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A PROPOSED METHODOLOGY FOR COMBUSTION TOXICOLOGY TESTING OF COMBINED HALON REPLACEMENT AGENT/JET FUEL INTERACTION

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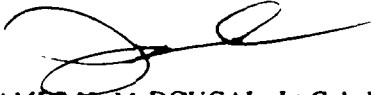
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The experiments reported herein were conducted according to the "Guide for the Care and Use of Laboratory Animals," Institute of Laboratory Animal Resources, National Research Council.

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

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FOR THE COMMANDER



JAMES N. McDOUGAL, Lt Col, USAF, BSC
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**A PROPOSED METHODOLOGY FOR COMBUSTION TOXICOLOGY
TESTING OF COMBINED HALON REPLACEMENT AGENT/JET FUEL INTERACTION**

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ABSTRACT

An international consensus to remove Chlorofluorocarbon (CFC) compounds from production and U.S. national policy to implement the resulting protocols has motivated the U.S. Air Force to embark on a program to find a suitable replacement for Halon 1211, currently used to extinguish flight line fires. This research addressed the feasibility of conducting a combustion toxicology (CT) program to assess the toxic products of the combustion interaction of JP-8 and the Group 1 or so-called "Near Term" candidate replacement agents for Halon 1211: HCFCs -123, -124, and -142b. A laboratory scale experiment benchmarked on large scale testing of a 150 ft² pool fire was developed on the basis of Froude scaling of the full scale fire to a 15 x 15 cm pan fire. A prototype apparatus was developed and investigation into the use of animal behavior methods as an indicator of human incapacitation was conducted. The result is a new method which may potentially be utilized for future toxicity studies of the combustion interaction of current and future U.S. Air Force fuels with various fire extinguishants.

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1. Introduction

The threat of ozone depletion and greenhouse warming has motivated the international community to mandate the replacement of halocarbon compounds used by various sectors of industry and the military. The 1987 Montreal Protocol, which went into effect in January 1989, limits the production of Halon and sets a schedule for its eventual phaseout (Grant, C.C., 1990). The Montreal Protocol targets five CFC's and three halon compounds: Halon 1301, 1202, and 2402 for total phaseout by the year 2000 (Licht, 1990).

The U.S. Air Force (USAF) is a major user of chlorofluorocarbons (CFC's) such as Halon 1211 and Halon 1301 for fire suppression roles in aircraft, in computer and communications facilities, and in flight line fire fighting. USAF discharges of Halon 1211 amounted to 783,000 pounds in 1986, over 28% of the U.S. total. The vast bulk of these discharges was due to the use of Halon 1211 in fire suppression training. Today the use of Halons in training is virtually nonexistent as a result of USAF compliance with a national plan to replace CFC's with substances which have low Ozone Depletion Potential (ODP) and low Greenhouse Warming Potential (GWP). A USAF Near Term program to replace Halon 1211, used in suppressing flight line Class B fuel fires, is progressing and various hydrochlorofluorocarbon (HCFC) agents are being considered as candidate agents. Future programs will assess Medium Term and Long Term replacement strategies for the Halons. Other than the primary requirement that the replacement compounds have a

significant capability to suppress Class B fires, the candidate agents must also meet certain ODP, GWP, and toxicity criteria (NIST, 1990). Toxicity testing of the replacement gases is mandated by the U.S. Environmental Protection Agency (EPA) and has in fact been partially carried out for a number of the leading candidates. The combustion toxicology (CT) of these candidates, both in a thermal degradation sense, and in combination with burning fuels, is not mandated by the EPA. The USAF is examining the need for a CT program which will determine the threat to mission performance caused by exposure of unprotected flight line personnel who often must initiate fire suppression actions prior to arrival of appropriately equipped fire department personnel, so-called "bandaid" fire suppression efforts. A CT program had not been conducted in the past on the interaction of Halon 1211 with fuels because CT is a newly emerging discipline with many uncertainties as to test procedures and evaluation of data.

2. Scope

The research described in this report investigated the feasibility of conducting a CT research program which will primarily address the interaction of JP-8, now the most common USAF aircraft fuel, with the leading candidates for near term Halon 1211 replacement: HCFC-123, HCFC-124, HCFC-142b, and an 80%/20% mixture of HCFC-123/HCFC-142b. The proposed CT program will also be capable of investigating both Medium Term and Long Term replacement agents as those programs evolve, as well as agent interaction with a variety

of fuel types.

A secondary goal of this research program was the conceptual design of an apparatus for CT testing of JP-8 fuel fire/HCFB interaction. The apparatus which evolved has a combustion section, analytic capability, an animal testing section, and appropriate controls and instrumentation.

3. General Research Procedure

The initial stages of research consisted of gathering information on the physical characteristics, fire suppression and combustion characteristics, toxicity, and combustion toxicity of JP-8, Halon 1211, HCFC-123, HCFC-124, and HCFC-142b. An on-line search of all relevant major databases was conducted to include the University of New Mexico Engineering Research Institute (NMERI) Halocarbon Database. The major thrust of analyzing the information obtained from these sources was to determine where gaps in knowledge about these substances exist and to determine if research should be conducted to provide the missing data.

The major standard CT models which are utilized by agencies which conduct CT research were reviewed for their applicability to the JP-8/HCFB CT program. These include the NBS, FAA, USF/NASA, and University of Pittsburgh methods. All of these methods rely on animal testing to provide end-point analyses of toxic effects. Current trends provide significant motivation to minimize the use

of animals in CT research and the use of analytic techniques is emphasized whenever possible. At this point in time it is envisioned that three series of experiments will be carried out.

Series 1 experiments would be laboratory scale, analytic experiments which will be used to determine the products of combustion of JP-8, and the products of interaction of the replacement agents and JP-8 in a scaled, laboratory fire scenario. The combustion products will be analyzed using a combination of Gas Chromatograph (GC), Mass Spectroscopy (MS) and Fourier Transform Infrared (FTIR) instrumentation. Interfaces with the instrumentation will be designed to rapidly gather and determine products in as automated a fashion as possible. An N-gas model or similar model could be utilized to serve as the means of evaluating the data gathered during the course of these experiments to evaluate toxic potential.

Series 2 experiments would be a limited set of animal tests in which the basic apparatus of the Series 1 experiments will be employed to replicate a set of the analytic series. These would be selected from the set of experiments which have the greatest likelihood of approximating large scale fire results.

Series 3 will be a set of large scale fires which approximate flight line fires and which will be conducted to gather data for use in benchmarking and comparing the Series 1 and 2 results.

Extensive contacts with the NMERI, the Midwest Research Institute, and the U.S. Air Force Engineering Center at Tyndall Air Force Base were made in order to insure the scenario developed for the large scale fires accurately represents the types of fires experienced on the flight line. Full scale test protocols have been developed and testing was carried out in August 1991. Data reduction is ongoing and results are expected in early 1992.

The hoped for result is a set of experiments which will be readily repeatable and standard in nature. This will allow future fire fighting agents, such as Group 2 and Group 3 agents, to be evaluated as they become available over the course of the next ten years.

4. Flight Line Fire Fighting Scenarios

The series of CT experiments must approximate actual flight line fires as realistically as possible. This is true not only for the Series 3 large scale tests, but also for the Series 1 and 2 laboratory scale tests. Issues such as oxygen availability, fire type and geometry, amount of fuel consumed, time to initial extinguishing actions, and the amount of Halon 1211 used on a typical fire must be assessed.

Contacts with the USAF Safety Office at Norton AFB, the Civil Engineering Center at Tyndall AFB, and with the Wright-Patterson AFB Fire Department provided some insights as to scenarios which

are realistic. In this regard a few major points need to be observed to produce a reasonable facsimile of a real world flight line fire.

First, hangar fires involving fuel and Halon replacement gases are considered to be rare because fueled aircraft are not allowed in hangar spaces. Additionally Halon is prohibited from being discharged in the hangar space. Consequently indoor fire scenarios probably need not be considered and laboratory simulations of fuel fires should provide for a free flow of air to the fire.

Second, flight line personnel are trained to approach to no closer than 30 feet to a flight line fire. The products of interaction from the laboratory scale experiments should provide for dilution of the interaction products to a level which corresponds to this nearest approach distance. Large scale fire scenarios will have instrumentation located to correspond somewhat to this most likely fire fighting distance.

Third, the nominal flight line fire occurs either due to accidental venting of fuel due to a malfunctioning fuel relief valve, or due to nacelle fires on the aircraft. The former type of fire is called a "running fuel fire." Both fire types involve a significant amount of combustion at human eye level and consideration should be given to the effects of this type of geometry on the development of all experiments.

5. Combustion Toxicity Testing Methods

Combustion research investigates a variety of fire development scenarios: smoldering, pyrolysis, and flaming conditions. The research under this program was restricted to flaming conditions for the fuel because this is the most feasible scenario.

Several standard laboratory scale test systems are available for combustion toxicity measurements. The following methods constitute the most frequently used approaches (Gad and Anderson, 1990):

- (a) DIN 53 436 Method
- (b) Federal Aviation Administration (FAA) Method
- (c) National Bureau of Standards (NBS) Method
- (d) Radiant Heat Test Method
- (e) University of Pittsburgh (PITT) Method
- (f) University of San Francisco (USF) Method

These methods can be classified by three general methodologies or combinations of these methodologies:

- (a) Tube Furnace: DIN, FAA, NBS, PITT
- (b) Crucible (Cup) Furnace: NBS
- (c) Radiant Heat

Additionally the various methods can be operated in a static (FAA, NBS) or dynamic modes (DIN, PITT), or a combination of static and dynamic modes (USF).

As an example of the dynamic method, the DIN procedure uses a moving annular electric oven which encloses a quartz combustion tube. The electric oven moves at a fixed rate along the length of the tube, thermally decomposing materials at a constant quantity of material per unit time. The disadvantages of the tube furnace are the relatively small sample which can be processed and the potential loss of smoke components on the walls of the combustion tube.

The static method as utilized in the NBS procedure allows larger samples to be processed, there is less opportunity for the loss of smoke components, and the cup furnace provides for close control of decomposition temperature. The disadvantages of this method are that air flow into the cup is limited, heat transfer to low density samples is inefficient, and there is no provision for continuous monitoring of the weight loss of the sample.

Schematics of the major apparatus are shown in the following five figures.

