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Next Generation Fire Suppression Technology Program FY 1999 Annual Report

Richard G. Gann

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FY1999 ANNUAL REPORT

Next Generation Fire Suppression Technology Program

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Richard G. Gann
Technical Program Manager
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I. INTRODUCTION

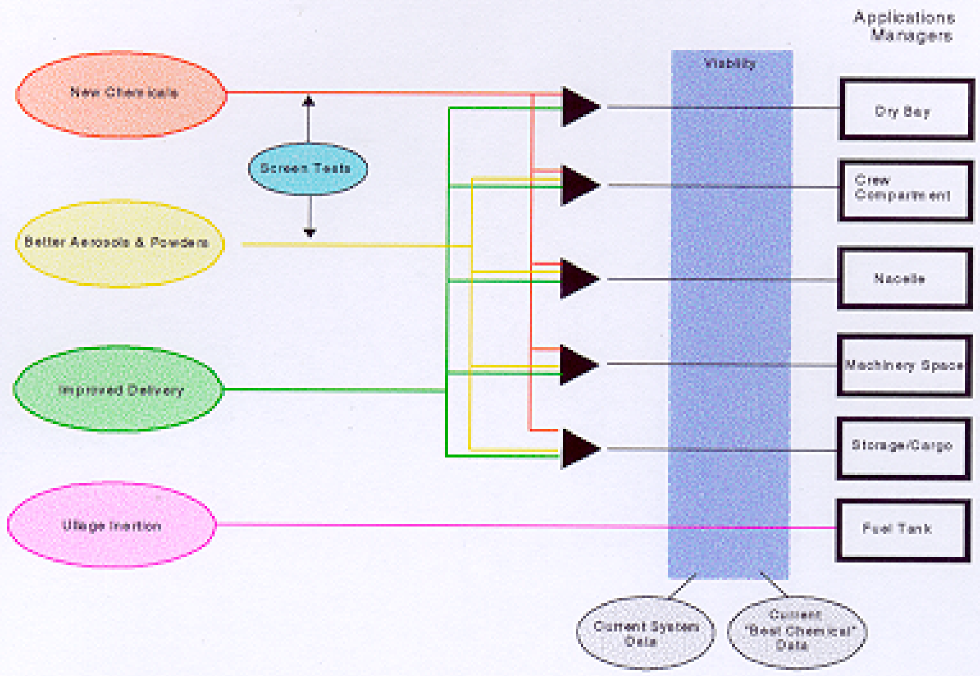
Halon 1301 (CF_3Br) has long been the choice for fire extinguishment in most weapon systems and mission-critical facilities. However, due to its high ozone-depletion potential, halon 1301 was banned from production as of January 1, 1994, under the Copenhagen Amendments to the Montreal Protocol on Substances that Deplete the Ozone Layer.

As part of its effort to eliminate its dependence on halon 1301, in FY1997 the Department of Defense (DoD) initiated its Next Generation Fire Suppression Technology Program (NGP). The goal of the 9-year, $46 million research program was to develop and demonstrate, by 2005, retrofitable, economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft, ships, land combat vehicles, and critical mission support facilities. The results are to be specifically applicable to fielded weapons systems. If successful, the NGP would eliminate DoD dependence on a substance no longer in national production, minimize any readiness impacts that could result if halon 1301 use restrictions were imposed in the future, and achieve these at greatly reduced cost.

Prior DoD efforts had identified viable, near-term halon alternatives for a wide variety of weapon system applications. These alternatives typically require weights and volumes that are double or triple that of halon 1301 for equivalent effectiveness. While they can be accommodated in new system designs, they pose a significant problem to existing weapon systems because of form, fit, and function constraints. Given the current extensions of in-service lives of fielded weapon systems, this problem could ultimately require DoD program managers to expend large amounts of funding and time for fire suppression system redesign and reconfiguration.

The potential fire locations for which alternatives to halon 1301 are sought include aircraft engine nacelles, dry bays, cargo bays, and fuel tanks; ground vehicle crew compartments; and shipboard machinery spaces and storage compartments. [Figure 1] These locations vary in size, shape and occupancy; the fuels are solids, vapors and liquids (pools and sprays); and the suppression times range from about 0.1 s to 100 s. The hazards to be avoided include harm to people, thermal damage, post-fire corrosion, loss of visibility, and overpressure. Successful candidates must thus do well in: fire suppression efficiency and reignition quenching, ODP, GWP, atmospheric lifetime, suppressant residue level, electrical conductivity, metals non-corrosivity and polymeric materials compatibility, long-term storage stability, low toxicity of the chemical and its combustion and decomposition products, speed of dispersion, safety and occupational health requirements. To be cost-effective, the suppressant and storage/delivery system must be of light weight and low volume, as well as compatible with the host designs of existing platforms.

Figure 1. NGP Research on Retrofitable Fire Suppression Technologies



The NGP has just completed its third year of research, having expended about 23 percent of the planned resources. Support from the NGP comes from DoD funding and cost sharing from the participating laboratories. To date, most of the DoD support has come from the Strategic Environmental Research and Development Program (SERDP), with additional support from the Army Tank and Automotive Command (TACOM).

The following Section highlights the new knowledge gained from the NGP research and the progress made towards the NGP Goal. Additional information on the strategy and status of the NGP can be found at the NGP web site: www.dtic.mil/ngp/.

II. TECHNICAL PROGRESS

A. NEW FLAME SUPPRESSION CHEMISTRY

The NGP is continuing the search for new chemicals that perform as well as CF_3Br, but without the environmental limitation. The research follows two directions: (a) learning more about how different chemicals effect suppression, then looking for optimal analogs and (b) identifying the best chemicals from the various families of chemicals. The principal desirable properties guiding the search are:

- Fire suppression efficiency at least comparable to halon 1301 and certainly higher than the HFCs.
- Short atmospheric lifetime (current preference of the order of a month), to keep ozone depletion, global warming and any future unidentified contamination issues to a minimum.
- Low toxicity relative to the concentration needed for suppression.
- Boiling point sufficiently low that for gaseous agents, an extinguishing concentration can be achieved within a specified time following discharge. An approximate upper limit is 80 °C, but slow evaporation may reduce this significantly for some chemicals.

Current NGP research has built on results from the prior years of the Program and findings of pre-NGP research to evolve a model for how fire suppressant additives quench flames. Flame propagation relies on fast reactions of the free radical pool (OH radicals and O and H atoms) with fuel molecules. In uninhibited flames, these three reactive species are in equilibrium with each other, but at concentrations well above equilibrium with their surroundings.

In the context of the NGP, flame suppressant additives can be viewed in three categories:

Halon-like suppressants. Globally, these suppress flames at about 3 percent by volume. The active species, such as a bromine atom, catalytically reduces the radical pool to a near-equilibrium level. The increased heat capacity from the additive reduces the flame temperature, further reducing the flame propagation reaction rates to the point where they can no longer sustain combustion. The chain length of the Br catalytic cycle has been estimated as about 7.

Super suppressants. These compounds contain a highly reactive entity, such as a metal or phosphorus atom. They are as much as two orders of magnitude more efficient than Br atoms at bringing the radical pool closer to equilibrium level, and thus are seen as highly efficient reducers of premixed *flame velocity*. However, a mass fraction similar to the halon-like chemicals is needed to reduce the flame temperature and thus the flame propagation kinetics to non-combustion-sustaining rates. The *extinguishing* concentrations thus appear to be only modestly lower than the halon-like chemicals, perhaps of the order of 1 percent.

