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METHODS DEVELOPMENT FOR MEASURING AND CLASSIFYING FLAMMABILITY/COMBUSTIBILITY OF REFRIGERANTS

Interim Report
TASK 2 - TEST PLAN

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PREFACE

This test plan was prepared by the Center for Global Environmental Technologies (CGET), the New Mexico Engineering Research Institute (NMERI), The University of New Mexico, Albuquerque, New Mexico 87131-1376 under Contract 660-52400 for the Air-Conditioning and Refrigeration Technology Institute (ARTI), 4301 N. Fairfax Drive, Suite 425, Arlington, VA 22203.

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ABBREVIATIONS AND ACRONYMS

AC	Alternating Current
ANSI	American National Standards Institute
ARTI	Air Conditioning and Refrigeration Technology Institute, Inc.
ASHRAE	American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc.
ASTM	American Society for Testing and Materials
CFC	Chlorofluorocarbon
DC	Direct Current
FTIR	Fourier-Transfer Infrared
HF	Hydrogen Fluoride
IR	Infrared
LFL	Lower Flammability Limit
MIE	Minimum Ignition Energy
NMERI	New Mexico Engineering Research Institute
PC	Personal Computer
UFL	Upper Flammability Limit
UV	Ultraviolet
VAC	Volts AC

SYMBOLS

°C	Degrees Celsius
cm	Centimeters
$d_{\|\|}$	Quenching distance
E	Energy .
F	Farads (Capacitance)
J	Joules
kHz	Kilohertz
kPa	Kilopascals
mL	Milliliters
mm	Millimeters
mg/m^3	Milligrams per cubic meter
mHz	Megahertz
psi	Pounds per square inch
psia	Pounds per square inch absolute
psig	Pounds per inch gauge
V	Voltage
ε_{eff}	Effective energy

1.0 INTRODUCTION

1.1 Background

Regulations on alternative refrigerants and concerns for the environment are forcing the refrigeration industry to consider the use of potentially flammable fluids to replace the chlorofluorocarbon (CFC) fluids currently in use. In some cases, these flammable fluids may result in the least environmental damage when considering ozone depletion, global warming, efficiency, and photochemical reactivity. Many potentially flammable fluids have proven to be effective when used either by themselves or as a part of a binary or ternary mixture. However, despite favorable initial test results, these fluids may not be acceptable to the general public if questions of safety cannot be adequately addressed. Significant research is being conducted to investigate the flammability of these materials.

One area of research is the determination of those conditions under which a refrigerant/air mixture can be used safely. American National Standards Institute/American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ANSI/ASHRAE) Standard 34-1992 currently classifies refrigerants based on the lower flammability limit (LFL) and the heat of combustion as determined by using the test method described in ANSI/ASTM E681-85. This test method uses a visual criterion for determining whether the refrigerant is flammable and is generally only valid at ambient and subambient pressure and relatively low temperatures. Additionally, the ignition of the mixture is accomplished by a spark generated between electrodes inside the test flask. This type of ignition may or may not be representative of a realistic threat. The use of this test method to determine the flammability of refrigerants has been questioned, and the objectives of this program are to establish the conditions under which refrigerants and refrigerant blends exhibit flammability and to develop appropriate methods to measure flammability.

1.2 Flammability Parameters

Not all combustible mixtures are considered flammable, and one of the difficulties in determining flammability is the definition of what constitutes flammability. According to Zabetakis,

> A combustible gas-air mixture can be burned over a wide range of concentrations—when either subjected to elevated temperatures or exposed to a catalytic surface at ordinary temperatures. However, homogeneous combustible gas-air mixtures are flammable, that is, they can propagate flame freely within a limited range of compositions. [1]

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[1] Zabetakis, Michael G., "Flammability Characteristics of Combustible Gases and Vapors," Bureau of Mines Report of Investigations 627, page 2, Bureau of Mines, Pittsburgh, PA, 1965.

We will use this definition for flammability, namely, that flames propagate freely through the gas-air mixture. The most dilute mixture that is flammable is known as the lower flammability limit (LFL) or lower limit, and the most concentrated mixture is known as the upper flammability limit (UFL) or upper limit. The paramount concept is that flame must propagate for the material to be flammable, and, with that in mind, we have borrowed liberally from the large body of combustion data to develop this test plan.

A second difficulty is the definition of the flammability limits themselves. Some researchers consider the LFL a unique fundamental material property[2] while others consider that there "is no convincing evidence for the existence of fundamental limits of inflammability, although theory suggests that there probably are such limits."[3] It is known that flames which can propagate upward may not always propagate downward, and that "carefully nurtured flames can be maintained well outside conventional limits"[4] using flat-flame burners. Pressure, temperature, catalytic effects, and other external factors influence flammability limits. One goal of this program is the development of a test technique that will determine realistic limits to reflect accurately the "true" flammability of refrigerants. One possible definition of "true" limits is that the limits should reflect the behavior of the flammable mixture in the environment in which the refrigerant is used.

Little has been published on the flammability of refrigerants. More data are available on the flammability of combustible gases, but the subject is almost always hydrocarbon fuels. Even more information is available on the ignition and propagation of flames through combustible mixtures. Therefore, the flammable refrigerant will be considered to have flammability properties similar to those of a hydrocarbon fuel, and other refrigerants in the mixture will be considered to be diluents or inertants. This concept will allow the application of vast amounts of combustion theory to the problem.

Combustion, and therefore flammability, generally cannot occur without the four legs of the fire tetrahedron—fuel, oxygen, heat, and sufficient free radicals to sustain the reaction. Unless sufficient fuel is available (at the LFL) or sufficient oxygen is available (at the UFL), the mixture is non-flammable. Unless the temperature reaches the ignition temperature, and heat is conveyed to the next layer of unburned gas, the mixture is non-flammable. And unless an adequate number of free radicals are available to sustain the reaction, the mixture is also non-flammable.

Gaseous fuels can burn in one of two ways. Fuel and air may be intimately mixed prior to burning (pre-mixed flames) or they may be initially separated and burned in the zone where they

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2. Grosshandler, William, ARI Flammability Workshop, March 8-9 1994, Chicago, IL, Air Conditioning and Refrigeration Institute, Arlington, VA 22203, 1994.

3. Linnett, JW., and Simpson, J.S.M., Limits of Inflammabilitv, Sixth Symposium (International) on Combustion, page 25, Reinhold Publishing Corporation, New York, NY, 1957.

4. Lewis, B., and Von Elbe, G., Combustion, Flames, and Explosion of Gases, 3rd Ed., page 326, Academic Press, Inc., Orlando, FL 32887, 1987.

mix (diffusion flames).[5] While flammable refrigerants may burn under either condition, most testing uses a pre-mixed flame rather than the diffusion flame (flowing, constant pressure systems are the exception). In reality, a realistic scenario for a flammable refrigerant could be an unconfined vapor cloud, which is not truly representative of either type of testing. For the purpose of this test program, only pre-mixed flames will be investigated due to the general acceptance of flammability results based on this type of testing.

Visual indications are only one of many indications that may be used to verify flammability. It may not be the most reliable method due to reactions at low temperatures that may produce cool flames or low-temperature explosions that, while producing luminosity, do not propagate on their own and thus do not meet the definition of flammability. Other indications of flammability that could potentially prove to be more reliable include the following:

a. Temperature rise. Does the ignition source raise the temperature above the limiting flame temperature of the mixture, which is required to sustain combustion?

b. Light. Are there non-visual methods—infrared or ultraviolet (IR or UV)—that can be more reliable and repeatable than visual?

c. Pressure rise. Both the magnitude of the pressure rise and the rate of the rise can be indicators of flammability.

d. Presence of radicals. It is known that combustion cannot occur without the presence of an adequate number of free radicals to sustain the reaction.

e. Presence of combustion products. Combustion can be indicated by the ratio of certain combustion products in the mixture.

f. Heat of reaction. Combustion can be indicated by the presence of a heat rise detected in bomb calorimetry.

g. Flame velocity. Combustion waves travel with a specific flame velocity that can be measured and analyzed to determine combustion.

h. Electrical properties. Electrical conductivity, ionization potential, dipole moments, and other electrical properties of the mixture may change after combustion.

Conceivably, each of these techniques could result in different limits of flammability depending upon the criteria. It is the purpose of this test program to propose and assess one or more reliable and repeatable test techniques to determine the flammability of refrigerants and refrigerant blends. Any experimental method should minimize the following quantities:[6]

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[5] Drysdale, D., An Introduction to Fire Dynamics, page 13, John Wiley and Sons, Chichester, England, 1985.

[6] Hertzberg, M., "The Theory of Flammability Limits - Natural Convection," Bureau of Mines Report of Investigations 8127, page 1, Bureau of Mines, Pittsburgh, PA, 1976.

a. Natural convection
b. Conductive/convection losses to walls
c. Radiative losses to walls
d. Selective diffusional demixing
e. Non-linear flow gradients (flame stretch)

Many parameters affect flammability and must be considered in the design and analysis of test methodology. Each of the factors below could affect the flammability limits:

a. Ignition source
b. Temperature of the mixture
c. Pressure of the mixture
d. Humidity of the air
e. Size and shape of the test vessel
f. Test vessel materials
g. Turbulence in the test vessel
h. Concentration of the components of the mixture
i. Reactivity of the components
j. Mixing of the components
k. Altitude of testing (may be a function of other factors such as pressure and air composition)

Each parameter will be discussed below.

1.2.1 Ignition Source

The ignition source may be the most critical parameter in determining repeatable flammability limits. Richard and Shankland[7] found differences of up to 12% in the LFL for R-32 when ignited with copper wire as compared to a match, and much greater differences have been found for more marginally flammable refrigerants such as R-141b. Except for autoignition, in which the temperature of the flammable gas is raised uniformly above the temperature required for ignition, most ignitions occur when a highly concentrated, but relatively small, region of high temperature raises the surrounding volume of flammable gas above its ignition temperature. If this reaction raises the temperature of the next layer of gas above its ignition temperature, the reaction continues

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[7] Richard, Robert G., and Shankland, Ian, "Flammability of Alternative Refrigerants," <u>ASHRAE Journal</u>, Vol. 34, No. 4, page 22, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA 30329, 1992.

and propagation of the flame occurs. If the next layer of gas is not ignited, the propagation is halted. Potential ignition sources, all of which provide this region of high temperature, include matches, pyrotechnic igniters (including electric matches), electric sparks, mechanical sparks, glowing wires, and hot surfaces. Alternating current (AC) sparks must be examined as well as the more traditional direct current (DC) sparks. Any potential source (for example, nichrome wire) must be examined to ensure that it does not have a catalytic effect on the reaction. Of the above sources, the two most likely to be repeatable are the match and the electric spark (AC or DC), and most flammability testing has been accomplished using those two ignition sources.

The electric spark is a very fast-acting ignition source, in the order of 10^{-8} to 10^{-7} seconds discharge time, and, therefore, the energy is highly concentrated. Sparks have been studied for years, primarily because of their importance in the internal combustion engine. Variables in this technique are given below:

a. AC versus DC. Testing at NMERI involving inertion of propane and methane by Halon 1301 has indicated that 120 volts AC (VAC) boosted through a transformer can ignite mixtures that cannot be ignited by a DC spark at any energy up to 100 J. However, the duration of the spark was not controlled.

b. Electrodes. The shape, diameter, separation distance, and materials may be critical. Most references indicate that above the quenching distance ($d_{||}$)—the maximum gap between electrodes that will successfully quench ignition—the shape of the ends of the electrodes is not important.[8] However, Lewis and von Elbe also state that for large spark energies, $d_{||}$ actually increases, due to the increased heat transfer produced by the turbulence of the larger spark.[9]

c. Position of the ignition source. It appears as if the majority of flammability testing, including the NMERI inertion work, has been conducted with the electrodes located approximately in the center of the apparatus. However, the procedures for testing in the ASTM flask do not specify a location of the electrodes, and indeed, the drawing of the apparatus indicates that the location should be somewhat lower than the center of the flask in Figure 1. Since ignition is measured by the upward propagation of flame, this would seem logical. On the other hand, Crescetti et al., have shown a correlation between the vertical location of the electrodes and the location of the flame front as a

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8. Sheldon, M., "Principles of Spark Ignition," Fire Protection, Vol. 165, page 28, Fire Protection Association, London, England, 1983.

9. Lewis, B., and Von Elbe, G., Combustion, Flames, and Explosion of Gases, 3rd Ed., pages 337-340, Academic Press, Inc., Orlando, FL 32887, 1987.

function of time.[10] Therefore, the vertical location of the electrodes in the ASTM flask will be considered as a variable.

d. Energy. Most electric sparks are produced by a capacitive discharge with many also having an inductive component. The energy level in a capacitive spark is defined by the stored electrical energy in the capacitors (½ FV^2) where F is the capacitance and V is the voltage to which the capacitors are charged (actually, the voltage before and after discharge must be considered). If there are no losses between the capacitor and the electrodes, all energy is transferred into the spark. However, it is possible that some energy will be required to initiate the spark and not all will be available to ignite the flammable mixture. The energy deposited at a sufficient temperature to initiate a freely propagating flame is called ε_{eff} and may be up to 2 orders of magnitude less than the stored energy, depending upon the voltage to which the capacitors were charged and the chamber volume size.[11] The energy loss due to the high-voltage transformer has been estimated at 85%.

e. Circuit parameters. (1) inductance in the ignition circuit results in a different type of spark than that without inductance[12] and (2) there is a fundamental difference in circuits that employ inductors in parallel or series to the capacitor. It has also been recognized that ignition energy is dependent not only on the resistance and capacitance of the circuit, but also on the product of the two, i.e., the discharge time constant.[13]

Matches have also been used for flammability testing. Matches are easily ignited using low voltage batteries or power supplies. Under most test conditions, matches have a higher energy content (one source reported 176 J)[14] than a spark with a time duration

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[10] Crescitelli, S., Russo, G., Tufano, V., Napolitano, F., and Tranchino, L., Flame Propagation in Closed Vessels and Flammability Limits, Combustion Science and Technology, Volume 15, pages 201-212, Gordon and Breach Science Publishers, Inc., New York, NY, 1977.

