decrease the time to extinguishment and correspondingly decrease the TDP.

Some applications require the protection of Class C fires. Appendix A of NFPA2001 contains a test method for determining the extinguishing concentration for energized fires. The standard also indicates that considerations should be given to the use of higher extinguishing concentrations for energized fires as well as increased thermal decomposition products [31]. Since the magnitude and functional form of TDP generations for C_6 F-ketone are comparable to other in-kind halocarbons for Class A and Class B, the same trend for Class C fires can be expected. Testing conducted in accordance with NFPA2001 can be conducted to quantify the TDP and agent extinguishing concentrations associated with Class C fires.

Finally, as discussed by Linteris [43], the effects of humidity levels can be studied. Not only does humidity have a direct effect on the flame, it has also been shown to affect TDP. This can be especially important since most locations where clean agent suppression is required have climate control, including humidity.

9.0 Reference List

[1] UNEP, **“Montreal Protocol On Substances that Delete the Ozone Layer – UNEP 1998 Assessment Report of the Halons Technical Options Committee,”** Halons Technical Options Committee, Kenya, March, 1999

[2] **“Regulation (EC) No 2037/2000 of the European Parliament and of the Council,”** Official Journal of the European Communities, June, 2000

[3] J.Z. Su, A.K. Kim, J.R. Mawhiney, **“Review of Total Flooding Gaseous Agents as Halon 1301 substitutes,”** Journal of Fire Protection Engineering, 8 (2), pp 45-64, 1996

[4] D.L. Albritton, P.J. Aucamp, G. Megie, R.T. Watson, **“Scientific Assessment of Ozone Depletion: 1998,”** World Meteorological Organization Global Ozone Research and Monitoring project – Report No. 44, Chapter 11, Geneva, 1999

[5] P.E. Rivers, **“Advancement in Sustainable Fire Suppression Development C6 F-ketone: A Novel New Halon Replacement Alternative to HFCs and PFCs,”** Halon Options Technical Working Conference, Albuquerque, NM, 2001

[6] B.D. Ditch, P.E. Rivers, S.D. Thomas, **“Thermal Decomposition Products Testing with L-15566,”** Halon Options Technical Working Conference, Albuquerque, NM, 2001

[7] P.J. DiNenno, E.W. Forssell, M.J. Peatross, M. Maynard, **“Evaluation of Alternative Agents for Halon 1301 in Total Flooding Suppression Systems – Thermal Decomposition Product Testing,”** Halon Options Technical Working Conference, Albuquerque, NM, 1993

[8] M. Meldrum, **“Toxicology of Substances in Relation to Major Hazards: Hydrogen Fluoride,”** Health and Safety Executive, ISBN 11 882100 8, 1993

[9] A.H. Mann, **“Possible Health Risks From Exposure to Hydrogen Fluoride Generated From the Use of Fluoride-Containing Fire Extinguishing Agents,”** Robens Institute of Industrial and Environmental Health & Safety, University of Surrey, Guildford, Surrey, United Kingdom, 1996

[10] D.P. Kelly, **“A Review of the Inhalation Toxicity of Hydrogen Fluoride,”** Halon Options Technical Working Conference, Albuquerque, NM, 1998

[11] W.J. Brock, **“Hydrogen Fluoride: How Toxic is Toxic? (A Hazard and Risk Analysis),”** Halon Options Technical Working Conference, Albuquerque, NM, 1999

[12] M.J. Peatross, **“A Review of Thermal Decomposition Product Testing of Halocarbon Fire Suppression Agents,”** Halon Options Technical Working Conference, Albuquerque, NM, 1998

[13] **“Regulations to Control Ozone Depleting Substances,”** UNEP and Stockholm Institute, 1996

[14] J.S. Curlin, **“The United Nations Environment Programme’s Role in Eliminating Halon Dependency in Developing Countries,”** Halons Options Technical Working Conference, Albuquerque, NM, 1998

[15] **“SNAP, 40 CFR Pars 9 and 82, EPA Final Rule,”** U.S. Environmental Protection Agency, 40 CFR Part 9 and 82, Volume 59, No. 53, March 18, 1994

[16] **“Voluntary Code of Practice for the Reduction of Emissions of HFC & PFC Fire Protection Agents,”** Halons Options Technical Working Conference, Albuquerque, NM, 2002

[17] D.L. Albritton, P.J. Aucamp, G. Megie, R.T. Watson, **“Scientific Assessment of Ozone Depletion: 1998,”** World Meteorological Organization Global Ozone Research and Monitoring project – Report No. 44, Chapter 10, Geneva, 1999

[18] **“Title VI of the Clean Air Act, Section 612: Safe Alternatives Policy,”** U.S. Environmental Protection Agency, 1997

[19] R.E. Tapscott, **“Short Course – Commercialized Halon Options*,”** Halons Options Technical Working Conference, Albuquerque, NM, 1998

[20] M.J. Molina, F.S. Rowland, **“Stratospheric Sink for Chlorofluoromethanes: Chlorine Atom-Catalyst Destruction of Ozone,”** *Nature*, Volume 249, June 28, 1974

[21] **“Stratospheric Ozone Depletion – A Focus on EPA’s Research,”** United States Environmental Protection Agency Office of Research and Development, March, 1995

[22] P. Rosenqvist, **“Emerging Issues in Stratospheric Ozone Protection Policy,”** The Earth Technologies Forum, The Conference on Climate Change and Ozone Protection Conference Proceedings, Washington, DC, 1998

[23] Center for Global Environmental Technologies (CGET) New Mexico Engineering Research Institute (NMERI) **“Halocarbon Nomenclature,”** Technical Update Series, Feb., 1996

[24] **“Final Report of the Halons Technical Options Committee,”** United Nations Environment Program Montreal Protocol Assessment Technology Review, 1989

[25] R.E. Tapscott, T.A. Moore, J.D. Mather, J.A. Vitali, **“Halon Replacement Research – A Historical Review of Technical Progress and Regulatory Decision Points,”** Halons Options Technical Working Conference, Albuquerque, NM, 1998

[26] R.E. Tapscott, **"Commercialized Halon Options,"** International CFC and Halon Alternatives Conference & Exhibition Conference Proceedings, 1995

[27] M.L. Robin, G.J. Walter, **"Progress Towards the Replacement of Halon 1211,"** International CFC and Halon Alternatives Conference & Exhibition Conference Proceedings, 1995

[28] P.O. Huston, **"Halon 1211 Replacement Agents, A Long Time in Development, Are Now Available,"** International Conference on Ozone Protection Technologies Conference Proceedings, Washington, DC, 1996

[29] R.E. Tapscott, **"Update on Total Flood Options,"** International Conference on Ozone Protection Technologies Conference Proceedings, Washington, DC, 1996

[30] R.E. Tapscott, G.D. Brabson, G. Gobeli, E.W. Heinonen, J.A. Kaizerman, J.L. Lifke, R.A. Patterson, **"Research on Advanced Agents as Halon Replacements,"** International Conference on Ozone Protection Technologies Conference Proceedings, Washington, DC, 1996

[31] **"NFPA 2001 – Standard for Clean Agent Fire Extinguishing Systems, 2000 Edition"**, National Fire Protection Association, 2000

[32] J.H. Seinfeld, S.N. Pandis, **"Atmospheric Chemistry and Physics – From Air Pollution to Climate Change,"** John Wiley & Sons, Inc., 1998

[33] R.D. Chambers, **Fluorine in Organic Chemistry,** John Wiley & Sons, 1973

[34] 3M Specialty Materials, **"Novec 1230 Fire Protection Fluid Product Information,"** 3M, June, 2001

[35] 3M Specialty Materials, **"3M Product Information Notebook – 3M Clean Extinguishing Agents CEA-614 (Perfluorohexane),** 3M

[36] **"NFPA 12A – Standard on Halon 1301 Fire Extinguishing Systems, 1997 Edition,"** National Fire Protection Association, 1997

[37] **"NFPA 12B – Standard on Halogenated Fire Extinguishing Agent Systems Halon 1211, 1973 Edition,"** National Fire Protection Association, 1973

[38] **"Cup Burner Flame Extinguishment Concentrations,"** Center for Global Environment Technologies (CGET) New Mexico Engineering Research Institute (NMERI), Albuquerque, New Mexico, May, 1998

[39] A.G. Guschin, Luisa T. Molina, M.J. Molina, Report Prepared for 3M Company, July, 1999

[40] S. Pinnock, M.D. Hurley, K.P. Shine, T.J. Wallington, T.J. Smyth, **"Radiative Forcing of Climate by Hydrochlorofluorocarbons and Hydrofluorocarbons,"** *Journal of Geophysical Research*, Vol. 100, D11, Pages 23,227-23,238, 1995

[41] R.D. Martinez, A.A. Buitrago, N.W. Howell, C.H. Hearn, J.A. Joens, **"The Near U.V. Absorption Spectra of Several Aliphatic Aldehydes and Ketones at 300 K,"** *Atmospheric Environment*, Vol. 26A, No. 5, pp. 785-792, 1992

[42] W.J. Brock, **"Cardiac Sensitization: Methods Development and Understanding the Hazard and Potential Risk,"** Halons Options Technical Working Conference, Albuquerque, NM, 1998