Thermal (non-catalytic) suppressants. These chemicals operate mainly by absorbing flame heat into multiple sensible heat modes, *e.g.*, vibronic absorption and endothermic phase changes. Gaseous compounds have been identified that can increase the thermal bath to quenching levels as low as 6 percent by mass. Adding the heat of vaporization can reduce this to below 2 percent by mass.

Thus, it appears that all these categories contain chemicals that are comparable to halon 1301 in suppression efficiency. Conversely, it remains to be seen whether it is possible to effect flame suppression at levels well below the halon efficiency (without blowing the flame out). This discussion also suggests that there may be a non-linear relationship between the chemical (catalytic) and thermal contributions of a suppressant.

NGP research has produced new findings on several promising suppressant chemicals:

- Aqueous lactic acid had previously been identified as a particularly effective thermal agent due to its high heat of vaporization. Calculated boiling points and latent heats of vaporization for the full range of lactic acid fraction in water show that both are nonlinear functions of water mole fraction. This suggests that certain mixtures may be particularly effective at extracting heat from a flame zone.

- Last year, methoxy-nonafluorobutane (HFE-7100, $H_3COC_4F_9$) was shown to be an efficient thermally active suppressant. New calculations of critical point data and ideal gas heat capacities, along with manufacturer's values for boiling and freezing points, vapor pressure, and liquid density have been added to the computer program PROFISSY (Properties of Fire Suppressant Systems). These can be used to predict the agent storage and discharge properties when pressurized with nitrogen.

  Using the Dispersed Liquid Agent Screen (DLAS, see discussion of Screening Tests below), the extinguishing concentration for HFE-7100 was determined to be 0.12 mass fraction and 0.016 mole fraction. Unpublished cup burner values from the New Mexico Engineering Research Institute and a 3M patent are 0.36 and 0.061 for gaseous HFE-7100, respectively. Thus, there is a significant advantage in getting the ether aerosol to the flame zone. For reference, the propane cup burner mass and mole fraction values for halon 1301 are 0.17 and 0.04, respectively.

Calculated values of the maximum flame temperature at extinction were obtained as a function of strain rate for several thermal suppressants (nitrogen, carbon dioxide, argon and helium). Experimental values of flame extinguishment concentrations of thermal agents could be predicted using a maximum flame temperature at extinction of 1550 K.

Extinguishing concentrations for these thermal agents were obtained using co-flowing methane and propane diffusion flames and compared with predictions from a detailed chemical kinetic modeling study from last year. The experimental extinguishing concentrations are considerably lower than predicted for an opposed flow burner, but the values are related by a constant value. The experimental extinguishing concentrations for the propane flame are considerably higher than for the methane flame. At the present time it is unclear why this should be so. Detailed chemical kinetic modeling of opposed-flow laminar diffusion flames, to be completed shortly, should provide additional insight.

Work has begun on developing a set of quantitative structure-activity relationships for compound volatility. These would be used in conjunction with values of agent discharge rates and the known dimensions of and thermal conditions in the fire compartment to determine whether compounds having a specified chemical structure can be expected to put out the fire in the required time frame (e.g., on the order 0.5 s in the case of an engine nacelle fire).

Previous research had shown that small amounts (*ca.* 10^{-4} mole percent) of $Fe(CO)_5$ are near the ideal limit at reducing premixed flame velocities. However, at higher concentrations the agent becomes less efficient, as the active iron species condense to form relatively inactive particles. Ferrocene, a decidedly less toxic iron-containing compound, produced nearly identical results, indicating that varying the binding state of the iron in the agent will not alter the flame suppression behavior.

Current research is examining two Mn-containing compounds, MMT (methylcyclopentadienyl manganese tricarbonyl) and monomanganese pentacarbonyl, to determine whether these known combustion modifiers offer significant improvement over iron-containing compounds. A chemical kinetic mechanism was assembled to examine the inhibition of these compounds. The calculations indicate no difference between the two Mn-containing chemicals. The reaction pathway is similar to the iron-containing compounds, with the Mn-containing compounds being 5-7 times less efficient at reducing burning velocity. Thus, further mechanistic investigation of these compounds is unwarranted.

Research continues on tropodegradable bromocarbons, bromine-containing compounds that are readily degraded in the lower atmosphere. For instance, bromoalkenes are expected to have atmospheric lifetimes of just a few days. Ten tropodegradable bromofluoro-alkenes and three bromofluoroamines were successfully synthesized or acquired from commercial and academic sources (Table 1). Upper limits of extinguishing concentrations were obtained using the NMERI 5/8-scale cup-burner, generally below 4%(v/v). Working with the Advanced Agent Working Group, acute inhalation toxicity "limit" tests of 8 of the tropodegradable bromofluoro-alkenes were performed at the Lovelace Respiratory Research Institute. For 4 of the tested compounds (#s 707, 873, 903, and 1116), rats exposed for 30 minutes to 5% (v/v) concentration survived and showed no aftereffects. These results substantially contributed to NGP predictive models for the acute inhalation toxicity of bromofluoro-alkenes, and additional bromofluoro-alkenes have now been identified for future work. Table 2 shows initial results for the 3 bromofluoro-amines.

Table 1. Tropodegradable Bromofluoro-Alkenes Acquired for Testing

CCOD ID[1]	Compound	Formula	Boiling point (°C)	Ext. Conc. (vol. %)	air conc.[3]	Toxicity[4]
707	1-Bromo-3,3,3-trifluoropropene	$CF_3CH{=}CHBr$	40	(3.5)[2]	-30 °C	OK
872	3-Bromo-3,3-difluoropropene	$CBrF_2CH{=}CH_2$	42	4.5	-30 °C	Y
873	2-Bromo-3,3,3-trifluoropropene	$CF_3CBr{=}CH_2$	34	2.6	-35 °C	OK
903	4-Bromo-3,3,4,4-tetrafluorobutene	$CF_2BrCF_2CH{=}CH_2$	54	3.5	-15 °C	OK
1116	2-Bromo-3,3,4,4,4-pentafluorobutene	$CF_3CF_2CBr{=}CH_2$	56	(3.8)	-15 °C	OK
1358	2-Bromo-3,3,4,4,5,5,5-heptafluoropentene	$CF_3CF_2CF_2CBr{=}CH_2$	78	(3.7)	-10 °C	Y
1359	2-Bromo-3-trifluoromethyl-3,4,4,4-tetrafluorobutene	$CF_3CF(CF_3)CBr{=}CH_2$	78	(3.3)	-10 °C	Y
1360	2-Bromo-3-trifluoromethoxy-3,4,4,4-tetrafluorobutene	$CF_3CF(OCF_3)CBr{=}CH_2$	75	(3.8)	-10 °C	Y
1391	1-Bromo-2-trifluoromethyl-3,3,3-trifluoropropene	$(CF3)_2C{=}CHBr$	63	(2.6)	-15 °C	N
1413	1-Bromo-4,4,4,3,3-pentafluorobutene	$CF_3CF_2CH{=}CHBr$	58	(3.1)	-15 °C	N

1 NMERI Chemical Compound Options Database ID
2 ( ) represent values that should be considered an upper limit for extinguishment
3 Predicted lowest application temperature assuming 5% extinguishing concentration, based on a calculation employing Trouton's Constant

[4] Acute inhalation toxicity testing: OK = tested, with no perceived effects; Y = tested, with some effects on the test animals; N = not tested

Table 2. Tropodegradable Bromofluoro-Amines

CCOD ID**	Compound	Formula	Boiling point (°C)	Ext. Conc. (vol. %)
1392	Bis(trifluoromethyl)-2-bromo-1,2,2-trifluoroethyl amine	$N(CF_3)_2(CHFCF_2Br)$	72	(2.4)*,**
1393	Bis(trifluoromethyl)-2-bromo-1,1,2-trifluoroethyl amine	$N(CF_3)_2(CF_2CFHBr)$	72	(2.4)*,**
1398	Bis(trifluoromethyl)-2-bromo-2-fluoroethylamine	$N(CF_3)_2(CH_2CF_2Br)$	80	(2.4)**

* Results of a 60/40 blend of CCODs 1392 and 1393

** ( ) reflect values considered to be upper bounds on extinguishment

New Flame Suppression Chemistry Publications

Babushok, V.I., Tsang, W., Linteris, G.T., and Reinelt, "Chemical Limits to Flame Inhibition," *Combustion and Flame* **115**, 551-560, 1998.