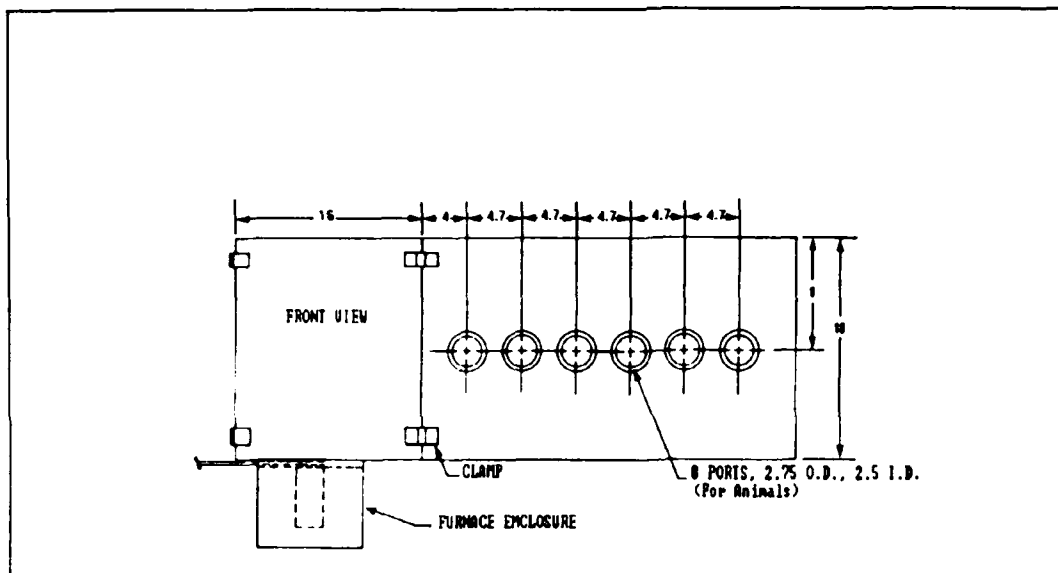


Figure 1. Standard NBS Combustion Toxicology Apparatus

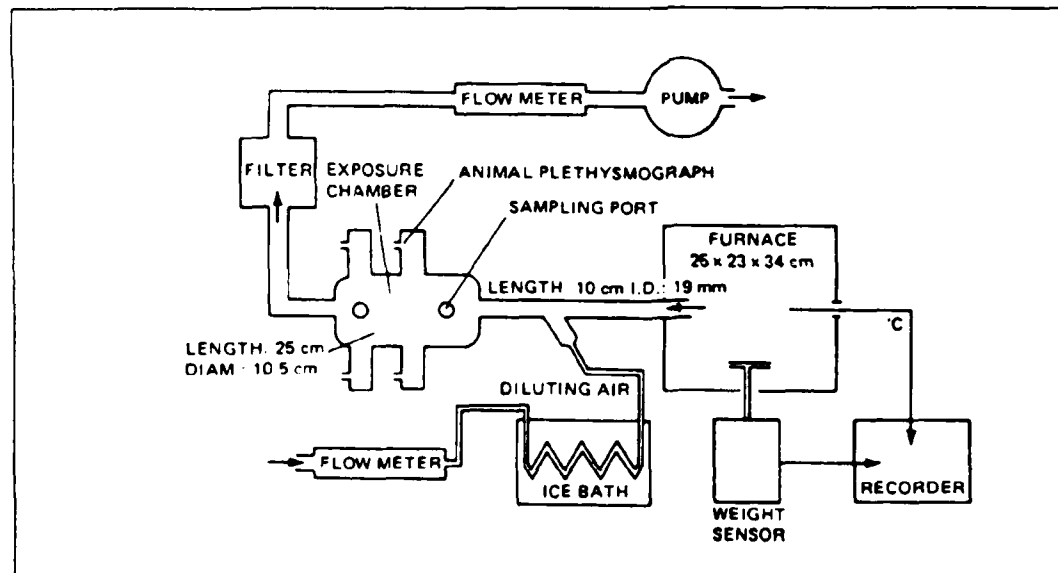


Figure 2. University of Pittsburgh Combustion Toxicology Apparatus

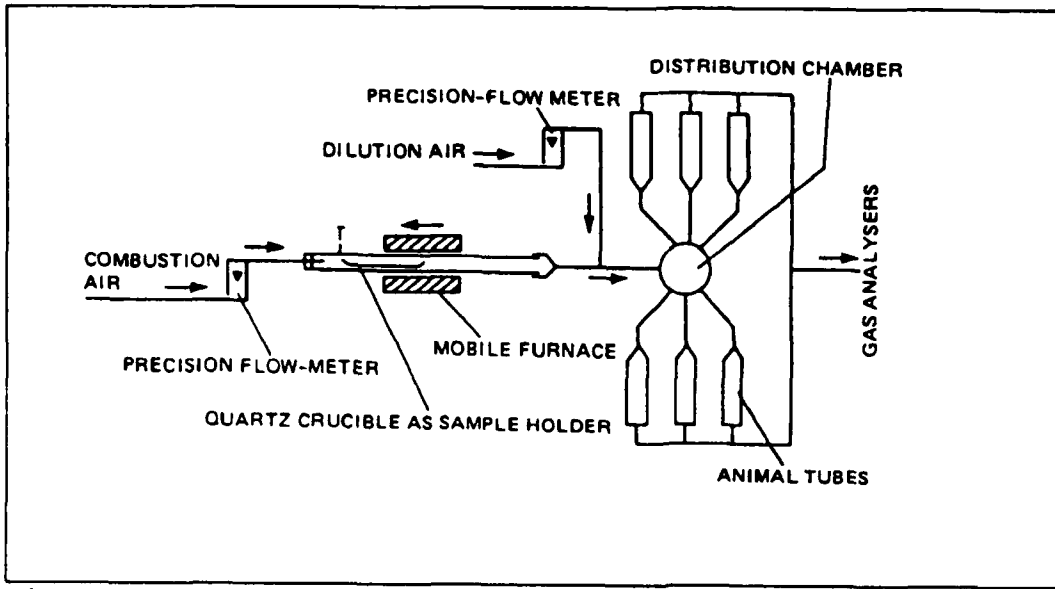


Figure 3. DIN 53436 Combustion Toxicology Apparatus

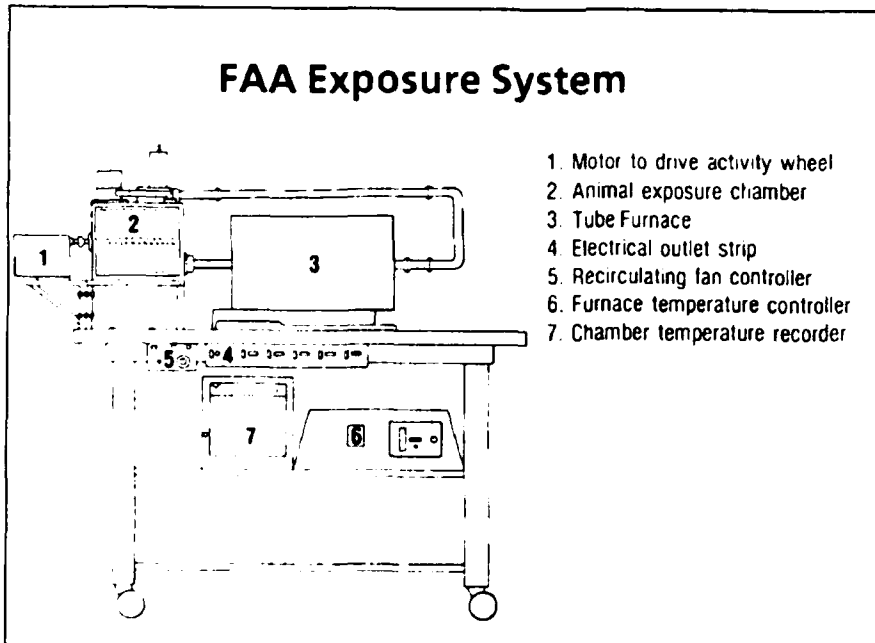


Figure 4. FAA Combustion Toxicology Test Apparatus

USF/NASA Exposure Chamber

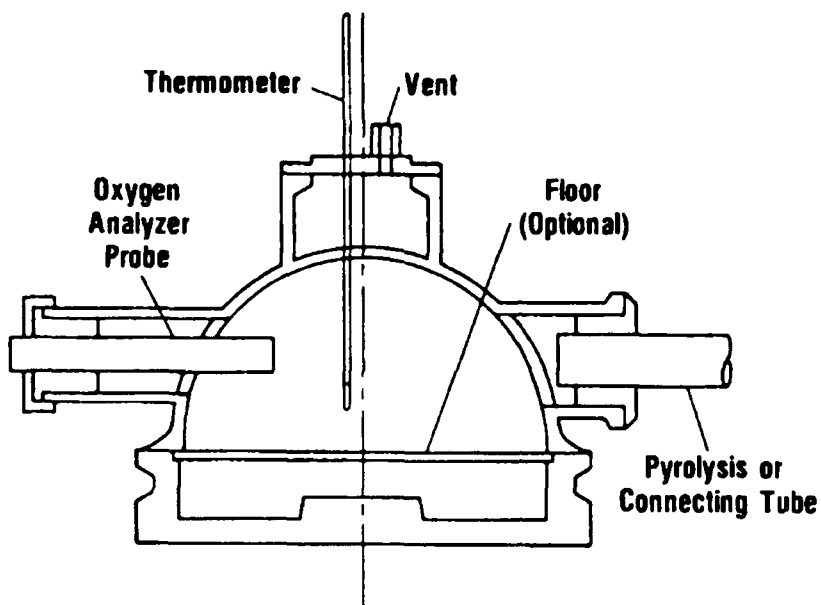


Figure 5. USF/NASA Combustion Toxicology Test Apparatus

Radiant heat devices decompose test samples by radiating infrared energy to the materials. Weight loss of materials can be continuously monitored and materials can be tested in their actual end-use configuration. Disadvantages cited are the variations in surface temperature, smoke interference with radiant heat transfer, and oxygen shortage during combustion.

All of these methods are designed specifically for animal testing and the literature does not indicate any efforts to employ analytic

techniques of evaluation in parallel with the animal studies. Selection of a method for the JP-8/HCFC CT studies would hopefully employ an apparatus and procedure which has the flexibility of incorporating both analytic evaluation techniques and animal studies for selected cases. The apparatus should be identical in its structure for both animal and analytic studies. Therefore it is envisioned that a hybrid system would be utilized which is instrumented to sample gases for analysis by GC, MS, FTIR, and on-line sensors and which has ports through which gases could be conducted to animal chambers. The strategy would be to conduct a series of consistent tests which would provide the same results for each combination of CT parameters. Thus if the fuel/oxygen/HCFC ratios were varied for the analytic tests, the same set of parameters and resulting conditions could be replicated for the animal testing.

6. Lethality versus Incapacitation

In both analytic and animal testing, the concentrations of toxic products which induce either lethality or incapacitation need to be considered. Additionally the mission readiness concerns of the USAF may indicate that, in fact, incapacitation, which occurs at lower concentrations, is the end point of interest for these studies.

The use of LC_{50} values to specify lethality of combustion products

has been heavily criticized due to the variety of methods used in its computation (Gad and Anderson, 1990). In the NBS Method the LC_{50} value is the ratio of the quantity of material that kills 50 percent of the animals to the chamber volume. For the PITT Method it is the quantity of material that kills 50 percent of the animals. In the DIN Method the weight loss of material and air dilutions are factored into the computation of the LC_{50} value. Another shortcoming of the LC_{50} nomenclature is that the exposure and post-exposure times for the various methods vary greatly. Consequently a fair amount of qualifying information is required to be able to compare LC_{50} numbers from different sources.

Computation of incapacitation involves the production of IC_{50} values, the concentration which incapacitates 50 percent of the test animals. In terms of incapacitation the most important combustion products are the narcotic (asphyxiant) gases CO and HCN (Purser, 1988).

Behavioral methods such as the leg-flexion shock avoidance test, the motor-driven activity wheel, and the pole-climb conditioned avoidance/escape response are among the commonly used incapacitation tests. A technique which does not require animal training is cage behavior in which the normal activity of animal control and exposure groups is analyzed for statistical differences. Behavioral work has been carried out on pure gases such as CO, HCL, HCN, and acrolein, as well as for combustion

atmospheres produced by materials. Concentration response curves, IC_{50} values, and concentration-time curves have been produced for some of the major toxicants. Using concentration-time (C*t) curves for CO, investigators have determined that the C*t time for incapacitation of rats exposed to CO is approximately one-third the CO C*t needed to produce lethality (Kaplan and Hartzell, 1984). A limited amount of this type of data is also available for HCN. In contrast the concentrations of HCL and acrolein needed to incapacitate rats is sufficiently high that the animals die shortly thereafter or produce a high rate of mortality in the 14 day post-exposure period (Kaplan, et al., 1985 and Crane, et al., 1985). These phenomena are attributed to the rat's relatively high tolerance of irritant gases. Figures 6. and 7. show C*t curves for CO and HCN. Figure 8. shows the time to loss of consciousness for rats for CO and HCN.