[43] G. Linteris, NIST, Private Communication, 2001

[44] J.C. Brockway, **"Recent Findings on Thermal Decomposition Products of Clean Extinguishing Agents,"** NFPA 2001 Committee Meeting, Ft. Lauderdale, FL, 1994

[45] M.J. Ferreira, C.P. Hanauska, M.T. Pike, **"Thermal Decomposition Products Results Utilizing PFC-410 (3M Brand PFC-410 Clean Extinguishing Agent",** Halon Options Technical Working Conference, Albuquerque, NM, 1992

[46] T.L. Miller, A.E.S. Green, **"A Survey of Techniques for Fire Suppressant Studies,"**

[47] W.T. Cochran, J.W. Cooley, D.L. Favin, H.D. Helms, R.A. Kaenel, W.W. Lang, G.C. Maling, D.E. Nelson, C.M. Radar, P.D. Welch, **What is the Fast Fourier Transform?,** Institute of Electrical and Electronics Engineers, Inc., 1967

[48] M.L. Robin, **"A Review of Thermal Decomposition Product Formation from Halocarbon Fire Suppression Agents: Suppression of Class A Fires,"** Halon Options Technical Working Conference, Albuquerque, NM, 1999

[49] T.A. Moore, D.S. Dierdorf, C. Hanauska, **"Decomposition Product Analysis of Halon Replacements: An Interlaboratory Comparison,"** Halons Options Technical Working Conference, Albuquerque, NM, 1996

[50] G.T. Linteris, M.D. King, A. Lui, C. Womeldorf, Y.E. Hsin, **"Acid Gas Production in Inhibited Diffusion Flames,"** Halon Options Technical Working Conference, Albuquerque, NM, 1994

[51] G.T. Linteris, G. Gmurczyk, **"Parametric Study of Hydrogen Fluoride Formation in Suppressed Fires,"** Halon Options Technical Working Conference, Albuquerque, NM, 1995

[52] R. Zalosh, S. Heyworth, **“Generalized Data Correlations for Extinguishing Times and Acid Concentrations in Fire Tests with Fluorinated Suppression Agents,”** Halons Options Technical Working Conference, Albuquerque, NM, 1996

[53] R.A. Filipczak, **“Relative Extinguishment Effectiveness and Agent Decomposition Products of Halon Alternatives Agents,”** Halon Options Technical Working Conference, Albuquerque, NM, 1993

[54] C.S. Miser, W.R. Davis, K.L. McNesby, S.H. Hoke, M.K. Leonnig, **“Measurement of Carbonyl Fluoride, Hydrogen Fluoride, and Other Combustion Byproducts During Fire Suppression Testing by Fourier Transform Infrared Spectroscopy,”** Halon Options Technical Working Conference, Albuquerque, NM, 1998

[55] M.R. Driscoll, P.E. Rivers, **“The Products of Thermal Decomposition in Intermediate Scale Testing,”** National Institute of Standards and Technology Annual Conference on Fire Research, Gaithersburg, MD, 1996

[56] B.C. Smith, **Fundamentals of Fourier Transform Infrared Spectroscopy,** 1996, CRC Press Inc.

[57] J. Seiter, **“Thermal Decomposition Testing with C_6 F-ketone,”** 3M Company Internal Technical Report, 2001

[58] R.S. Sheinson, H.G. Eaton, B.H. Black, R. Brown, H. Burchell, A. Maranghides, C. Mitchell, G. Salmo, W.D. Smith, **“Halon 1301 Replacement Total Flooding Fire Testing, Intermediate Scale,”** Halons Options Technical Working Conference, Albuquerque, NM, 1994

[59] J.Z. Su, Z. Liu, A.K. Kim, M Kanabus-Kaminska, E. Lusztyk, **“Gas Measurement Using FTIR, GC/MS and Ion Selective Electrode Methods in Fire Suppression Tests,”** Halons Options Technical Working Conference, Albuquerque, NM, 1997

[60] S.H. Hoke, M.L. Clay, K.L. McNesby, C.S. Miser, M.K. Leonnig, S. Polyanski, C. Herud, W. Bolt, **“Comparison of Methods for Measuring Hydrogen Fluoride Gas as a Fire Suppression By-Product,”** Halons Options Technical Working Conference, Albuquerque, NM, 1997

[61] R.S. Sheinson, A. Maranghides, H.G. Eaton, D. Barylski, B.H. Black, R. Brown, H. Burchell, P. Byrne, T. Friderichs, C. Mitchell, M. Peatross, G. Salmon, W. Smith, F.W. Williams, **“Total Flooding Real Scale Fire Testing with Halon 1301 Replacements,”** International CFC and Halon Alternatives Conference & Exhibition Conference Proceedings, Washington, DC, 1994

[62] J.Z. Su, A.K. Kim, **“Full-Scale Evaluation of Gaseous Fire Suppressants,”** International Conference on Ozone Protection Technologies Conference Proceedings, Washington, DC, 1996

[63] S.H. Modiano, K.L. McNesby, W. Bolt, C. Herud, **“Quantitative Measurements by Fourier-Transform infrared spectroscopy of toxic gas production during inhibition of JP-8 fires by CF_3BR and C_3F_7H,”** *Applied Optics*, Vol. 35, No.21, July 1996

[64] A. Chattaway, J. Griggs, D.J. Spring, **“Halon Replacement Decomposition Product Studies,”** Halons Options Technical Working Conference, Albuquerque, NM, 1996

[65] R.S. Sheinson, A. Maranghides, H.G. Eaton, D. Barylski, B.H. Black, R. Brown, H. Burchell, P. Byrne, T. Friderichs, C. Mitchell, M. Peatross, G. Salmon, W.D. Smith, F.W. Williams, **“Large Scale (840 m3) HFC Total Flooding Fire Extinguishment Results,”** Halons Options Technical Working Conference, Albuquerque, NM, 1995

[66] R. Hansen, G. Black, **“United States Coast Guard Full-Scale Shipboard Testing of Alternative Gaseous Agents,”** Halons Options Technical Working Conference, Albuquerque, NM, 1994

[67] A.K. Kim, J.Z. Su, J.R. M. Kanabus-Kaminska, **“Full-Scale Fire Testing of HFC-277ea and HCFC Blend A,”** Halons Options Technical Working Conference, Albuquerque, NM, 1996

[68] R.S. Sheinson, H.G. Eaton, B.H. Black, R. Brown, H. Burchell, G. Salmon, J. St.Aubin, W.D. Smith, **“Total Flooding Fire Suppressant Testing in a 56m3 (2000 ft^3) Compartment,”** Halons Options Technical Working Conference, Albuquerque, NM, 1993

[69] T.A. Moore, D.S. Dierdorf, S.R. Skaggs, **“Intermediate-Scale (645 ft^3) Fire Suppression Evaluation of NFPA 2001 Agents,”** Halons Options Technical Working Conference, Albuquerque, NM, 1993

[70] D.S. Deirdorf, T.A. Moore, S.R.Skaggs, **“Decomposition Products Analysis During Intermediate-Scale (645 ft3) and Laboratory-Scale (6.18 ft3) Testing of NFPA 2001 Agents,”** Halons Options Technical Working Conference, Albuquerque, NM, 1993

[71] R. Hansen, R. Richards, G.G. Back, T. Moore, **“USCG Full-Scale Shipboard Testing of Gaseous Agents,”** Proceedings of 1994 International CFC and Halon Alternatives Conferences, Washington DC 1994

[72] R.S. Sheinson, **“Halon Alternatives – Compartment Total Flooding Testing,”** Proceedings of 1991 International CFC and Halon Alternatives Conference, Baltimore, MD, December, 1991

[73] S.P. Baldwin, R. Brown, H. Burchell, H.G. Eaton, G. Salmon, J. St. Aubin, R.S. Sheinson, W.D. Smith, **"Halon Replacements: Cup Burner and Intermediate Size Fire Evaluation,"** CFC and Halon Alternatives Conference, Washington, D.C., 1992

[74] R.S. Sheinson, A. Maranghides, H.G. Eaton, D. Barylski, B.H. Black, R. Brown, H. Burchell, P. Byrne, T. Friderichs, C. Mitchell, M. Peatross, G. Salmon, W.D. Smith, F.W. Williams, **"Total Flooding Real Scale Fire Testing with Halon 1301 Replacements,"** International Conference on CFC and Halon Alternatives, Washington, D.C., 1994

[75] W.D. Smith, R.S. Sheinson, H.G. Eaton, R. Brown, G. Salmon, H. Burchell, J. St.Aubin, **"Halon Acid Evaluation in an Intermediate-Scale Halon 1301 Replacement Suppressant Test,"** Proceedings Sixth International Fire Conference, Interflam 1993, Oxford, England

[76] R.S. Sheinson, J.K. Musick, H.W. Carhart, **"HF and HBr Production From Full Scale CF_3Br (Halon 1301) Fire Suppressant Tests,"** *Journal of Fire & Flammability*, Vol. 12, July, 1981

[77] K.L. McNesby, R.G. Daniel, A.W. Miziolek, S.H. Modiano, **"Optical Measurement of Toxic Gases Produced during Firefighting Using Halons,"** *Applied Spectroscopy*, Vol. 51, Number 5, 1997