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Skaggs, R.R., Daniel, R.G., Miziolek, A.W., and McNesby, K.L., "Spectroscopic Studies Of Inhibited Opposed Flow Propane/Air Flames," *Proceedings of 1999 Joint Meeting of the United States Sections of the Combustion Institute*, Washington, DC, 1999.

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Fleming, J.W., "Chemical Fire Suppressants: How Can We Replace Halon?," *Proceedings of the Fall Technical Meeting of the Eastern States Section of the Combustion Institute*, pp. 16-23, Raleigh, NC, 1999.

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Pitts, W.M., Yang, J.C., Huber, M.L., and Blevins, L.G., "Characterization and Identification of Super-Effective Thermal Fire Extinguishing Agents—First Annual Report," National Institute of Standards and Technology Internal Report, NISTIR 6414, 58 p., 1999.

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

Tapscott, R.E. and Mather, J.D., "Tropodegradable Fluorocarbon Replacements for Ozone Depleting and Global Warming Chemicals," *Journal of Fluorine Chemistry*, submitted for publication, 1999.

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

Mather, JD., and Tapscott, R.E., "Next-Generation Fire Suppression Technology Program: NMERI/CGET Projects Overview," *Proceedings of the 1998 Halon Options Technical Working Conference*, Albuquerque, 1998.

Tapscott, R.E., and Olivares-Sooley, M.G., "A Decision Tree for Global Environmental Impact Screening," *Proceedings of the1998 Halon Options Technical Working Conference*, Albuquerque, 1998.

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

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B. SUPPRESSANT SCREENING TESTS

As planned, the NGP research to develop a set of efficient, accurate screening tests for new suppressant chemicals is drawing to a close, with completion expected in FY2000. Protocols for progressive evaluation of compounds for environmental impact, toxicity, and materials compatibility have been completed and published. Evaluation of inhalation toxicity using a human pharmacokinetic model and a test for fire suppression efficiency of gases and liquid aerosols are nearly complete. Significant progress has been made on a method for screening the effectiveness of a suppressant in transient release.

The Dispersed Liquid Agent Screen (DLAS) is now in steady use both to obtain suppression efficiency data on candidate suppressant fluids and as a research tool. A final report, including full documentation of the apparatus and its use, has been published. Two modifications have been made to the apparatus to enhance its operation. The apparatus is also suitable for evaluating powder agents when a powder delivery system is integrated into the current system.

- The test section has been modified to minimize the corrosive damage from the HF generated by fluorinated suppressants.

- The suppressant sprays from the nebulizer have been characterized using a Phase Doppler Particle Analyzer. This is because the suppressant performance may depend on the droplet size, and different fluids may produce different droplet diameter distributions under the same nebulizer conditions. For several fluids of widely varying density, viscosity and surface tension (water, 30 % and 45 % potassium lactate by mass, and 1000 mg/L and 2000 mg/L sodium dodecyl sulfate), the differences in the average droplet size were found to be within ±15% (Figure 2). The effect of this variation in droplet size was found to affect the blow-off velocity (a measure of extinction efficiency) by under ±15% (Figure 3). These variances are well within useful tolerance for a screen apparatus. The standard operating protocol uses a reference delivery rate based on these results.

Figure 2. Effect of Fluid and Fluid Flow on Droplet Size

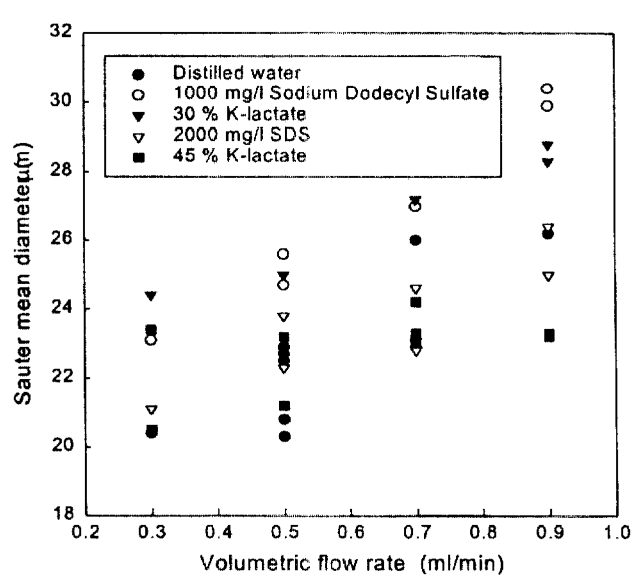
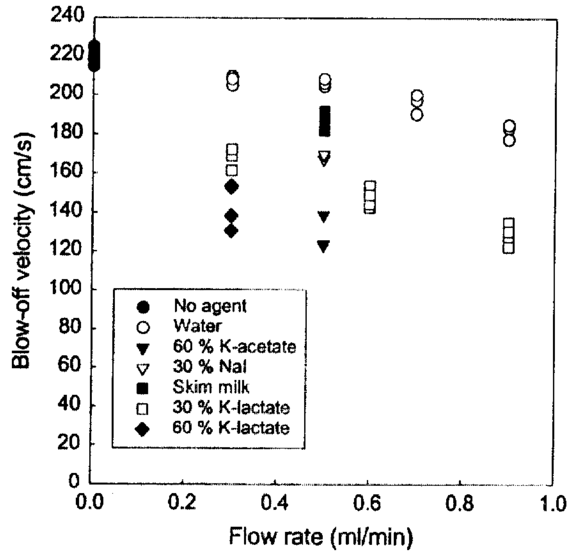


Figure 3. Effect of Fluid and Fluid Flow on Flame Extinction Effectiveness



The screening tool for the effectiveness of suppressants that are impulsively discharged is well on its way to completion. The following analyses of the Transient Application, Recirculating Pool Fire (TARPF) agent effectiveness screen (Figure 4) have been completed:

- The effectiveness of CF_3Br in suppressing an aerodynamically stabilized propane pool fire was compared to that of N_2. The resulting suppression concentrations scale with the corresponding cup burner values.

- Direct numerical simulation of the flow over various obstacles in the TARPF has been conducted to help interpret the experimental results and extend them to other conditions. Figure 5 shows three snapshots of a simulation of a propane flame stabilized behind a 25 mm high baffle. The first image shows the flame before injection of the agent (nitrogen). The second image shows how the flame is distorted in a vortex as the speed upstream roughly doubles due to the agent injection. The third image shows the flame restabilizing after the agent has been injected. In this case, the flame is not extinguished.