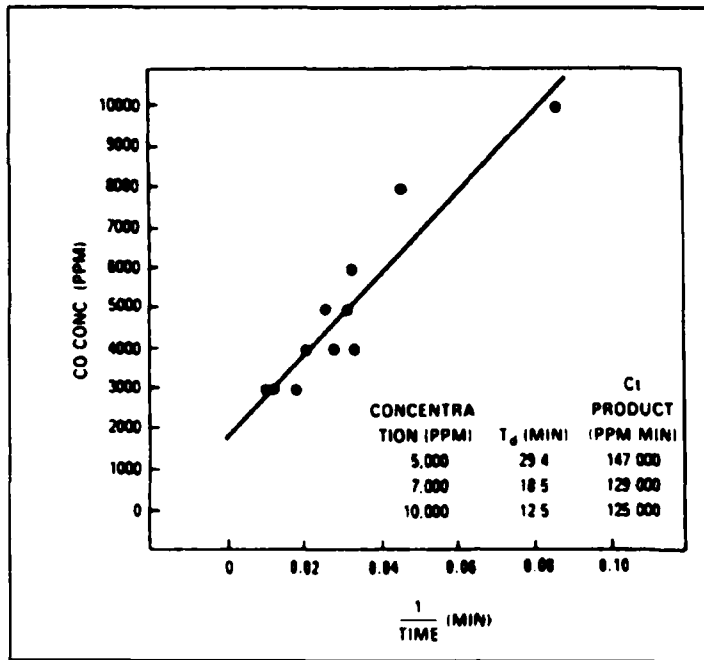


Figure 6. C*t Curve for Lethality and C*t Lethality Products for CO for Rats

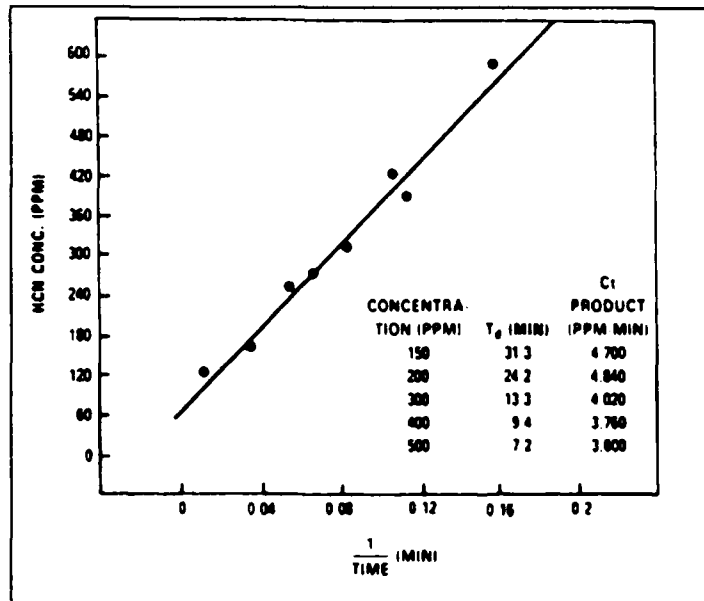


Figure 7. C*t Curve for Lethality and C*t Lethality Products for HCN for Rats

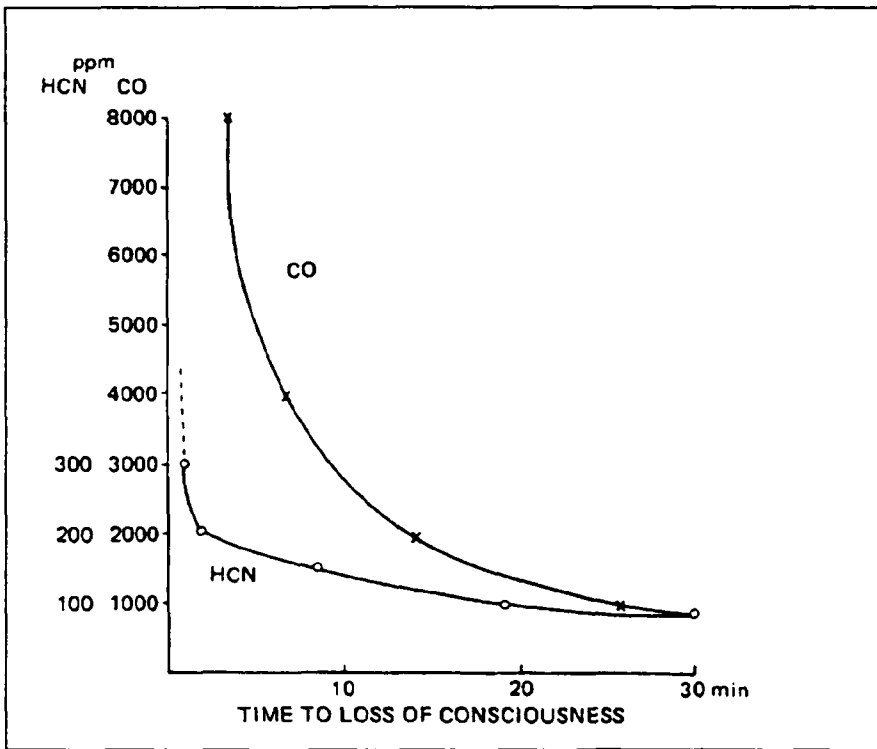


Figure 8. Time to Loss of Consciousness for Rats for CO and HCN

The use of analytic studies alone is generally considered to be inadequate. Even when the major toxicants can be identified there is a great deal of uncertainty because of possible biological interactions. This makes the analytical prediction of toxicity a highly speculative art rather than a hard science. An example of an analytical approach is a study conducted by the FAA which developed a methodology to determine the time to incapacitation based on the yield of nine combustion gases: CO, HCN, H₂S, NO₂, SO₂, HCl, CH₂O, HBr, and HF (Spurgeon, 1978). A three gas model involving CO, H₂S, and HCN was also derived from the test data.

The bottom line is that the use of animals in combustion toxicology studies is necessary not only to detect the presence of unusual or unexpected gases, but also to detect biological interaction between common gases, such as may occur between CO and CO₂ and between CO and HCN. The problem then reduces to determining the split in effort between purely analytical studies and animal testing. At this stage it appears that significant worthwhile and useful information can be gathered in analytical studies and incorporated into N-gas or other models to assess toxic potential. A selected range of the analytical studies would be then replicated for animal studies to provide the added assurance that unusual or unexpected effects are or are not occurring. A suitable N-gas model, based on JP-8/halocarbon interactions, which adequately represents lethality and/or incapacitation, would have to be constructed for interpretation of the analytical data. Appendix A contains a summary of toxicity data for the major combustion products anticipated for the JP-8/HCFE CT research.

7. JP-8 Characteristics and Considerations

JP-8 is a kerosene jet fuel which is rapidly becoming the primary jet fuel for the USAF. It is a mixture of straight and branched chain paraffins, naphthalenes (cycloparaffins), and aromatic hydrocarbons, with carbon chain lengths that range from C8 to C17 carbon atoms per molecule. It is a yellow to straw colored, mobile, low volatile, oily liquid with a kerosene-like odor. Its physicochemical properties include: (Sax, 1989 and Gosselin, et al., 1984)

Molecular Weight: 170.35 for $C_{12}H_{26}$
Specific Gravity: 0.81
Boiling Point: 175 to 325 °C
Flash Point: > 38 °C

JP-8 is miscible with absolute alcohol, ethers, chloroform, carbon disulfide, and carbon tetrachloride. It more effectively resists gunfire crash-induced fuel fires and explosions compared to other fuels, has more BTU's per gallon, and a lower vapor pressure. As a result of these properties, aircraft range is increased and evaporative fuel losses are decreased. On the negative side, JP-8 has slightly degraded capabilities in ground starting and altitude relight for jet aircraft due to its lower volatility (Martel, 1987).

JP-8 has numerous advantages over JP-4, the fuel which it is replacing, although it is more expensive. JP-8 has ranged from

\$0.015/gal to \$0.045/gal more expensive to procure than JP-4. JP-8 was derived from Commercial Jet A-1 fuel, a low-freezing point kerosene fuel. JP-4 is a mixture of gasoline and kerosene fractions, has a high volatility which gives a high probability of fire in post-crash scenarios of combat aircraft, in excess of 80%. JP-8 differs slightly from Commercial Jet A-1 fuel in that it contains a fuel system icing inhibitor and a corrosion/lubricity improver as additives. Table 1 shows some of the major differences between JP-4 and JP-8 (AFWAL/POSF, 1987).

| Parameter | JP-4 | JP-8 |
|-----------------------------------|-----------|-----------|
| Density (kg/m ³) | 751 - 802 | 775 - 840 |
| Normal Average (lb/gal) | 6.34 | 6.71 |
| Distillation Range, °F | 50 - 500 | 300-500 |
| Flash-point, °F, min. | N/A | 100 |
| Reid vapor pressure, psi at 100°F | 2.0 - 3.0 | N/A |
| Aromatics, volume %, max. | 25 | 25 |
| Freeze Point, °F, max. | -72 | -53 |
| Heat of Combustion, BTU/lb, min. | 18,400 | 18,400 |
| Normal Average, BTU/lb | 18,710 | 18,550 |
| Heat of Combustion, BTU/gal, | 118,600 | 124,500 |

Table 1. Comparison of JP-4 and JP-8 Properties

JP-8 is expected to provide significant savings over JP-4 through reduced evaporation losses, reduced handling costs, reduced fuel

related fires and explosions, reduced aircraft maintenance and downtime costs, and a reduction in combat and peacetime aircraft losses.

JP-8 has a mean lethal dose or LD_{50} of kerosene in an average 70 Kg adult of approximately 6 ounces or 180 milliliters, that is, 2.6 ml/Kg (Gosselin, et al., 1984). Aspiration of kerosene in humans results in acute, fulminating, hemorrhagic, and often fatal bronchopneumonia. A few milliliters may be fatal in these incidents. Investigators have reported that a little as 0.1 - 0.2 ml of kerosene administered in the trachea can cause death. Kerosene and other similar hydrocarbon mixtures with viscosities of less than 70 SSU (Saybolt Seconds Universal) at 38°C have been shown to be highly toxic by aspiration (NIOSH, 1977). A time-weighted Threshold Limit Value (TWA-TLV) of 63 ppm has been recommended for JP-8 (Stokes, 1990). NIOSH has recommended a TWA-TLV of 14 ppm (100 mg/m³), however the basis of this recommendation was a material with higher aromatic and naphthalene content which does not adequately approximate the toxicity of JP-8 (NIOSH, 1977). In comparison, the recommended TLV for the more volatile JP-4 is 200 ppm (Bishop, 1983). The Material Safety Data Sheet (MSDS) for JP-8 lists a TLV-TWA of 100 ppm, a TLV short-term exposure limit (TLV-STEL) of 200 ppm, and a PEL/TWA (OSHA) of 500 ppm (MSDS, 1985).

A study which exposed rats and mice to JP-8 vapors at 0, 500, and

1000 mg/m³ for 90 days showed increased mortality and some effects on kidney function. The renal effects could not be readily projected for human exposure due to male rat renal protein peculiarity (Mattie, et al., 1989).

In handling JP-8 for test purposes several precautions must be observed. According to the MSDS, JP-8 causes minimal eye irritation and is moderately irritating to the skin. Inhalation may be irritating to the upper respiratory tract and high concentrations may result in CNS depression and/or chemical pneumonitis. Ingestion may result in vomiting. Long term effects on rats have indicated skin cancer, kidney damage, and tumors. A JP-8 fire must be extinguished with water fog, foam, dry chemical, or CO₂. A direct stream of water is not recommended. Chemical resistant gloves and other clothing are recommended to minimize contact and a respirator should be used if testing occurs in an area where the TLV guidelines may be exceeded. The flash point of JP-8 is a minimum of 100°F and consequently it is necessary to keep the fuel away from heat sources, sparks, and flames.