[78] S.H. Hoke, C. Herud, **"Real-Time Analysis of Halon Degradation Products,"** Halon Options Technical Working Conference, Albuquerque, NM, 1993

[79] M.L. Robin, **"Development of a Standard Cup Burner Apparatus and Procedure,"** International Conference on Ozone Protection Technologies Conference Proceedings, 1997

[80] **"Cup Burner Values for Halons and Halon Replacements Candidates,"** Center for Global Environment Technologies (CGET) New Mexico Engineering Research Institute (NMERI), Albuquerque, New Mexico, June 10, 1994

[81] T.A. Moore, S.R. Skaggs, **"An Analysis of the Cup Burner,"** International Conference on CFC and Halon Alternatives, Washington, D.C., 1992

[82] C. Warren, **"3M Company Stability Testing,"** Private Communication, 2001

[83] A.M. Leber, **"Early Warning Fire Detection,"** International CFC and Halon Alternatives Conference & Exhibition Conference Proceedings, Washington, DC, 1994

[84] M.J. Peatross, E.W. Forssell, **"A Comparison of Thermal Decomposition Product Testing of Halon 1301 Alternative Agents,"** Halons Options Technical Working Conference, Albuquerque, NM, 1996

10.0 Appendix

A. Wet Chemistry Calculations

A1.1 Calibration and Gas Phase Concentration Calculation

This section describes the calculation of gas-phase HF in the test enclosure from ISE measurements. The ISE was calibrated from standard solution, Figure 16.

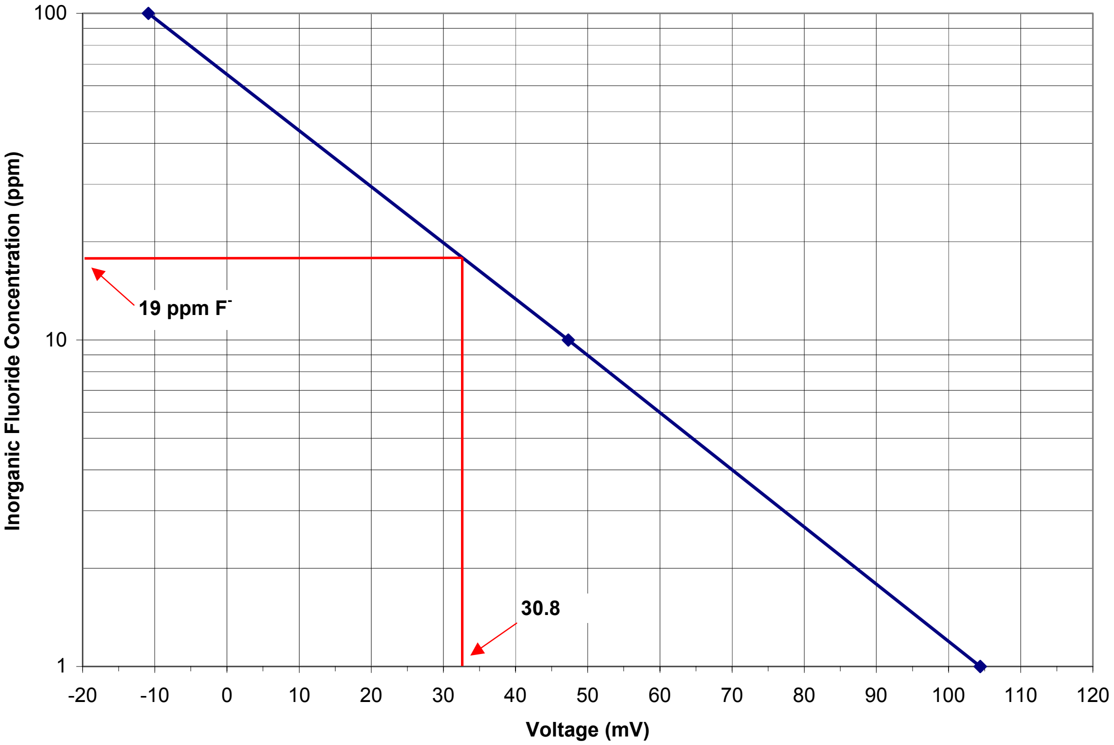


Figure 16, Typical Calibration Curve for ISE analysis.

Interpolating the voltage reading along the y-axis yields the corresponding F^- concentration in solution. Equations 4-12 convert F^- concentrations to HF mass in sample solution assuming a solution with a density of 1 g/ml.

[Eq. 4]
$$19\,ppmF^- = 19\frac{\mu gF^-}{1x10^6\,\mu g - solution}\left(1x10^6\,\frac{\mu g}{ml}\right) = 19\frac{\mu gF^-}{ml - solution}$$

The absolute mass, Equation 5, is found by multiply by the solution volume.

[Eq. 5]
$$19\frac{\mu gF^-}{ml}(20ml - solution) = 380\,\mu gF^-$$

The corresponding HF mass is found by multiplying by the ratio of molecular weights, Equation 6.

[Eq. 6] $$380\mu g F^{-}\left(\frac{20\mu g HF}{19\mu g F^{-}}\right) = 400\mu\text{gHF}$$

Using the ideal gas law, calculate the partial HF gas volume in the sample bulb, Equation 7.

[Eq. 7] $$\frac{400\mu g HF}{1x10^{6}\frac{\mu g}{g}}\left[\frac{\left(82.05\frac{ml\cdot atm}{g\cdot mol-K}\right)(293K)}{1atm\left(20\frac{gHF}{g\cdot ml}\right)}\right]1000\frac{\mu l}{ml} = 480\mu l \text{ partial volume of HF}$$

The gas phase concentration in ppm (volume basis) is found using the sample bulb volume (250 ml), Equation 8.

[Eq. 8] $$480\mu l HF\left(\frac{1x10^{6}}{250{,}000\mu l}\right) = 1920\,ppmHF$$

A1.2 Maximum C_6 F-ketone Hydrolyzed During Neutralization Time

The following calculations use the same test results as above. Note that these calculations are only applicable to tests run during the neutralization time study, with no fire. The simplest hydrolysis mechanism for C_6 F-ketone, in the presence of a strong base (i.e. NaOH), is illustrated in Equations 9 and 10. In addition, this mechanism accounts for the greatest amount of C_6 F-ketone hydrolyzed.

[Eq. 9] $$CF_3CF_2C(O)CF(CF_3)_2 + H_2O \rightarrow CF_3CF_2COOH + CF_3CFHCF_3$$

[Eq. 10] $$CF_3CFHCF_3 \xrightarrow{NaOH} CF_3CF = CF_2 + HF$$

From Equations 9 and 10, a 1:1 molar ratio of C_6 F-ketone of HF during hydrolysis is identified. Therefore, the amount of C_6 F-ketone hydrolyzed can be determined by assuming the ideal gas law, Equation 11.

[Eq. 11] 1 mol C_6 F-ketone = 1 mol HF

or

$$1920\,ppm_{HF} = 1920\,ppm_{C_6F-ketone}$$

Using the HF concentration found in Equation 8 and the 1:1 molar ratio of C_6 F-ketone to HF found in Equation 12, the maximum percent C_6 F-ketone hydrolyzed can be calculated.

[Eq. 12] $$\frac{1920\,ppm_{C_6F-ketone(Hydrolyzed)}}{42000\,ppm_{C_6F-ketone}}x100 = 4.57\,\%\text{-}C_6\text{ F-ketone hydrolyzed}$$

A1.3 Theoretical Maximum TDP Calculations

It is possible to determine the theoretical maximum HF production for a given test. It is necessary to use a simplified system where all fluorine in the structure is converted to hydrogen fluoride. Then 1 mol of C_6 F-ketone produces 12 mol HF. Therefore, the maximum HF production for C_6 F-ketone at 4.9% is based on the 12:1 ratio of fluoride ion, Eq. 13.

[Eq. 13] $$\left[49000\,ppm_{C_6F-ketone}\right]*\left[12\right]=588000\,ppm_{HF}$$

This assumes complete decomposition of C_6 F-ketone. This simple model can also be used to determine the approximate percentage of C_6 F-ketone decomposed during a test. For example, if a 3.7 kW fire produced 5000 ppm_{HF}, then a minimum of 0.42% C_6 F-ketone decomposed, Eq. 14.