[11] Hertzberg, Martin, Conti, Ronald, and Cashdollar, Kenneth, Spark Ignition Energies for Dust-Air Mixtures: Temperature and Concentration Dependencies, Twentieth Symposium (International) on Combustion, pages 1682-1683, The Combustion Institute, Pittsburgh, PA 15213, 1984.

[12] Allsop, G., and Guenault, E.M., The Incendivity of Electric Sparks in Relation to the Characteristics of the Circuit, Third Symposium (International) on Combustion, page 344, The Williams and Wilkins Co., Baltimore, MD, 1949.

[13] Li, G., and Wang, C., "Comprehensive Study on Electric Spark Sensitivities of Ignitable Gases and Explosive Powders," Journal of Electrostatics, Vol. 11, page 331, Elsevier Scientific Publishing Company, Amsterdam, The Netherlands, 1982.

[14] Skaggs, S.R., Heinonen, E.W., Moore, T.A., and Kirst, J.A., Low Ozone-Depleting Halocarbons as Total-Flood Agents: Volume 2: Laboratory-Scale Fire Suppression and Explosion Prevention, NMERI OC 92/26, page 46, New Mexico Engineering Research Institute, Albuquerque, NM 87106, September 1993. (Draft)

much longer than a spark and have resulted in wider flammability limits than electric sparks or heated wires. It must be assessed whether matches provide a realistic ignition source in the small test volumes used in flammability testing.

Lewis and von Elbe describe ignition by hot-wires and heated metal bars.[15] These sources will be considered as potential ignition sources in this program.

The minimum ignition energy (MIE) for various hydrocarbons has been extensively studied for years.[16,17] According to Bradford and Finch, "in all cases which have been examined, more electrical energy is necessary to bring about ignition of mixtures near the limits than in the middle zone of inflammability." [18] Therefore, the MIE must be examined not only at the stoichiometric fuel-to-air ratio, but at the limits as well and as a function of composition. However, it is believed that rather than devote significant effort to determine precisely the MIE for various concentrations of agents, it is more critical to develop a representative source that provides repeatable and reliable ignition of the mixture with a known energy.

1.2.2 Temperature

In general, the higher the initial temperature, the wider the flammability limits. This occurs because less energy is required to bring the flammable mixture to its flame temperature. The mixture will ignite without an external source when raised to its auto-ignition temperature. Zabetakis[19] has suggested that the LFL of a hydrocarbon at any temperature can be estimated by drawing a line between the room temperature LFL and 0% concentration at 1300 °C (Figure 1). If this estimation can be extrapolated to flammable refrigerants, or if a similar estimation can be made, the amount of testing at elevated temperature can be minimized.

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15. Lewis, B., and Von Elbe, G., Combustion, Flames, and Explosion of Gases, 3rd Ed., pages 373-380, Academic Press, Inc., Orlando, FL 32887, 1987.

16. Ballal, D.R., and Lefebvre, A.H., The Influence of Flow Parameters on Minimum Ignition Energy and Quenching Distances, Fifteenth Symposium (International) on Combustion, pages 1473-1481, The Combustion Institute, Pittsburgh, PA 15213, 1974.

17. Blanc, M.V., Guest, P.G., Von Elbe, G., and Lewis, B., Ignition of Explosive Gas Mixtures by Electric Sparks III. Minimum Ignition Energies and Quenching Distances of Mixtures of Hydrocarbons and Ether with Oxygen and Inert Gases, Third Symposium (International) on Combustion, pages 363-367, The Williams and Wilkins Co., Baltimore, MD, 1949.

18. Bradford, B.W., and Finch, G.I., The Mechanism of Ignition by Electric Discharges, Second Symposium on Combustion, pages 112-126, The Combustion Institute, Pittsburgh, PA 15213, 1965.

19. Zabetakis, Michael G., "Flammability Characteristics of Combustible Gases and Vapors," Bureau of Mines Report of Investigations 627, pages 22-24, Bureau of Mines, Pittsburgh, PA, 1965.

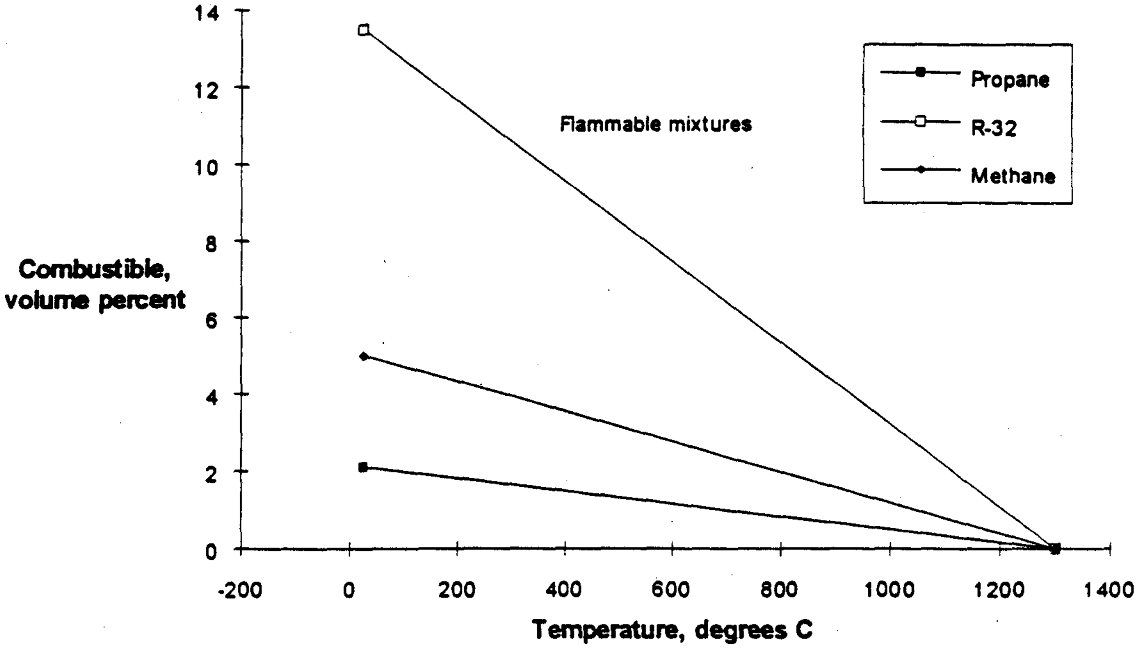

Figure 1. Effect of Temperature on Lower Limits of Paraffin Hydrocarbons in Air at Atmospheric Pressure (from Reference 19).

1.2.3 Pressure

Pressure effects are among the most difficult of all the factors affecting flammability to quantify, and in some cases, trends presented in different sources are contradictory. It is fairly well understood that higher pressures affect the UFL much more than the LFL. For example, Drysdale reports the UFL of methane as 60% and the LFL as 4% at 200 atmospheres (as compared to 15% and 5% at 1 atm)[20], indicating a significant widening of the limits. On the other hand, Coward and Jones state that increases in pressure above that of atmospheric do not always widen the limits and for some mixtures, the range of flammability is lowered with increasing pressure.[21]

At lower pressures some disagreements also occur. Drysdale indicates that pressures below atmospheric do not affect the flammability limits providing that the pressure is

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[20] Drysdale, D., An Introduction to Fire Dynamics, page 89, John Wiley and Sons, Chichester, England, 1985.

[21] Coward, H.F., and Jones, G.W., "Limits of Flammability of Gases and Vapors," Bureau of Mines Bulletin 503, pages 3-4, Bureau of Mines, Pittsburgh, PA, 1952.

above 10.1 kPa (0.1 atmosphere) and the compound remains either a gas or a liquid.[22] Egerton states that "a reduction of the pressure below 760 mm (*of Hg*) always causes both limits to converge until they coincide at some critical pressure below which no propagation can occur"[23] (although he does not state how rapidly this convergence occurs). However, Lovachev[24] has reported that Lewis and von Elbe were uncertain that a lower pressure limit independent of vessel size could exist. He also reported instances of flammability limits at extremely low pressures, although he concluded that ignition effects may have played a part in those tests. While these three statements may not be totally inconsistent (the conditions under which the conclusions were made were not described), the fact that some controversy appears to occur indicates that difficulty in measuring the flammability limits at low pressures exists. Therefore, care must be taken to define upper and lower pressure requirements that are reasonable and will not impact the flammability limits.

1.2.4 Humidity

While it has long been known that water vapor can affect the kinetics of a reaction, it has been only recently that the flammability behavior of R-245ca has been analyzed with respect to the moisture content of the air.[25,26] It has been postulated that more than one combustion reaction is possible depending upon whether adequate water vapor is present. This dichotomy occurs primarily where the number of fluorine atoms is greater than the number of hydrogen atoms and the flammability of refrigerants, such as R-134a, R-245ca, and R-245fa, may be affected by this phenomenon. Effectively, as refrigerant concentration, temperature, and pressure were kept constant, the flame characteristics intensified as the moisture content increased from 10 to 60% relative humidity. Therefore, any test methods developed must consider the relative humidity of the air.

In a personal correspondence, Dr. N. D. Smith of EPA noted some interesting observations regarding attempts to obtain known moisture levels in the ASTM E-681 flammability tests. In one series of 21 consecutive flammability tests, the same amount of

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[22] Drysdale, D., An Introduction to Fire Dynamics, page 88, John Wiley and Sons, Chichester, England, 1985.

[23] Egerton, A.C., Limits of Inflammability, Fourth Symposium (International) on Combustion, page 10, The Williams and Wilkins Co., Baltimore, MD, 1953.

[24] Lovachev, L.A., Babkin, V.S., Bunev, V.A., V'yun, A.V., Krivulin, V.N., and Baratov, A.N.,"Flammability Limits: An Invited Review," Combustion and Flame, Vol. 20, pages 281-282, Elsevier Science Publishing Co., New York, NY 10017, 1973.

[25] Smith, N.D., Ratanaphruks, K., Tufts, M., and Ng, A.S., "R-245ca: A Potential Far-Term Alternative for R-11," ASHRAE Journal, Vol. 35, No. 2, pages 19-23, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA 30329, 1993.

[26] Smith, N.D., ARI Flammability Workshop. March 8-9 1994, Chicago, Illinois, Air Conditioning and Refrigeration Institute, Arlington, VA 22203, 1994.

water (96 micrograms) was injected into the evacuated flask and allowed to evaporate and the resulting pressure exerted by the water vapor was recorded. For the first 20 runs, when the sphere was not cleaned between runs, the pressure of the water vapor declined after each test. When the flask was rinsed with DI water and dried in the oven for several minutes, the vapor pressure returned to the original value. In a similar discovery, the actual pressure was 37% lower than the predicted value - 1.57 kPa versus 2.47 kPa (11.8 torr versus 18.7 torr).

One potential explanation involves the adsorption of water vapor by the inside glass surface of the flask. The glass surface itself adsorbs water vapor, accounting for the discrepancy between the predicted and actual values. When hydrogen fluoride (HF) is formed as a result of combustion, it clings to the surface, providing radicals to facilitate the adsorption of the water vapor. As more tests are run without cleaning the sphere, more HF builds up. This observation underscores the importance of cleaning the inside of the flask, especially when zeroing in on the LFL or the UFL.

1.2.5 Test Vessel Size and Shape

Much of the accepted flammability results were developed in the Bureau of Mines in the 150-cm high by 5-cm diameter explosion or (flame) tube. In several studies it was determined that flammability limits were affected by the quenching effects of the vessel walls under 5 cm, but were generally unaffected over 5 cm.[27] Likewise, it was determined that explosion spheres of 5 liters (20.2 cm diameter) give similar results to larger vessels for R-32 flammability testing.[28]

However, the behavior of flammability limits in free space has not been studied extensively. Lovachev indicates that "the flammability limits of ammonia-air flames in free space were found to be wider than for a standard tube. This indicated that there are mixtures capable of burning in free space only."[29] Therefore, any limits determined in the confined spaces of the ASTM flask or explosion sphere must be regarded as approximate if the true flammability situation is an unconfined cloud of refrigerant.

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[27] Lewis, B., and Von Elbe, G., Combustion, Flames, and Explosion of Gases, 3rd Ed., page 324, Academic Press, Inc., Orlando, FL 32887, 1987.

[28] ICI Chemicals, KLEA 32 Blends: Flammability Characteristics, page 1, ICI Chemicals and Polymers, March 1992.

[29] Lovachev, L.A., "Flammability Limits-A Review," Combustion Science and Technology, Vol. 20, page 211, Gordon and Breach Science Publishers, Inc., New York, NY, 1979.

1.2.6 Test Vessel Material

Although for the most part flammability has been determined by the time that the flame front has reached the walls of the test vessel, two different properties could affect the flame front after that point. First, different materials have different heat conduction values, affecting the temperature of the flame front. Second, various types of materials tend to affect the free radicals differently, promoting different kinetics at the wall of the vessel.

One additional parameter to be considered is the cleanliness and condition of the ASTM flask. Repeated testing may eventually etch the Pyrex®, affecting both the actual results of the flammability testing and the visual observation of the tests. The observations of Dr. Smith reported in Section 1.2.4 illustrate this point.

1.2.7 Turbulence in the Test Vessel

Turbulence affects the development of the flame front. Drysdale[30] indicates that turbulence increases the rate of flame propagation through a mixture, but the effect is difficult to quantify. Significant research has been conducted on the effect of turbulence on coal dust explosions[31] and to a lesser extent flammable gases.[32] Any testing needs to consider that turbulence is a variable; consequently, turbulence should be reduced to as low a level as possible.

1.2.8 Composition of the Components of the Mixture

Two component factors determine the flammability of the mixture in air: the weight (or volume) fraction of each constituent element in a binary or ternary mixture, especially when only one of the constituents is flammable; and the total concentration of the mixture with air. Methods such as the Critical Flammability Ratio[33] can provide a good estimate of the flammability of any ratio of constituents if the weight percentage required to provide non-flammability to the flammable refrigerant is known for each individual constituent. One additional factor that must be considered is the purity of the individual constituents.

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[30] Drysdale, D., An Introduction to Fire Dynamics, pages 111-113, John Wiley and Sons, Chichester, England, 1985.