8. Toxicity of Group 1 Halon Replacements

Based largely on the amount of toxicity information available, the candidate halon replacement agents are divided into three groups. Group 1 agents are HCFC's, FC's, and CFC's which are intended as near term replacements for Halon 1211, which have been produced in bulk in the past, are now being produced, or are being developed

for near-term production, and for which significant toxicity studies, up to and including chronic studies, have been performed or are now in progress. HCFC-123, -124, and -142b have emerged as the primary Group 1 candidates for replacing Halon 1211 for fire fighter training and are the subject of the current CT effort. The properties of Halon 1211 and the desired properties of the replacement agents are shown in Table 2 (Nimitz et al., 1989).

| Property | Halon 1211 | Replacement Agent |
|---|------------|-------------------|
| Flame suppression, % (cup burner test) | 3.2 | < 10 |
| ODP relative to CFC-11 = 1.0 | 2.7 | < 0.05 |
| Boiling point, °C | -3 | -15 to 60 |
| Vapor pressure, psia at 25 °C | 33 | 5 to 40 |
| Gas heat capacity, cal/g-°C at 25 °C | 0.11 | > 0.09 |
| Heat of vaporization, cal/g | 32 | > 25 |
| Toxicity, TLV ^a , % | 5 | > 3 |
| Cost, \$/lb | 2 to 4 | < 10 |

^a TLV= Threshold Limit Value for 1-minute exposure in humans

Table 2. Properties of Halon 1211 and Desired Replacement Agent

The following sections describe the state of toxicity knowledge for the proposed Halon replacement agents.

a. HCFC-123 (CAS #306-83-2)

Halocarbon No. 123, also known as HCFC-123, has the chemical formula CHCl_2CF_3 or 2,2-Dichloro-1,1,1-trifluoroethane. Its basic physical properties are shown in Table 3. along with those of HCFC-124 and HCFC-142b.

| Property | HCFC-123 | HCFC-124 | HCFC-142b |
|-------------------------------|----------|----------|-----------------|
| Est. flame supp. conc., % | 6.7 | 8.8 | 11.0 |
| Boiling Point, °C | 28 | -12 | -10 |
| Vapor pressure, psia at 25 °C | 13 | - | 53 ^a |
| Gas Heat Capacity, cal/g | 0.163 | 0.197 | 0.197 |
| Heat of Vaporization, cal/g | 40.1 | - | 57 ^b |
| ODP | 0.02 | 0.018 | 0.05 |
| GWP | 0.017 | - | 0.34 |
| Relative Cost | 3 | 3+ | 2 |

^a Estimated by means of the Clausius-Claperyon Equation

^b Estimated by means of Trouton's Rule

Table 3. Properties Summary for Selected Group 1 Agents

HCFC-123 is considered to have low acute toxicity, with an acute inhalation LC_{50} of 28,000 to 50,000 ppm for rats, a dermal LD_{50} of greater than 2 g/Kg in rats and rabbits, and a lethal oral dose for rats of 9 g/Kg (EPA, 1990). It is a mild ocular irritant and

produces minimal dermal irritation and eye irritation in rabbits. Cardiac sensitization as measured in an epinephrine challenge test is seen in dogs in concentrations of 20,000 ppm or greater. CNS depression occurs in rats at 5,000 ppm and greater in acute, short-term, and subchronic inhalation studies.

HCFC-123 has been shown to cause liver toxicity in studies performed with rats and dogs. At concentrations of 10,000 ppm pathological changes in dog livers have been reported but not in those exposed to 1,000 ppm (Crowe, 1978).

In vitro (Barsky and Butterworth, 1976; Callandar, 1989) and in vivo tests (Muller and Hoffman, 1988) suggest that HCFC-123 induces neither gene nor chromosomal mutations and it is reasonable to suggest that there is no reason to suspect it as a germ cell mutagen.

No information on oncogenic potential is available and ongoing efforts are expected to report their results in 1993.

Some evidence of maternal toxicity of HCFC-123 has been reported in rat and rabbit studies (Culik and Kelly, 1976), although the results are termed inconclusive.

b. HCFC-124 (CAS #2837-89-0)

HCFC-124 has a chemical formula of CHClFCF_3 , or 2-Chloro-1,1,1,2-

tetrafluoroethane. Its physical properties are listed in Table 3. above.

HCFC-124 has very low acute toxicity with an LC_{50} for acute inhalation exposure in rats from 230,000 to greater than 360,600 ppm (Hazelton, 1976; Kelly, 1990). Cardiac sensitization with an epinephrine challenge test was noted in dogs at concentrations of 25,000 ppm and greater (Mullin, 1976). No effect was noted at 10,000 ppm. CNS depression was noted in acute and subacute studies at greater than 50,000 ppm.

HCFC-124 has been shown to cause absolute and relative liver weight changes in rats in a subchronic study (Industrial Biotest Laboratory, 1977). Further evaluations are ongoing.

Tests for chromosomal and gene mutations have provided no evidence of mutation.

No information is available on the oncogenic potential of HCFC-124 and it has not been adequately tested for developmental toxicity. HCFC-124 has not been tested for reproductive toxicity.

c. HCFC-142b (CAS #75-68-3)

HCFC 142b has the chemical formula $CClF_2CH_3$ or 1-Chloro-1,1-difluoroethane. Its physical properties are listed in Table 3.

HCFC-142b has very low acute toxicity with and LC_{50} for 30 minutes exposure greater than 300,000 ppm (Lester and Greenberg, 1950). Epinephrine challenge tests on dogs produced cardiac arrhythmia at 50,000 ppm (Mullin, 1969).

HCFC-142b has not been adequately tested for neurotoxicity or for developmental toxicity.

HCFC-142b was mutagenic in an Ames assay (Jagannath, 1977; Longstaff and McGregor, 1978; Longstaff, et al., 1984) and provided a weak positive response when tested in its ability to induce chromosomal aberrations in the bone marrow of male rats (Pennwalt, 1980). It is generally concluded that HCFC-142b does not present a mutagenic hazard to man.

Oncogenic potential for HCFC-142b is considered to be low.

HCFC-142b has not been adequately tested for developmental toxicity.

d. Toxicity Summary

Table 4. is a summary of the toxicity testing of the major Group 1 candidates.

| Test Series | HCFC-123 | HCFC-124 | HCFC-142b |
|------------------------|----------------|----------|----------------|
| Acute Toxicity | T | T | T |
| Cardiac Sensitivity | T | T | T |
| Neurotoxicity | P | NT | NT |
| Subchronic Toxicity | T | O | T |
| Mutagenicity | T | T | T |
| Oncogenicity | O | P | T |
| Developmental Toxicity | T ^a | O | T ^b |
| Reproductive Effects | P | NT | NT |

^a Tested in rats and rabbits, inconclusive in rats.

^b Tested in one species only, results inconclusive.

T = Tested at this endpoint

NT= Not tested at this endpoint

P = Testing planned at this endpoint

O = Testing ongoing for this endpoint

Table 4. Status of Testing Programs for Group 1 Candidates.

9. Combustion Toxicity of Group 1 Halon Replacement Agents

A recent test program at AAMRL was conducted to assess the toxicity of the thermal degradation products of several candidate Halon replacement agents, among them HCFC-123. In addition R-22 and R-141b were tested and the results compared to similar tests on Halons 1211 and 1301 (Elves, et al., 1990). The order of toxicity based on thermal degradation was:

R-22 > HCFC-123 > Halon 1211 > R-141b > Halon 1301

In the post-exposure analysis of the Male Fisher 344 rats utilized in the evaluation, all tissues appeared normal with the exception of HCFC-123 exposed animals at the highest concentrations.

10. Dynamics of Pool Fires

10.1 Experimental Data on Pool Fires

The laboratory scale experiment is envisioned to be designed to reasonably approximate a typical shallow pool fire because this is a typical scenario for a flight line fuel fire. Much of the research to determine the burn rates and heat release rates from fuel fires was carried out by Russian scientists in the 1950's (Blinov and Khudiakov, 1957). Their investigation covered hydrocarbon liquid fires ranging in diameter from 3.7×10^{-3} m. to 22.9 m. In general pool fires exhibit differing dominant heat transfer mechanisms dependant on the size of the pool. For diameters less than 0.03 m. the flames are laminar. The rate of burning falls with increasing diameter. For large diameters, greater than 1.0 m., the flames are fully turbulent and the burn rate is independent of diameter. In the transition range, $0.03 < D < 1.0$ m. transitional behavior between laminar and turbulent mechanisms occurs. In small diameter fires conductive heat transfer is the dominant mechanism while in large diameter fires radiation predominates.

The basic governing equations for surface burn rate and heat generation in pool fires are:

$$\dot{m}'' = \dot{m}_\infty'' (1 - e^{-k\beta D}) \quad (1)$$

$$\dot{Q}_c = \dot{m}'' \Delta H_c A_f \quad (2)$$

where:

- \dot{m}'' = burn rate, Kg/m²-s
- \dot{m}_∞'' = burn rate, infinite pool, Kg/m²-s
- D = diameter, m
- $k\beta$ = extinction-absorption coefficient of the flame
- \dot{Q}_c = heat release rate, MJ/s
- ΔH_c = combustion energy, MJ/Kg
- A_f = pool area, m²

The variation of burning rates of pool fires with pool diameter is shown in Figures 9. and 10. using cylindrical pans to simulate the pool geometry (Hottel, H.C., 1959). In Figure 9. burn velocity and the ratio of flame height to pan diameter are plotted for a range of fuels for pool diameters from 0.37 cm to 22.9 m. The lower set of curves gives burning velocity in mm/min as a function of pan diameter while the upper set gives the flame height to pan diameter ratio. The diagonal lines on the lower curve are constant Reynolds numbers based on pan diameter. The flame geometry of a pool fire is such that the flame diameter is a function of the spill size and the rate of burning and the flame height is directly related to the flame diameter and type of fuel, the latter having a characteristic burn rate.

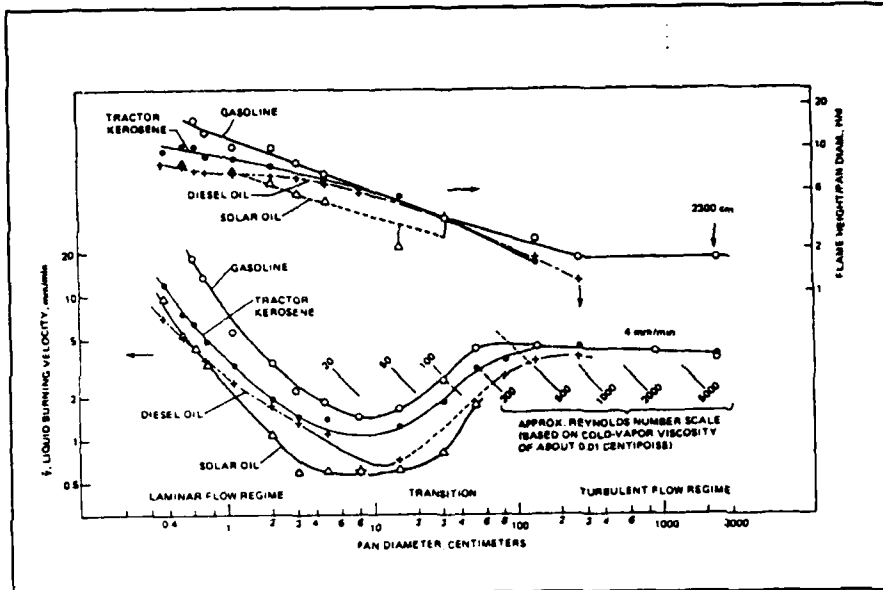


Figure 9. Burning Rates and Flame Heights for Hydrocarbon Fuel Fires

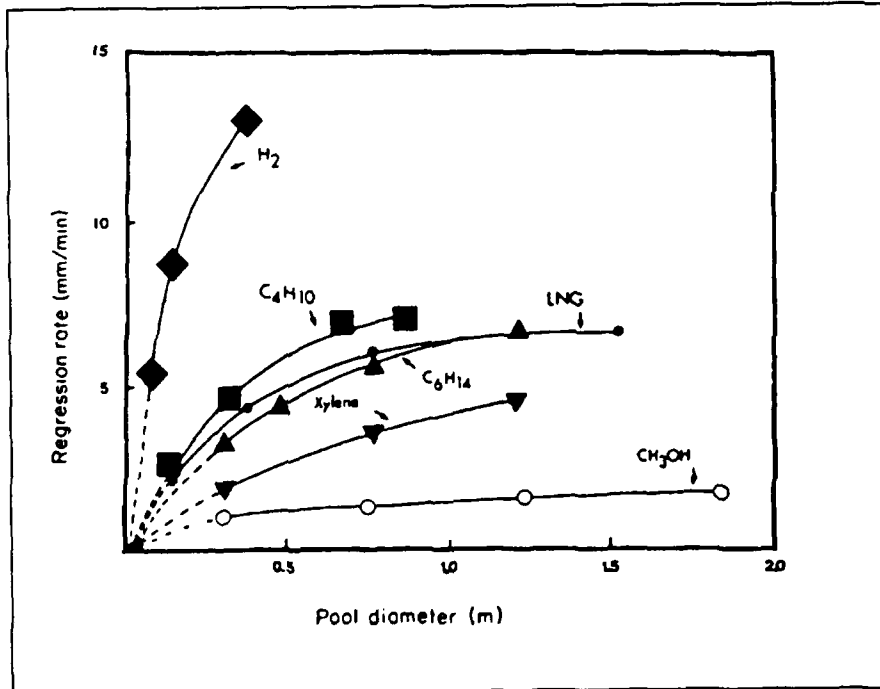


Figure 10. Limiting Regression Rates for Pool Fires

Figure 11. shows the surface burn rate and mass burn rate for hydrocarbon pool fires on land as a function of the thermochemical properties of the fuel (Zabetakis and Burgess, 1961).