[Eq. 14] $$\frac{\frac{5000\,ppm_{HF}}{12}}{49{,}000\,ppm_{C_6F-ketone}}x100=0.85\%C_6F-ketone_{Decomposed}$$

A2.1 Wet Chemistry Test Results

Table A3.1 - C_6 F-ketone at 4.2% (v/v)
Class B Test with a 9 Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (ppm HF)
13,17	3.7	9	4291
12,16,19	1.7	11	3160
7-9,11,15	0.6	10	1356
10,14,18	0.1	6	943

B. FTIR Parameters

B1.1 Pathlength and Transfer Line Recovery Determination

Instrument Pathlength Determinations

Cell: 10cm

File ID	Date / Time	Pathlength (meters)	Error+-	% D from mean
c0003.abs	3/28/01 11:20	0.106	1.91E-04	2.91%
c0005.abs	3/29/01 10:17	0.104	1.61E-04	0.97%
c0005.abs	3/30/01 9:09	0.104	1.86E-04	0.97%
c0002.abs	4/2/01 11:15	0.103	1.66E-04	0.00%
c0002.abs	4/3/01 8:19	0.102	2.03E-04	0.97%
c0002.abs	4/4/01 9:11	0.103	1.98E-04	0.00%
c0002.abs	4/5/01 9:07	0.101	1.75E-04	1.94%
c0002.abs	4/6/01 8:46	0.101	1.84E-04	1.94%
	Average:	0.103		

Sampling and Analytical System Mass Transfer Verification

Cell: 10cm

Cylinder Concentration: 1999 ppm

File ID	Date / Time	Pathlength (meters)	Error+-	% D from mean
c0004.abs	3/28/01 11:22	0.106	1.89E-04	2.91%
c0005.abs	3/28/01 11:23	0.106	1.90E-04	2.91%
c0006.abs	3/29/01 10:18	0.104	1.71E-04	0.97%
c0007.abs	3/29/01 10:19	0.104	1.74E-04	0.97%
c0006.abs	3/30/01 9:10	0.104	1.88E-04	0.97%
c0007.abs	3/30/01 9:11	0.104	1.90E-04	0.97%
c0003.abs	4/2/01 11:16	0.103	1.71E-04	0.00%
c0004.abs	4/2/01 11:17	0.103	1.70E-04	0.00%

c0003.abs	4/3/01 8:20	0.102	2.10E-04	0.97%
c0004.abs	4/3/01 8:21	0.102	2.08E-04	0.97%
c0003.abs	4/4/01 9:12	0.103	1.96E-04	0.00%
c0004.abs	4/4/01 9:13	0.103	1.94E-04	0.00%
c0003.abs	4/5/01 9:08	0.101	1.73E-04	1.94%
c0004.abs	4/5/01 9:09	0.101	1.74E-04	1.94%
c0003.abs	4/6/01 8:46	0.101	1.88E-04	1.94%
c0004.abs	4/6/01 8:47	0.101	1.86E-04	1.94%
	Average:	0.103		

Cell: 1cm

File ID	Date / Time	Pathlength (meters)	Error+-	% D from mean
c0002.abs	3/28/01 12:45	0.013	9.14E-05	0.00%
c0002.abs	3/29/01 10:40	0.013	9.90E-05	0.00%
c0003.abs	3/30/01 10:44	0.013	9.52E-05	0.00%
c0002.abs	4/2/01 12:57	0.013	9.06E-05	0.00%
c0003.abs	4/3/01 10:38	0.013	9.92E-05	0.00%
c0003.abs	4/4/01 10:46	0.013	1.03E-04	0.00%
c0002.abs	4/5/01 10:46	0.013	1.00E-04	0.00%
c0002.abs	4/6/01 10:26	0.013	9.87E-05	0.00%
	Average:	0.013		

Sampling and Analytical System Mass Transfer Verification

Cell: 1cm

Cylinder Concentration: 20010

File ID	Date / Time	Pathlength (meters)	Error+-	% D from mean
c0003.abs	3/28/01 12:47	0.013	9.14E-05	0.00%
c0004.abs	3/28/01 12:48	0.013	9.10E-05	0.00%
c0003.abs	3/29/01 10:41	0.013	9.95E-05	0.00%
c0004.abs	3/29/01 10:44	0.013	9.93E-05	0.00%
c0004.abs	3/30/01 10:45	0.013	9.58E-05	0.00%
c0005.abs	3/30/01 10:46	0.013	9.53E-05	0.00%
c0003.abs	4/2/01 12:58	0.013	9.12E-05	0.00%
c0004.abs	4/2/01 12:59	0.013	9.14E-05	0.00%
c0002.abs	4/3/01 10:37	0.013	9.85E-05	0.00%
c0004.abs	4/3/01 10:39	0.013	9.96E-05	0.00%
c0004.abs	4/4/01 10:47	0.013	1.04E-04	0.00%
c0005.abs	4/4/01 10:48	0.013	1.03E-04	0.00%
c0003.abs	4/5/01 10:47	0.013	9.99E-05	0.00%
c0004.abs	4/5/01 10:48	0.013	9.97E-05	0.00%
c0003.abs	4/6/01 10:26	0.013	9.79E-05	0.00%
c0004.abs	4/6/01 10:27	0.013	9.79E-05	0.00%
	Average:	0.013		

B1.2 AutoQuant CLS Method

```
Method Name: B236 CEA
Method Type: AutoQuant 3.0

Linear Analysis mode
Temperature & Pressure Adjustments: OFF
Mass Emission Computations: OFF

Method Parameters:
 Wavenumber range:          650.00 - 4500.00
 Fingerprint zoom:          650.00 - 1400.00
 Path Length =                   0.013
 Interfere Criterion =            2500

 Gain number =                       1
 Apodization =              Triangle
 Phase Correct =            Mertz
 Resolution =                      0.5
 Baseline Correction:       Linear

Compound: Ethylene
 Alarms: Disabled
 Output: Disabled

 Spectrum: J2KETY.SPC
                            Primary:    Yes
                            Reference concentration = 206.60
                            Region #1: 880.86 - 1017.19

Compound: L15566
 Alarms: Disabled
 Output: Disabled

 Spectrum: 74C6KETONE.SPC
                            Primary:    Yes
                            Reference concentration = 74.16
                            Region #1: 952.00 - 1326.00
```

```
Method Name: Noranda
Method Type: AutoQuant 3.0

Non-Linear Analysis mode
Temperature & Pressure Adjustments: OFF
Mass Emission Computations: OFF

Method Parameters:
 Wavenumber range:          650.00 - 4500.00
 Fingerprint zoom:          650.00 - 1400.00
 Path Length =                         19.8
 Interfere Criterion =                 2500

 Gain number =                          0.5
 Apodization =              Triangle
 Phase Correct =            Mertz
 Resolution =                           0.5
 Baseline Correction:       Linear

Compound: C2 Acid
 Alarms: Disabled
 Output: Disabled

 Spectrum: 100C2ACI.SPC
                            Primary:        Yes
                            Reference concentration = 100.00
                            Region #1:      1077.01 - 1116.35

Compound: C2F6
 Alarms: Disabled
 Output: Disabled

 Spectrum: 46_8C2F6.SPC
                            Primary:        Yes
                            Reference concentration = 46.75
                            Region #1:      1110.40 - 1130.75

Compound: C3F8
 Alarms: Disabled
 Output: Disabled

 Spectrum: 53_4C3F8.SPC
                            Primary:        Yes
                            Reference concentration = 53.36
                            Region #1:      986.02 - 1022.02
```

```
Compound: CF4
 Alarms: Disabled
 Output: Disabled

 Spectrum: 23_06CF4.SPC
                               Primary:            Yes
                               Reference concentration = 23.06
                               Region #1:          1255.84 - 1284.03

Compound: CO
 Alarms: Disabled
 Output: Disabled

 Spectrum: C2_100CO.SPC
                               Primary:            Yes
                               Reference concentration = 99.90
                               Region #1:          2128.30 - 2156.50

Compound: COF2
 Alarms: Disabled
 Output: Disabled

 Spectrum: COF2_17.SPC
                               Primary:            Yes
                               Reference concentration = 17.30
                               Region #1:          1864.26 - 2003.72

Compound: Ethylene
 Alarms: Disabled
 Output: Disabled

 Spectrum: J2KETY.SPC
                               Primary:            Yes
                               Reference concentration = 206.60
                               Region #1:          876.55 - 1053.07

Compound: Hexafluoropropene
 Alarms: Disabled
 Output: Disabled

 Spectrum: HFPEZ1A.SPC
                               Primary:            Yes
                               Reference concentration = 11.37
                               Region #1:          1160.44 - 1192.11
                               Region #2:          1363.52 - 1422.03
```

```
Compound: HF
 Alarms: Disabled
 Output: Disabled

 Spectrum: 72HF3M.SPC
                              Primary:            Yes
                              Reference concentration = 72.00
                              Region #1:          4128.48 - 4208.73

Compound: HFC134A
 Alarms: Disabled
 Output: Disabled

 Spectrum: 1112TZ1A.SPC
                              Primary:            Yes
                              Reference concentration = 11.40
                              Region #1:          1098.55 - 1225.07

Compound: L15566
 Alarms: Disabled
 Output: Disabled

 Spectrum: C0094.SPC
                              Primary:            Yes
                              Reference concentration = 69.05
                              Region #1:          793.24 - 866.61

Compound: PFIB
 Alarms: Disabled
 Output: Disabled

 Spectrum: PFIBSP~1.SPC
                              Primary:            Yes
                              Reference concentration = 10.00
                              Region #1:          977.23 - 1004.33
                              Region #2:          1047.05 - 1066.67

Compound: PFIButane
 Alarms: Disabled
 Output: Disabled

 Spectrum: I_PFIB.SPC
                              Primary:            Yes
                              Reference concentration = 10.00
                              Region #1:          885.43 - 1005.41
```

```
Compound: SiF4
 Alarms: Disabled
 Output: Disabled

 Spectrum: SIF4_21.SPC
                                Primary:                 Yes
                                Reference concentration = 21.10
                                Region #1:               957.19 - 1096.51

Compound: Tetrafluoroethylene
 Alarms: Disabled
 Output: Disabled

 Spectrum: C2F4_2.SPC
                                Primary:                 Yes
                                Reference concentration = 45.50
                                Region #1:               1167.33 - 1189.40



Method Name: Ambient Pathlength
Method Path: C:\AUTOQ3\METHODS\AMBPATH\AMBPATH.ME
Method Type: AutoQuant 3.0

Non-Linear Analysis mode
Temperature & Pressure Adjustments: OFF
Mass Emission Computations: OFF

Method Parameters:
 Wavenumber range:              650.00 - 4500.00
 Fingerprint zoom:              650.00 - 1400.00
 Path Length =                                 20.01
 Interfere Criterion =                          2500

 Gain number =                                   0.5
 Apodization =                  Triangle
 Phase Correct =                Mertz
 Resolution =                                    0.5
 Baseline Correction:           Linear
```

```
Compound: Ety
 Alarms: Disabled
 Output: Disabled

 Spectrum: J2KETY.SPC
                              Primary:            Yes
                              Reference concentration = 206.60
                              Region #1:          902.36 - 1010.17
```