[31] Pu, Y.K., Jarosinski, J., Johnson, V.G., and Kauffman, C.W., Turbulence Effects on Dust Explosions in the 20-Liter Spherical Vessel, Twenty-third Symposium (International) on Combustion, pages 843-849, The Combustion Institute, Pittsburgh, PA 15213, 1991.

[32] Coward, H.F., and Jones, G.W., "Limits of Flammability of Gases and Vapors," Bureau of Mines Bulletin 503, pages 3-4, Bureau of Mines, Pittsburgh, PA, 1952.

[33] Dekleva, T.W., Lindley, A.A., and Powell, P., "Flammability and Reactivity of Select HFCs and Mixtures", ASHRAE Journal, Vol. 35, No. 12, page 46, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA 30329, 1993.

1.2.9 Reactivity of the Components

For the most part, the refrigerants used are very stable components; however, even stable components may react with outside chemicals such as lubricants or other fluids. In inertion testing using ethylene oxide and R-12 in the NMERI explosion sphere, a regular pressure decrease was noted prior to ignition. This was believed to be due to the ability of the ethylene oxide to polymerize. Reactivity is not considered to be a problem in either test or field situations and will be evaluated on a case-by-case basis rather than consequent to testing for each mixture.

1.2.10 Mixing of the Components

The ASTM E-681 method requires stirring for at least 5 minutes to obtain complete mixing and thermal equilibrium, with final trials to be made at longer mixing times. During initial inertion testing in the NMERI sphere, it was determined that repeatable results required thorough mixing of the fuel, air, and inertant. A electronic box fan was installed inside the sphere and allowed to run at least 1 minute to ensure proper mixing. Total mixing of all components is required in any test technique for consistency in the evaluation of flammability in a laboratory environment.

1.2.11 Altitude

Coward and Jones state that the normal variations of atmospheric pressures do not appreciably affect the limits of flammability[34]. However, the local atmospheric pressure at some locations may differ considerably from the 101 kPa (14.7 psia) sea level value. For example, the average barometric pressure at Albuquerque, with an altitude in excess of 1524 m (5000 ft), is approximately 84.1 kPa (12.2 psia). All NMERI sphere tests were performed at 101 kPa, which required the addition of approximately 17.2 kPa (2.5 psi) additional air to the sphere to compensate for the altitude. The ASTM method, which is performed at local atmospheric due to the requirement to rest the stopper on the top of the flask to allow proper venting of the explosion, does not accommodate additional pressure. An analysis of the effects of altitude will be performed.

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[34] Coward, H.F., and Jones, G. W., "Limits of Flammability of Gases and Vapors," Bureau of Mines Bulletin 503, page 3, Bureau of Mines, Pittsburgh, PA, 1952.

2.0 PROPOSED TEST APPARATUSES

The following test apparatuses have been identified as potential vehicles to develop a new test technique for determination of the flammability of refrigerants:

a. NMERI explosion sphere
b. ASTM E-681 test flask
c. Bomb calorimeter
d. Light emission detector
e. Flame tube or other glass vessel

A brief description of each follows, with pros and cons for each apparatus and a projection of modifications or additional research required for each one.

2.1 NMERI Explosion Sphere

The NMERI explosion sphere[35] (Figure 2) was constructed to investigate the ability of halocarbons to inert propane and methane. It was designed to screen large numbers of halocarbons to determine which ones required the least weight and volume of inerting agent to reduce the explosive overpressure to 1 psi or less, which was considered the definition of an explosion. In addition to its intended use, it has also been used to test inertants using refrigerants such as R-32, R-152a, and R-142b as fuels. As part of this series of tests, upper and lower flammability limits were found for these flammable refrigerants, although precise limits were not determined due to time limitations. In all cases, however, the flammability limits were narrower than reported using other test facilities, reflecting the trend that less inerting agent was required in the NMERI explosion sphere than in other apparatuses. The difference in NMERI results was the subject of a paper presented in 1993.[36]

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[35] Skaggs, S.R, Heinonen, E.W., Moore, T.A., and Kirst, J.A.,Low Ozone-Depleting Halocarbons as Total-Flood Agents: Volume 2: Laboratory-Scale Fire Suppression and Explosion Prevention, NMERI OC 92/26, pages 18-31, New Mexico Engineering Research Institute, Albuquerque, NM 87106, September 1993. (Draft).

[36] Heinonen, E.W., "The Effect of Ignition Source and Strength on Sphere Ignition Results," Proceedings of the Halon Alternatives Technical Working Conference 1993, pages 565-576, New Mexico Engineering Research Institute, Albuquerque, NM 87106, 1993.

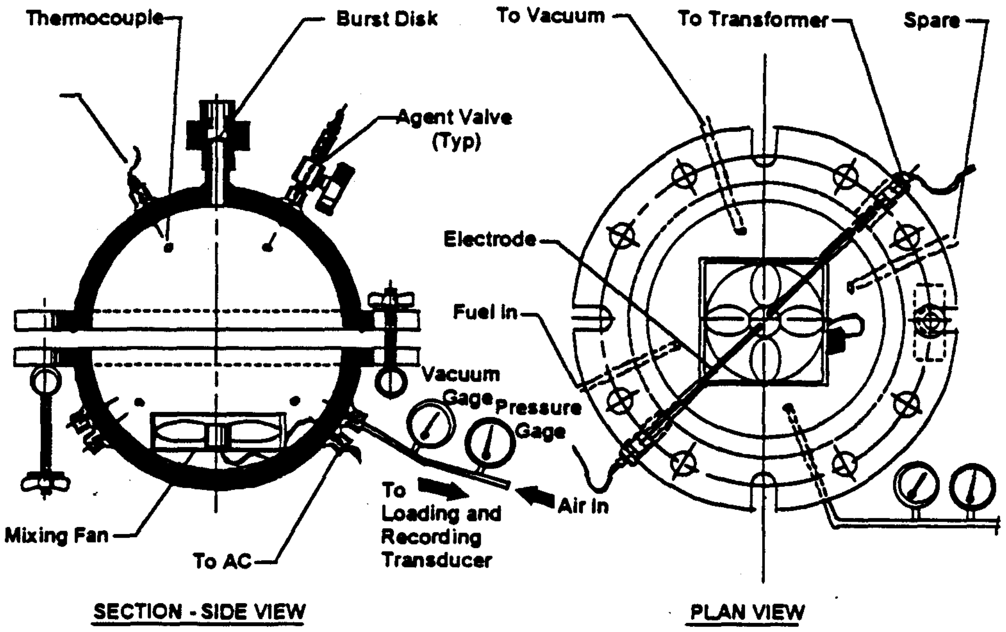

Figure 2. NMERI Explosion Sphere.

PROS: Procedures have been developed and results for inerting have been shown to be repeatable and reliable. Flammability limits for some flammable refrigerants have already been determined, although not to a great degree of accuracy. The measure of flammability—an overpressure of 1 psi—is quantifiable and repeatable. Because of the steel construction of the sphere, the effect of increased pressure can be examined.

CONS: An explosion sphere is not readily available for every user. It has to be custom-built. There is no indication that the chosen explosion limit, or any other arbitrary pressure limit, corresponds to flammability.

ADDITIONAL WORK: The ignition system has not been optimized. The electrodes have flat ends rather than the more efficient rounded or pointed, and the electrode separation was set at 6 mm, similar to that of other test techniques but nonetheless not optimized. As part of the ignition research, many factors will be investigated.

The Hewlett-Packard computer system used for control and data collection is slow and limited in channels, and data cannot be transferred to a personal computer (PC) for analysis and plotting. Therefore, a PC-based control and data collection system will be developed and the software rewritten to work on a PC. This will allow additional pressure transducer, thermocouple, and humidity measuring channels to be connected and accelerate data collection and analysis significantly.

2.2 ASTM E-681 Flask

This apparatus[37] is the standard device used to determine flammability of refrigerants.

PROS: The standard is well accepted and many potential testers already have the equipment. The test is easy to run, and there is a vast body of data available. The effect of temperature can be measured easier in this device than with the sphere.

CONS: Results for this test are subjective, depending in part upon the visual indication of flammability. The ignition source is not precisely denoted. "Test data available at present are inadequate to establish any measure of repeatability or reproducibility."[37]

ADDITIONAL WORK: Because of the general acceptance of this method, it appears logical that the test equipment and methodology should be modified using to the additional precision and automation available in the NMERI explosion sphere. This would involve a comparison of test results derived from the standard ASTM Standard E-681 method with those derived from a modified test technique. This modified technique could include more precise measurement of the partial pressures of the components, measurement of the overpressure using a precise transducer, control of the water vapor content in the air, and better control of ignition. A comparison could then be made between visual indications and pressure and temperature increases to assess how well flammability is determined by a visual trace. Size effects could also be examined by replacing the 5-liter flask by a 12-liter flask and repeating tests.

2.3 Bomb Calorimeter

Fedorko et al. used a bomb calorimeter in their evaluation of the flammability of R-22.[38] They did not consider the small size of the bomb (65 mm in diameter and 342 mL in volume), a handicap because they reported 50 mm (5 cm) as the limit of the quenching effects of the walls. Bomb calorimetry is a simple method to determine the heat of combustion, and it appears logical that the LFL and UFL, can also be determined by noting the lowest and highest concentrations under which combustion occurs. NMERI has available a Paar 1341 plain jacket oxygen bomb calorimeter,[39] which is apparently the same model used by Fedorko.

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[37] ASTM Standard E-681-85 (Reapproved 1991) Standard Test Method for Concentration of Flammability of Chemicals, American Society for Testing and Materials, Philadelphia, PA 19103, 1991.

[38] Fedorko, G., Fredrick, L.G., and Hansel, J.G., "Flammability Characteristics of Chlorodifluoromethane (R-22)-Oxygen-Nitrogen Mixtures," ASHRAE Transactions, No. 3097, pages 716-724, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA 30329, 1993.

[39] Instructions for the 1341 Plain Jacket Oxygen Bomb Calorimeter, Manual Number 147, Parr Instrument Corporation, Moline, IL. n.d.

PROS: Test procedures are well defined, results are precise, and many testers would have access to such a device.

CONS: Both the explosion sphere and the ASTM flask have been extensively used to measure the limits of flammability for numerous materials, but the bomb calorimeter has apparently been used by only a few researchers. It is uncertain to what degree of accuracy the LFL and UFL can be calculated and how well they might compare with the results determined from other apparatuses. The volume in this particular bomb is small. Precise measurement of the refrigerant would be required. Most testing is done at pressures above atmospheric, although atmospheric testing is possible.

ADDITIONAL WORK: For pressures above atmospheric, an analysis must be made to determine whether the refrigerants to be tested can generate adequate partial pressures to allow concentrations equal to the UFL or LFL to be injected in the bomb.

2.4 Light Emission Detection Device

This device would involve measuring individual photons as they are generated after the ignition. A schematic is shown in Figure 3.

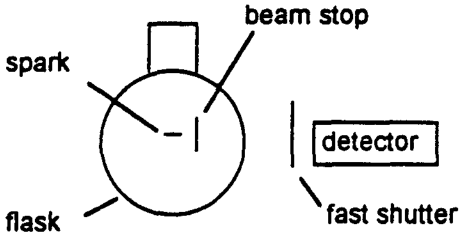


Figure 3. Light Emission Detection Device.

A photon detector would be aimed at the ignition point. A fast shutter would block the spark at the time of ignition but open to allow viewing immediately afterward. Photons emitted from the gas would be counted and combustion indicated.

PROS: This could be a precise indication of whether a combustion event has occurred.

CONS: The apparatus is not yet constructed and may not be practical. There has been no correlation between photon emission and flammability, and photon emission may occur long before visible ignition indications.

ADDITIONAL WORK: NMERI will investigate the feasibility of such a device, and construct a device if cost allows. Dr. Edward A. Walters (Chemistry Department, University of New Mexico) has several additional devices that may prove to be suited to this work; he will be an advisor to this phase of the work.

2.5 Other Test Vessels

Much of the early flammability results were obtained in flame tubes or other such devices. During the course of testing, design and construction of an apparatus similar to one of those early devices may prove useful to compare results.

PROS: It would be useful to repeat some early tests with more sophisticated instrumentation to investigate whether simple, repeatable results could be generated.

CONS: This reinvestigation would involve another complexity to the test program.

ADDITIONAL WORK: Planning, construction, and test method development would be required.

3.0 INSTRUMENTATION

3.1 Data Acquisition System

The data acquisition currently in use for the sphere is based on a Hewlett-Packard 86 computer. It does not have multi-channel data recording capability nor does it allow data transfer to a PC for data analysis and plotting. Therefore a new data acquisition system based on a 486 33-mHz PC has been developed for testing in both the sphere and the flask, using a National Instruments® 16-channel data acquisition card and LabWindow® software. This system will support 16 analog input channels, 2 analog output channels, and 8 digital input/output channels, as well as a clock and other functions. It will monitor loading of the air and components and control either the charging and discharging of the capacitors or the operation of other ignition systems. Data will be recorded and stored during a 10-second test window consisting of 2 seconds prior to ignition and 8 seconds following ignition. A signal indicating the time of ignition will be recorded and shown on all plots. Data will be recorded at 10 kHz per channel and displayed as pressure and temperature versus time plots immediately after test completion. All data, including information on the test parameters, will be stored in a format suitable for import into standard spreadsheet and database applications.

3.2 Standard Test Instrumentation

For all tests conducted in the sphere and flask, the following data will be recorded.

3.2.1 Temperature

At least two, and possibly three, channels of temperature data will be taken. Temperature will be measured at locations above the ignition point, below the ignition point, and possibly along the wall of the vessel. For testing in the sphere, two Type K thermocouples will be used. For testing in the flask, a faster response time device such as a thermistor may be used. Temperature measurements will be taken continuously before and after test and recorded during the 10-second test window.

3.2.2 Pressure

The blast overpressure produced in the sphere as a result of the explosion will be measured using a Druck 0-206 kPa (0-30 psi) pressure transducer. It was chosen because of its accuracy in measuring lower pressure explosions near the flammability limits. The minimum pressure rise that can be measured using this transducer should be in the range of 0.7 kPa (0.1 psi). The pressure inside the sphere will be plotted with respect to time; the rate of pressure rise will also be calculated.

