SCREENING TESTS FOR ALTERNATIVE SUPPRESSANTS FOR IN-FLIGHT AIRCRAFT FIRES

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1. THE NEED FOR SCREENING TESTS

A primary component of the Next Generation Fire Suppression Technology Program (NGP) was the examination of the "world" of chemistry, seeking to identify chemicals that merited examination under practical fire suppression conditions or to enable a finding that no previously unidentified such chemicals existed. Performing this survey required a protocol for rapid and inexpensive screening of literally thousands of chemicals to identify those relatively few agents worthy of further examination as alternative fire suppressants.

There are multiple, critical chemical properties whose beneficial values promoted the widespread use of halon 1301 (CF_3Br) and which would affect consideration of alternative fire suppressants. These are fire suppression efficiency, quenching of flame re-ignition, ozone depletion potential (ODP), global warming potential (GWP), atmospheric lifetime, suppressant residue, electrical conductivity, corrosivity to metals, compatibility with polymeric materials, stability under long-term storage, toxicity of the chemical and its combustion and decomposition products, and speed of dispersion. Estimation of these values needed to be obtained using minimal mass of the chemicals for cost and toxicity reasons.

A testing hierarchy was needed to ensure that the most unique chemicals and the properties that were deemed most important and used the least chemical were determined first. Figures of merit for each property and a testing/estimating sequence and target values were also needed. The NGP built on prior methods used to screen chemicals[1], an NGP-organized workshop on agent compatibility with people, materials and the environment[2], and other formal and informal procedures.

2. GENERAL APPROACH

For a single candidate suppressant, performing a full battery of screening tests for the 12 properties listed above could require about 4 moles of chemical, about 8 days, and $15,000.[1] Thus, the first order of business was to identify which of the 12 properties should be the subjects for initial screening. This decision was based on the properties deemed most important for a successful chemical, easiest to determine, and most likely to disqualify a chemical. A second task was to identify efficient and reasonably accurate screening tests, recognizing that these would not necessarily be the tests used in the final acceptance of an agent. The selection was based on ease of operation for these types of chemicals, the extent of prior data available, the amount of chemical required, and the relevance of the figure(s) of merit to the NGP applications. Existing methods were adapted or new methods were developed to meet anticipated needs. The third task was to set an order of screening tests to perform. As will be seen below, not all of the screening tests were routinely used.

For each property to be screened, a three-step process was followed:

1. Determine whether there was a value in the published literature.

2. Estimate the value of the property from the values for analogous compounds. If available, make use of quantitative structure-activity relationships (QSARs).

3. Perform the selected screening test.

The expanse of organic and inorganic chemistry was sorted into chemical families. Each family was characterized by one or more chemical features, e.g., the presence of a carbon-carbon double bond or a bromine atom. Since a family might include hundreds of individual chemicals, a small number of most likely prospects were identified that had desirable values of the screening properties, determined using the first two of the steps above. Any laboratory tests were then performed as described in the remainder of this paper.

3. AGENT PROPERTIES TO BE SCREENED

The following properties were identified as most affecting the desirability of a chemical compound as a halon 1301 alternative:

- Fire suppression efficiency. The target was a fire suppression efficiency better than HFC-125 and preferably comparable to that of halon 1301.

- Atmospheric lifetime. The NGP aimed for lifetime estimates of the order of one month. Halon 1301 has an estimated atmospheric lifetime of 65 years.[3]

- Effectiveness of low-temperature dispersion. Thermodynamic calculations showed that a typical suppressant chemical will have an equilibrium concentration of at least 5 volume % at -40 °C if its boiling point is below 20 °C.

- Low toxicity. The criterion was the suppressing concentration should be lower than the lowest observed acute exposure level (LOAEL) for inducing cardiac arrhythmia.

These properties are not entirely independent. For example, the molecules in fluids with low boiling points are generally small, i.e., composed of few atoms. Some of the molecular features that lead to short atmospheric lifetime, such as a carbon-carbon double bond, require more atoms, which will increase the boiling point. The presence of atoms that provide efficient flame extinguishment, such as a bromine atom, may increase toxicity.

4. FIRE SUPPRESSION EFFICIENCY SCREENING

4.1 Estimation of Values

The first step in obtaining an approximate value for the concentration of a chemical compound needed to extinguish a flame was based on the known efficiency of analogous compounds. In general, candidate compounds belonged to one of three categories:

- Physically active molecules. Pitts's thorough study of these chemicals became the basis for assessing candidates of this type.[4]

- Reactive molecules. There are some atoms, e.g., F, that can be extracted from the suppressant molecule by a hydrogen atom from the flame, but which play no further role

in the quenching of the flame. There were flame extinguishment data for some fluorocarbons and hydrofluorocarbons.

- Catalytic molecules. These contained Br, I, P, and/or some metal atoms. NGP research and testing refined this list as the Program evolved.

4.2 Cup Burner

The most commonly used apparatus for examining fire suppressant chemicals is the cup burner, and it was the workhorse of this Program. The NGP used the NMERI cup burner[5] with n-heptane as the fuel. An assessment consumed ≈0.03 moles of the chemical if the extinguishing concentration was about 5 volume %.