- Discussions with suppliers of solid propellant gas generators (SPGG) have lead to the design of an SPGG agent injection system that should accommodate safely 1 to 100 g of propellant. Preliminary tests of SPGGs have been successful.

Figure 4. Schematic of TARPF (dimensions in mm)

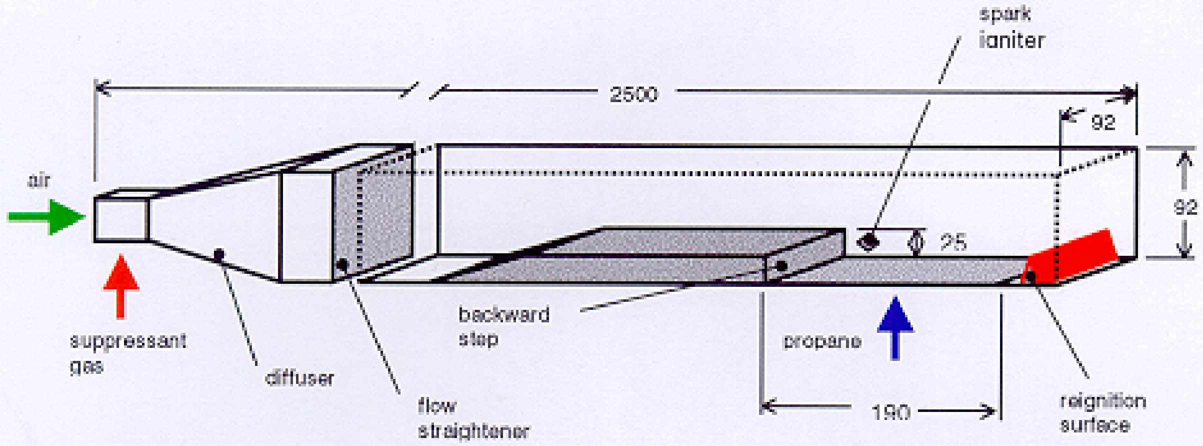


Figure 5. Computer Simulation of a Stabilized Propane Flame in the TARPF

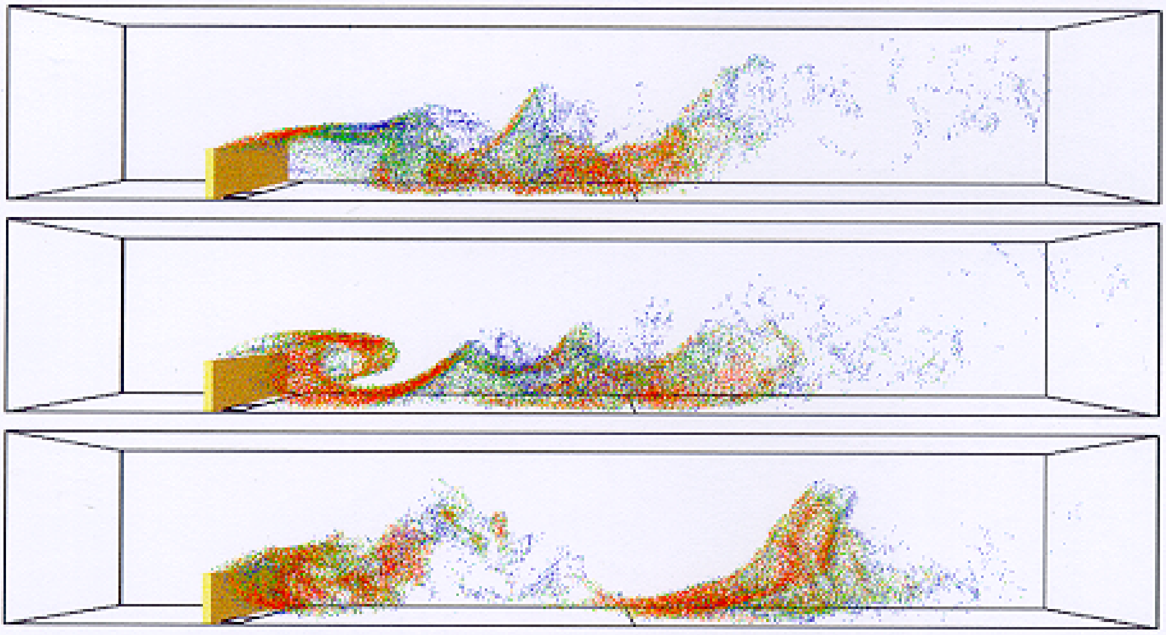
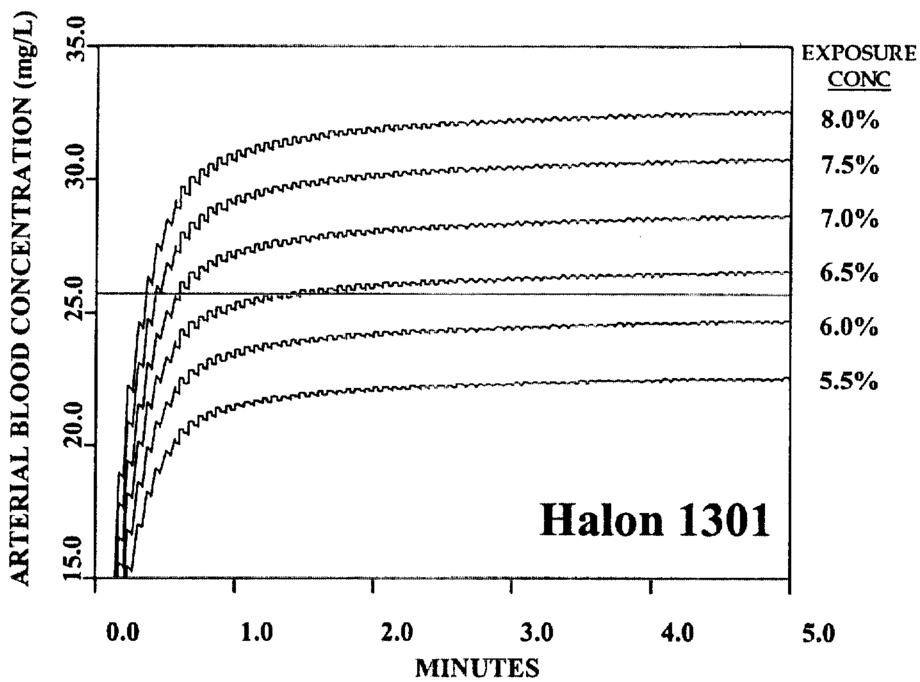


Figure 6. Monte Carlo simulations of humans exposed to halon 1301. The simulation lines represent the mean + 2 standard deviations resulting from 1000 Monte Carlo simulations. The horizontal line at 25.7 mg/L represents the lowest arterial blood concentration measured at 5 minutes in a group of 6 dogs exposed to halon 1301 at the cardiac sensitization LOAEL of 7.5%.



The development of a physiologically based pharmacokinetic (PBPK) model of a human system to describe the short-term inhalation of volatile halogenated hydrocarbons is nearing completion. This model incorporates a breath-by-breath description of respiration and follows the inhaled suppressant to the bloodstream. Use of the model has also been demonstrated for both retrospective examination of prior exposures and prospective examination based on known potential exposure scenarios or on known targeted endpoints.