3.2.3 Humidity

The water vapor content has not been considered a variable in much of the reported testing, including that conducted by NMERI. A Vaisala temperature and humidity probe model Humitter 5OY has been procured to measure the relative humidity in the test vessel prior to adding the refrigerant and after the refrigerant has been added and mixed. The operating humidity range is 0-100% with an accuracy of ±3% from 10-90% relative humidity. To prevent exposure of the probe to overpressure and products of combustion, humidity will be measured in a chamber external to the test device.

3.2.4 Ignition Energy

The ignition energy in a DC spark is a user-selected value based on the capacitance of the capacitors and the voltage to which the capacitors are charged. Given the energy required and the value of the capacitance, the computer calculates the required voltage using the formula $E=(\frac{1}{2}FV^2)/0.85$, where the 0.85 factor is a commonly-used factor to account for the efficiency of the transformer. The capacitors are then automatically charged to the required voltage. A similar formula will be developed for AC sparks based on the circuit design. .

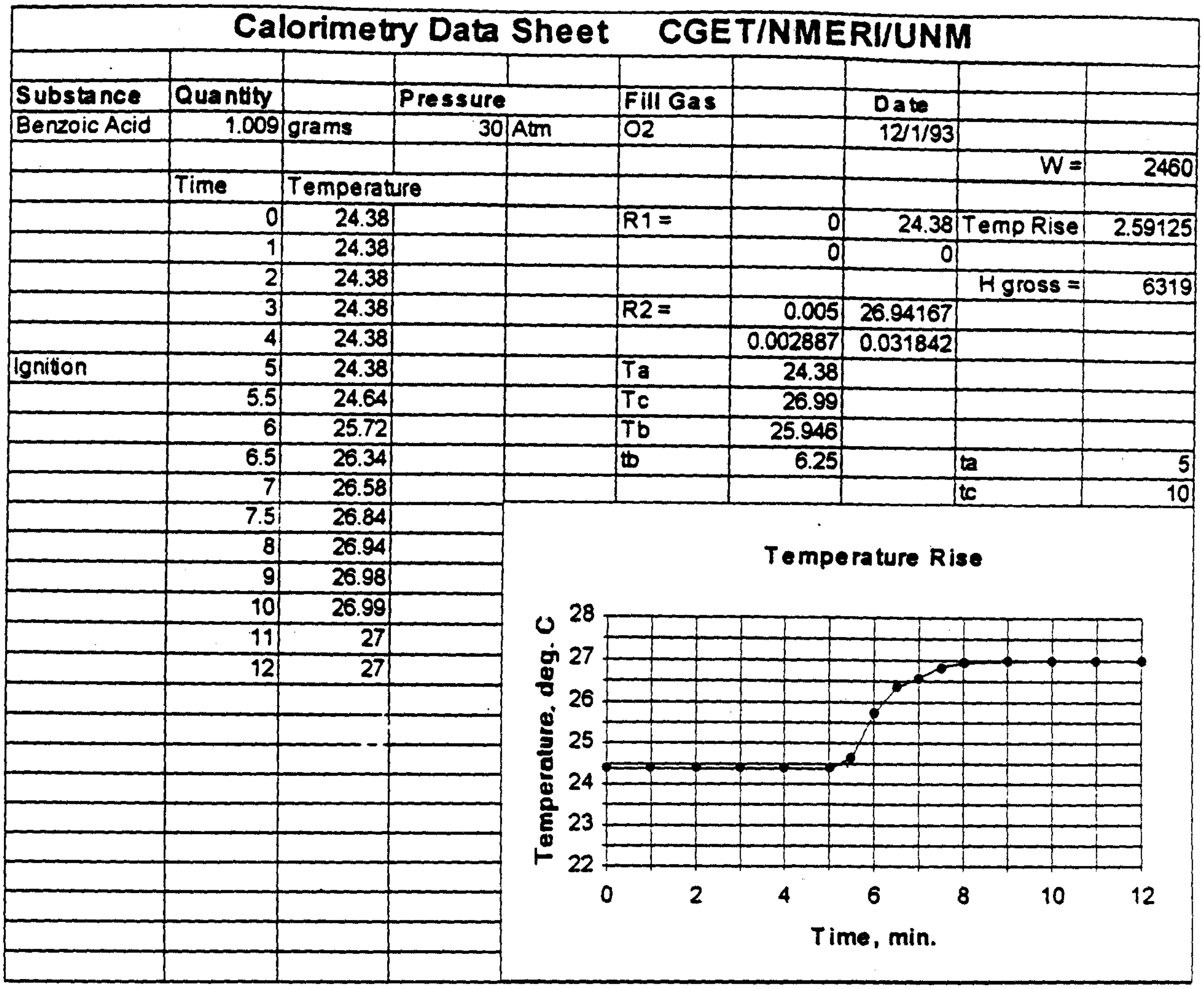
In addition to the instrumentation listed above, any testing conducted in a flask or other vessel allowing visual access to the interior will be recorded on videotape.

3.3 Special Instrumentation

In addition to the standard instrumentation required for each test, special instrumentation will be employed to measure selected test parameters. The two instances where special instrumentation may be used include the bomb calorimeter and the FTIR for use in the flask.

3.3.1 Bomb Calorimeter

NMERI has developed a program for Microsoft EXCEL to record and plot temperature data and calculate the heat of combustion for bomb calorimeter tests (Figure 4). While this spreadsheet is set up for a solid substance, it is easily modified for a gas.



Calorimetry Data Sheet CGET/NMERI/UNM									
Substance	**Quantity**		**Pressure**		**Fill Gas**		**Date**		
Benzoic Acid	1.009	grams	30	Atm	O2		12/1/93		
								W =	2460
	Time	Temperature							
	0	24.38			R1 =	0	24.38	Temp Rise	2.59125
	1	24.38				0	0		
	2	24.38						H gross =	6319
	3	24.38			R2 =	0.005	26.94167		
	4	24.38				0.002887	0.031842		
Ignition	5	24.38			Ta	24.38			
	5.5	24.64			Tc	26.99			
	6	25.72			Tb	25.946			
	6.5	26.34			tb	6.25		ta	5
	7	26.58						tc	10
	7.5	26.84							
	8	26.94							
	9	26.98							
	10	26.99							
	11	27							
	12	27							

Figure 4. Typical EXCEL Spreadsheet for Bomb Calorimeter Results.

3.3.2 Fourier Transform Infrared Spectrometer

NMERI has successfully used this FTIR to measure both the initial concentration of fuels and diluents in fire suppression tests and the concentrations of decomposition products after combustion. NMERI uses a Perkin-Elmer Model 2000 FTIR, with a capability to take up to 20 samples per second, depending upon resolution. This technique is intended for use in the ASTM flask test procedure, and IR windows will be inserted into one or more of the 5-liter flasks to allow the beam to penetrate the Pyrex®.

Figure 5 shows IR transmission spectra of R-23 taken before and after R-23 was used to extinguish a fire illustrating the data that can be generated by the FTIR. R-23 is a representative fluorocarbon similar to the refrigerants to be used in this test program. The lowest detectable concentrations of substances is estimated to be in the range of 5 to 10 parts per million.

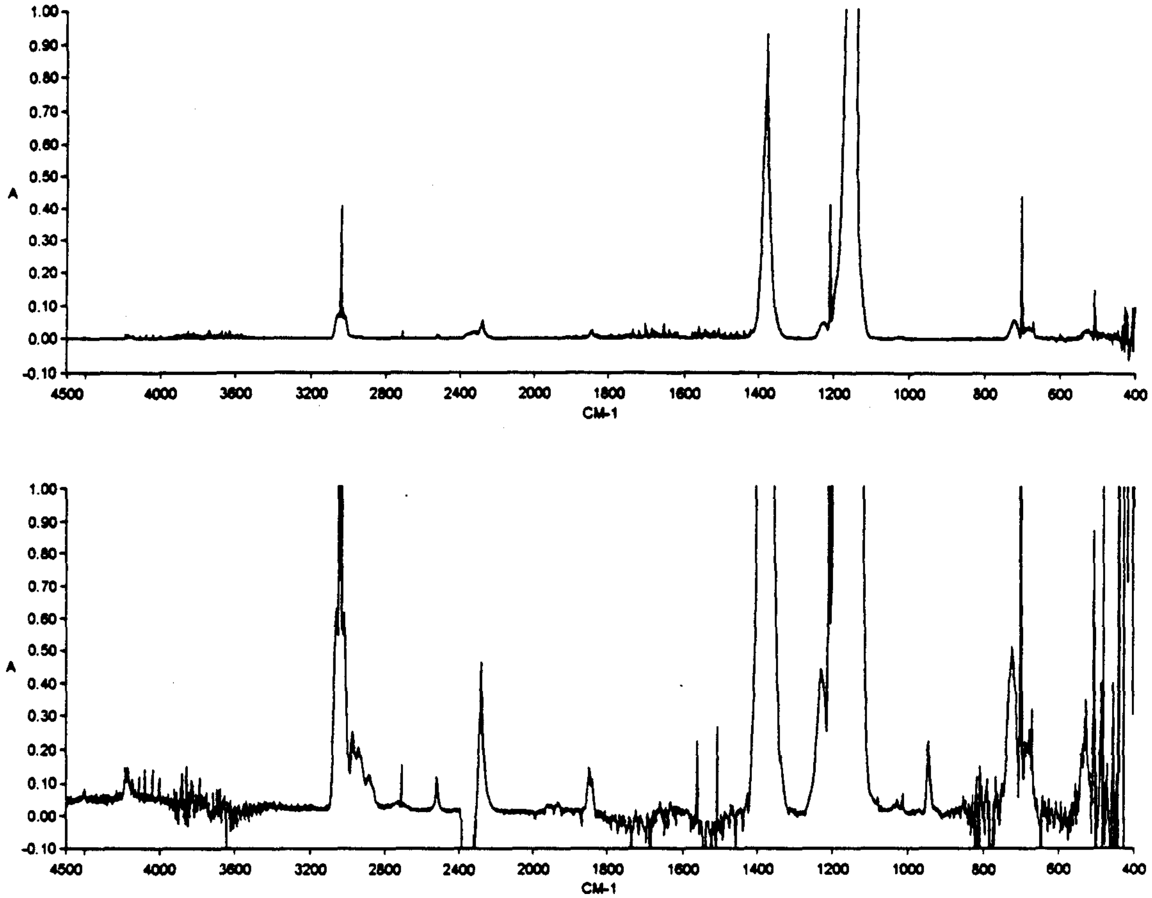


Figure 5. FTIR Spectra of R-23 Before Extinguishment of a Fire (Top) and After Extinguishment of a Fire (Bottom).

It is anticipated that the FTIR will be used for three separate measurements: (1) the concentrations of the components of the refrigerant blend and the concentration of that blend in air; (2) the determination that combustion has occurred by measuring the presence of byproducts such as carbon monoxide, hydrogen fluoride, and carbonyl fluoride; and (3) the concentrations of each of the byproducts as a function of time. This last measurement could be significant in determining whether combustion will continue or die out.

4.0 TEST MATRIX

Eleven parameters that could affect the flammability of the refrigerants were identified in Section 1. Eight of those parameters have been selected for initial testing, and Table 1 is a matrix of each of the parameters with respect to the equipment that will be used for the testing. Most, if not all, of the initial testing will use either propane (because of the body of previous data) or R-32 as the fuel, with the proposed ternary mixture tested as part of the concentration investigation. No additional test vessel apparatus has been included at this time.

TABLE 1. TEST PARAMETER/EQUIPMENT MATRIX*

Parameter	NMERI Explosion Sphere	ASTM E-681 Test Flask	Bomb Calorimeter	Light Emission Detector
Ignition	X	X	—	X
Temperature	—	X	—	—
Pressure	X	—	X	—
Humidity	X	X	—	—
Vessel Size	X	X	X	—
Vessel Material	X	X	—	—
Turbulence	X	—	—	—
Mixing	X	X	—	—
Concentration	X	X	X	X

* Other test vessels not included in matrix at this time.

Because of the large number of variables for the sphere and flask testing, an experimental strategy will be developed based on statistics.[40] This strategy serves several purposes, the major ones of which are to (1) screen a large number of variables to determine which are the most important, and (2) estimate the effects of several factors simultaneously. By employing these statistical techniques, the number of tests will be reduced and all significant factors should be identified.

The following discusses how each of the parameters in Table 1 will be evaluated.

4.1 Ignition

Section 1 described how critical the source of ignition is to flammability. One difficulty in using the ASTM E-681 standard method is that the ignition source is only approximately identified, and there is no confirmation that variations in the construction and use of the ignition system in accordance with ASTM E-681 will not lead to variations in the flammability limits. The output power requirement from the transformer is specified as approximately 30 mA at 15 kV. Since the transformer specified is a "luminous tube transformer" (really a neon or fluorescent tube

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[40] Strategy of Experimentation, Revised Edition, October 1975, E.I. Du Pont De Nemours & Co., Wilmington, DE 19898, October 1975.

transformer), there is no guarantee that output is consistent between devices since these are generally not precision devices.

4.1.1 Bench Tests

The first step will be to quantify the energy in the standard NMERI ignition source by measuring the voltage and current. Other techniques for developing a spark will be investigated to quantify the effects of spark generation on flammability tests. Non-electrical techniques such as matches and heated wires will be explored. The goal of this effort is to develop a simple ignition source that can be assembled from readily available parts and produce a standard amount of energy regardless of the test apparatus and conditions.

Measurement of the output current and voltage is complicated by the high voltage; standard measurement equipment by itself is inadequate to measure either voltage or current at such high voltages, and high-voltage probes and additional equipment are required in the measurement process. To provide a baseline for this project, NMERI will perform the following research prior to beginning ignition testing:

1. Measure the energy across the spark gap for the standard NMERI ignition spark. Most testing has been conducted at 70 J stored energy, with an 85% efficiency factor for the transformer factored in. This efficiency factor will be evaluated during this phase of testing by measuring the transformer input voltage and current and the output current and voltage. The charging voltage and capacitance will be varied and the output voltage and current waveforms recorded on a Nicolet recording oscilloscope. From the output waveform, the energy can be calculated. Both AC sparks and DC sparks will be investigated, with the duration of the AC spark being an additional variable.