A volatile chemical was pre-mixed in air and flowed into the chimney. For low volatility chemicals (boiling point such that the equilibrium concentration in air was near or below the extinguishing concentration), a metered flow of agent aerosol (from a nebulizer) was carried by a metered flow of air into a heated glass column and fully evaporated.[5] The cup burner chimney was heated to eliminate condensation of the agent on the glass surface. (See Figure 1.)
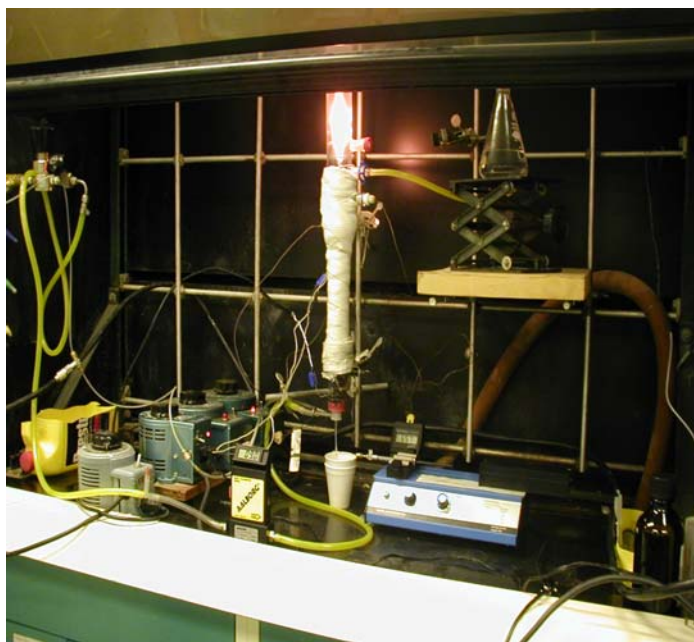
Figure 1. Heated Cup Burner for Appraising High-boiling Flame Suppressants.

Using these approaches, the apparatus was usable to address compounds with boiling points from at least -57 °C (halon 1301) to 130 °C. In some cases, only a very small mass of sample could be obtained. For these, the value was estimated, and a single test was performed to establish an upper bound.

4.3 Dispersed Liquid Agent Fire Suppression Screen (DLAFSS)

4.3.1 Need for a Liquid Agent Screen

Fluid suppressants, stored as liquids under pressure, dispense as both vapor and droplets. When they reach the flame zone, the droplets absorb additional heat, cooling the flame as they vaporize. This heat of vaporization can be a significant contribution to the agent's flame

suppression efficiency. The cup burner, dispensing only gases, does not capture this additional benefit. For the NGP, Yang and co-workers designed, constructed, and demonstrated an apparatus that can perform the screening of liquid agents in a well-controlled setting.[6]

4.3.2 General Description

The apparatus consists of:

- a burner that generates a flame whose properties make it appropriate for examining liquid aerosol suppressants and whose extinguishment is readily observed,

- a wind tunnel that produces a flow field in which the droplets are transported to the flame in a well characterized manner, and

- a liquid droplet generator that generates small amounts of liquid aerosol agent of controlled and known dimension.

The device can also be used to screen gaseous fire suppressants.

The burner is a sintered stainless steel cylinder, 1.58 cm in diameter and 3.18 cm long, of the type devised by Tsuji.[7] Burners like this have been extensively used to study flame structure and flame extinction using inert gases[8], halons[9], and powders.[9] Propane, which is a moderately sooting fuel, is ejected uniformly from the cylinder surface. The counterflow flame is laminar, two-dimensional, and very stable. The fuel and the oxidizer flows can be independently adjusted. The flame is easily observed, and the blow-off limit (abrupt transition from an enveloped flame, Figure 2a, to a wake flame, Figure 2b) can be ascertained with ease and high reproducibility.

(a)   (b)
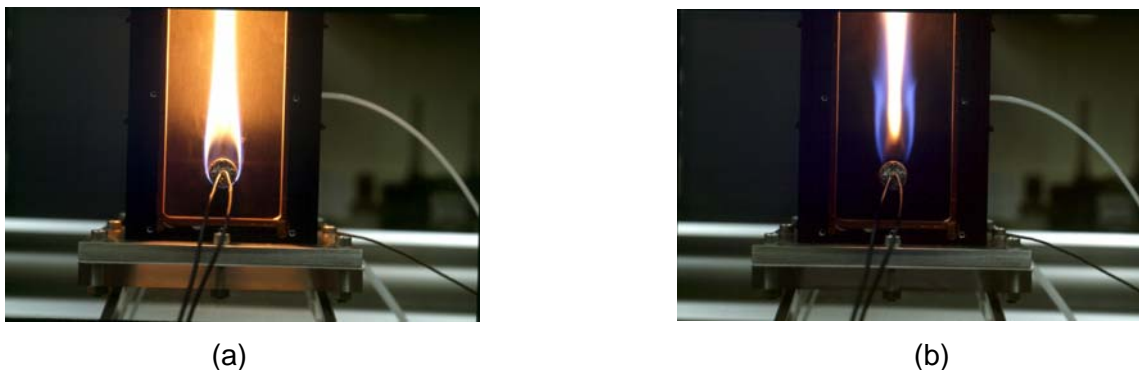
Figure 2. An Enveloped Flame (a) and a Wake Flame (b).