B1.3 Detection Limit Summary

Detection Limit Summary

Instrument ID: L
File ID: L28mar01 (C0001)
Background: Room Air

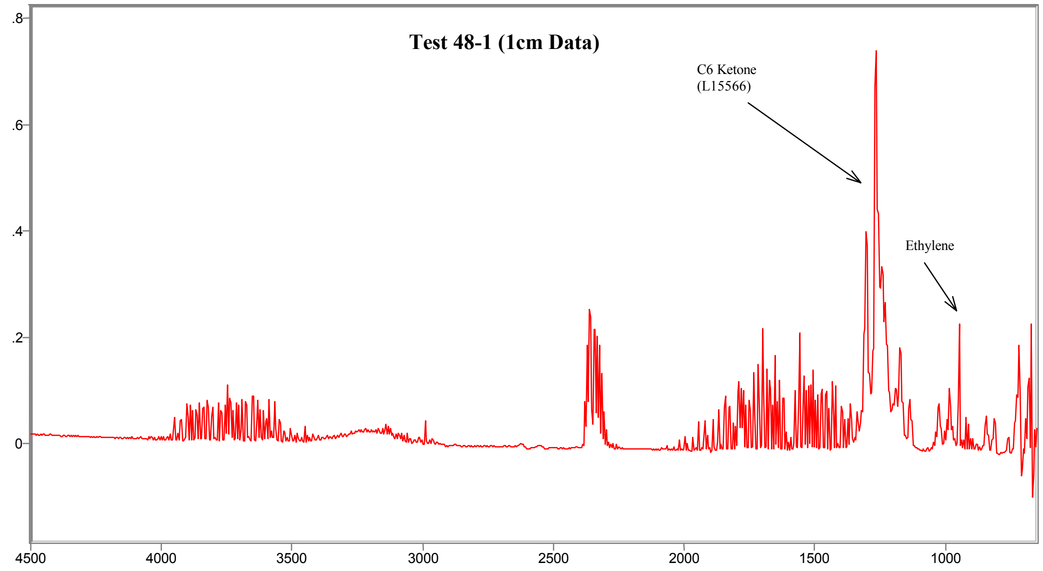
Analyte	Analytical Region cm^{-1}	Detection S-Factor	3X S-Factor	Reference Standard (ppm-m)	Pathlength (m)	Detection Limit (ppmv)
C4F10	900	0.0072	0.0215	20.17	0.013	33.3
CO	2140	0.0092	0.0277	99.90	0.013	213
COF2*	1944	0.0380	0.1140	17.30	0.013	152
Ethylene	950	0.0026	0.0078	206.6	0.013	124
HF	4039	0.0087	0.0260	72.00	0.013	144
L15566 (C6F12O)	1000	0.0065	0.0195	69.05	0.013	103

Instrument ID: M
File ID: M02apr01(c0005)
Background: Room Air

Analyte	Analytical Region cm^{-1}	Detection S-Factor	3X S-Factor	Reference Standard (ppm-m)	Pathlength (m)	Detection Limit (ppmv)
C4F10	900	0.0070	0.021	20.17	0.103	4.11
CO	2140	0.0153	0.046	99.90	0.103	44.6
COF2*	1944	0.0990	0.297	17.30	0.103	49.9
Ethylene	950	0.0042	0.013	206.6	0.103	25.3
HF	4039	0.0123	0.037	72.00	0.103	25.7
L15566 (C6F12O)	1000	0.0071	0.0214	69.05	0.103	14

* The MDL fro COF2 was higher than anticipated due to an interferant peak in this region from the high level of agent in the sample spectra.

B2.1 Representative Spectra



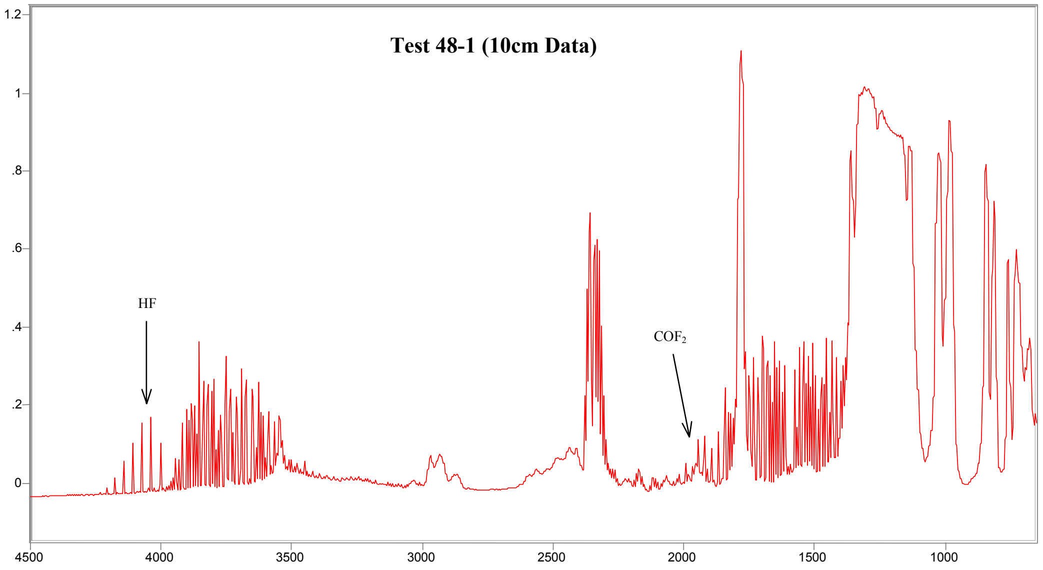
Absorbance / Wavenumber (cm-1)

Stacked X-Zoom CURSOR

File # 1 = C0060

4/3/01 1:39 PM Res=None

test 48-1 dil w/ety,1lpm,amb,0.013m,L



Absorbance / Wavenumber (cm-1)

Stacked X-Zoom CURSOR

File # 1 = C0065

4/3/01 1:39 PM Res=None

Test 48-1,2lpm,amb,0.1m,M

B3.1 FTIR Test Results

Table B2.1 - C_6 F-ketone at 4.9% (v/v)
Class B Test with a 3-Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (ppm HF)	Maximum TDP (ppm COF_2)
42	3.7	4.7	1753	280
43	1.7	4.3	1140	153
45	0.6	3.7	370	61
46	0.1	2.0	11	0

Table B2.2 - C_6 F-ketone at 5.9% (v/v)
Class B Test with a 3-Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
47	3.7	3.8	1517	220
48	1.7	4.2	1177	163
49	0.6	4.2	647	87
50	0.1	2.5	70	0

Table B2.3 - C_6 F-ketone at 4.9% (v/v)
Class B Test with a 9-Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
32	3.7	11.0	2847	490
33	1.7	11.3	1817	270
34	0.6	10.0	810	97
35	0.1	8.7	147	0

Table B2.4 - C_6 F-ketone at 5.9% (v/v)
Class B Test with a 9-Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
36	3.7	9.0	2700	447
37	1.7	9.3	1617	223
38	0.6	9.7	857	107
39	0.1	4.3	90	0

Table B2.5 - C_6 F-ketone at 4.9% (v/v)
Class B Test with a 25+ Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
54	3.7	22.0	4377	790
53	1.7	32.3	3550	627
52	0.6	28.7	1863	267
51	0.1	25.3	207	0

Table B2.6 - C_6 F-ketone at 5.9% (v/v)
Class B Test with a 25+ Second Discharge

Test	Fire Size (kW)	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
58	3.7	12.3	3777	650
57	1.7	20.7	2433	397
56	0.6	21.0	1150	147
55	0.1	18.8	106	0

Table B2.7 - C_6 F-ketone at 4.9% (v/v)
Class A Test with a 9-Second Discharge

Test	Fuel	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
60	Cotton	16.0	1500	225
61	PE Pipets	8.0	515	76
59	Wood	45.5	3340	495

Table B2.8 - C_6 F-ketone at 5.9% (v/v)
Class A Test with a 9-Second Discharge

Test	Fuel	Ext. Time (s)	Maximum TDP (PPM HF)	Maximum TDP (ppm COF_2)
3	Cotton	11.5	850	112
64	PE Pipets	13.8	2070	235
62	Wood	9.0	835	135

C. Publications

B.D. Ditch, P.E. Rivers, S.D. Thomas, **“Thermal Decomposition Products Testing with L-15566,”** Halon Options Technical Working Conference, Albuquerque, NM, 2001

Thermal Decomposition Product Testing with L-15566

Benjamin D. Ditch, Paul E. Rivers, Scott D. Thomas
3M Specialty Materials Division

Abstract

3M has developed a new class of compounds of which one, 3M Experimental Product L-15566, has shown potential for both total flooding and streaming applications [8]. L-15566 is C6 ketone, or perfluoro-2-methyl-3-pentanone, or $C_6F_{12}O$, or $CF_3CF_2C(O)CF(CF_3)_2$. This new fire protection fluid provides the right combination of performance, safety, and sustainable environmental properties as well as economic viability for commercial acceptance. Understanding the balance requires knowledge of key properties and of the extinguishing effectiveness.