2. Vary the type of ignition spark. The standard NMERI spark boosts the discharge of a bank of capacitors charged to a low voltage (approximately 165 V) to a voltage estimated to be over 10,000 V using a transformer. An alternate method of generating the high voltage spark is to charge the capacitors to the required 10,000 V and discharge the capacitors directly across the spark gap. NMERI has obtained a high-voltage power supply and capacitors adequate to store the energy and will measure the energy across the spark gap using different circuit configurations having the same output voltage.

3. Investigate the effect of electrode shape on ignition. The effect of electrode shape was mentioned in Section 1, with a statement that, in most cases, the shape of the electrode does not affect the quenching distance, except where the spark energy is large, as may be the case here. NMERI has constructed an electrode holder with a micrometer to control precisely the separation of the electrodes. The energy in the spark gap will be measured with three different electrode shapes: standard flat end, hemispherical ends, and pointed ends. The minimum and maximum distances for which a spark occurs will be

measured as a function of the energy. Depending upon the results of this study, one or more of the different-shaped electrodes may be used in flammability tests.

4. Investigate minimum ignition energy. Determination of the minimum ignition energy and quenching distances in gaseous mixtures is described in ASTM Standard E-582-76 (reapproved 1981).[41] At this time, MIE testing is not recommended as a part of this program as any reliable ignition source would be far greater in energy than the minimum. However, a means of generating sparks in the millijoule range will be investigated during this phase of the effort to provide a source of low energy sparks for the sphere and flask testing. One method of measuring extremely low overpressures, from which small spark energies may be determined, is to measure the motion of fluid in a capillary tube open to the explosion.

5. Develop alternate ignition sources. One of the goals of the program is to compare the effects of several different types of ignition sources. NMERI scientists have recently developed a methodology of igniting a match head within the NMERI sphere using copper wire wrapped around the match head and taped to each of the ends of the electrodes. A low voltage (24-V) battery supplied the energy to ignite the match. Several different types of matches, including kitchen matches, paper matches, model rocket electric matches, and M-100 series electric matches maybe tested. Methods using heated wire or a fuse wire (similar to that in a bomb calorimeter) together with the electrodes will be developed and quantified if possible. A method to generate a precisely-timed AC spark of known frequency and duration will also be developed and the energy quantified using the methods outlined above. Sources that potentially will give representative and worst-case results will be identified for sphere and flask testing.

4.1.2 NMERI Explosion Sphere

Ignition methods that have proven effective in the bench tests will be employed to find the LFL and UFL for propane. Propane has been extensively used in prior testing both at NMERI and elsewhere and offers a good opportunity for comparison of the methods to past results. Based on the propane results, one or more ignition methods and conditions will be used to test R-32 and binary and ternary combinations of R-32, R-125, and R-134a at a one bar, 25 °C, no-turbulence condition. Results will be compared to those of Dekleva, et al., and Richard and Shankland. The energy of the ignition source will be a variable in the statistical experimental method in those cases where the energy can be varied.

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[41] ASTM Standard E 582 - 76 (Reapproved 1981) Standard Test Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixtures, American Society for Testing and Materials, Philadelphia, PA 19103, 1985.

4.1.3 ASTM E-681 Test Flask

A similar test matrix will be conducted in the ASTM flask using the same or similar ignition conditions as in the sphere. Overpressure measurements will be taken and a comparison of the visual indications compared to the overpressure levels. Optical windows (thallium bromoiodide, also known as KRS-5) will be glued into at least one flask to allow measurement of the concentrations of both the refrigerant(s) prior to ignition as well as the combustion products. Using this flask, the light emission detector may also be employed to quantify any concentration differences between visual observation and initial light.

It is probable that all tests will be conducted at local atmospheric pressure at Albuquerque, NM (approximately 84 kPa (12.2 psia)) because of the requirement to release the cover hold-down devices prior to mixing and test. If the pressure inside the flask is raised above the local atmospheric pressure, there is a good chance that the mixture will leak from the flask prior to ignition.

After these tests, two standard ignition sources—one for representative and one for worst case—will be described. They may be two levels of the same source (for example, 40- and 70-J electric sparks) or two different ignition methods. These will be used as the primary ignition sources for the remainder of the testing, although there may be some instances where additional sources will be employed to investigate other parameters.

4.2 Temperature

Section 1.2.2 indicated a possible relationship that could provide an estimation of LFL as a function of temperature. If this relationship, or a similar relationship, could be confirmed for R-32 and other flammable refrigerants, it would not be necessary to conduct significant amounts of testing to determine the LFL at any temperature at atmospheric pressure. .

4.2.1 ASTM E-681 Test Flask

NMERI has constructed a test chamber based on an oven with a maximum temperature in excess of 100 °C. Tests will be run at 100 °C to investigate how the LFL and UFL are affected. One potential problem is to assure that the electrodes have reached the same temperature as the flask and its contents. Other researchers have had to use radiative sources to heat the electrodes. Most likely, the two limits for screening would be room temperature and 100 °C.

4.3 Pressure

The effects of pressure have been extensively studied in the past, although there is still some disagreement as to how increases or decreases to atmospheric pressure affect flammability limits. The intent of flammability testing in this program is not to test at extremely high or low pressures, but rather to quantify the effects of relatively small changes and to determine a range of insensitivity over which standardized testing can take place. This range has been tentatively identified as 50 to 303 or 404 kPa (0.5 atm to 3 or 4 atm). Both the explosion sphere and the bomb calorimeter are projected for pressure testing.

4.3.1 NMERI Explosion Sphere

The initial test pressure can be raised to several atmospheres in the NMERI sphere, provided that the flammable component concentration is near the flammability limits and the full overpressure from a stoichiometric or near-stoichiometric explosion is not developed. Likewise, tests can be run with initial pressure below atmospheric, which may be required in order to have a one-to-one comparison with the flask method, which will be run at the local atmospheric condition. Since components are introduced into the sphere using the partial pressure method, it is simple, once the final precise values are known, to calculate the required partial pressure of each components in the mixture.

4.3.2 ASTM E-681 Test Flask

As was mentioned in Section 4.1.3, it is likely that all flask tests will be conducted at the local Albuquerque atmospheric. Baseline sphere tests will be run at that overpressure to facilitate comparison.

4.3.3 Bomb Calorimeter

It was reported earlier that this technique is not widely used for flammability testing. Selected mixtures will be tested in the bomb calorimeter to investigate how well the flammability limits can be determined. If this apparatus can be used for this purpose, tests to determine the flammability at initial pressures higher than are available in the sphere will be conducted.

4.4 Humidity

The humidity of the air will be controlled by using dry air (air, zero gas has been selected) and injecting water (in mg/m^3) into the test apparatus in the amount required to provide the desired relative humidity. A Vaisala humidity probe has been procured. For all tests, the relative humidity of the air will be measured prior to the addition of any other component. Before any flammability testing is undertaken, trials will be conducted to determine the amounts of water required to provide the required relative humidity in the various test apparatuses used. A plot of relative humidity as a function of the amount of water will be made, allowing the operator to read the required amount of water to achieve the desired relative humidity from the plot. Humidity testing is planned in both the sphere and the flask. Humidity will be kept at 50% as a standard and varied between 5% and 95% to investigate the effects of humidity.

The test vessel (sphere or flask) will be evacuated and filled with dry air to the required air pressure. The required volume of water (in microliters) will be injected into the vessel and allowed to evaporate. The relative humidity will be measured and additional water injected if necessary to raise the humidity to the desired level. The final relative humidity of the air within the test vessel prior to any test will be recorded.

4.5 Test Vessel Size and Shape

Several options will be explored to investigate the vessel size. Originally, it was planned to construct a new sphere somewhat larger than the current sphere. Later, it was proposed to construct a cylindrical insert to fit between the flanges of the current sphere, increasing the volume but not increasing the diameter of the cylindrical system. A third option being considered is to use a 12-liter flask and/or a 22-liter flask to compare results to those from the 5-liter flask. This would involve the modification of an existing test enclosure as the enclosure developed for the 5-liter flask will not accommodate a larger flask. The modifications would require the replacement of side and top panels with blow-out panels and other minor modifications. A fourth option is the purchase or manufacture of a vessel of a different shape, possibly to include a burette or tube. This option has been previously discussed in Section 2.5 as the fifth proposed test apparatus.

4.6 Test Vessel Material

This is considered a secondary effect, and little effort will be made to test for it. However, since both a stainless steel explosion sphere and a Pyrex® flask will be available, testing will be conducted using identical methods to identify any differences that can be attributed to the material type. An investigation will also be made to determine whether any operational scenarios could involve materials that could potentially affect the flammability limits.

4.7 Turbulence

The effect of turbulence on ignition and flame propagation was described in Section 1.2.7. The explosion sphere uses an internal fan to mix the components. This fan will be adapted by a variable voltage source to provide variable turbulence within the sphere. The LFL and UFL will be measured as a function of turbulence (probably qualitative rather than strictly quantitative, that is, under no-, low-, medium-, and high-turbulence conditions).

4.8 Mixing

The standard ASTM method uses a magnetic stirring bar to mix the components. A modified stirring bar (possible with fins) and fan-mixing techniques will be developed and compared to the ASTM method to investigate how well the components are mixed. Using the flask with the optical windows and a Fourier-Transfer Infrared (FTIR) spectrometer, the concentration of each component in the center of the flask can be measured as a function of time. This will permit the determination of whether all components are mixed during 5 minutes that is called out in ASTM Standard E-681-85. An alternate method would be to remove a sample from the flask at different times, and locations, measure the concentrations in the FTIR, and plot concentration as a function of time and location. A confirmation will be made that the current method is acceptable or a revision to that method will be suggested.

4.9 Concentration

Significant research has already been reported on the flammability of R-32 blends, especially combined with R-125 and R-134a in binary and ternary blends.[42] A test series will be run using both the ignition sphere and the ASTM flask and each of the selected ignition sources to confirm the results presented in Reference 41. The details of this matrix will be decided after the results of the previous testing have been analyzed. A modified test methodology, based on analysis of all the relevant parameters, will be selected and the R-32 blends tested.

Flammability diagrams, which illustrate the flammability of a fuel when a diluent (inertant) is added, are generated by plotting the concentration of fuel versus the concentration of diluent required to make the mixture inflammable, as shown in Figure 6. In this case, the fuel is propane, and the diluent is Halon 1301. All regions within the curve are flammable, and all regions outside the curve are not flammable. In the case of previous NMERI testing, the criterion was 1 psi overpressure. R-32 will be tested using a binary blend (either 50:50 or another ratio) of R-125 and R-134a as the diluent to investigate the flammability using other overpressure criteria for flammability. Overpressure levels of 0.5, 2.5, and 10 psi are suggested.

4.10 Repeatability

Repeatability is not one of the flammability criteria, but it is nonetheless critical to investigate the repeatability of the methods developed. One test methodology based on a single apparatus will be selected as the preferred refrigerant flammability test method. A sufficient number of tests at one point will be conducted to determine the precision, bias, completeness, representativeness, and comparability of the data. These tests will demonstrate the repeatability of the data, and allow comparison of results with other test apparatuses. Both propane and the selected R-32/R-125/R-134a blend will be tested.

---

[42] Dekleva, T.W., Lindley, A.A., and Powell, P., "Flammability and Reactivity of Select HFCs and Mixtures", ASHRAE Journal, Vol. 35, No. 12, pages 45-47, American Society of Heating, Refrigerating and Air-Conditioning Engineers, Atlanta, GA 30329, 1993.

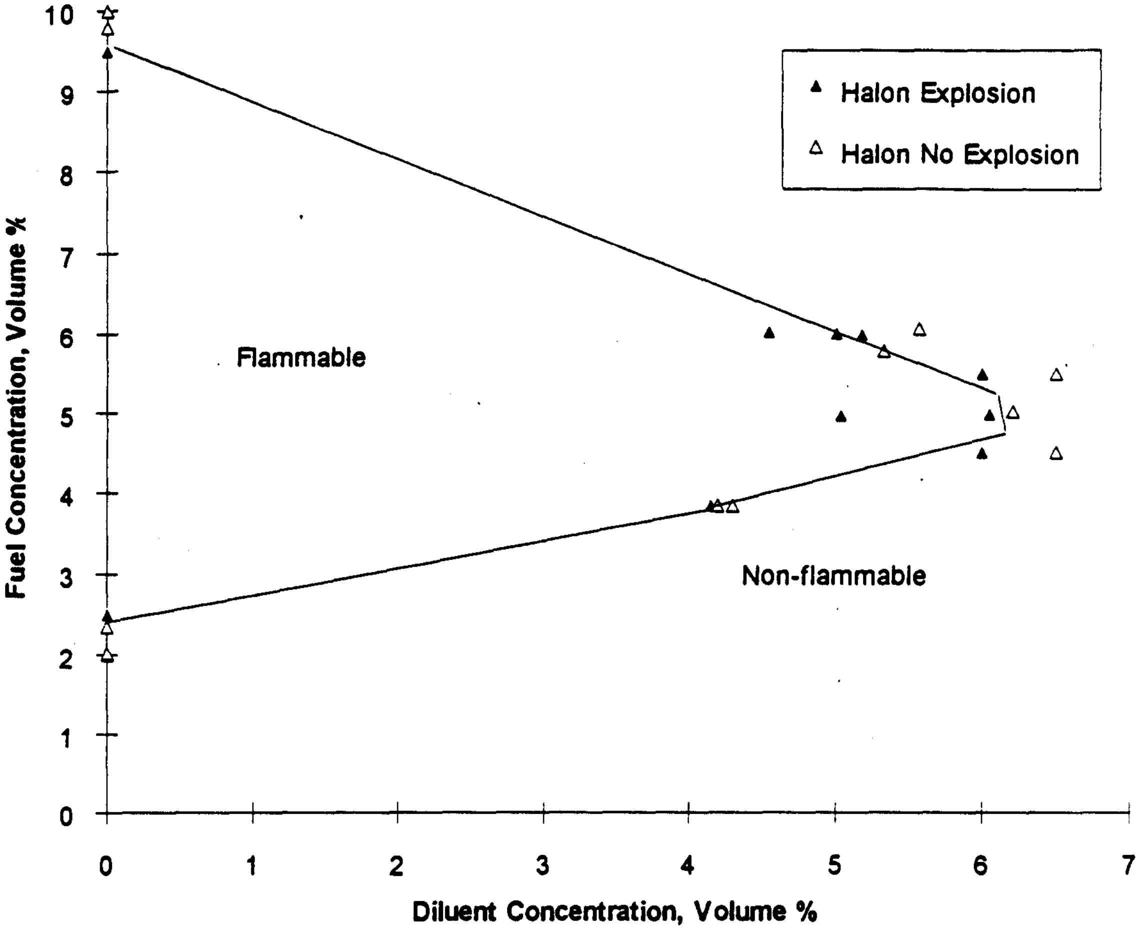

Figure 6. Flammability Curve, Halon 1301 /Propane.