The liquid droplets were generated using a commercially available small glass nebulizer of the type used in inductively-coupled plasma atomic emission spectroscopy. The droplet size distribution was measured using a two-component Phase Doppler Particle Analyzer with a Doppler Signal Analyzer. For a range of fluids, the Sauter mean diameter was 20 µm to 30 µm, and about 90 % of the droplets fell within ±5 µm of the mean value.

Suppressant performance was determined by increasing the air flow at a fixed liquid agent application rate until blow-off occurred. Table 1 lists some values for aqueous solutions.

Water and the aqueous agents studied here were found to be more effective than CF_3Br, compared to the propane cup burner value (mass fraction of 0.17 for CF_3Br).[6] The

computational study by Lentati and Chelliah[10] also demonstrated that 20 µm water droplets are more effective at extinguishing an opposed-flow methane diffusion flame than CF_3Br.

Table 1. Liquid Agent Effectiveness Relative to Water.

| Agent	*Nominal* agent mass %	m_{water}/m_{agent}
Water	2.6	1.0
60 % potassium acetate	0.8	4.0
30 % sodium iodide	1.3	2.0
Skim milk	1.6	1.6
30 % potassium lactate	1.2	2.0
60 % potassium lactate	0.6	4.0

4.4 Transient Application, Recirculating Pool Fire Apparatus (TARPF)

4.4.1 Genesis of the Apparatus

Both the cup burner and the DLAFSS determine the minimum concentration of agent needed to suppress a flame by increasing the agent flow slowly until a critical volume fraction is achieved in the oxidizer stream and flame extinction is observed. In practice, however, agents designed to replace CF_3Br are discharged rapidly. The TARPF is a robust and repeatable means to evaluate the effectiveness of different formulations at these fast application rates. It was derived from prior work by Hirst and Sutton[11], Hamins and coworkers[12], Takahashi and coworkers[13], and Grosshandler and coworkers.[14]

As shown in figure 3, the TARPF is a small wind tunnel in which is placed a propane diffusion burner. A step obstruction just upstream of the burner also enables investigation of re-ignition scenarios. Re-ignition was effected by directing a stream of JP-8 droplets onto the heated obstruction after flame suppression. Gaseous agents were metered from pressurized vessels. Aerosol agents were dispensed using a hollow-cone atomizer. When positioned at upstream locations, the spray appeared to fill the entire air passage cross section. For a solid propellant gas generator (SPGG), the injected mass and injection time interval were controlled by discharging the SPGG into a "pre-chamber," from which a selected fraction entered the wind tunnel. (The SPGG discharge time was consistently 20 ms ± 1 ms, less than one-third the shortest N_2 or CF_3Br injection interval.) This hardware allowed standard size gas generators (which contain significantly more material than is required for suppression in the TARPF) to be evaluated by repeating the test sequence and incrementally increasing the fraction of SPGG effluent allowed to flow into the TARPF air stream. For the results included below, the hybrid generator consisted of 20 g of compressed argon and 0.7 g of a solid propellant, which at equilibrium converts to KCl (s), H_2O, N_2 and a small amount of CO_2.[15]