The thermal decomposition products (TDP) resulting when halocarbon alternatives are discharged to extinguish a fire has been studied. Work performed by 3M and others has shown that acid-gas production by halon alternatives is between 2 and 10 times greater than that of halon 1301. It has also been shown that the three key factors resulting in thermal decomposition production are the fire size-to-volume ratio, the agent volumetric concentration, and the discharge time [6].

Testing conducted in 3M's 1.28-m^3 (45-ft^3) “box” included class B fires and class A fires. The three variables in the test matrix are fire size, agent discharge time, and agent concentration. TDP are then quantified using on-line FTIR analysis. The TDP data are compared with other commercially available halon alternatives previously tested.

It should be noted that small-scale TDP testing for comparative purposes is only one method of determining the expected performance. Full-scale demonstrations incorporating actual field conditions can yield results not anticipated in small-scale tests.

Introduction

The halon alternative search, for critical use applications, with the right combination of performance, safety, and environmental characteristics has been the subject of considerable research by the fire protection industry over the past decade. While halons excel in performance and safety, the presence of chlorine and bromine in their molecular structure has been proven to be very destructive to the earth’s ozone layer. It is therefore paramount for a replacement agent to be sustainable environmentally, not only with a zero ozone depletion potential (ODP) but also have a minimal persistence in the environment.

3M has developed a new class of compounds of which one, L-15566, has shown potential applications as an alternative to commercially available halon replacements. L-15566 is C6 ketone, or perfluoro-2-methyl-3-pentanone, or $C_6F_{12}O$, or $CF_3CF_2C(O)CF(CF_3)_2$. The focus of this paper is an analysis of thermal decomposition products (TDP) testing and comparison to other commercial halon alternatives.

Studies such as Meldrum and Robens Institute provide analyses indicating levels at which TDP can be dangerous. Meldrum concluded that the dangerous toxic load (DTL), for various animals, is 12000 ppm-minutes. In other words the DTL for a 30-minute HF exposure is 400 ppm [4]. The Robens Institute study found that the highest tolerable HF concentration, for human subjects, was 120 ppm for a 1-minute exposure [7].

Previous work done at 3M, and elsewhere, has shown that the main factors affecting TDP are duration of fire exposure, fire size, and agent concentration. Therefore a testing matrix was developed to consider fire size, discharge time and agent concentration.

Methodology

Test Enclosure

Testing was conducted at 3M in a 0.91x0.91x1.7-m^3 (3x3x5-ft^3) "box", constructed of 1.3-cm (0.5-in) thick polycarbonate walls, reinforced with a 5-cm (2-in) angle iron frame. This provides a 1.28-m^3 (45-ft^3) total floodable volume. Two doors, located at different heights on opposing walls, allow access to the box once it is sealed. The doors are equipped with 4 compression latches and a rubber seal to ensure an airtight seal. The rest of the openings in the box are located on the other two walls. Ventilation is accomplished by an air inlet valve located near the bottom of the enclosure and an outlet valve located on the opposite wall and near the enclosure top. Both of these valves are controlled by solenoids. Three additional openings allow for 0.64-cm-dia (¼-in) Swagelok™ bulkhead fittings, which can be used for gas sampling. Fires are located on the enclosure floor on a 7.5-cm (3-in.) riser. Surrounding the fire is a metal baffle, which measures 38x38x20.3–cm^3 (15x15x8in^3), that is used to reduce turbulence around the fire and eliminate a possible "blow-out" of the fire. A complete schematic of the box is seen in Figures 1a and 1b.

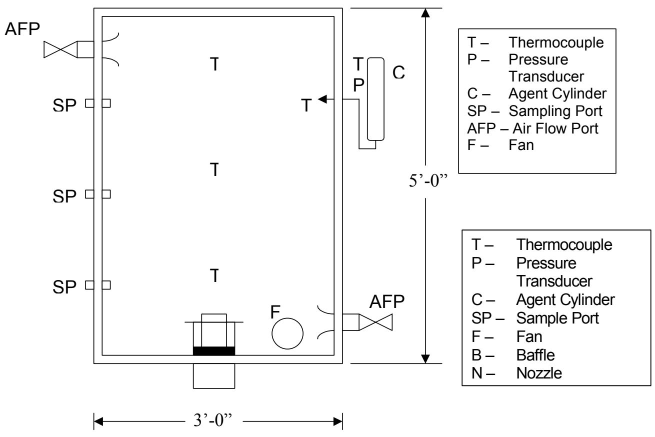


Figure 1a. Side View

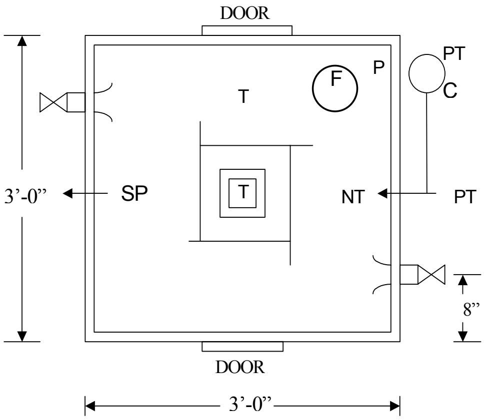


Figure 1b. Top View

Instrumentation

The box is equipped with 5 Omega™ Type K stainless-steel thermocouples. A thermocouple tree, consisting of three thermocouples evenly spaced in the vertical direction, is orientated directly over the fire. The two other thermocouples are used to measure temperatures around the nozzle during discharge, one is located in the discharge stream 2.5 cm (1 in) from the nozzle and the other is located inside the piping immediately before the nozzle.

Two Omega™ PX-102 sealed gauge pressure transducers with a working range of 0 to 344 kPa (0 to 500 psi) measure pressure in the cylinder and at the nozzle. Data are collected by an Omega™ DaqBook 100 with one Omega™ DBK 19 card for pressure transducer data and one Omega™ DBK 13 card for thermocouple data. The data collection system is run by an IBM™ ThinkPad™ 600E utilizing LabTech Notebook™ v 10.02 software.

Discharge Apparatus
Agent is stored in a 3.8-l (1-gal.) Whitey™ stainless-steel cylinder fitted with a valve at the base. The cylinder is connected to the nozzle by a simple piping network of 0.64-cm-dia (¼ in) pipe bolted to the exterior of the box, with a ball valve for discharge. The discharge nozzle is located on a side wall, centrally in the horizontal direction, on the upper quarter point in the vertical direction.

Agent Concentration Calculations
Two agent concentrations were chosen: cup burner and cup burner + 20%. In accordance with NFPA 2001, the initial total volumetric agent concentration was determined as the cup-burner minimum extinguishing concentration for heptane, as established by a recognized testing lab. An increased agent concentration was based on the minimum heptane cup-burner value plus a 20% safety factor. Agent mass required to produce the desired agent concentrations in the box were calculated as follows:

$$W = \frac{V}{s}\left(\frac{C}{100 - C}\right)$$

where, W is the mass of the agent in lb (kg), V is the enclosure volume in ft^3 (m^3), C is the agent design concentration (volume percent), and s is the agent specific volume (m^3/kg) at 1 atm. and ambient temperature [3].

Discharge Time
Discharge times of 3 s, 9 s, and 25+ s were chosen to compare with previous testing done [2] [6]. The discharge time is controlled by the flow rate (orifice size) of the discharge nozzle. Initial testing was conducted to determine which nozzles were needed to produce the desired discharge time, the results of those tests are presented in Table 1.

Table 1 Nozzle Discharge Times

	Agent Discharge Time		
Agent Concentration	3 Seconds	9 Seconds	20+ Seconds
Cup Burner (4.9%)	Spraying Systems; TP8020	Spraying Systems; TP8005	Spraying Systems; TP8001
Cup Burner + 20% (5.9%)	Spraying Systems; TP8020	Spraying Systems; TP8006	Bete Company; NF0300

The computer data acquisition allowed for the experimental determination of the discharge and extinguishing time for each test [5]. A typical pressure history is listed in Figure 2, below.