5.0 DATA ANALYSIS PLAN

The goal of this project is to develop a test methodology to determine the concentration of a flammable refrigerant or refrigerant blend at the LFL and the UFL under a set of reference conditions using some not-yet determined criteria for flammability. The set of reference conditions is defined by the parameters described in Sections 4.1 through 4.8, and the criteria for flammability will be developed during this program. Data analysis will consist of determining the sensitivity of each parameter with respect to the refrigerant concentrations at the LFL and the UFL and identifying those with the greatest effect. Once these have been identified, acceptable values of each of the parameters can be specified based on a realistic evaluation of the conditions the under which the refrigerant could be exposed during operation.

Data will be available on IBM-compatible files from the data acquisition computer, on hand-written data sheets, which will be prepared for all tests, and on videotape, which will be used to record all tests with visual indications of flammability. The computer screens showing the loading conditions and the plots of pressure and temperature versus time will be printed using the print screen option.

APPENDIX A. SAFETY PLAN

A. PURPOSE

This safety plan covers all work on testing flammable refrigerants in the NMERI explosion sphere or the ASTM E-681 test flask apparatus to be conducted in the NMERI/CGET Chemistry Laboratory (901 University SE, Albuquerque, NM). It identifies the agency responsible for each of these test areas. All references to the test throughout this safety plan will pertain to the tests to be conducted at the above location. The detailed safety rules which are applicable to this project are documented herein. The following safety documents are applicable to this test: (1) OSHA Standards 29 CFR 1910 and 29 CFR 1926 and (2) the NMERI Safety Manual.

B. OVERALL SAFETY RESPONSIBILITY

NMERI/CGET, as Test Director, is responsible for enforcing the overall safety program for the test. The Test Director or the NMERI Safety Officer, or the designated representative, will act as the Safety Officer during all tests.

C. SAFETY AREAS

The safety requirements are divided in to the following areas: general safety; explosive safety; and refrigerant and combustion byproducts safety.

D. GENERAL SAFETY

The responsibility for general safety resides with NMERI. The authority to execute specific safety directives is delegated to the Test Director.

1. Safety Briefing

The Test Director will brief all personnel on the safety hazards associated with the testing.

2. Visitors

Visitors will not be allowed at the test site during testing without approval of the Test Director or the Senior Technician. Visitors will be instructed on applicable safety regulations.

3. Individual Safety Responsibility

Careful attention to potential hazards involved in work dealing with flammable and explosive gases and liquids and products of combustion must be stressed in all levels of responsibility. The purpose of the safety rules outlined herein is to present the most important safety elements in this test series. These rules do not cover all the possible hazards or safety precautions necessary at the site. As new problems arise, new safety measures will be established to cope with them. In the interim, common sense must be applied to ensure that safety prevails. This entire safety plan shall be closely followed by all personnel and enforced by all supervisors. The procedures contained herein shall be accepted as minimum standards until such time as the Test Director, with the concurrence of the NMERI Safety Officer, authorizes deviation therefrom.

4. Accident Reporting (Emergency)

a. Scope: This standard procedure is intended as a guide to ensure expedient handling and care of personnel injured in an accident or disaster. All post-emergency reporting and investigation of an accident will be performed in accordance with applicable NMERI regulations and is not considered to be within the scope of this standard procedure.

b. Responsibility: Every person involved in this testing must be completely familiar with the emergency reporting procedures established by this plan and must implement these procedures immediately in the event of an accident. The Test Director Must familiarize all supervisors with this standard procedure. The supervisors must familiarize subordinate personnel with the procedures established by this plan.

c. Emergency reporting procedures: In the event of an accident at the test site, the following procedures will be followed:

1. The senior supervisor at the accident scene will direct appropriate first aid. Caution will be exercised to prevent aggravation of an accident-related injury.
2. Albuquerque Fire and Rescue will be called at 911.
3. The Test Director or, alternatively, the Senior Technician, shall determine the seriousness of the accident. If the accident is not serious enough to require emergency hospitalization or ambulance service, the injured person will be taken to a doctor or hospital by normal means of transportation.
4. First Aid. The Test Director will ensure than an adequate supply of first aid items is maintained at the test site. These items will be properly stored and periodically inspected to ensure their availability in case of an emergency.

E. SPECIFIC SAFETY REQUIREMENTS

1. NMERI Explosion Sphere

While the sphere has been designed and tested to withstand pressures well in excess of those expected during testing, and a rupture disk assembly is provided to vent pressures over 150 psi, certain safety precautions shall be followed during testing. Testing will occur under a ventilation hood to exhaust gases in case the rupture disk activates, and an enclosure capable of deflecting particles shall surround the chamber during testing (the fume hood will be closed). Only personnel required for testing shall be in the area, and they shall be protected from potential explosion.

2. ASTM E-681 Test Flask

The explosion flask apparatus has been designed in accordance with ASTM Standard E-681-85 (reapproved 1991) using an existing oven modified as the enclosure. All operating and safety procedures prescribed in Chapters 7 and 9 of that document will be followed. Additionally, those safety precautions listed in the section on the NMERI explosion sphere will also be followed. In particular, the following procedures will be followed:

a. Only air will be used as the oxidizer.

b. Tests will only be conducted using fuel concentrations demonstrated in the sphere testing to be near the LFL or the UFL.

c. All testing will be conducted in the fume hood.

d. Care must be taken when removing the flask from the enclosure. The stopper and flask must be rotated together toward the front of the enclosure to provide clearance for the removal of the flask. Special care must be taken when removing the flask during elevated temperature testing at elevated temperatures.

3. Other Test Apparatus

Additional apparatus-specific safety instructions will be developed for each piece of equipment prior to any testing being accomplished.

F. REFRIGERANT AND BYPRODUCTS SAFETY

An evaluation of the toxicity of each refrigerant, including neat toxicity and toxicity of byproducts, has been performed by CGET for prior testing. Neat refrigerant handling and transfer procedures used in other NMERI/CGET laboratory testing will be followed. Exhaust fans in the hoods will be turned on at all times. Agent cylinder connections and fittings will be checked with a hand-held halocarbon detector or by bubble-checking with "snoop." Combustion byproducts will be exhausted through a cryotrap filled with liquid nitrogen, which is capable of capturing particulates before they are exhausted through the house vacuum system. Protective gloves, goggles, and breathing apparatus shall be available for all personnel involved in testing. Appendix B provides copies of the Material Safety Data Sheets (MSDSs) for all refrigerants, fuels, and cryogenic materials.

APPENDIX B

MATERIAL SAFETY DATA SHEETS FOR CANDIDATE AGENTS AND FUELS

Material Safety Data Sheet

From Genium's Reference Collection
Genium Publishing Corporation
1145 Catalyn Street
Schenectady, NY 12303-1836 USA
(518) 377-8855

GENIUM PUBLISHING CORP.

No. 61
NITROGEN
(Revision A)

Issued: April 1980
Revised: April 1986

SECTION 1. MATERIAL IDENTIFICATION

21

MATERIAL NAME: NITROGEN

DESCRIPTION: Gas supplied in cylinders (2000+ psig) or cold liquid supplied in vented Dewar containers.

OTHER DESIGNATIONS: N_2, CAS #7727-37-9, ASTM #D1933

MANUFACTURER/SUPPLIER: Available from several suppliers, including:
Air Products & Chemicals, Inc., Industrial Gas Division, PO Box 538, Allentown, PA 18105; Telephone: (215) 481-4911
Airco Industrial Gases of the Boc Group, Inc., 575 Mountain Avenue, Murray Hill, NJ 07974; Telephone: (201) 464-81000
Union Carbide Corp., Linde Div., 39 Old Ridgebury Rd., Danbury, CT 06817; Telephone: (203) 794-5300

HMIS
H: 2
F: 0
R: 0
PPE*
*See Sect. 8

0
3 0
-
(Liquified)

R 1
I 1
S 2 (Liquid)
K 0

SECTION 2. INGREDIENTS AND HAZARDS

SECTION 2. INGREDIENTS AND HAZARDS	%	HAZARD DATA
Nitrogen, CAS #7727-37-9	>99.5	No TLV Established.
Oxygen, CAS # 7782-44-7	< 0.5	

SECTION 3. PHYSICAL DATA

Boiling Point, 760 mm Hg ... -320.4°F (-195.8°C)
Vapor Density (Air = 1) ... 0.967
Solubility in Water @ 20°C, Vols./100 vols. ... 1.6
Density (liq.), g/cm³ ... 0.8
Melting Point ... -345.7°F (-209.86°C)

Critical Temperature ... -232.8°F (-147.1°C)
Critical Pressure, Atm ... 33.5
Molecular Weight ... 28.01
Expansion Ratio, Liquid to Gas @ 70°F ... 1:696

Appearance and odor: A colorless, odorless, tasteless gas or a cryogenic liquid.

SECTION 4. FIRE AND EXPLOSION DATA

Flash Point and Method	Autoignition Temp.	Flammability Limits in Air	LOWER	UPPER
Not Found	Not Found	Nonflammable	Not Found	Not Found

Use extinguishing media that are appropriate to the surrounding fire. Do not discharge solid streams of water into liquid N_2. Use water spray to cool fire-exposed containers or, if desirable, to increase the rate of evaporation of the liquid if the increased rate can be controlled (cryogenic liquid will rapidly freeze water). Nitrogen is a nonflammable material that will not support combustion. It presents no unusual explosion hazard unless the compressed gas is exposed to fire; then containers may rupture violently. Nitrogen cylinders are equipped with pressure-relief devices that are designed to vent N_2 when they are exposed to elevated temperatures and pressures. When liquid nitrogen is spilled it can release a rapidly vaporizing cloud that will create an oxygen-deficient atmosphere.

SECTION 5. REACTIVITY DATA

Nitrogen is stable when stored in closed containers. It does not polymerize. Nitrogen is noncorrosive and is nearly inert at room temperature. At high temperatures it can combine with oxygen to form oxides, and with hydrogen to form ammonia. When heated with carbon in the presence of alkalies or barium oxide it may form cyanides. It can form nitrides with lithium, silicon, calcium, strontium, and barium when it is at a red heat.

It has been reported that nitrogen can be oxidized explosively by ozone.

Lithium and titanium at an elevated temperature can burn in a nitrogen atmosphere. Berylium can be ignited in a mixed nitrogen-and-carbon dioxide atmosphere.

Nitrogen will react with oxygen in the presence of sparking (from an electric arc or a gas-fired furnace) to produce nitric oxide gas.

SECTION 6. HEALTH HAZARD INFORMATION

Nitrogen is not listed as a carcinogen by the NTP, IARC, or OSHA.
This material is nontoxic and is classified as a simple asphyxiant by virtue of its displacement of oxygen. Symptoms of exposure depend on the degree and the duration of oxygen deficiency. They can include increased frequency and volume of breathing, increased pulse rate, muscular incoordination, fatigue, nausea, vomiting, and collapse. Inhalation of pure nitrogen atmosphere produces immediate loss of consciousness; death follows unless air/oxygen breathing can be quickly restored.
Contact with liquid nitrogen or cold vapors can cause cryogenic burns (severe frostbite/freeze burns).
FIRST AID: CONTACT WITH LIQUID NITROGEN: Promptly flush areas affected with lots of tepid water to reduce freezing of tissue. (Do not apply direct heat to affected areas!) Do not rub frozen areas. Loosely apply dry, sterile, bulky dressings to protect area from infection and from further injury. Get medical help.*
INHALATION: Caution! Would-be rescuers need to be concerned with their own safety in oxygen-deficient areas. Use self-contained breathing equipment. Remove victim to fresh air. Quickly restore and/or support his breathing as required, administering oxygen if available. Get medical help.*
INGESTION: Get medical help.* ACUTE EFFECTS: Gas - Simple asphyxiation by displacement of oxygen. Liquid - Cryogenic burns. PRIMARY ENTRY: Inhalation
* GET MEDICAL ASSISTANCE = In plant, paramedic, community. Get medical help for further treatment, observation, and support after first aid.

SECTION 7. SPILL, LEAK, AND DISPOSAL PROCEDURES

Notify safety personnel of major nitrogen leaks or spills. Shut off leak if you can do so without risk. Evacuate all personnel from the danger area until ventilation can restore a safe oxygen level. Emergency personnel need self-contained breathing equipment. Minor leaks (which are dangerous in enclosed areas) can be detected by painting the suspected area of leakage with a soap solution. Prevent liquid nitrogen from contacting vulnerable steel structures and vehicle tires (see sect. 9). Allow spilled liquid to evaporate.

DISPOSAL: Remove a liquid nitrogen container or leaking cylinder outdoors or place into a hood with good forced ventilation. Allow gas to discharge at a moderate rate. Defective cylinders should be tagged to indicate defect. Close the valve and return the defective cylinder to supplier.