Extensive experiments and computer simulations were conducted to determine the effects of the experimental parameters on the mass of suppressant needed for extinguishment by CF_3Br and N_2. The effect of the baffle height was negligible. An air velocity difference of a factor of 4.5 had a 30 % effect. Up to about 880 °C, the temperature of the re-ignition surface had no effect. Above 890 °C, reignition always occurred regardless of the mass of N_2 added. The same effect was found for CF_3Br, but at a dividing temperature that was about 50 °C higher.
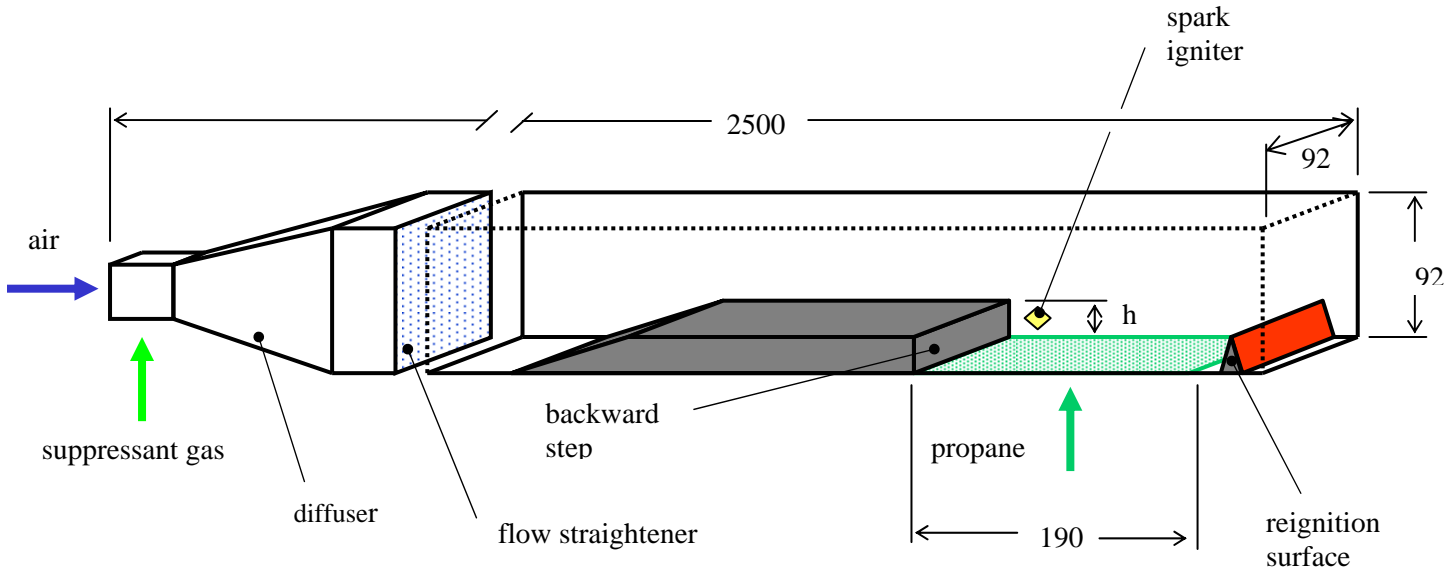
Figure 3. Schematic of Step-stabilized Pool Fire Apparatus. Dimensions in mm.

The effectiveness of the gaseous agents was compared to that of the SPGG through use of a simple agent mixing model to describe the suppression phenomena.[16,12] As shown in Figure 4, the minimum volume fraction of agent for suppression, normalized by the cup burner value, correlates with $[1 - \exp(-\Delta t/\tau)]^{-1}$, where Δt is the injection time interval and τ characterizes the mixing time behind the obstacle in the flow. Thus, for the first time, both compressed and solid-propellant generated gases can be compared side by side, and the effect on performance of various SPGG designs can be unambiguously discriminated.
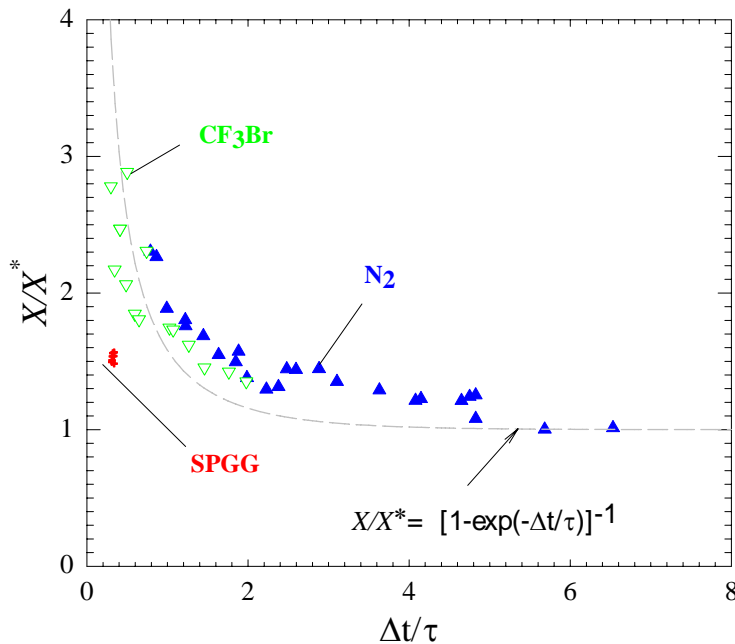
Figure 4. Normalized Mole Fraction as a Function of Non-dimensional Injection Interval.

4.5 Summary of Fire Suppression Efficiency Screens

Because of the expected diversity of physical and chemical properties of candidate fire suppressants, the NGP developed three apparatus for screening fire suppression efficiency. The cup burner was the workhorse for examination of the chemicals. The DLAFSS was available for assessing those chemicals with high boiling points and high heats of vaporization. The TARPF was available for appraising those chemicals and delivery systems for which it was expected that burst delivery would significant modify the interpretation of data obtained using the cup burner. The three different types of laboratory diffusion flames produced similar relative values for inert suppressants. The DLAFSS produces the most conservative results.

5. ATMOSPHERIC LIFETIME SCREENING

5.1 Factors Affecting Atmospheric Harm

The NGP screening protocol had its roots in the 1990 development of screening procedures for ODP and GWP.[1] It was updated and refined as the result of a 1997 NGP workshop[2] and constraints on the agent chemistry resulting from the other properties being screened. The principles that determined the NGP screening protocol were:

- Both ODP and GWP are directly related to the lifetime of a test substance in the atmosphere. The greater the persistence of a chemical, particularly within the troposphere, the greater the potential for adverse effects on the global environment.