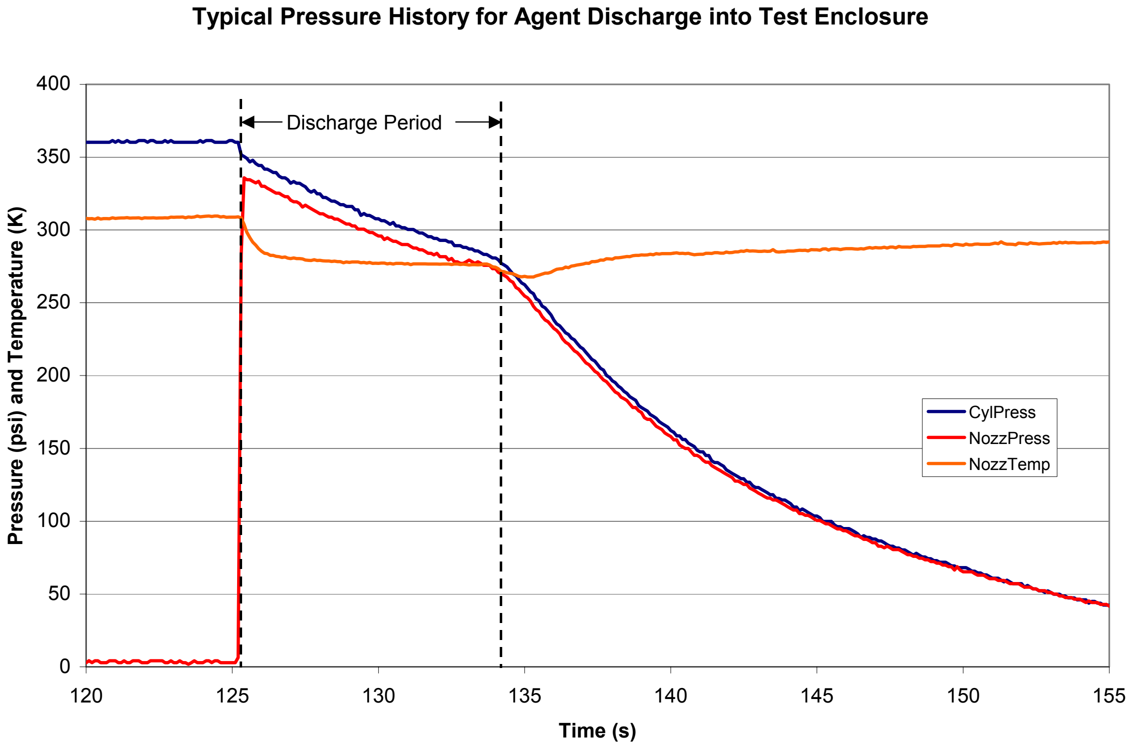


Figure 2

Fire Size

The four different fires sizes used in this study were chosen to compare with previous work [2] [6]. A cone calorimeter was used to determine the heat release rates of the four square pans, which measure, 2-cm (0.75-in), 4.5-cm (1.75-in), 7-cm (2.75-in), and 9.5-cm (3.75-in). The corresponding heat release rates for these pans when filled with heptane are, 0.1 kW, 0.6 kW, 1.7 kW, and 3.7 kW, respectively. For each test, the pans were filled to the top with fresh heptane immediately before the test. New heptane is used for each test to prevent agent build-up in the fuel.

FTIR Analysis Procedure and Setup
Two MIDAC I Series Model FTIR spectrometers were used for this field test. Each spectrometer was configured with a ZnSe beam splitter. A 1-cm, unheated stainless-steel gas cell utilizing ethylene as a diluent was used to acquire L-15566 concentration data. TDP concentrations, which are orders of magnitude less than L-15566 concentrations, were acquired using a 10-cm, unheated, stainless steel gas cell. The spectrometers had an ultimate resolution of 0.5 cm-1 apodized, and were coupled with 110V gas sampling pumps and portable computers for data acquisition.

The extractive gas sampling system used for the enclosure testing consisted of approximately 3-m of 0.64-cm-dia PTFE tubing leading into the gas cells. Each spectrometer and its sampling system were operated independently. TDP samples were drawn from the box through a 3-m-long, 0.64-cm-dia PTFE sampling line into the spectrometers. Samples were continuously pumped through the sample line and the gas cells at a flow rate of 1 and 2 lpm for the 1-cm and 10-cm gas cells, respectively. Flows were verified on site using a Dry Cal™ flow- meter. Three, 2.5-min spectra were taken for every test. The maximum HF concentration was determined by taking the greatest of the 3 spectra.

Test Procedure
Immediately before each test begins the calibrated heptane pan is filled to the top with heptane. The test begins when the fuel is ignited, at which time the access door is sealed and the FTIR machines are turned on. The 60-s pre-burn occurs with both the box inlet and outlet valves open, minimizing combustion product buildup and oxygen depletion. The valves are then closed, and 5 seconds later the agent is discharged. After extinguishment, the fan inside the enclosure is turned on to thoroughly mix the enclosure volume. The box remains sealed during the FTIR analysis cycle.

Results

The maximum HF concentration is determined through FTIR analysis. Figure 3 presents results for class B testing. The data are linearly regressed for comparison purposes. HF production is a monotonically increasing function of fire size. It is also seen that there is a relationship between the agent exposure time to the fire (i.e. discharge time) and the HF production.

L-15566 is also useful in extinguishing class A fires. As can be seen in Figure 4, the HF production from the class A fires is lower than for Class B fires. This is consistent with previous work and shows that heptane was a good choice for a “worst-case” scenario for HF production [6].

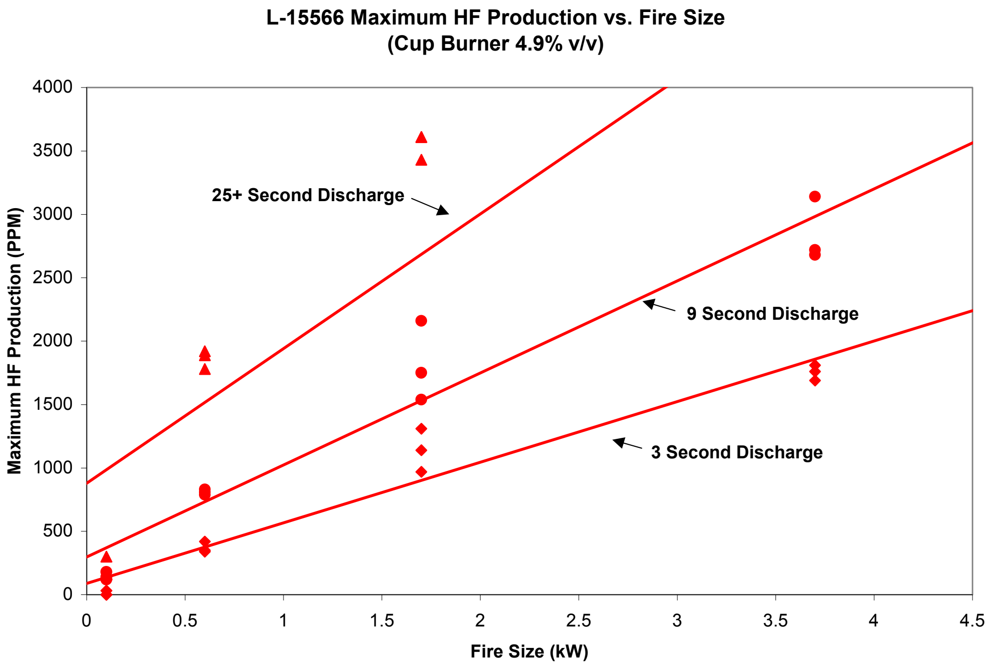


Figure 3

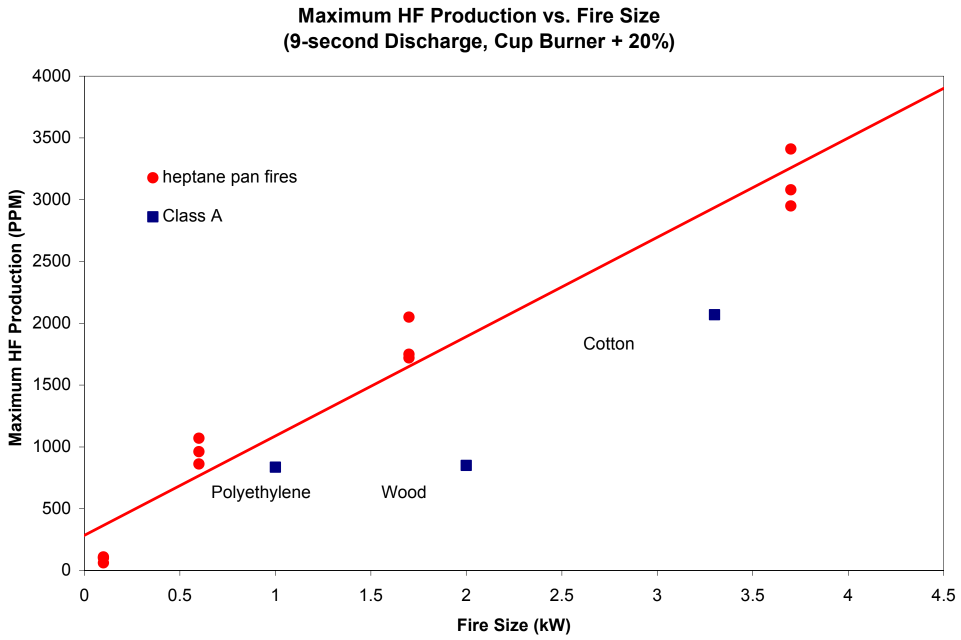


Figure 4

Figure 5 shows a comparison of the maximum HF production for various agents resulting from exposure to a fire. The fire sizes are normalized to allow the comparison of TDP irrespective of test compartment size. In terms of thermal decomposition production, L-15566 is directly comparable to other commercially available halon alternatives [4].