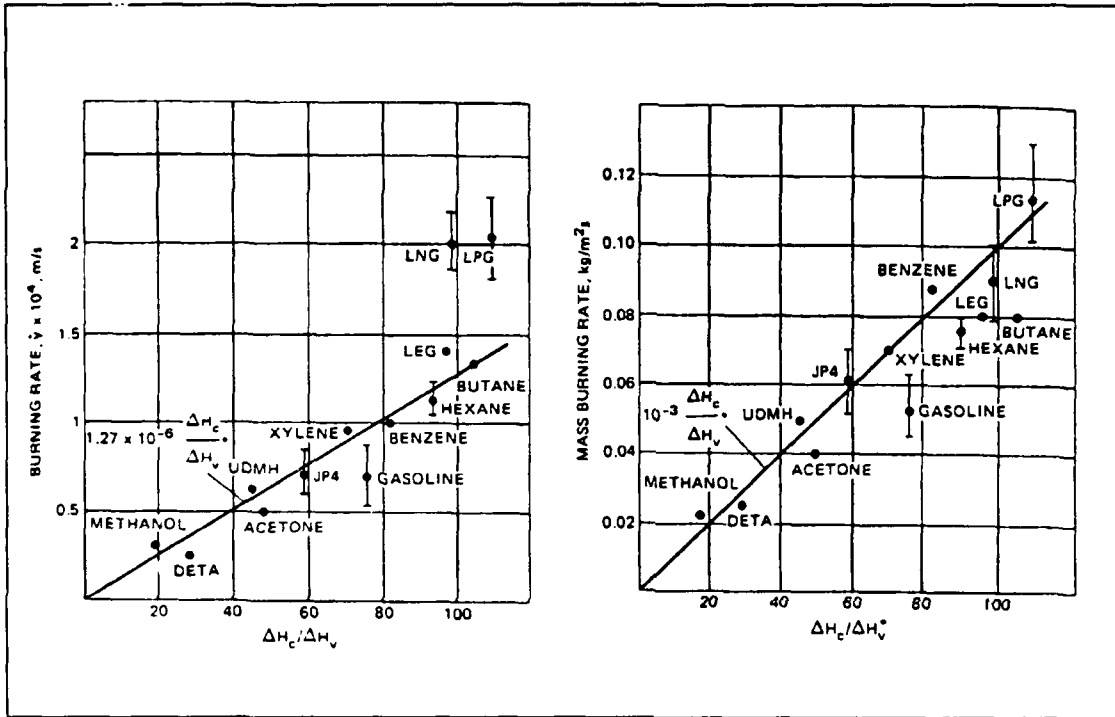


Figure 11. Burn Rate and Mass Burn Rate of Hydrocarbon Fuels on Land versus Thermochemical Properties

In a pool fire the rate of supply of volatiles from the fuel surface is the mechanism which controls the rate of heat transfer from the flame to the fuel (Figure 12.).

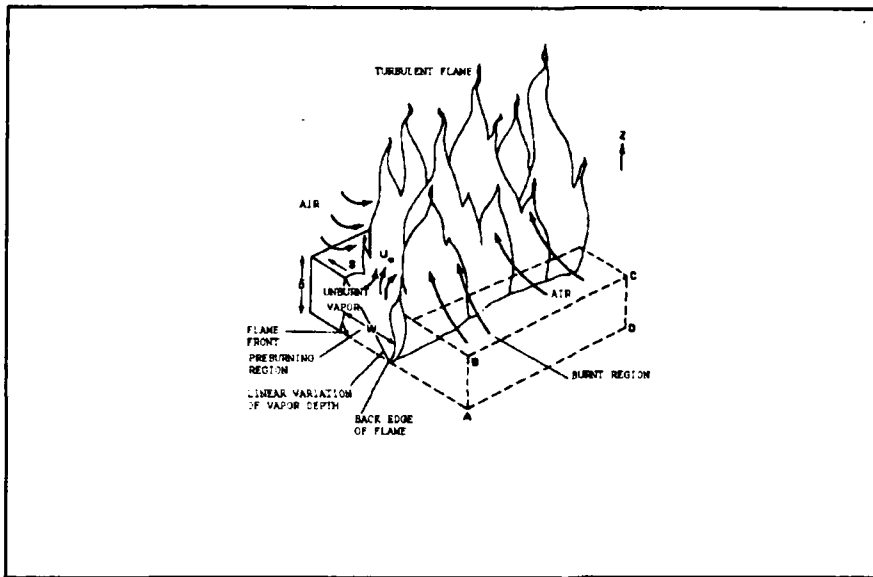


Figure 12. Depiction of the Unconfined Burning of a Flammable Vapor Cloud

The temperature of the pool layers is distributed such that only the surface layers are heated as shown in Figure 13. In fact the surface temperature of a freely-burning liquid is slightly below its boiling point and as the more volatile fuel components burn off, the surface temperature will rise.

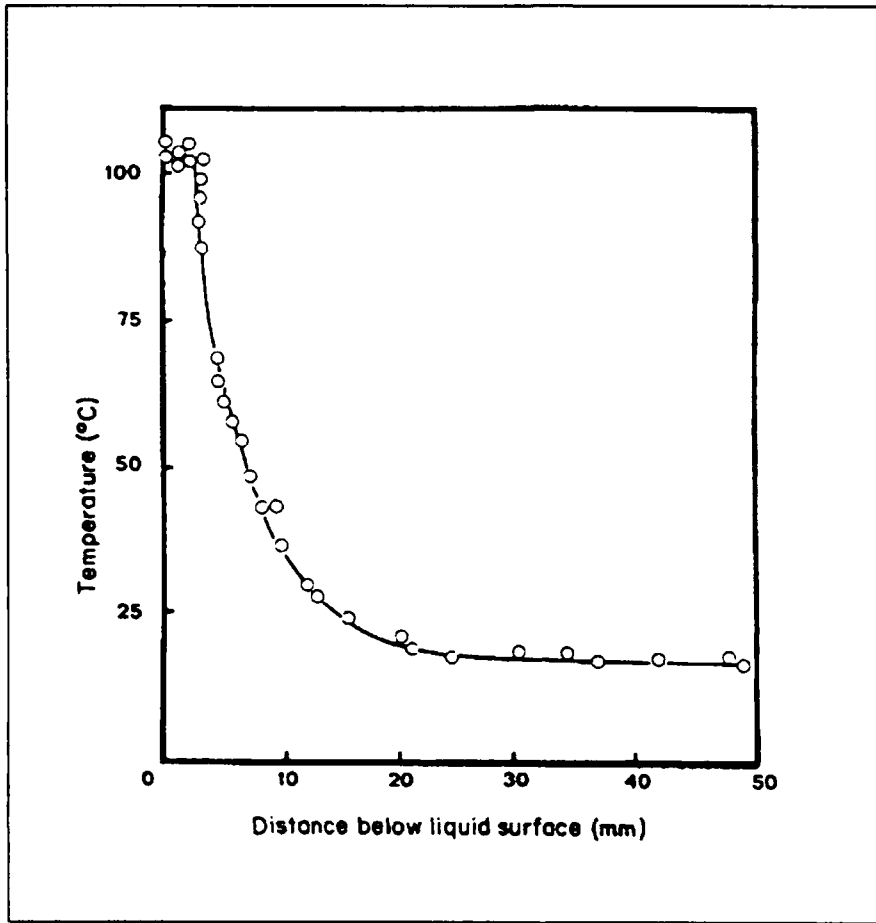


Figure 13. Temperature Distribution Below the Surface for n-Butanol for a 36 mm Diameter Steady Burning Pool

10.2 Scaling of a Pool Fire Experiment

The following physical parameters for JP-4 and kerosene were utilized in preliminary studies of scaled pool fires because similar data for JP-8 has not yet been developed.

| | <i>Kerosene</i> | <i>JP-4</i> |
|--------------------------------------|-----------------|-------------|
| $\rho, \text{kg/m}^3$ | 820.0 | 760.0 |
| $\Delta h_c, \text{MJ/Kg}$ | 43.2 | 43.5 |
| $\dot{m}'' , \text{Kg/m}^2\text{-s}$ | 0.039 | 0.051 |
| $k\beta, \text{m}^{-1}$ | 3.5 | 3.6 |

Table 5. Fire Related Parameters for JP-4 and Kerosene

For the purposes of creating a lab scale experiment, two pool trays were fabricated to determine a suitable scale JP-8 fire which would adequately simulate a large scale fire and which could be readily handled in a laboratory. The trays were 15 x 15 cm and 30 x 30 cm in size, approximating a laminar fire and a transition fire respectively. The scale of the fires was observed and the burn rate was determined both analytically and experimentally. The preliminary results of comparing analytical and experimental pool fires are shown in Table 6. and Figure 14.

PHYSICAL PROPERTIES

| | |
|--------------------------|--------|
| Density, Kg, m3 | 800 |
| κ Beta, m-1 | 3.5 |
| m-dot infinity, Kg, m2-s | 0.04 |
| Square Pan, length m | 0.15 |
| Equivalent Diameter, m | 0.1893 |
| Area, m2 | 0.0225 |
| m-dot, Kg, m2 s | 0.0179 |

EXPERIMENTAL RESULTS

| Run, # | 1 | 2 | 3 | 4 | 5 | 6 |
|--------------------------|-------|-------|-------|-------|-------|-------|
| Air Temperature, deg C | 25 | 25 | 25 | 25 | 25 | 25 |
| Fuel Temperature, deg C | 100 | 115 | 95 | 105 | 90 | 75 |
| Wind, mph | 15 | 15 | 15 | 15 | 15 | 15 |
| Fuel Volume, ml | 50 | 100 | 150 | 200 | 250 | 500 |
| Fuel Mass, Kg | 0.040 | 0.080 | 0.120 | 0.180 | 0.200 | 0.400 |
| Fuel Depth, cm | 0.222 | 0.444 | 0.667 | 0.889 | 1.111 | 2.222 |
| Burn Time, s(calculated) | 99.4 | 198.9 | 298.3 | 397.7 | 497.1 | 994.3 |
| Burn Time, s(observed) | 93 | 200 | 285 | 285 | 395 | 595 |

Table 6. Burn Times for Scale Model Pool Fires

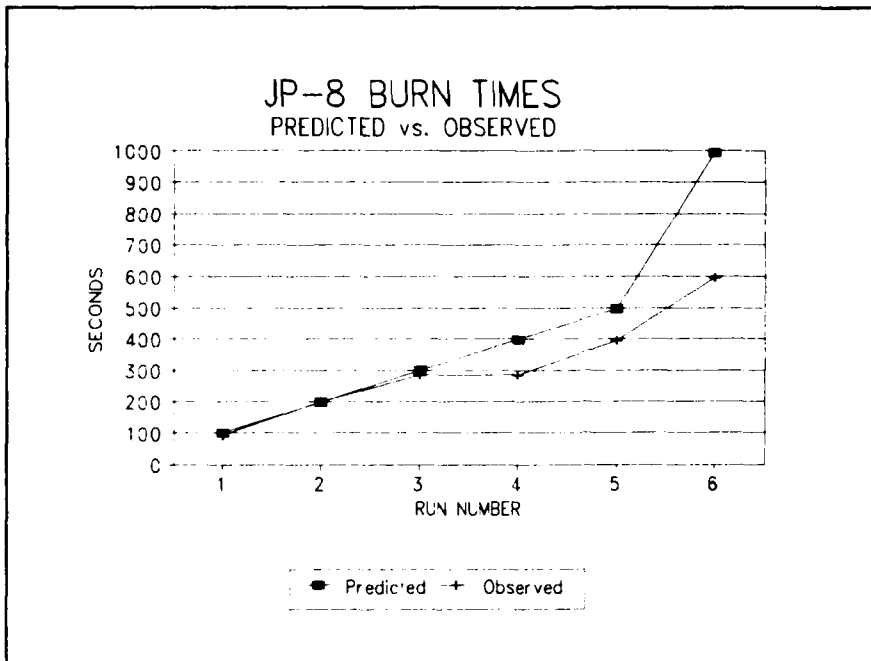


Figure 14. JP-8 Burn Times for Scale Model Pool Fires

As a consequence of conducting the test burns the basic size of a laboratory scale fire was set at a 15 x 15 cm tray. The 30 x 30 cm tray produced a fire size and energy output which were greater than what could be reasonably handled in a laboratory setting. One difficulty is that the equivalent diameter of the 15 x 15 cm tray places it in a transition range in terms of flame behavior and combustion activity. However it is believed that, in terms of the CT aspects, the issue of laminar versus turbulent convection is a second order effect which does not have appreciable effect on the experiment.