- The tropospheric lifetime of a chemical is largely determined by the reactivity with respect to OH radicals and absorption of in the VIS-UV region of the solar spectrum.

- ODP is also directly related to the presence of certain atoms in a compound's chemical formula. Simple atmospheric models give results adequate for use in developing screening tests.[17] Halon 1301 has an estimated ODP value of about 13.

- GWP is directly related to the capability of a test compound to absorb radiation in the region of the "atmospheric window" between 7 μm and 13 μm. Test compounds which are weak absorbers in this region are unimportant with regard to global warming.

5.2 The Screening Protocol

Estimation of the atmospheric impact of candidate fire suppressant considered several properties. The following is the sequence that was typically followed:

- A small molecule that did not contain Cl, Br, I or N was generally "passed."

- For a larger molecule or one that contained one or more of the four atoms, but contained a feature that bespoke a high rate of reactivity in the troposphere, its reaction rate with OH was estimated using structure-activity relationships.[18] The potential of the molecule to absorb VIS-UV radiation was also estimated.

- The reaction rate was measured for a molecule that appeared well in the prior step and in the screens for fire suppression effectiveness and volatility. The method of choice for this determination is the flash-photolysis resonance fluorescence technique.[19,20,21]

Under the NGP, Huie and coworkers developed a refined method to predict atmospheric lifetimes for new classes of halogenated compounds.[22,23,24] At the heart of the method is a computational

scheme for OH reaction rate constants for those compounds for which hydrogen abstraction would be expected to be the dominant reaction mechanism. Combining calculations with new measurements of ultraviolet absorption spectra, they then estimated atmospheric lifetimes of a set of bromine-containing compounds for which no data had been reported. Table 2 shows some results of these calculations and measurements.

Table 2. Atmospheric Lifetimes (years), from Theory and from OH Reactivity Measurements, for Selected Molecules.

	Atmospheric Lifetime (theory)	Atmospheric Lifetime (from meas.)	Theory/Meas.
CH_2Br_2	0.1	0.25	0.5
CH_3F	6.4	2.9	2.2
CH_3Cl	1.5	1.5	1.0
CH_3Br	2.5	2.0	1.3
CH_2F_2	3.6	5.6	0.6
CH_2FCl	1.7	1.4	1.2
CH_2Cl_2	0.43	0.46	0.9
CH_2ClBr	0.54	0.49	1.1
CH_2Br_2	0.57	0.42	1.4
CHF_3	400	263	1.5
CHF_2Cl	13.2	12.7	1.0
CHF_2Br	6.0	5.6	1.1
$CHFCl_2$	1.2	2.1	0.6
$CHCl_3$	0.15	0.51	0.3
CH_2FBr	1.9	Unknown	
$CHFBr_2$	0.49	Unknown	
$CHFClBr$	0.73	Unknown	
$CHCl_2Br$	0.16	Unknown	
$CHClBr_2$	0.12	Unknown	

6. VOLATILITY SCREEN

For a chemical to be successful as a total flooding agent, it must evaporate and fill a space to the desired concentration within the time available for extinguishment. Estimation of this capability entails two properties: (1) the equilibrium vapor pressure at the ambient temperature in the fire compartment and (2) the rate of evaporation to achieve that vapor pressure.

The Clausius-Clapeyron equation, Equation (1), was used to estimate whether a given compound could achieve the required extinguishment concentration upon discharge. T_b is the boiling point, in Kelvins, at a pressure, P_b. T_2 and p_2 are the ambient temperature and pressure, respectively. Trouton's constant, t_c was set at the typical value of 88 J/K-mol.

$$p_2 = P_b 10^{**}\{(0.052)\, t_c\, [1-(T_b/T_2)]\} \tag{1}$$

Figure 5 shows the maximum boiling point of a compound that can give a desired concentration of the agent at 101 kPa, 1 atm.

The estimation of evaporation rates is much more difficult. In general, the NGP used the finding of Yang and Pitts that if the agent boiling point was below the ambient temperature, the agent would flash evaporate. If the boiling point were higher than the ambient temperature, then for

efficient dispersion, the agent had to be atomized efficiently. Otherwise it would settle to the bottom of the engine nacelle or dry bay and evaporate slowly.