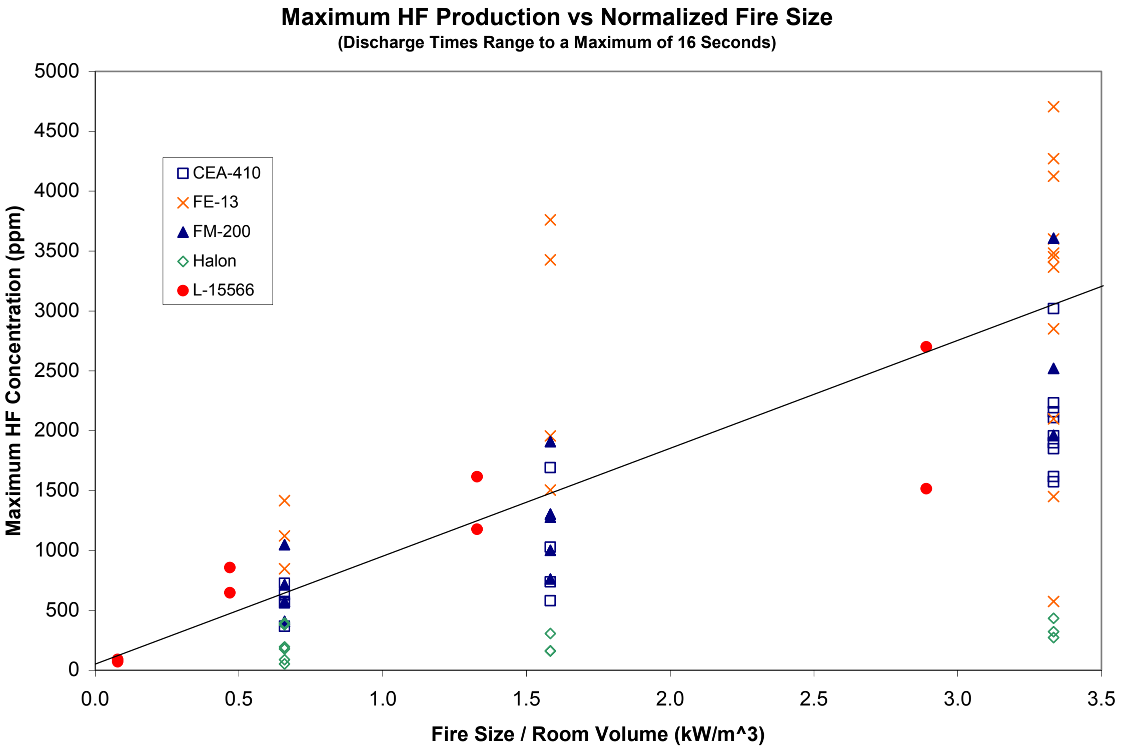


Figure 5. Comparision of TDP for halon alternatives.
(Peatross *et al.*[4] plus L-15566 data)

Discussion and Conclusion

The tests in this report are representative of fire conditions in real hazard scenarios. For example, the maximum fire size tested in this study is 3.7 kW, similar to the typical fire size for a circuit board, which is on the order of 3 to 5 kW according to industry experts. Figure 6 below can be used as a tool such that the TDP can actually be predicted for a given room size. A system is then engineered to limit TDP below hazardous levels through effective design.

The importance of effective design is indicated by studies examining the effects of TDP exposure. One such study, conducted on animal subjects by Meldrum, sets the dangerous toxic load (DTL) at 12000 ppm-minutes. In other word, the DTL for a 30-minute HF exposure is 400 ppm [4]. Another study conducted by the Robens Institute found that the highest tolerable HF concentration for a 1 min human exposure was 120 ppm [7]. Figure 6 shows that when typical room sizes are considered, in most cases, L-15566 produces tolerable levels of TDP.

L-15566 showed comparable performance in TDP testing to currently commercially available halon alternatives. The tests conducted showed the ability to extinguish fires with a variety of different fuels under a wide range of conditions. Note that small-scale TDP testing only provides a means for comparing performance; full-scale demonstrations should be conducted to validate small-scale results.

Test results show a relationship between HF production and fire size as well as with discharge time and agent concentration. In all instances, a shorter exposure time to fire result in a lower TDP generation. The emphasis for system design should therefore be on early fire detection and rapid discharge.

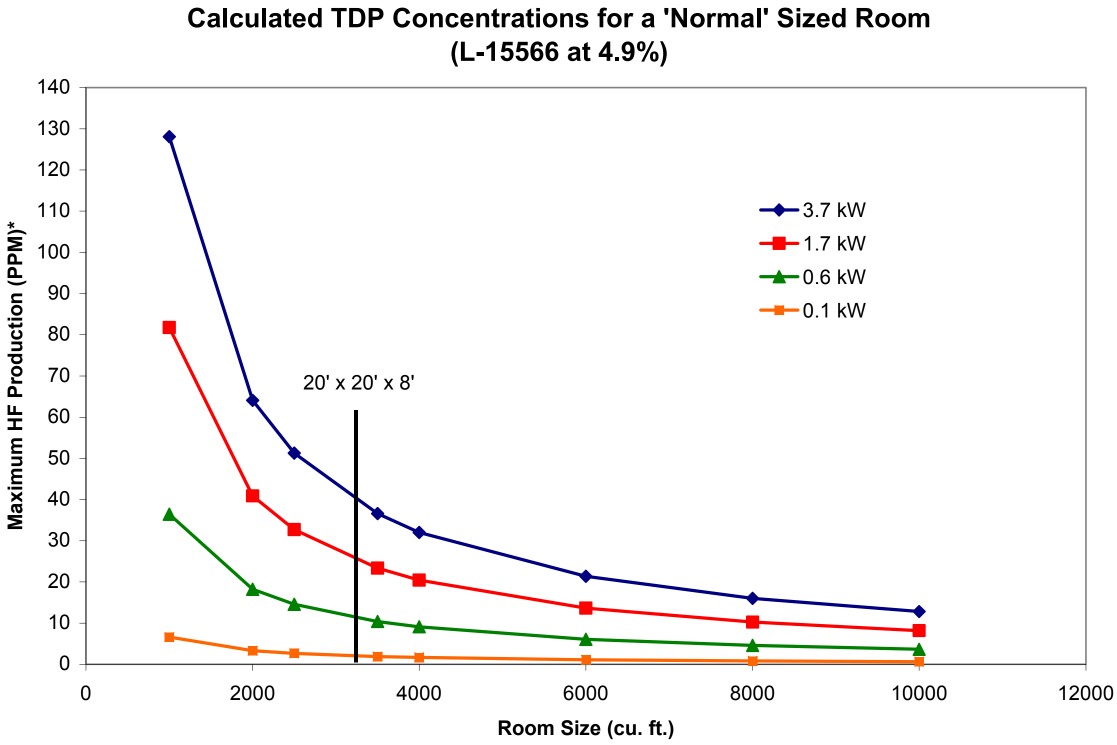


Figure 6

References

[1] P.J. DiNenno, E.W. Forssell, M.J. Peatross, Michelle Maynard, "Evaluation of Alternative Agents for Halon 1301 in Total Flooding Fire Suppression Systems – Thermal Decomposition Product Testing –" Halon Options Technical Working Conference Proceedings, Albuquerque, NM, 1993.

[2] Brockway, J, "Recent Findings on Thermal Decomposition Products of Clean Extinguishing Agents," NFPA 2001 Technical Committee on Alternative Protection Options to Halon, Meeting Minutes, page H-5, Ft. Lauderdale, FL, 19-22 September, 1994.

[3] NFPA 2001, *Standard for Clean Agent Fire Extinguishing Systems,* 2000 Edition.

[4] M.J. Peatross, E.W. Forssell, “A Comparison of Thermal Decomposition Product Testing of Halon 1301 Alternative Agents,” Halon Options Technical Working Conference Proceedings, Albuquerque, NM, 1996.

[5] The SFPE Handbook of Fire Protection Engineering, 2nd Edition.

[6] M.J. Ferreira, C.P. Hanauska, M.T. Pike, “Thermal Decomposition Product Results Utilizing PFC-410 (3M Brand PFC-410 Clean Extinguishing Agent),” Halon Options Technical Working Conference Proceedings, Albuquerque, NM, 1992.

[7] A.H. Mann, “Possible Health Risks From Exposure to Hydrogen Fluoride Generated from the Use of Fluorinated-Containing Fire Extinguishing Agents,” prepared for 3M by the Robens Institute, University of Surrey, Guildford, Surrey, United Kingdom, 1996

[8] P.E. Rivers, “Advancement in Sustainable Fire Protection Development C6 F-ketone: A Novel New Halon Replacement Alternative to HFCs and PFCs,” Submitted to Halon Options Technical Working Conference Proceedings, Albuquerque, NM, 2001.