The selection of a suitable sized pan to simulate a pool fire requires that the physical dimensions, flows, temperatures, and pressures be scaled by a process known as Dimensional Analysis and Buckingham's Theorem. The strategy is to select the dimensionless groups, such as the Reynolds and Prandtl numbers, which must be preserved in order to have a suitably scaled model (Cheremisinoff, 1981). The number of dimensionless groups which should be preserved in order for the model to have the same response as the real flightline fire is quite large. Therefore two methods involving dimensionless groups have evolved in the study of fire dynamics in order to simplify the modeling process: Froude modeling and pressure modeling.

Froude modeling is suitable where viscous forces are relatively unimportant and velocities are scaled with the square root of the principal dimension. In Froude modeling the geometry of the system must be preserved. The Froude number is expressed as follows:

$$\text{Froude Number (Fr)} = \frac{u_m^2 \rho}{l g \Delta \rho} \quad (3)$$

where: u_m = maximum velocity
 ρ = density
 l = flame height
 g = acceleration due to gravity
 $\Delta \rho$ = density change

The Froude number has a physical interpretation as the ratio of:

$$\frac{\textit{inertia forces}}{\textit{viscous forces}}$$

There are correlations which give the flame height of the fire as a function of thermal output:

$$l = 0.23 \dot{Q}_c^{2/5} - 1.02D \quad (4)$$

where: l = flame height
 $\dot{Q}_c^{2/5}$ = rate of heat release
 D = fire diameter

Pressure modeling handles both laminar and turbulent flow and preserves the Grashof number, defined as:

$$\text{Grashof Number (Gr)} = \frac{g}{\mu^2} \left(\frac{\rho}{\Delta\rho} \right) \rho^2 l^3 \quad (5)$$

where: g = acceleration due to gravity
 μ = dynamic viscosity
 ρ = density
 $\Delta\rho$ = density change
 l = flame height

Physically the Grashof number may be described as the ratio of:

$$\frac{\text{buoyancy forces} \times \text{inertia forces}}{(\text{viscous forces})^2}$$

Although there are advantages to either modeling method, the pressure method requires that the pressure be varied to maintain similitude between physical reality and the laboratory model. Thus a scaling of an object 1 m. high to a 0.1 m. experimental scale would require a pressure scaling from 1 atm to 31.6 atm (Drysdale, 1985). This would be highly impractical for the models envisioned here. Since it can be assumed that viscous forces are not important in the pool fire scenario, Froude modeling would suffice for the modeling of the pool fire.

The calculation of the modeling parameters utilizes the following equation set:

$$\dot{Q}_c = \dot{m}'' \Delta H_c A_f \quad (2)$$

$$l = 0.23 \dot{Q}_c^{2/5} - 1.02 D \quad (6)$$

$$u_o = \dot{Q}_c^{1/5} k \left(\frac{z}{\dot{Q}_c^{2/5}} \right) \quad (7)$$

$$\frac{2 g \Delta T_o}{T_o} = \left(\frac{k}{c} \right)^2 \left(\frac{z}{\dot{Q}_c^{2/5}} \right)^{2 \eta - 1} \quad (8)$$

where: \dot{Q}_c = thermal output, Kw
 \dot{m}'' = surface burn rate, Kg/m²-s
 ΔH_c = thermal capacity, MJ/Kg
 A_f = Fire Area, m²
 u_o = Flame Velocity, m/s
 k, c, η = Constants
 g = 9.8 m/s²
 z = Flame Height at Centerline of Fire, m
 T_o = Ambient Temperature, 20°C
 ΔT_o = Temperature Rise of Flame, °K

The August 1991 NMERI full scale test burn utilized a 150 ft² pool fire. Using the methods described above the following parameters for that fire, using JP-4, can be predicted.

| | |
|---|----------|
| Fire Area, m ² | = 13.94 |
| Equivalent Diameter, m | = 4.21 |
| Mass Burn Rate/Area, Kg/m ² -s | = 0.051 |
| Heat Release Rate, KJ/s | = 30,925 |
| Flame Height, m | = 10.1 |
| Flame Centerline Velocity, m/s | = 21.51 |
| Centerline Temperature, °C | = 873.5 |
| Froude Number | = 4.67 |

Scaling the full scale fire to a 15 cm x 15 cm laboratory scale model provides the following parameter sets based on Froude scaling:

| | |
|---------------------------|----------|
| Fire Area, m ² | = 0.0225 |
| Equivalent Diameter, m | = 0.169 |
| Heat Release Rate, KJ/s | = 0.50 |

The result is a fire that provides a low, controllable heat release rate and that can be readily handled in a laboratory setting. The unanswered difficulty with this model is that the actual control of the heat release rate in practice will be very difficult. Although not entirely satisfactory the combustion air delivery rate to the pool fire may have to be controlled to insure the low burn rate required for proper scaling.

**11. Design Aspects and Constraints for JP-8/Fire Suppressant
Combustion Toxicology Test Apparatus**

The apparatus designed to establish the combustion toxicity of the interaction of JP-8 and the candidate Halon replacement agents must be able to adequately portray a realistic fire scenario by producing concentrations of fumes and particulates that are reasonably close to real fire concentrations. As a consequence of this scaling problem, a number of important issues need to be resolved to adequately design the CT apparatus for these studies.

The first issue is the collection of large scale experimental data and the design of a laboratory scale experiment to mimic the large scale results. To accomplish this, the previously mentioned full scale fire scenario was created by NMERI. The fire was a combination of a running fuel fire and a 150 ft² pool fire. Data was collected from this fire by the Midwest Research Institute (MRI). Among the critical data that were collected were the variation of CO and particulates at a distance from the fire that is a likely fire fighting distance. The laboratory scale fire for CT testing can mimic the conditions found in the large scale fire. The question then remains whether the exact conditions found in the large scale fire should be replicated or whether the concentrations should be increased or decreased because animal threshold effects for lethality and incapacitation may differ from human effects by significant amounts for some compounds.

A second issue is whether lethality or incapacitation should be used as the measure of CT effects. As noted in section 6 of this report, each product of combustion will have a significant difference in concentration for lethality versus incapacitation. On the one hand, the use of incapacitation as a measure of CT effects runs parallel with general USAF desires to assess mission capability. On the other hand incapacitation experiments are much more difficult to execute in some types of experiments because animals must be trained in one or more behavioral patterns, the degradation of which is a measure of incapacitation. This involves a significant amount of additional time and expense to ready and execute the experiment. The potential use of untrained behavior as a measure of incapacitation would significantly reduce the preparation time. One final point is that the degradation of behavior is a fairly subjective measure of performance while lethality is a straightforward measure of effect. It can be argued that the relationship between lethality and incapacitation is known for some of the major combustion constituents such as CO and HCN. Thus it may be possible to forecast the overall concentration of combustion atmosphere at which incapacitation would occur. Another possibility is to design the experiment with enough flexibility to accept either incapacitation or lethality studies.

A third issue is the burn time and fire suppressant injection timing of the CT experiment. Preliminary rudimentary experiments with JP-8 indicate that may be difficult to obtain burn times in

with JP-8 indicate that may be difficult to obtain burn times in excess of 10 minutes without resorting to pumping of fuel into the chamber, an unnecessary complication. Thus the exposure time of the animals will probably be limited to approximately 10 minutes. The requirement to inject the fire suppressant and generate the new combustion atmosphere must also be accommodated in the protocol. Another possibility is to create an experimental scenario which exposes the animal chamber to a sequence of clean air, JP-8 combustion atmosphere, JP-8/fire suppressant atmosphere, and finally clean air. This sequence would reasonably approximate a real world fire. Previous work performed at AAMRL used a cycle time of 90 minutes (Elves, et al., 1990):

| | |
|-------------|-------------------------------|
| 0 - 15 min | Agent On/Animals in Chamber |
| 15 - 45 min | Desired Nominal Concentration |
| 45 - 60 min | Agent Off |
| 60 - 90 min | Nominal Concentration = 0 |
| > 90 min | Animals Out |

At the present time it would appear that a 40 minute cycle would be appropriate for JP-8/HCFC interaction in a CT experiment:

| | |
|-----------------|----------------------------------|
| 0 min | Animals In |
| 0 - 10 minutes | Fresh Air Circulation |
| 10 min | Ignite JP-8 |
| 10 - 20 minutes | JP-8 Burn |
| 20 minutes | Inject HCFC |
| 20 - 25 minutes | Fire Suppression/Gas Interaction |
| 25 - 30 minutes | Purge Gases |
| 30 - 40 minutes | Fresh Air Circulation |
| > 40 minutes | Animals Out |

A fourth issue is whether or not a dose response curve can or should be generated for these CT experiments. A nominal dose response curve would involve a fairly simple scenario such as would be the case for the thermal degradation of one of the HCFC's conducted in an NBS or FAA test apparatus. The JP-8/fire

suppressant CT experiment does not lend itself very well to generation of a dose response curve because in fact two or more sets of events are occurring. The first event is a JP-8 fire while the second is a JP-8/fire suppressant interaction event. A dose response curve would be a plot of concentration-time (C*t) versus time employing Haber's Rule which hypothesizes that the product of concentration and time for a given effect such as lethality is approximately constant. The question here is what is the product whose concentration is being utilized to generate the curve. Initially it would be the concentration of JP-8 combustion atmosphere and particulates. At a later point in time it would also include the addition of the products of JP-8/fire suppressant interaction. A carefully qualified C*t relationship could be generated which is specific to the experiment and the combination of fuel and fire suppressant involved.

A number of features of the CT experiment can in fact be forecast ahead of time, prior to the acquisition of large scale fire test experimental data. The animals must receive an adequate supply of oxygen during the course of the experiment to insure that oxygen deprivation is not a cause of lethality. The temperature of the animal chamber must also be maintained to insure that the animals do not perish as a consequence of heat stress. Lethality should be a result of toxic gases and aerosols alone (NRC, 1977; NRC, 1978).

The preliminary design of the CT apparatus for conducting JP-8/HCFC

studies is shown in Figure 15. It incorporates features which minimize smoke aerosol deposition, allow highly repeatable experiments, provide for precise control of conditions, and utilize computer controls to the maximum for sequencing monitoring, and analysis.