- One important use of the model is the prediction of safe exposure duration for a given agent used at a known extinguishing concentration. Figure 6 and Table 7 show the results of a Monte Carlo simulation for halon 1301. Similar tables were prepared for CF_3I, HFC-125, HFC-227ea, and HFC-236fa. Extension of the model to other suppressants requires:
    - Partition coefficients, *i.e.*, solubility of the chemical into blood and other body tissues
    - Metabolic rate, the rate at which chemical is broken down by the body
    - LOAEL for cardiac sensitization measured in beagle dogs or other endpoint
    - Arterial blood concentrations measured in beagle dogs exposed at the LOAEL concentration (without epinephrine challenge). (Data should be collected over a ten minute period, with the five minute data point being the most critical)

Table 3. Time for Safe Human Exposure at Stated Concentrations for Halon 1301

Halon 1301 concentration		Time in Minutes Based on LOAEL in Dogs of 7.5%
% v/v	PPM	
5.5	55,000	5.00
6.0	60,000	5.00
6.5	65,000	1.33
7.0	70,000	0.59
7.5	75,000	0.42
8.0	80,000	0.35

Three publications were found that presented data on releases of Halon 1211 and/or Halon 1301 in aircraft. Model calculations of inhalation hazard have been performed using these data.

The NGP research to develop a computational screening tool for a suppressant's atmospheric lifetime and infrared absorption is continuing.

- The calculated rate constants for the reaction of OH with halomethanes are in good agreement with their experimental counterparts, establishing the viability of *ab initio* calculations as the basis of a screening tool.

- Calculations for the reactions of OH with several fluoroethanes and the ethers derived from them have reproduced the experimental trends, with predictions in absolute reactivity within a factor of three. Calculations are being extended to ethers with several carbons and containing fluorine along with one or more bromine atoms.

Suppressant Screening Test Publications

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C. NEW AND IMPROVED AEROSOL SUPPRESSANTS

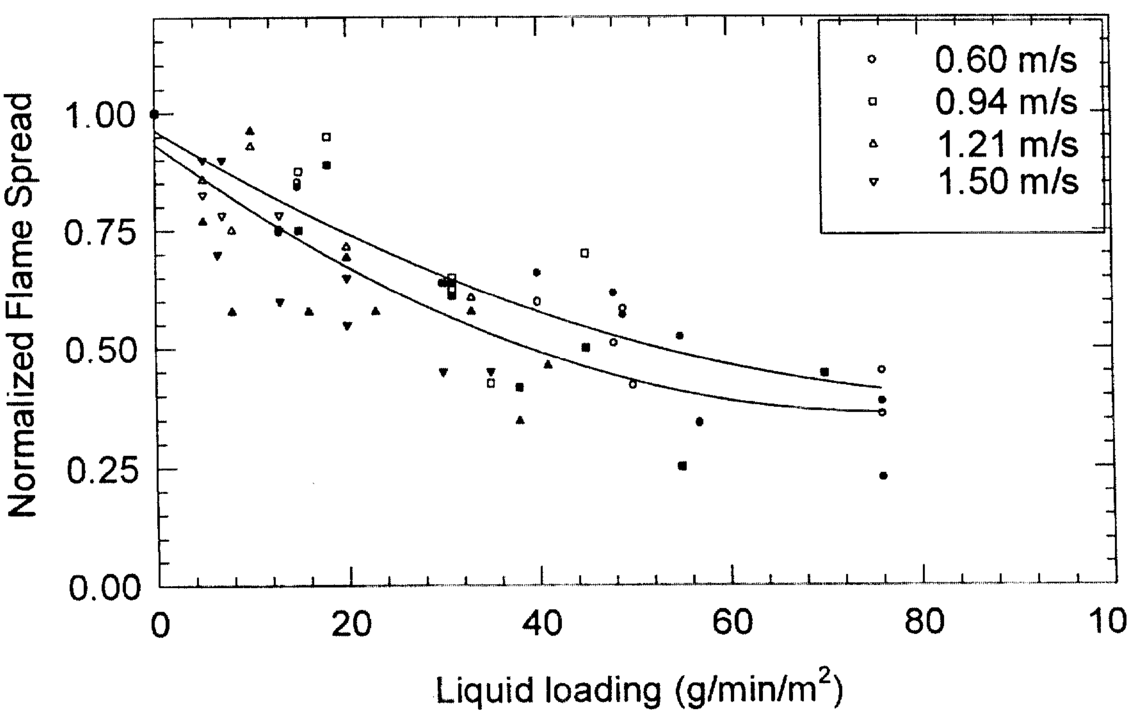
Nearly all suppressants of interest emerge from pressurized storage containers as liquids or powders, along with a gaseous component. The properties of the aerosol (a) determine its transport effectiveness to the fire, (b) the magnitude of its effect on the flames, (c) its ability to quench condensed-phase fuels, and (d) its impact on preventing reignition. The values of the aerosol properties that optimize each of these may be uniform for the four impacts or may be in conflict. This section deals with the latter three of these impacts.

NGP studies of water droplets injected into propane/air and methane/air counterflow non-premixed flames have identified the optimal droplet diameter ranges for suppression effectiveness. Droplets with diameters ≤18 μm completely evaporated before reaching the stagnation plane at every strain rate measured. A significant number of droplets with diameters ≥30 μm survived in most propane/air flames. Droplets larger than 42 μm were much less efficient at suppression.

- These water mist concentrations approach the predicted limit based on comparison of the physical effect of water mist's sensible enthalpy and heat of vaporization to gaseous thermal agents.
- For the droplet sizes and flame strain rates measured, extinction effectiveness appears to correlate with the degree of evaporation. Thus, for water aerosols, if all of the water droplets can evaporate in or near the flame, water is as effective as halon 1301 on a mass basis.

Droplet diameter variation was found to have a minimal impact on flame spread rate across a PMMA surface. The rate decreased almost linearly with the mass of water incident on the surface (Figure 7).

Figure 7. Variation in Flame Spread with Liquid Loading. The open symbols were obtained with 0.3 mm PMMA, and the closed symbols were obtained with 0.64 mm PMMA sheet. The symbol shapes correspond to different air velocities.



Droplet diameter and velocity measurements from a mono-disperse spray onto a hot plate showed that buoyancy had a significant impact on the droplet velocities and diameters. The droplet velocity slows to half the injection velocity causing the faster and cooler droplets to collide and coalesce with the droplets in front of them near the surface of the hot plate. Therefore, it is important to model coalescence in fire suppressions scenarios. Further study of this phenomenon with non-evaporating droplets is in progress.

The NGP has developed a two-color planar pyrometer which can measure the surface temperatures of smoldering and charring surfaces. This equipment will be used to obtain surface temperatures for a charring fire under the influence of a spray mist.