SECTION 8. SPECIAL PROTECTION INFORMATION

Provide adequate general and local exhaust ventilation to prevent workplace atmospheres from becoming oxygen deficient (minimum O_2 volume = 18%). Provide air-supplied or self-contained breathing equipment for emergency or nonroutine situations where the nitrogen level is excessive. Use a safety line and a standby worker when respirator-protected personnel enter a hazardously nitrogen-enriched area. (The standby worker should have a self-contained breathing apparatus immediately available.) Those working with liquid nitrogen should wear approved insulating gloves, safety glasses, and other protective clothing as required by use conditions to prevent any skin contact with liquid nitrogen. Cuffless trousers should be worn outside high-topped shoes. Safety shoes are recommended for those handling cylinders of gases.

Wear safety gloves and approved insulated gloves. Use air-supplied or self-contained breathing apparatus.

Contact lenses pose a special hazard; soft lenses may absorb irritants, and all lenses concentrate them.

SECTION 9. SPECIAL PRECAUTIONS AND COMMENTS

STORAGE SEGREGATION: Store in a cool, dry, well-ventilated, low fire-risk area. Protect containers against physical damage.
SPECIAL HANDLING/STORAGE: Protect containers from extremes of temperature and weather. (Do not allow any part of a compressed gas cylinder to be exposed to temperatures above 125°F [51.6°C]). Follow general safety procedures for handling and securing compressed gas cylinders. Liquid nitrogen storage areas should be kept clean and free from flammable materials. Make sure that liquid nitrogen containers are properly vented to prevent buildup of pressure. All pressure equipment and process lines should be designed so that the minimum burst pressure is at least four (4) times the expected maximum pressure. Certain materials are unsuitable for service in contact with liquid nitrogen because they become extremely brittle and can be readily shattered by impact.

DOT Classification: Nonflammable Gas UN1066 (Compressed); UN1977 (Cryogenic Liquid)
LABEL: Nonflammable Gas
Data Source(s) Code: 1, 4-11, 14, 17, 25, 51, 63, 82, 84. CK

Approvals 1/87.
Indust. Hygiene/Safety 12-86
Medical Review

Genium Publishing Corporation
1145 Catalyn Street
Schenectady, NY 12303-1836 USA
(518) 377-8854

Material Safety Data Sheets Collection:

Sheet No. 380
Propane

Issued: 10/84 Revision: B, 4/90

Section 1. Material Identification

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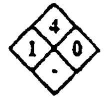
Propane Description: Derived from petroleum and natural gas. Propane is obtained by the so-called "stabilization process" using fractional distillation under pressure. Propane is widely used as a fuel gas, sometimes mixed with butane; as refrigerant, gas enricher, extractant, aerosol propellant, mixture for bubble chambers; in hydrocarbon oxidation, flame control of weeds, and organic synthesis.
Other Designations: CAS No. 0074-98-6; C_3H_8; dimethylmethane; liquified propane; *n*-propane; propyl hydride.
Manufacturer: Contact your supplier or distributor. Consult the latest *Chemicalweek Buyers' Guide*(73) for a suppliers list.

R 1
I 1
S 3*
K 4
* Liquid

NFPA


HMIS
H 1
F 4
R 0
PPG†
† Sec. 8

Section 2. Ingredients and Occupational Exposure Limits

Propane, ca 100%

OSHA PEL	ACGIH TLV, 1989-90*	NIOSH REL, 1987	Toxicity Data†
8-hr TWA: 1000 ppm, 1800 mg/m³	None established	None established	None listed

* ACGIH (1989-90) labels propane a simple asphyxiant (control at 18 vol % minimum oxygen).
† Monitor NIOSH, RTECS (TX2275000) for additional toxicity data.

Section 3. Physical Data

Boiling Point: -43.8 °F/-42.1 °C at 1 atm
Melting Point: -309.4 °F/-189.7 °C
Vapor Pressure: 760 mm Hg at -43.8 °F/-42.1 °C
Vapor Density (Air = 1): 1.56 at 32 °F/0 °C
Molecular Weight: 44.09 g/mol
Specific Gravity (H_2O = 1 at 39 °F/4 °C): 0.58 at -44.0 °F/-42.2 °C
Water Solubility: Slightly soluble

Appearance and Odor: A colorless gas at room temperature and 1 atm pressure, propane can be liquified by lowering and/or raising the temperature. Liquified propane is an unspecified mixture of propane, various butanes, and propylene. Although odorless when pure, propane can have an odor like natural gas. It has an odor threshold of 5,000 to 20,000 ppm, but odor is not an adequate warning to prevent overexposure.

Section 4. Fire and Explosion Data

Flash Point: -156 °F/-105 °C	Autoignition Temperature: 842 °F/450 °C	LEL: 2.1% v/v	UEL: 9.5% v/v

Extinguishing Media: If feasible, stop flow of gas. Use water to cool fire-exposed containers, tanks, surroundings, and to protect personnel working on shutting off gas flow. If you cannot stop the gas flow, direct water spray, dry powder, or carbon dioxide at flame area. *Do not completely extinguish flame unless gas flow is shut off!* Propane burns with a luminous, smoky flame.
Unusual Fire or Explosion Hazards: This material can be a dangerous fire and explosion hazard when mixed with air or exposed to heat and flame. Vapors may flow on surfaces for considerable distances, reach an ignition source, and flash back. One volume of propane requires about 25 volumes of air for complete combustion.
Special Fire-fighting Procedures: Since fire may produce toxic fumes, wear a self-contained breathing apparatus (SCBA) with a full facepiece operated in the pressure-demand or positive-pressure mode. Continue cooling containers with water well after fire is extinguished. Fight massive cargo fires with unmanned hose holders or monitor nozzles. If this is not feasible, withdraw from the area and allow the fire to burn. Be aware of runoff from fire control methods. Do not release to sewers or waterways.

Section 5. Reactivity Data

Stability/Polymerization: Propane is stable when stored as a liquid in steel tanks under its own vapor pressure. Hazardous polymerization cannot occur.
Chemical Incompatibilities: Propane reacts vigorously with oxidizers and explosively with chlorine dioxide (ClO_2). A violent exothermic reaction occurs with barium peroxide and heat.
Conditions to Avoid: Propane can produce carbon monoxide when oxidized with a deficiency of oxygen. When sufficient oxygen is present, burning propane forms carbon dioxide and water. Propane can be a pyrolysis product of polyvinyl chloride, sytrene-acrylonitrile, acrylonitrile-butadiene-styrene, and polyacrylonitrile.
Hazardous Products of Decomposition: Thermal oxidative decomposition of propane can produce acrid smoke and irritating fumes.

Section 6. Health Hazard Data

Carcinogenicity: Neither the NTP, IARC, nor OSHA lists propane as a carcinogen.
Summary of Risks: This material is an asphyxiant. If sufficiently concentrated to reduce the oxygen level below 18% in inhaled air, symptoms such as rapid respiration, mental dullness, incoordination, poor judgement, and unconsciousness may result. If the oxygen concentration is reduced to 6% to 8% or less, unconsciousness leading to death occurs. Contact with liquified gas can produce frostbite and severe skin burns which could result in serious impairment.
Medical Conditions Aggravated by Long-Term Exposure: None reported.
Target Organs: Central nervous system.
Primary Entry Routes: Inhalation.
Acute Effects: Exposure to propane vapors can cause eye and respiratory tract irritation, headache, dizziness, and vomiting. At high concentrations, propane may have anesthetic properties. Direct contact with liquid propane can cause severe skin burns.
Chronic Effects: None reported.
FIRST AID
Eyes: Flush immediately, including under the eyelids, gently but thoroughly with flooding amounts of running water for at least 15 min.
Skin: *Quickly* remove contaminated clothing. After rinsing affected skin with flooding amounts of water, wash it with soap and water.
Inhalation: Remove exposed person to fresh air and support breathing as needed. Emergency response personnel should be concerned with their own safety in oxygen-deficient areas. Use SCBA for rescue attempts in oxygen-deprived environments.
Ingestion: Ingestion is unlikely because of propane's physical properties. However, if liquid propane is ingested, severe cold injury to the mouth and oral cavity results. Monitor the airway, have trained medical personnel administer oxygen, and seek medical attention.
After first aid, get appropriate in-plant, paramedic, or community medical support.
Physician's Note: For frostbite, consider rapid rewarming at 108 °F/42 °C. Do not institute rewarming unless complete rewarming can be assured. A variety of pharmacologic agents to help restore perfusion to the tissues may be appropriate.

Section 7. Spill, Leak, and Disposal Procedures

Spill/Leak: Notify safety personnel, evacuate the hazard area, eliminate all heat and ignition sources, and supply maximum explosion-proof ventilation to keep the concentrations well below the lower flammability limit. Personnel involved in leak stoppage should use SCBAs and protect against direct contact with the liquified gas. Ventilate closed spaces before entering them. Follow applicable OSHA regulations (29 CFR 1910.120).

Disposal: Contact your supplier or a licensed contractor for detailed recommendations. Follow applicable Federal, state, and local regulations.

EPA Designations

RCRA Hazardous Waste (40 CFR 261.33): Not listed

CERCLA Hazardous Substance (40 CFR 302.4): Not listed

SARA Extremely Hazardous Substance (40 CFR 355): Not listed

SARA Toxic Chemical (40 CFR 372.65): Not listed

OSHA Designations

Listed as an Air Contaminant (29 CFR 1910.1000, Table Z-1)

Section 8. Special Protection Data

Goggles: Wear protective eyeglasses or chemical safety goggles, per OSHA eye- and face-protection regulations (29 CFR 1910.133).
Respirator: Follow OSHA respirator regulations (29 CFR 1910.134) and, if necessary, wear a NIOSH-approved respirator. For emergency or nonroutine operations (cleaning spills, reactor vessels, or storage tanks), wear an SCBA.
Warning: Air-purifying respirators do *not* protect workers in oxygen-deficient atmospheres.
Other: Wear impervious gloves, boots, aprons, and gauntlets to prevent skin contact. Neoprene or polyurethane protective clothing is recommended.
Ventilation: Provide general and local explosion-proof ventilation systems to maintain airborne concentrations below the OSHA PEL (Sec. 2). Local exhaust ventilation is preferred since it prevents contaminant dispersion into the work area by controlling it at its source.[103]
Safety Stations: Make available in the work area emergency eyewash stations, safety/quick-drench showers, and washing facilities.
Contaminated Equipment: Never wear contact lenses in the work area: soft lenses may absorb, and all lenses concentrate, irritants. Remove this material from your shoes and equipment. Launder contaminated clothing before wearing.
Comments: Never eat, drink, or smoke in work areas. Practice good personal hygiene after using this material, especially before eating, drinking, smoking, using the toilet, or applying cosmetics.

Section 9. Special Precautions and Comments

Storage Requirements: Store and use propane cylinders an[illegible]ks in well-ventilated area, away from heat, direct sunlight, ignition sources, oxidizing agents, and cylinders of oxygen or chlorine. Follow [illegible]andard procedures for handling cylinders and tanks of flammable, compressed gas. Provide protection against damaging cylinders and tanks. All engineering systems should be of maximum explosion-proof design and electrically grounded and bonded.
Engineering Controls: Avoid vapor inhalation and liquid contact with skin. Use only with adequate ventilation and appropriate personal protective gear. Propane is a serious fire and explosion hazard and should be handled accordingly. Do not expose to any heat or ignition source.

Transportation Data (49 CFR 172.101, .102)

DOT Shipping Name: Liquified petroleum gas
DOT Hazard Class: Flammable gas
ID No.: UN1075
DOT Label: Flammable gas
DOT Packaging Requirements: 173.304, 173.314, 173.315
DOT Packaging Exceptions: 173.306

IMO Shipping Name: Propane
IMO Hazard Class: 2.1
IMO Label: Flammable gas
IMDG Packaging Group: –
ID No.: UN1978

MSDS Collection **References:** 73, 84, 88, 100, 101, 103, 124, 126, 127, 132, 136, 138
Prepared by: MJ Allison, BS; Industrial Hygiene Review: DJ Wilson, CIH; Medical Review: MJ Hardies, MD P5

DU PONT

MATERIAL SAFETY DATA SHEET

INTERIM

IDENTIFICATION

NAME
HFC-125

FORMULA
CHF_2-CF_3

MANUFACTURER/DISTRIBUTOR
E. I. du Pont de Nemours & Co. (Inc.)

ADDRESS
Wilmington, DE 19898

CHEMICAL FAMILY
Hydrogenated Haloethanes

TSCA INVENTORY STATUS
Under EPA review

SARA/TITLE III STATUS
See ADDITIONAL INFORMATION Section

PRODUCT INFORMATION PHONE
(800) 441-9450

MEDICAL EMERGENCY PHONE
(800) 441-3637

TRANSPORTATION EMERGENCY PHONE
CHEMTREC (800) 424-9300

PHYSICAL DATA

BOILING POINT
-48.5°C (-55.3°F)

LIQUID DENSITY
1.248 g/cc at 2°C (68.0°F)

VAPOR DENSITY (Air = 1)
4.2

SOLUBILITY IN WATER
0.5% by wt. at 37.8°C (100°F)

FORM
Liquefied Gas

COLOR
Colorless

PERCENT VOLATILE BY VOLUME
100

VAPOR PRESSURE
190 psia at 25°C (77°F)

FREEZING POINT
-103°C (-153.4°F)

APPEARANCE
Clear

ODOR
Slight Ethereal

H-09101 Date: 5/89

HAZARDOUS COMPONENTS

MATERIAL(S)	CAS NO.	APPROXIMATE %
Ethane, Pentafluoro	354-33-6	100

HAZARDOUS REACTIVITY

STABILITY
Material is stable. However, avoid open flames and high temperatures.

INCOMPATIBILITY
Alkali or alkaline earth metals—powdered Al, Zn, Be, etc.

DECOMPOSITION
This compound can be decomposed by high temperatures (open flames, glowing metal surfaces, etc.) forming hydrofluoric acids and carbonyl halides.

POLYMERIZATION
Will not occur.

FIRE AND EXPLOSION DATA

FLASH POINT
Will not burn

FLAMMABLE LIMITS IN AIR, % BY VOL.
LOWER Not applicable
UPPER Not applicable

AUTOIGNITION TEMPERATURE
Not determined

AUTODECOMPOSITION TEMPERATURE
Not determined

FIRE AND EXPLOSION HAZARDS
Cylinders may rupture under fire conditions. Decomposition may occur.