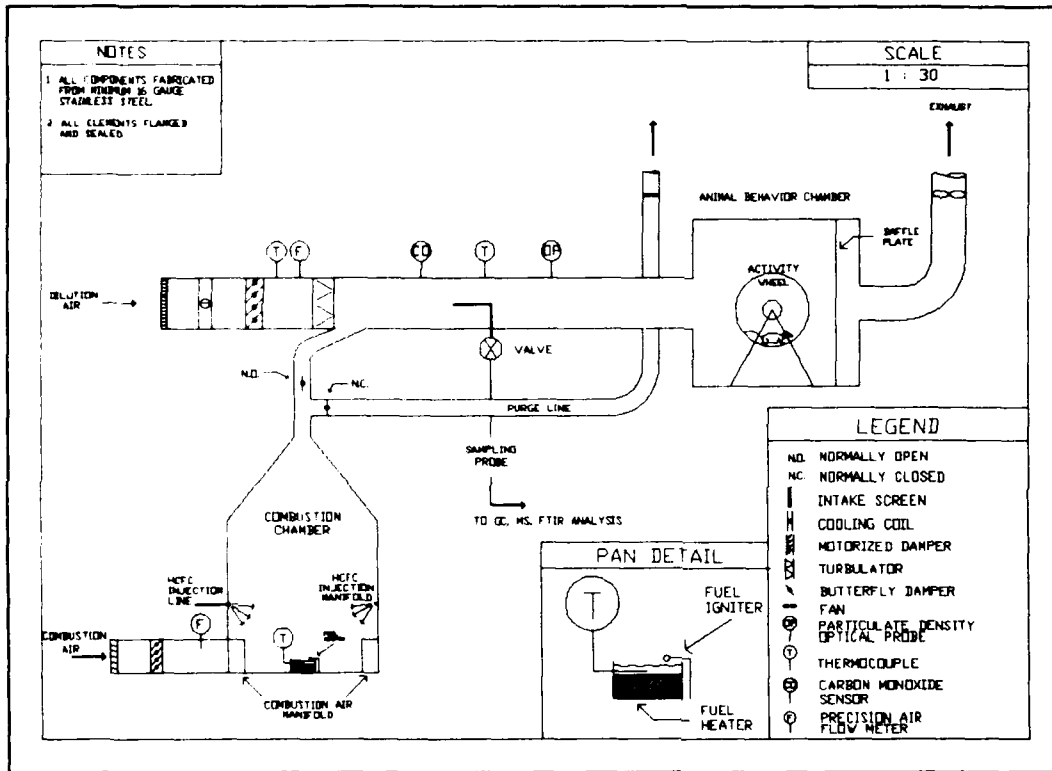


Figure 15. Preliminary Design of a Combustion Toxicology Apparatus for Analysis of JP-8/HCFC Interaction

12. Animal Testing Aspects

The downstream side of the apparatus for simulation of JP-8/HCFC interaction is envisioned as a chamber suitable for use in animal behavior. Appendix B is a summary of animal behavior testing methods that were examined for their applicability and utility for this purpose.

The general categories of animal behavior which could be utilized are either trained behavior or untrained behavior. Each category has advantages and disadvantages. Primary in the decision to utilize one method over another will be time and cost. The trained behavior approach has major disadvantages when the effort required to train the animals is taken into account and when somewhat subjective criteria must be employed to determine the loss of function. Consequently untrained animal behavior is an attractive possibility, especially in light of the research progress into various schemes for assessing various end points associated with loss of coordination and loss of ambulatory capability. Several methods which are potentially useful in the JP-8/HCFC CT research program are Home Cage Behavior, the Running Wheel, and the Rotorod. Another potential new development which should be considered is a combination of Running Wheel and Rotorod. This latter device can be highly automated together with the combustion chamber to provide highly reliable data and repeatable experiments. Appendix B contains a summary of untrained animal behavior knowledge for use in determining the final configuration of the animal chamber.

13. Conclusions/Recommendations

This research program had the primary purpose of determining the feasibility of performing CT testing of the interaction of JP-8 with Halon replacement fire suppression agents. It can be concluded that this CT test program is indeed feasible. However there are several qualifications which must be made to specify how the results would be interpreted, expressed, and utilized:

(1) The CT program described here differs from conventional CT efforts in that it consists of flaming combustion rather than pyrolysis.

(2) The end-point of the CT program is incapacitation corresponding to degradation of USAF mission performance. Additionally the test program contains several phases (burn, suppression, purge) which makes a straightforward statement of lethality or LC_{50} difficult to achieve.

(3) The desired outcome, without good correlation of animal effects to human behavior, is a comparison of Halon replacement agent effects with the effects of a relatively benign Halon 1301 or even with the presently utilized flight line fire suppression gas, Halon 1211.

With regard to the combustion chamber portion of the apparatus, the following recommendations are made:

(1) The pan size for simulation of the pool fire should be on the order of 15 x 15 cm in size.

(2) Accommodation should be made for varying dilution air inserted into the apparatus to allow the concentrations of the combustion products to be varied to, above, and below the fire scenario concentrations.

(3) All measures which can be utilized to prevent deposition of

smoke aerosols on the walls of the apparatus should be employed.

(4) The apparatus should employ computer controls to insure repeatability of test protocols.

(5) Mixing of combustion products and dilution air should employ measures to insure a thoroughly mixed gas enters the animal chamber.

(6) Control should emphasize CO as the target gas for dilution.

(7) A second control system should insure that temperature reaching the animal temperature are $< 34^{\circ}\text{C}$.

It is recommended that the animal behavior be conducted in the following manner:

(1) Use a combination Running Wheel/Rotorod as the apparatus for assessing animal response to the products of combustion.

(2) Utilize sets of 10 trials per scenario to provide statistically significant data.

(3) Measure times to loss of coordination (animal drops off Rotorod) and loss of ambulatory capability (animal ceases ambulation).

APPENDIX A

BASIC TOXICOLOGICAL DATA

| COMPOUND | LC ₅₀ | REF. | TLV _{TWA} | REF. | TLV _{STEL} | REF. |
|---------------------------------|------------------|------|--------------------|------|---------------------|------|
| C ₃ H ₄ O | 13 | b | 0.1 | a | 0.3 | a |
| Br ₂ | 750 | b | 0.1 | a | 0.3 | b |
| COBr ₂ | --- | | --- | | --- | |
| COCl ₂ | --- | | 0.1 | a | --- | |
| COF ₂ | 360 | b | 2 | c | 5 | c |
| CO ₂ | | | 5000 | a | 30000 | a |
| CO | 1807 | b | 50 | a | 400 | a |
| CH ₂ | 472 | b | 1 | a | 2 | a |
| Cl ₂ | 293 | b | 0.5 | a | 1 | a |
| HBr | 2858 | b | 3 | a | --- | |
| HCl | 4701 | b | 5 | a | --- | |
| HCN | 484 | b | 10 | a | --- | |
| HF | 1276 | b | 3 | a | --- | |
| H ₂ S | 444 | b | 10 | a | 15 | a |
| NH ₃ | --- | | 25 | a | 35 | a |
| NO | 593 | b | 50 | a | --- | |
| NO ₂ | 88 | b | 3 | a | 5 | a |
| SO ₂ | 2520 | b | 2 | a | 5 | a |

Appendix A References

- a. 1990-1991 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, American Conference of Governmental Industrial Hygienists, 1990.
- b. Newton Irving Sax Richard J. Lewis, Sr. Dangerous Properties of Industrial Materials, Van Nostrand Reinold, 1989.
- c. Newton Irving Sax Richard J. Lewis, Sr. Hazardous Chemicals Desk Reference, Van Nostrand Reinold, 1989.

APPENDIX B

TESTING ANIMAL INCAPACITATION

1. Incapacitation versus Lethality

Traditionally the lethal concentration of a gas or smoke has been determined by exposing animals to various concentration levels until 50 percent of the animals die within a specified time period. This is defined as the LC_{50} value. A problem arises when the concentration necessary to incapacitate or impair the animal from performing a specific task is to be determined. The first and foremost concern is to define what constitutes incapacitation. Different tasks require various levels of cognitive ability and incapacitation in one situation is not the same as incapacitation in a different situation. Although behavioral studies are not new to toxicology, no standard test or set of tests for determining, both qualitatively and quantitatively, the level of incapacitation, have been widely accepted (Kaplan et al., 1983). The need for such a standard procedure is critical for determining the concentration levels at which incapacitation occurs in animals and the degree of that incapacitation.

2. Animal Testing Methods

Some of the testing procedures used in the past for determining changes in animal behavior during and following exposure have been maze tests, homecage activity tests, open-field tests, startle

response tests, rotorod tests, and wheel tests. Each testing procedure looks for differences between the exposed and control groups of animals. Each test has advantages and disadvantages and measures different parameters such as activity or cognitive ability.

2.1 Mazes

The two most commonly used of the maze tests are the "T" and Figure Eight. The "T" Maze is used post-exposure to test for a reduction in cognitive abilities. The "T" Maze does not require animal training, but the animals may be conditioned to the maze prior to testing to assess the decrement in their baseline behavior as a measure of toxic effect. It is basically a swimming test through a series of 6 to 9 T-shaped passages arranged to form water-filled mazes (Figure 16). The time it takes for the animal to complete the maze and the number of wrong turns it makes are recorded and compared to a control animal. The Figure Eight is shaped like the number eight and is also used post-exposure (Figure 17). It differs from the "T" Maze in that it is not a swimming test and it measures level of activity rather than cognitive ability of the animal. A series of 8 photocells connected to a microcomputer record the level of locomotor activity. A possible disadvantage of the Figure Eight Maze is that it takes 1-2 hours for rats to achieve habituation because of its level of complexity. However the Figure Eight Maze can be used to measure "exploratory activity" without habituation in as little as 20 minutes.

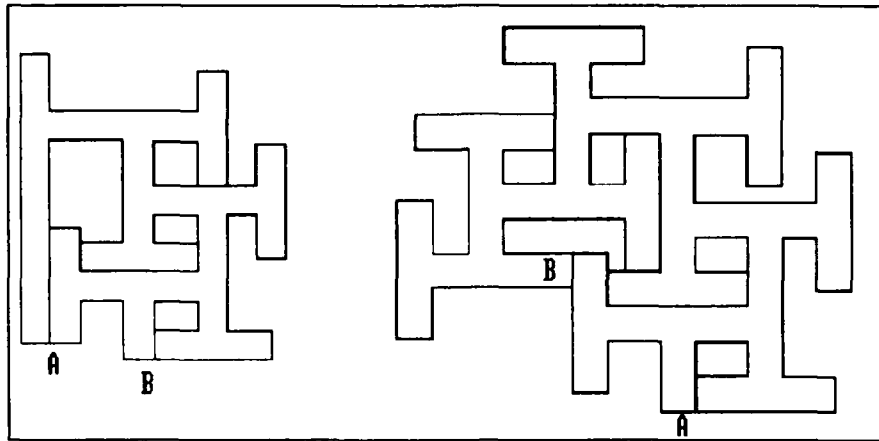


Figure 16. Biel Maze (left) and Cincinnati Maze (right) containing "T" units (Voorhees, 1987)

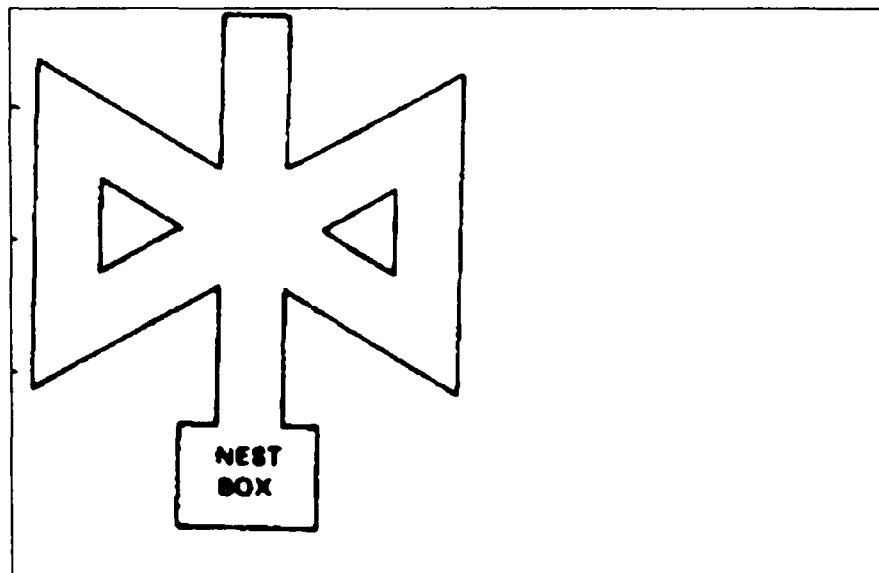


Figure 17. Schematic of "Residential Maze" Variant of Typical Figure Eight Maze with Nesting Box

2.2 Open Field

The Open-Field Test measures animal activity by dividing a large square box into smaller equal squares and counting animal movement between squares. This is done visually, with photocells, or by using a pressure sensitive grid. Due to its simplicity the habituation time for the Open-Field Test is about 15 minutes.