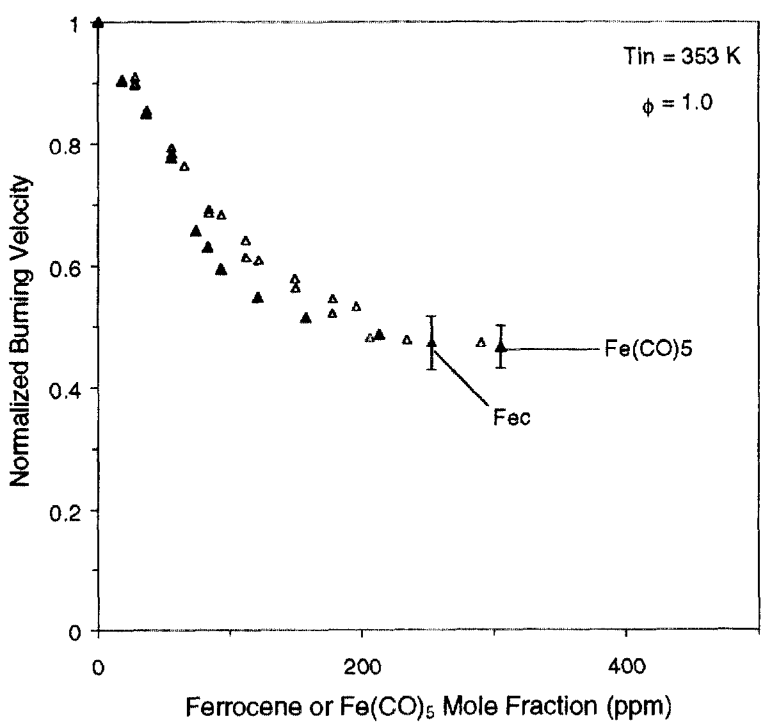
It is important to know the conditions under which fine droplet sprays can suppress the fireballs experienced in aircraft dry bay and ground vehicle crew compartment fires. Calculations for fine sprays (diameters <50 μm) indicate nominally complete evaporation near the flame front. Thus, for these small droplets, other parameters such as the droplet transport time to the fireball should be considered.

It is possible to encapsulate a practical mass of a suppressant onto an inert host for transport to the fire. A large weight fraction of $Fe(CO)_5$ can be absorbed into zeolites (33 %) and aerogels (up to 200%). Further, thermogravimetric analysis showed that at 250 °C a large fraction of the $Fe(CO)_5$ is desorbed. Flame tests will allow assessment of whether the agent can be liberated in the time available in a flame.

- Some matrix materials (*i.e.*, zeolites) can exacerbate the pyrophoricity of $Fe(CO)_5$, likely due to reaction with residual absorbed water. However, ferrocene has been shown to be as effective as $Fe(CO)_5$ (Figure 8) and is less toxic and pyrophoric.

- Combining iron compounds with HFCs is not an effective combination because stable iron-halogen species act as sinks for active gas-phase iron compounds.

Figure 8. Comparison of Premixed $CH_4/O_2/N_2$ Flame Inhibited by Ferrocene and $Fe(CO)_5$



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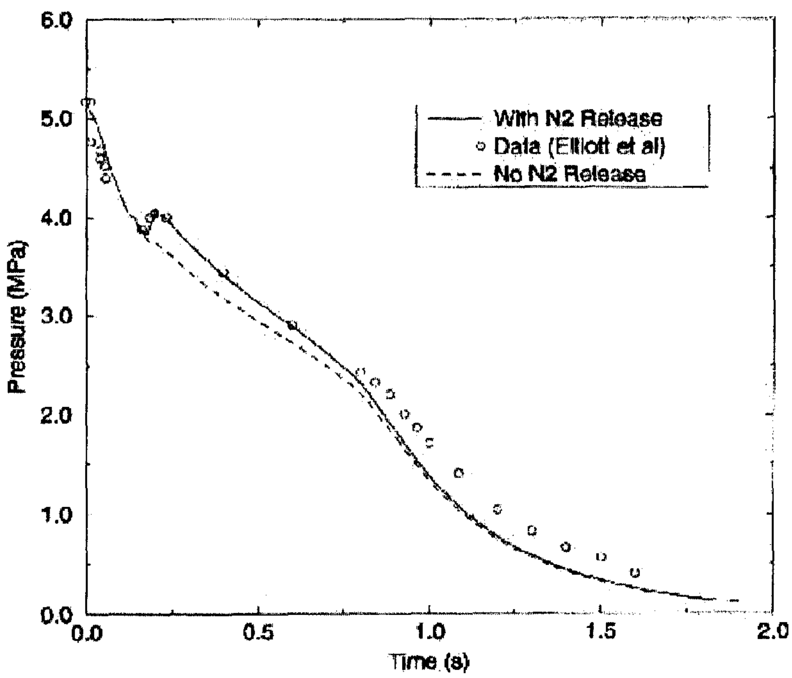
D. IMPROVED SUPPRESSANT DELIVERY

The complement to identifying new suppressants is improving the efficiency of getting the suppressant to the site of the fire. This comprises storage and discharge technology, transport through any distribution piping and transport once the agent has been dispensed from the storage/distribution hardware.

Replacement fluids must function within the existing distribution plumbing. Replacing the piping is a major cost in retrofit and is to be avoided. Therefore one has to know how a new, multi-phase chemical will behave in a long run of bent pipe.

- The new computer code for prediction of two-phase fire suppressant flows during discharge, begun last year, is now nominally complete. The user can select water, halon 1301, CO_2, HFC-227ea or HFC-125 as the suppressant. The software tracks both the fluid and nitrogen as a pressurizing gas. Figure 9 compares the vessel pressure calculations with published data (Elliott *et al.*, "Flow of Nitrogen-Pressurized Halon 1301 in Fire Extinguishing Systems," JPL Publication 84-62, 1984). The code is portable to a variety of commonly used operating systems. A tutorial and workshop on the code is being planned for spring, 2000.

Figure 9. Comparison of Calculated Supply Vessel pressure with Experimental Data

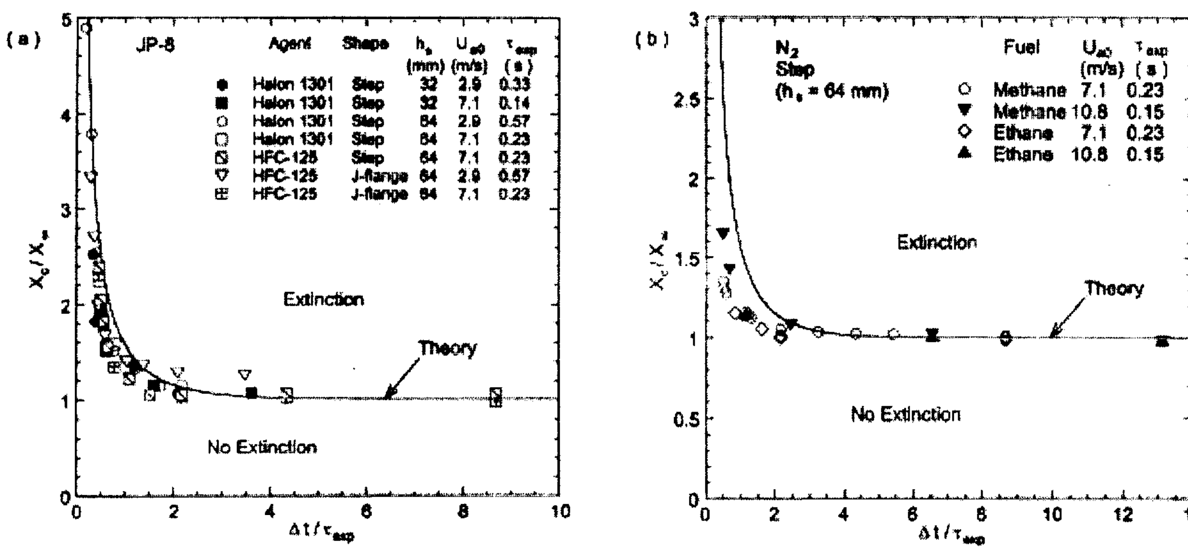


- Advanced instrumentation for the facility to verify these suppressant flow and discharge predictions has been installed. Measurement capabilities include instantaneous mass flow of fluid during transient discharge from the source vessel (using a differential pressure transducer), fluid temperatures along the discharge pipe (using film thermocouples with response times on the order of milliseconds), and void fraction (using a capacitance sensing probe). Numerous test data have been collected using HFC-227ea. During a test run transient measurements of local pressure at five different locations in the system, local temperature at five locations, void fraction at the end of the pipe, and mass flow rate out of the discharge vessel are recorded.