Thus, the NGP utilized a compound's boiling point as the screen for volatility. This was generally obtainable from the literature or the supplier. For unknown boiling points, either a microscale technique[25] or an isoteniscope[26] was used.
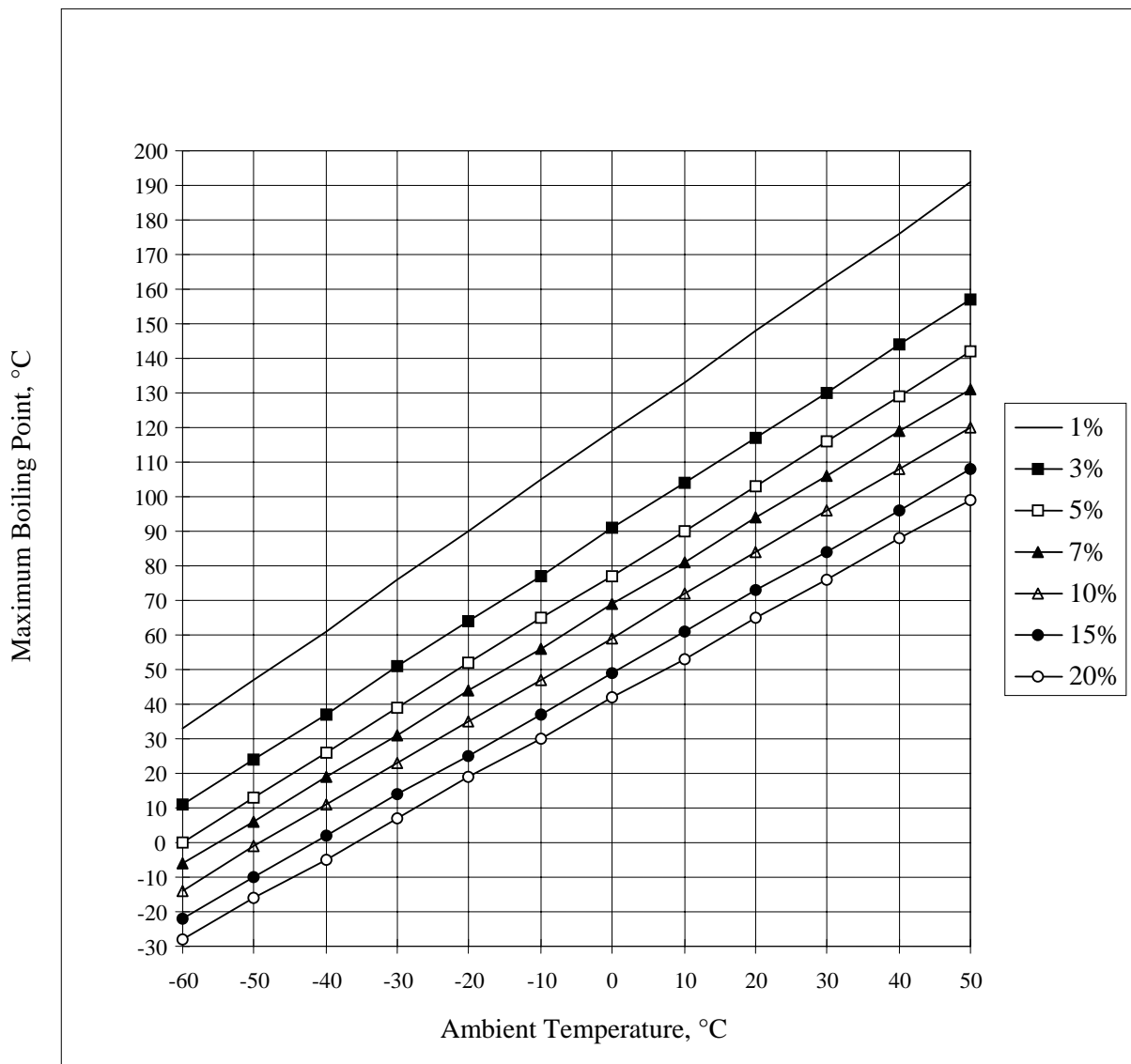

Figure 5. Estimated Maximum Boiling Points That Can Achieve Given Concentrations as Function of Ambient Temperature, Calculated for t_c = 88 J/K-mol.

7. TOXICITY SCREEN

7.1 Hazards and Regulation

There are a variety of acute toxic effects that can results from exposure to a fire suppressant chemical. These include sensory irritation, incapacitation, or even death. The NGP was concerned with the full range of such effects. Most of the candidate chemicals that were likely to

meet screening requirements for fire suppression efficiency and volatility were halocarbons. Thus, while the toxicity screening effort was formulated with the full breadth of possible chemicals in mind, there was a focus on halocarbons.

It has been recognized for decades that a principal toxic effect of halocarbon agents is cardiac sensitization.[27] This is the sudden onset of cardiac arrhythmias caused by a chemical sensitization of the heart to epinephrine (adrenaline). Under the EPA SNAP Program, cardiac sensitization values help define the use restrictions placed on a replacement chemical.

There are no regulatory testing guidelines for conducting a cardiac sensitization study. However, the procedure most often followed for evaluating exposure to agents that might potentially evoke a cardiac sensitization response is the cardiac sensitization test performed in beagle dogs.[28] The results of this test are expressed in terms of the LOAEL (lowest observed adverse effect level) and the NOAEL (no observed adverse effect level). LOAEL data obtained from this test are very conservative and very rarely have people died as a result of exposure to the halons.

7.2 Steps in the Screening Process

7.2.1 Use Published Values

There are multiples sources available, e.g., Chemical Abstracts, National Library of Medicine, NIOSH, EPA, Merck Index. While there often were data for the established compounds, such as HFCs and HCFCs, there were few data for the new candidate fire suppressants.