2.3 Homecage Activity

The Homecage Activity Test measures eating, drinking, rearing, and horizontal activity right in the animals home environment. The animal's rearing and horizontal activity is measured by mounting photocells on aluminum brackets outside the plexiglass cage and recording and logging the activity level via microcomputer (Figure 18). The animal's eating and drinking behaviors are also monitored in 24 hour increments. Although there is disagreement as to the reliability of homecage behavior tests due to the large amount of variability among animals, there is also evidence to suggest that, among activity tests, homecage behavior testing can provide a comprehensive measure of toxicity.

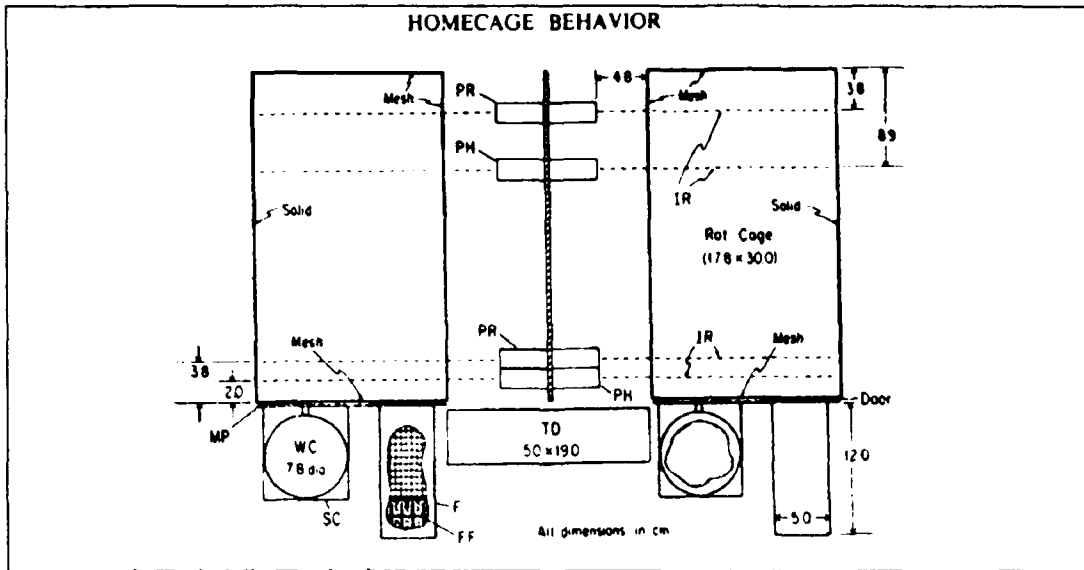


Figure 18. Homecage Behavior Apparatus

2.4 Startle Response

The Startle Response Test detects the time for an animal to respond to a noise or some other stimulus. The animal is placed in a cage and allowed an adaptation period before the stimuli are administered. The mammalian startle reflex in a rat is exhibited as an abrupt contraction of the flexor musculature that yields a momentary crouching posture. This test can be useful in evaluating the effects of some CNS toxins.

2.5 Rotorod

The Rotorod Test is a mechanical method for measuring animal incapacitation. After some training, a rat will remain on a

rotating rod above an electrified grid to avoid being shocked. When the animal cannot remain on the rod or cannot jump back on the rod within a designated time, the animal is considered incapacitated (Kaplan et al., 1983). It should be noted that the level of incapacitation is still open to debate because it is possible that the rat could still perform other less complicated tasks.

2.6 Running Wheel or Rotating Wheel

A rotating wheel is a motor-driven exercise wheel on which the rat walks or runs for the purpose of testing cognitive ability. When the rat begins to slide or tumble it is said to be incapacitated (Kaplan et al., 1983). It is hypothetically possible to assign different levels of difficulty based on the speed of the wheel and to correlate them to varying degrees of incapacitation. Some researchers argue that walking and running are reflex type activities, hence the rotating wheel does not test cognitive ability. Further research is required in this area before definitive conclusions can be drawn.

The running wheel is a wheel that is driven by the rat walking or running on it and therefore is a measure of activity. A counter is attached to count the number of revolutions in a given time period. A disadvantage is that the animal may not run or walk voluntarily without some training or other method of encouragement. A baseline must be determined to compare the treated animals with the controls and it is difficult to observe subtle differences of significance.

REFERENCES

AFWAL/POSF, 1987. Cost Savings Possible with AF Conversion to JP-8 as its Primary Fuel. AFWAL-TR-87-2037, Wright-Patterson AFB, Ohio.

Barsky, F.C. and Butterworth, B.E., 1976. In Vitro Mutagenicity Studies of 2,2-dichloro-1,1,1-trifluoroethane. Haskell Laboratory Report No. 581-76., August 3, 1976.

Bishop, E.C., et al., 1983. USAF OEHL Report 83-128EH111DGA, Brooks AFB, Texas.

Blinov, V.I. and Khudiakov, G.N., 1957. The Burning of Liquid Pools, Doklady Akademi Nauk SSSR, **113**: 1094.

Callander, R.D., 1989. HCFC 123 - An Evaluation Using Salmonella Mutagenicity Assay. Imperial Chemical Industries Limited, Central Toxicology Laboratory, Alderly Park, Macclesfield, UK. Report No. CTL/P/2421.

Cheremisinoff, N.P., 1981. Fluid Flow: Pumps, Pipes, and Channels. Ann Arbor Science Publishers, Inc., Ann Arbor Michigan, 115-127.

Crane, C.R., et al., 1985. Inhalation Toxicology IV. Times to Incapacitation and Death for Rats Exposed Continuously to Atmospheric Hydrogen Chloride Gas. FAA-AM-85-4, Civil Aeromedical Institute, Oklahoma City, Oklahoma, Federal Aviation Administration.

Crowe, C.D., 1978. Ninety-day Inhalation Exposure of Rats and Dogs to Vapors of 2,2-dichloro-1,1,1-trifluoroethane (FC-123). Haskell Laboratory Report No. 229-78.

Drysdale, D., 1985. An Introduction to Fire Dynamics. John Wiley and Sons, Chichester, U.K., 149-151.

Elves, R., et al., 1990. Combustion Toxicity of Halon Replacements, AAMRL ongoing study.

Gad, S.C. and Anderson R.C., 1990. Combustion Toxicology, CRC Press, Boca Raton, Florida, 1-202.

Gosselin, et al., 1989. Clinical Toxicology of Commercial Products, Fifth Edition, Williams and Wilkins, 220-224.

Grant, C.C., 1990. Life Beyond Halon, Fire Journal, **84**: 52-59.

Hazelton Laboratories America, Inc., 1976. LC₅₀ of G124 in Rats, Final Report. Project No. 165-163, Vienna, Virginia.

Hottel, H.C., 1959. Certain Laws Governing Diffusive Burning of Liquids, Fire Research Abstracts and Reviews, Vol 1, 177.

Industrial Bio-Test Laboratories, 1977. 90-Day Subacute Inhalation Toxicity Study with Nenetron 124 in Albino Rats. IBT Report No. 8562-09345, Northbrook, Illinois.

Jagannath, D.R., 1977. Mutagenicity Evaluation of Isotron 142b. Study performed by Litton Bionetics, Inc., Kensington, Maryland. LBI Project NO. 20838.

Kaplan, H.L., Grand, A.F., and Hartzell, G.E., 1983. Combustion Toxicology: Principles and Test Methods, Technomic Publishing Company, Lancaster, Pennsylvania, 1-179.

Kaplan, H.L. and Hartzell, G.E., 1984. Modeling of the Toxicological Effects of Fire Gases: I. Incapacitating Effects of Narcotic Fire Gases. Journal of Fire Science, 2: 286.

Kaplan, H.L., et al., 1985. Effects of Combustion Gases on Escape Performance of the Baboon and the Rat. Journal of Fire Science, 3: 228.

Lester, D. and Greenberg, L.A., 1950. Acute and Chronic Toxicity of Some Halogenated Derivatives of Methane and Ethane. Arch. Ind. Hyg. Occup. Med., 2: 335-344.

Licht, 1990. Chlorofluorocarbons (CFC) Recovery and Source Reduction, Charles Licht Engineering Associates Inc., study performed for the Illinois Department of Energy and Natural Resources, ILENR/RE-AQ-90/14.

Longstaff, E. and McGregor, 1978. Mutagenicity of a Halocarbon Refrigerant Monochlorodifluoromethane (R-22) in Salmonella Typhimurium. Toxicology Letters, 2: 1-4.

Longstaff, E. et al., 1984. Genotoxicity and Carcinogenicity of Fluorocarbons: Assessment by Short-Term in Vitro Tests and Chronic Exposure in Rats. Toxicology and Applied Pharmacology, 72: 14-34.

Martel, C.R., 1987. Military Jet Fuels, 1944-1987. AFWAL-TR-87-2062, Wright-Patterson Air-Force Base, Ohio.

Mattie, D.R., et al., 1989. A 90-Day Continuous Vapor Inhalation Toxicity Study of JP-8 Jet Fuel Followed by 20 or 21 Months of Recovery in Fischer 344 Rats and C57BL/6 Mice, Poster Session at the 28th Annual Meeting of the Society of Toxicology, February 27 - March 3, 1989.

Muller, H. 1988. HCFC 123 Micronucleus Test in Male and Female NMRI Mice After Inhalation. Pharma Research Toxicology and Pathology, Hoechst Aktiengesellschaft, Frankfurt am Main, Germany, Report No. 88.1340.

Mullin, L.S., 1969. Cardiac Sensitization. Haskell Laboratory Report No. 354-69.

MSDS, 1985. Material Safety Data Sheet (MSDS) for Shell Turbine Fuel, JP-8, Shell Oil Company, Houston, Texas.

NIST, 1990. Preliminary Screening Procedures for Replacements for Halon 1211 and 1301, NIST Technical Note 1278, August 1990.

NRC, 1977. Fire Toxicology: Methods for Evaluation of Toxicity of Pyrolysis and Combustion Products. NRC Committee on Fire Toxicology, Report No.2, National Academy of Sciences, Washington, DC.

NRC, 1978. Smoke and Toxicity (Combustion Toxicology of Polymers), Vol. 3, Publication NMAB 318-3, NRC Committee on Fire Safety Aspects of Polymeric Materials, National Academy of Sciences, Technomic Publishing Company, Westport, Connecticut.

Nimitz, J.S., et al., 1989. Survey of Candidate Fire Extinguishing Agents, International CFC & Halon Conference, October 10-11, Washington, DC.

NIOSH, 1977. Criteria for a Recommended Standard -- Occupational Exposure to Refined Petroleum Products, DHEW Publication No. (NIOSH) 77-192.

Pennwalt Corporation, 1980. A Dominant-Lethal Inhalation Study with Fluorocarbon 142b in Rats. Project No. 79-7288. Study performed by Bio/dynamics Inc., East Millstone, New Jersey.

Purser, D.A., 1988. Chapter 1-14, Toxicity Assessment of Combustion Products, SFPE Handbook of Fire Protection Engineering, Society of Fire Protection Engineers, Boston, Massachusetts.

Sax, N.I., 1984. Dangerous Properties of Industrial Materials, 7th Ed., Van Nostrand Reinhold Company, New York, 3: 2386.

Spurgeon, J.C., 1978. The Correlation of Animal Response Data with Yields of Selected Thermal Decomposition Products for Typical Aircraft Interior Materials, FAA-NA-78-45, National Aviation Facilities Experimental Center, Federal Aviation Administration, Atlantic City, New Jersey.

Stokes, M.J. 1990. Health Exposure Guideline for JP-8 Vapor, contained in Memorandum, EHT/AAMRL, 22 October 1990.

Voorhees, C., 1987, Neurotoxicology and Teratology, 9: 235-241

Zabetakis, M.G. and Burgess, D.S., 1961. Research in Hazards Associated with the Production and Handling of Liquid Hydrocarbon Pool Fires, U.S. Bureau of Mines Report No. RI-5707.