A principal reason for the historic overdesign of halon 1301 systems was to overwhelm the impedance of suppressant distribution by the extensive clutter in the space. NGP engineers are quantifying these penalties for different fuels (methane, ethane, JP-8), fire suppressants (halon-1301, HFC-125, nitrogen) and bluff body shapes (step, baffle, J-flange). These results will both quantify the potential gains from redesigned distribution systems and assist in screening for the effectiveness of candidate suppressants.

An NGP model based on a well-stirred reactor describes the rate of agent entrainment into the recirculation zone. It relates the free stream agent concentration and injection period to the critical concentration needed for extinguishment and a characteristic mixing time for entrainment into the recirculation zone. Figure 10 shows that this model captures the normalized agent mole fraction at extinction as a function of agent injection period for a range of flow conditions, agents, and clutter shapes.

Figure 10. Calculated and Measured Normalized Extinction Concentrations as a Function of Normalized Agent Residence Time



Based on these results, a fire suppression system should be designed to provide a critical concentration of agent for a period at least three or four times the characteristic mixing time of the system.

NGP research is developing new types of solid propellant gas generators (SPGGs) that have high flame suppression efficiency, yet little negative impact on the environment or the weapons system. The first of these formulations are aimed at both reducing SPGG combustion temperatures and increasing flame suppression.

- One approach directs a rapid gas generator exhaust discharge of additive-enhanced propellant formulations into a flame zone. Two formulations are being considered:
  - 5-amino tetrazole(5-AT) and potassium perchlorate (KP), with an elastomeric binder, with and without decabromodiphenyl ether, added as a chemically active flame inhibitor
  - Potassium carbonate or nitrate.

- A second approach directs the hot gas generator discharge from an "inert" solid propellant across an "activated" agent bed and entrains a chemically active additive into the gas stream and carries it to the flame zone. Activated coolant bed formulations under consideration include granular magnesium carbonate coolant "activated" by deposits of varied levels of potassium iodide and potassium carbonate.

Improved Suppressant Delivery Publications

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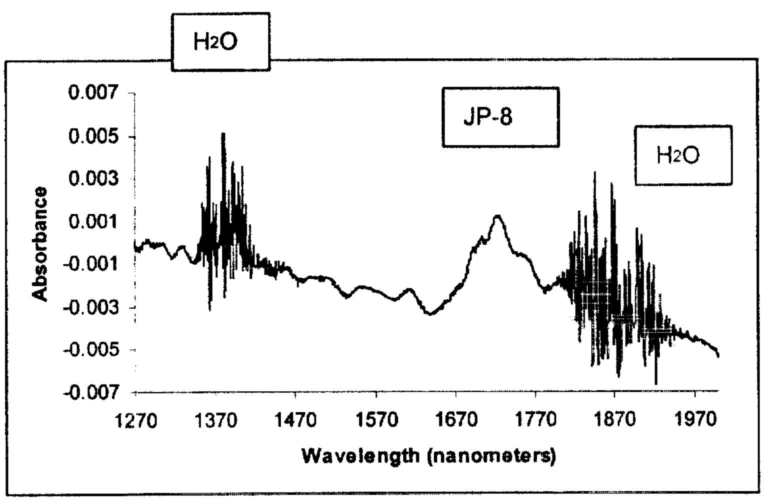
E. VIABILITY OF NEW SUPPRESSANT TECHNOLOGIES

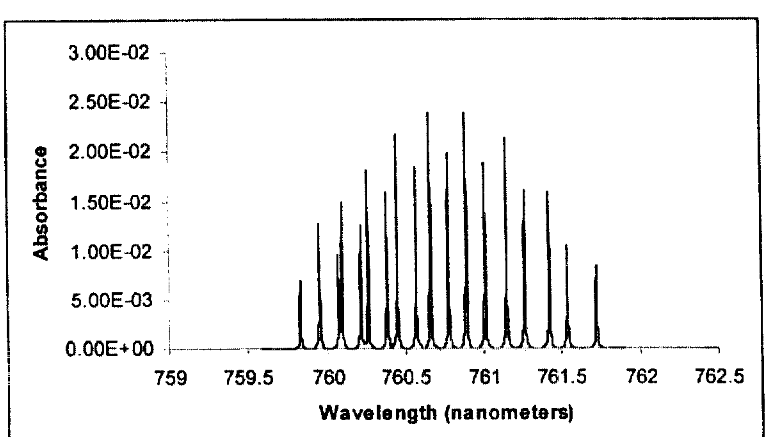
The success of new NGP technologies requires (1) that the laboratory research replicate the suppression phenomena in real-scale fires and (2) that the NGP be able to demonstrate that candidate fire suppression methods are quenching flames as they would under the threats experienced in the field. Meeting both of these needs entails improved instrumentation in the test articles already owned by the Military Department laboratories.

- NGP researchers are complementing prior instrumentation advances by developing a time-resolved (10 ms), multi-point, fieldable, fiber-coupled, near-infrared tunable diode laser-based sensor for measurement and detection of combustible mixtures of oxygen and hydrocarbon fuels (heptane and JP-8) before, during and after the fire suppression event of 250 ms duration. Detection of fuel and oxygen concentration is especially important after the suppression event in order to predict the possibility of reignition. Two separate lasers, one to detect each species, are combined to produce the probe beam. Initial tests of this system have shown that detection of fuel and oxygen at the anticipated levels is feasible (Figure 11).

Figure 11. Measured Near-infrared Absorbance in the Region Near JP-8 Vapor at 355 K, and the Calculated Absorbance Spectrum of O_2



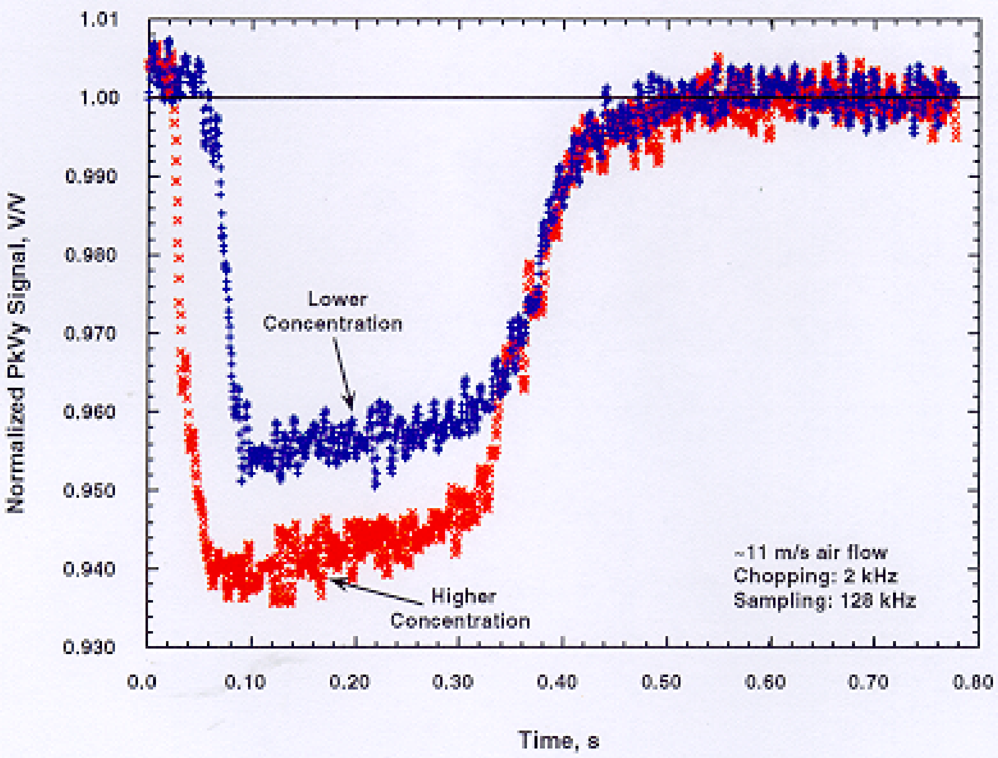
JP-8 vapor, 10 cm path length
355K, $4 cm^{-1}$ resolution,
256 scans.