7.2.2 Derive Values from Quantitative Structure-activity Relationships (QSARs).

Skaggs et al.[29], Vinegar[30], and Grzyll et al.[31,32] have extracted some such toxicity trends.

7.2.3 Conduct Non-animal Tests

The NGP was unable to identify any established test of this type for estimating cardiac sensitivity to a compound. However, there is some evidence to support a relationship between the tendency of a chemical toward cardiac sensitization and its relative solubility in polar (e.g., water) and non-polar (e.g., octanol) liquids.[33,34,35] A compound would be characterize by its relative solubility in the two fluids, i.e., a partition coefficient, K_{OW}. Table 3 shows an approximate correlation between this ratio and the tendency of anesthesia agents, which are chemically similar to the halons, to cause cardiac arrhythmias in people.

Table 3. Partitioning (K_{OW}) and Arrhythmia Properties of Selected Anesthetics.[36,37]

Property	Halothane	Enflurane	Isoflurane	Desflurane	Sevoflurane
Oil-water Ratio[a]	220	120	170	19	55
Arrhythmia[b]	+++	+	+	~	~

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

[b] The symbols "+++," "+," and "~" reflect, in order, a decreasing tendency of the anesthetic to induce arrhythmias in human patients during anesthesia. The last of these indicates only a slight tendency.

Experimental determination of the octanol-water partition coefficient, K_{OW}, using reverse phase high pressure liquid chromatography is rapid and requires only a few mg of the compound.

Values of K_{OW} may also be estimated from the contributions of molecular fragment-based terms plus correction factors.[38] Different algorithms can give different results, so some experience is needed to select or develop an appropriate version for the particular chemicals under consideration. Table 4 shows some agreements and disparities between two methods and experimental data. It is probable that the use of calculated partition coefficient values to develop predictions of trends in LOAEL performance works best when only applied to narrowly defined groups of compounds.

Table 4. Comparison of Calculated and Measured Values of Log K_{OW} of Selected Halocarbons

Compound	Log K_{OW} * (calculated)	Log K_{OW} ** (calculated)	Log K_{OW} (measured)	LOAEL (volume %)
CF_3Br (halon 1301)	1.83	1.59	1.86	7.4
$CHBrF_2$	1.85	0.98	NA	3.9
$CH_2=CBrCF_3$	2.14	2.49	NA	1.0
CF_2ClBr (halon 1211)	2.17	1.90	2.1	1.0
CF_3I	2.22	2.01	NA	0.4
C_3HF_7	2.35			10.5

* Molinspiration Cheminformatics algorithm (http://www.molinspiration.com)
** Syracuse Research Corporation algorithm (http://esc.syrres.com)

A wide range of *in vitro* methods has been developed for specific toxic endpoints.[2] These methods expose a test chemical to organ preparations, isolated tissue preparations, single cell suspensions, or tissue culture systems. The preparation is determined by the mechanism of effect of the chemical on humans. Caution should be exercised when utilizing *in vitro* techniques because many factors, such as absorption and transport processes, influence the toxicity of a chemical. Thus, it was not deemed wise to rule out further consideration of a candidate based exclusively on the results of a single *in vitro* test. Of more importance, the NGP could find no *in vitro* method that was established as predictive of the standard dog exposure test.

7.2.4 Conduct Live Animal Tests

Performing the dog exposure tests was not feasible for the large number of chemicals under consideration by the NGP. This was because the testing takes about two months, requires about 30 moles of chemical, and costs nearly $100 k. The NGP conducted an extensive search for methods that would predict the LOAEL and NOAEL values to within 2 mole %. However, no accurate screening procedure existed to obviate the need for the standard dog exposure test. In fact, such testing of two otherwise promising chemicals generated negative results.

A protocol containing a more comprehensive set of toxicity tests was developed by Dodd and co-workers.[39] This included tests for genotoxicity, subchronic toxicity, carcinogenicity, development and reproductive toxicity, among others. However, the NGP identified no compounds that progressed to that level of testing.

7.3 Time-dependence of Toxic Hazard

Should a suppression system discharge into an occupied area, people could be exposed to a high concentration of the agent for a relatively short time. There is a time lag in the concentration of

the agent at the body site where the toxic effect will occur. Then, as the suppressant dissipates, the occupant breathes a lower concentration. Thus, the eventual dose (the integral of local agent concentration and time) reaching the sensitive site can be far lower than the exposure (the integral of the environmental concentration overt the exposure time).

Under sponsorship of the EPA and the NGP, a team of toxicologists at the Air Force Research Laboratory modified a physiologically-based pharmacokinetic (PBPK) model of a human to include time-dependent representation of the cardiovascular system and lungs that will allow simulation of the outcome of short-term exposures to fire suppressant chemicals. [40, ,41,42,43] This is an important improvement over commonly used PBPK models that use steady-state descriptions to describe uptake of chemical via the lung and subsequent transfer of chemical to arterial blood.