O_2, 1 m path length,
296K, calculated using
HITRAN database.

Research is also continuing on developing an instrument for measuring agent concentration with a 10 ms time response, fast enough for quantification of the transient agent concentration during the suppression of the fastest fires involving military systems. Tests of a second-generation version of the Differential Infrared Agent Concentration Sensor (DIRRACS-2) (Figure 12) showed that the device is able to follow HFC-125 discharges with acceptable signal-to-noise ratio (improved by a factor of 20) and time response (improved by a factor of 10). The next stage in the development of the DIRRACS-2 will be the assembly of two portable units to be deployed in the field.

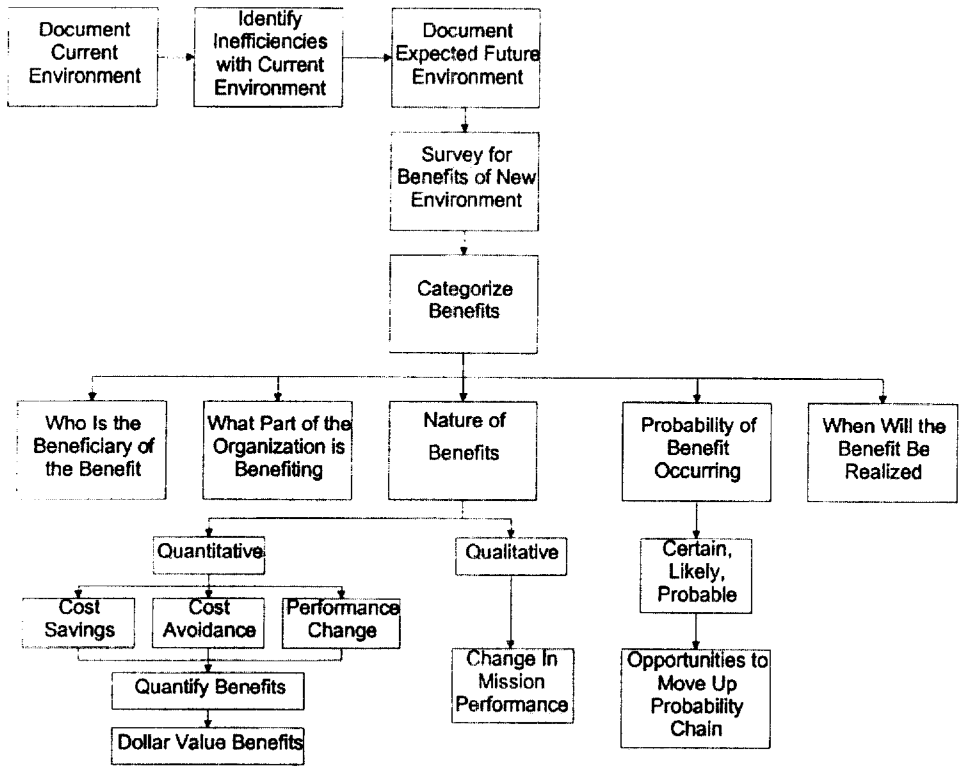
Figure 12. Concentration of HFC-125 During and After 250 ms Releases in the Transient Application Recirculating Pool Fire (TARPF) Facility



There are a large number of contributing factors that must be considered when making a decision to retrofit a fire suppression system (or not). These include both objective cost factors and subjective value factors. Accordingly, the NGP is developing a methodology to quantify a fire suppression technology by its total, life cycle cost and to enable superimposing on this a subjective value system.

The data gathering for and formation of the baseline (halon 1301) case has been completed, as has the structuring of the cost benefit analysis process. The latter provides a framework for evaluating a range of weapons systems, taking financial and technical variables into consideration. Figure 13 displays a framework for qualifying benefits. Expert Choice will be the methodology for evaluating benefits.

Figure 13. Framework for Quantifying Benefits



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F. IMPROVED FUEL TANK INERTION

Research in this area has been limited. There are only two aircraft that currently use halon 1301 to inert fuel task when entering combat, the F-16 and the F-117. The Air Force is considering the use of CF_3I for this application. Should this decision be positive, then alternative technologies for fuel tank inerting will not be an NGP task.

NGP staff have begun a project to assess current status of alternate systems that had in prior decades shown promise for fuel tank inerting. Tasks underway include assessment of in-flight fuel tank operating environments and identification of whom to consult in gathering information about these alternate systems.

III. WHAT LIES AHEAD?

The planned support for the NGP has been reset to a 9-year, $20 M effort, of which two thirds has been committed through FY2000. This change necessitates a new NGP goal, which is:

> "Develop and demonstrate, by 2005, technology for economically feasible, environmentally acceptable and user-safe processes, techniques, and fluids that meet the operational requirements currently satisfied by halon 1301 systems in aircraft."

The focus on aircraft stems from the reliance of the aircraft survivability engineering teams from all three Military Services on NGP research to meet their fire suppression needs. Thus, the updated program:

- addresses the predominant fires occurring in aircraft dry bays and engine nacelles;
- does not include fuel tank inerting since the Air Force is in the final stages of evaluating CF_3I for this use;
- focuses resources on identifying and examining promising chemicals and precepts for their effective storage, dispersion and distribution; and
- pertains to both current and planned platforms.

Over the next two years, the NGP will deliver the following, building on NGP research to date:

- analysis of the world of useful chemicals, identification of the best places to look for alternative suppressants, and a first set of "best looks;"
- a suite of screening tests and guidance for their use;
- a method for determining and comparing the total life-cycle costs of new fire suppression technologies; and
- definition of what diagnostic information is needed to characterize the outcome (beyond flames out or not) of real-scale tests so that program managers have confidence in the program "products" they are considering.

From that point forward, the NGP will produce:

- specific chemicals that meet the requirements in the goal statement,
- verified precepts for improved suppressant delivery, and
- validated modeling to guide the selection of optimal dispensing conditions, nozzle locations, etc. for the variety of nacelle and dry bay configurations, but
- limited toxicity testing and full-scale experiments.

Throughout the research, the NGP Technical Coordinating Committee will continue to maintain close contact with the aircraft survivability engineers and platform managers in the Military Departments. As appropriate research questions arise, they will become candidates for NGP investigation.