A PBPK model provides the quantitative link between a (possibly time-varying) exposure concentration and the blood levels of the chemical achieved following inhalation. The model requires a considerable amount of input data: cardiac sensitization LOAEL; arterial concentration measured after 5 min of exposure of beagles to the LOAEL concentration; partition coefficients of the chemical in blood, liver, fat, and muscle; metabolic constants, and human blood flows and tissue volumes.

Figure 6 shows the result of simulations of the concentration of halon 1301 in human blood during exposure to six different constant concentrations of the suppressant in air. The horizontal line at 25.7 mg/L represents the lowest arterial blood concentration measured at 5 min in a group of 6 dogs exposed to halon 1301 at the cardiac sensitization LOAEL of 7.5 %.
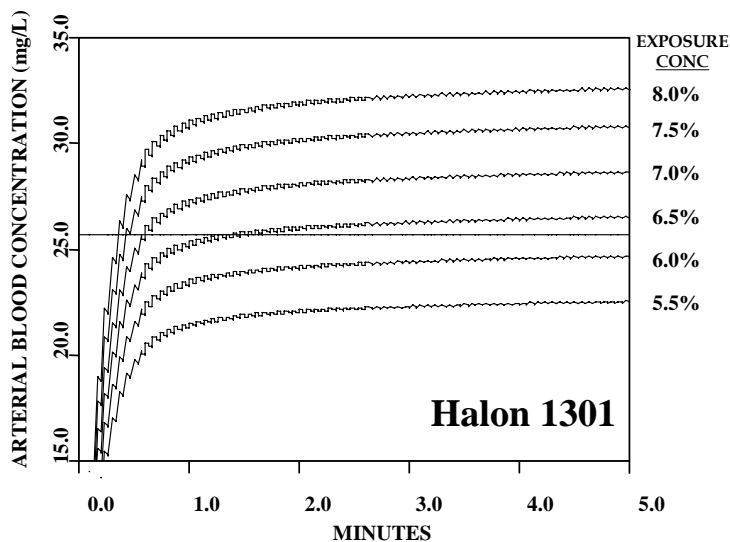
Figure 6. Simulations of Humans Exposed to Various Concentrations of Halon 1301.

A comparison can be made between the concentration for safe 5 min exposure and the recommended design concentration of agent for extinguishing a fire. As can be seen in Table 5, the safe 5 min exposure for halon 1301 occurs at 5.5 % which is 2.0 % below the LOAEL. The design concentration for fire extinguishment is 5 %.[44] Thus, the PBPK simulation suggests that it is not safe to stay for 5 min in a halon 1301 environment that will put out a fire. Halon 1301

has a long history of safe use, which points to the conservative nature of the cardiac sensitization endpoint, which ultimately determines the target arterial concentration, which in turn is used for determining safe exposure time.

The importance of this to approval of a fire suppressant is significant. The specifications for safe exposure design of halon 1301 and potential replacement chemicals for use as total flooding agents in a fire-fighting scenario do not take into consideration the pharmacokinetics of the agents and the relationship between the exposure concentration and the internal concentration actually associated with a cardiac event.

Table 5. Time for Safe Human Exposure at Stated Concentrations for Halon 1301

Halon 1301 Concentration (mole %)	Time (min)
5.5	5.00
6.0	5.00
6.5	1.33
7.0	0.59
7.5	0.42
8.0	0.35

The PBPK model thus can provide a defensible approach and appropriate tools for decision makers, who are tasked with balancing performance and personnel safety issues, to evaluate the acute toxicity potential of inhaled fire suppressants.

7.4 Limit Tests

The need to spend time and resources to obtain a once traditional "LC_{50} value" for a halon replacement candidate is discouraged in favor of a single limit test. The purpose of the limit test is to evaluate mammalian toxicity following a single dose or exposure of the halon replacement candidate. A traditional limit test involves exposing several rats to a single, conservative dose of chemical for a fixed period of time and determining whether this dose is lethal.[45] For gaseous chemicals, inhalation is the most important route of exposure, whereas for liquids, skin contact may be more important than inhalation. For volatile candidate fire suppressants, a typical exposure is to a concentration of 10 volume % for 15 minutes, both of which are likely in excess of the exposure of people were the chemical eventually used as a fire suppressant.

8 Application of Screen Tests

In practice, it was generally easy to eliminate candidate chemicals from further consideration based on the most basic screening procedures.

- The NGP relied most heavily on cup burner data and the presence of one or more chemically active atoms for estimating a chemical's fire suppression efficiency. Only compounds whose extinguishment concentration was measured or estimated to be below 5 mole % were considered further.

- Next, compounds whose boiling points were above 20 °C were eliminated from further consideration. For fluids with slightly higher boiling points, similar fluids were considered to see if there might be a lower boiling member of the chemical family.

- Third, a chemical continued under consideration if it had a feature that rendered it tropodegradable, i.e., likely to have a short atmospheric lifetime.

- Most of the compounds considered were of unknown toxicity, so in relatively few cases could a confident safe exposure value be assigned. For compounds that were successful in the first three properties, a limit test would be performed. Success there would lead to a dog exposure test. In practice, no animal tests were performed for agents for in-flight fire suppression.

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