EXTINGUISHING MEDIA
As appropriate for combustibles in the area.

SPECIAL FIREFIGHTING INSTRUCTIONS
Use water spray to cool containers. Self-contained breathing apparatus (SCBA) may be required if cylinders rupture and contents are released under fire conditions.

HEALTH HAZARD INFORMATION

PRINCIPAL HEALTH HAZARDS (Including Significant Routes, Effects, Symptoms of Overexposure, and Medical Conditions Aggravated by Exposure)

Inhalation of high concentrations of vapor is harmful and may cause heart irregularities, unconsciousness, or death. Intentional misuse can be fatal. Vapor reduces oxygen available for breathing and is heavier than air. Liquid contact causes frostbite.

Individuals with preexisting diseases of the central nervous or cardiovascular system may have increased susceptibility to the toxicity of excessive exposures.

HFC-125 has very low acute inhalation toxicity. No deaths occurred in rats exposed to concentrations of HFC-125 up to 100,000 ppm for four hours.

SKIN: Contact with liquid can cause frostbite

EYE: Contact with liquid can cause frostbite

CARCINOGENICITY

HFC-125 is not listed as a carcinogen by IARC, NTP, OSHA, or ACGIH.

EXPOSURE LIMITS

AEL (Du Pont): 1000 ppm (8- & 12-hour TWA)

SAFETY PRECAUTIONS

Avoid breathing high concentration of vapor. Use with sufficient ventilation to keep employee exposure below recommended limits. Avoid contact of liquid with skin and eyes. Wear chemical splash goggles and lined butyl gloves. Do not allow product to contact open flame or electrical heating elements because dangerous decomposition products may form.

FIRST AID

IF HIGH CONCENTRATIONS ARE INHALED: Immediately remove to fresh air. Keep persons calm. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

IN CASE OF EYE CONTACT: Immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

IN CASE OF SKIN CONTACT: Flush skin with water after excessive contact. Treat for frostbite if necessary. Seek medical assistance if irritation is present. Wash contaminated clothing before reuse.

IF SWALLOWED: Ingestion is not considered a potential route of exposure.

NOTE TO PHYSICIANS

Because of possible disturbances of cardiac rhythm, catecholamine drugs, such as epinephrine, should be used with special caution only in situations of emergency life support.

PROTECTION INFORMATION

GENERALLY APPLICABLE CONTROL MEASURES

Normal ventilation for standard manufacturing procedures is generally adequate. Local exhaust should be used when large amounts are released. Mechanical ventilation should be used in low places.

PERSONAL PROTECTIVE EQUIPMENT

Lined butyl gloves should be used to avoid prolonged or repeated exposure. Chemical splash goggles should be available for use as needed to prevent eye contact. Under normal manufacturing conditions, no respiratory protection is required when using this product. Self-contained breathing apparatus (SCBA) is required if a large release occurs.

DISPOSAL INFORMATION

SPILL, LEAK OR RELEASE

NOTE: Review FIRE AND EXPLOSION HAZARDS and SAFETY PRECAUTIONS before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Dike spill. Prevent liquid from entering sewers, waterways or low areas.

Ventilate area, especially low places where heavy vapors might collect. Remove open flames. Comply with Federal, State, and local regulations reporting releases.

WASTE DISPOSAL

Recover by distillation or remove to permitted waste disposal facility. Comply with Federal, State, and local regulations.

SHIPPING INFORMATION

DOT (172.101)

PROPER SHIPPING NAME
Compressed Gas, N.O.S.
(Pentafluoroethane)

HAZARD CLASS
Nonflammable Gas

UN NO.
UN 1956

DOT LABEL(S)
Nonflammable Gas

DOT/IMO (172.102)

PROPER SHIPPING NAME
Compressed Gases, N.O.S.
(Pentafluoroethane)

HAZARD CLASS
Nonflammable Gas, 2.2

UN NO.
UN 1956

SHIPPING CONTAINERS
Cylinders

ADDITIONAL INFORMATION

STORAGE CONDITIONS
Clean, dry area. Do not heat above 125°F.

NPCA-HMIS RATINGS

Health	1
Flammability	0
Reactivity	1
Personal Protection	-

Personal Protection rating to be supplied by user depending on use conditions.

SARA/TITLE III HAZARD CATEGORIES AND LISTS

<u>Product Hazard Categories</u>:

Chronic Health	- No
Acute Health	- Yes
Fire Hazard	- No
Pressure Hazard	- Yes
Reactivity Hazard	- No

<u>Lists</u>:

Extremely Hazardous Substance	- No
CERCLA Hazardous Substance	- No
Toxic Chemicals	- No

DATE OF LATEST REVISION/REVIEW: 5/89
PERSON RESPONSIBLE FOR MSDS: K. P. BROWN
Du Pont Company
Chemicals & Pigments Department
Chestnut Run Plaza
P.O. Box 80709
Wilmington, DE 19880-0709
(302) 999-5072

DuPont
Material Safety Data Sheet

HFC-32

6027FR Revised 4-NOV-1993 Printed 20-JUL-1994

CHEMICAL PRODUCT/COMPANY IDENTIFICATION

Material Identification

Corporate MSDS Number : DU005983
CAS Number : 75-10-5
Formula : CH2F2
CAS Name : METHANE, DIFLUORO-

Company Identification

MANUFACTURER/DISTRIBUTOR
DuPont
1007 Market Street
Wilmington, DE 19898

PHONE NUMBERS
Product Information : 1-800-441-9442
Transport Emergency : CHEMTREC: 1-800-424-9300
Medical Emergency : 1-800-441-3637

COMPOSITION/INFORMATION ON INGREDIENTS

Components

Material	CAS Number	%
METHANE, DIFLUORO- (HFC-32)	75-10-5	100

HAZARDS IDENTIFICATION

Potential Health Effects

Inhalation of high concentrations of vapor is harmful and may cause heart irregularities, unconsciousness, or death. Intentional misuse or deliberate inhalation may cause death without warning. Vapor reduces oxygen available for breathing and is heavier than air. Liquid contact can cause frostbite.

HUMAN HEALTH EFFECTS:

Contact with the liquid may cause frostbite. Overexposure by inhalation may lead to temporary alteration of the heart's electrical activity with irregular pulse, palpitations, or inadequate circulation.

Individuals with preexisting diseases of the central nervous or cardiovascular system may have increased susceptibility to the toxicity of excessive exposures.

(HAZARDS IDENTIFICATION - Continued)

Carcinogenicity Information

None of the components present in this material at concentrations equal to or greater than 0.1% are listed by IARC, NTP, OSHA or ACGIH as a carcinogen.

FIRST AID MEASURES

First Aid

INHALATION
If high concentrations are inhaled, immediately remove to fresh air. Keep person calm. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

SKIN CONTACT
In case of contact, flush skin with plenty of water for at least 15 minutes. Treat for frostbite if necessary by gently warming affected area. Get medical attention if irritation is present.

EYE CONTACT
In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

INGESTION
Ingestion is not considered a potential route of exposure.

Notes to Physicians

Because of possible disturbances of cardiac rhythm, catecholamine drugs, such as epinephrine, should only be used with special caution in situations of emergency life support.

FIRE FIGHTING MEASURES

Flammable Properties

Flash Point : Not determined
Flammable limits in Air, % by Volume
LEL : 14
UEL : 31
Autoignition : 648 C (1198 F)

Fire and Explosion Hazards:

Flammable. Cylinders are equipped with temperature and pressure relief devices but still may rupture under fire conditions. Use water spray to cool cylinders and tanks.

(FIRE FIGHTING MEASURES - Continued)

Extinguishing Media

Water Spray, Water Fog, Dry Chemical.

"Alcohol" Foam. Carbon Dioxide (CO_2).

Fire Fighting Instructions

Keep container cool with water spray. If gas exiting container ignites, stop flow of gas. Do not put out the fire unless leak can be stopped immediately. Self-contained breathing apparatus (SCBA) is required if containers rupture and contents are released under fire conditions.

ACCIDENTAL RELEASE MEASURES

Safeguards (Personnel)

NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL) sections before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Accidental Release Measures

If a spill can cause a concentration in excess of 1,000 ppm, turn off valves and ignition sources. Evacuate area. Ventilate area, especially low or enclosed places where heavy vapors might collect. Wear self-contained breathing apparatus (SCBA).

If this product is released and not recovered, or is recovered as a waste for treatment or disposal, the CERCLA Reportable Quantity is 100 lbs. (release of an unlisted Hazardous Waste characteristic of ignitability).

HANDLING AND STORAGE

Handling (Personnel)

Avoid breathing high concentrations of vapors. Avoid liquid contact with skin or eyes. Use with sufficient ventilation to keep employee exposure below recommended limits. Lines and equipment which will contain HFC-32 should be pretested with nitrogen using soapy water to detect leaks.

Storage

Clean, dry area. Do not heat above 52 deg C (125 deg F).

EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering Controls

Normal ventilation for standard manufacturing procedures is generally adequate. Local exhaust should be used when large amounts are released. Mechanical exhaust should be used in low or enclosed places. Ground all equipment and cylinders before use. Use explosion-proof electrical equipment rated Class I, Group D in Division 1 locations. In Division 2 locations, all spark-producing electrical equipment must be explosion-proof and rated Class I, Group D. Non-sparking motors need not be explosion-proof.

Personal Protective Equipment

Impervious gloves and chemical splash goggles should be worn when handling the liquid. Fire protective clothing (NOMEX) with antistatic control should be worn when handling this product. Under normal manufacturing conditions, no respiratory protection is required when using this product. Self-contained breathing apparatus (SCBA) is required if a large release occurs.

Exposure Guidelines

Exposure Limits

HFC-32

PEL (OSHA)	None Established
TLV (ACGIH)	None Established
AEL * (Du Pont)	1000 ppm, 8 & 12 Hr. TWA

* AEL is Du Pont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.

PHYSICAL AND CHEMICAL PROPERTIES

Physical Data

Boiling Point	-51.7 C (-61.1 F)
Vapor Pressure	248 psia at 25 deg C (77 deg F)
Vapor Density	1.85 (Air = 1.0) at 25 deg C (77 deg F)
Freezing Point	-136 C (-213 F)
% Volatiles	100 WT%
Solubility in Water	0.44 WT% @ 25 C (77 F) (248 psia)
Odor	Slight ethereal
Form	Gas
Color	Clear, colorless
Density	1.14 g/cc at 25 deg C (77 deg F) - Liquid

STABILITY AND REACTIVITY

Chemical Stability

Material is stable. However, avoid open flames and high temperatures.

Incompatibility with Other Materials

Incompatible with alkali or alkaline earth metals- powdered Al, Zn, Be, etc.

Polymerization

Polymerization will not occur.

Other Hazards

Decomposition : Decomposition products are hazardous. This material can be decomposed by high temperatures (open flames, glowing metal surfaces, etc.) forming hydrofluoric acid and possibly carbonyl fluoride.

TOXICOLOGICAL INFORMATION

Animal Data

Inhalation 4-hour LC50: >760,000 ppm in rats

The effects from single exposure by inhalation include lethargy, and temporary loss of mobility in hind limbs that was regained in less than an hour after the end of the exposure. Cardiac sensitization occurred in 1 of 12 dogs exposed to a concentration of 250,000 ppm. Repeated exposure in guinea pigs exposed by inhalation caused some bleeding in the lungs and liver discoloration; the kidney and spleen were also abnormal. No animal test reports are available to define carcinogenic, embryotoxic or reproductive hazards. Tests in bacterial cell cultures demonstrate no mutagenic activity.

DISPOSAL CONSIDERATIONS

Waste Disposal

Reclaim by distillation, incinerate or remove to a permitted waste facility. Comply with Federal, State, and local regulations.

This product may be an RCRA Hazardous Waste on disposal due to the ignitability characteristic.

TRANSPORTATION INFORMATION

Shipping Information

DOT/IMO
Proper Shipping Name : LIQUIFIED GASES, FLAMMABLE, N.O.S. (DIFLUOROMETHANE)
Hazard Class : 2.1
UN No. : 1954
DOT/IMO Label : FLAMMABLE GAS

IATA
Proper Shipping Name : LIQUIFIED GASES, FLAMMABLE, N.O.S. (DIFLUOROMETHANE)
Hazard Class : FLAMMABLE GAS
UN No. : 3161
Hazard Label : FLAMMABLE GAS

Shipping Containers

Cylinders
Ton Tanks

REGULATORY INFORMATION

U.S. Federal Regulations

TSCA Inventory Status : Reported/Included.

TITLE III HAZARD CLASSIFICATIONS SECTIONS 311, 312

Acute : Yes
Chronic : No
Fire : Yes
Reactivity : No
Pressure : Yes

LISTS:

Extremely Hazardous Substance	-No
CERCLA Hazardous Material	-(*)
Toxic Chemicals	-No

*See Disposal Information.

HFC-32 is a flammable gas as defined by OSHA in 29CFR 1910.1200(c). Use of this product may require compliance with 29CFR 1910.119, Process Safety Management of Highly Hazardous Chemicals.

OTHER INFORMATION

NFPA, NPCA-HMIS

NPCA-HMIS Rating

Health	1
Flammability	4
Reactivity	1

Personal Protection rating to be supplied by user depending on use conditions.

The data in this Material Safety Data Sheet relates only to the specific material designated herein and does not relate to use in combination with any other material or in any process.

Responsibility for MSDS : DuPont Chemicals
Address : Engineering & Product Safety
P. O. Box 80709, Chestnut Run
Wilmington, DE 19880-0709

# Indicates updated section.

End of MSDS

Allied
Signal

Allied-Signal Inc.
Engineered Materials Secto
P.O. Box 1139R
Morristown, NJ 07962-1139

PRODUCT SAFETY DATA SHEET

TRADE NAME: HFC-32 CAS.NO.: 75-10-4

CHEMICAL NAME: Difluoromethane

FORMULA: CH_2F_2

ADDRESS:
Allied-Signal Inc.
Engineered Materials Sector
P. O. Box 1139R
Morristown, NJ 07962

CONTACT: Director, Product Safety Phone: 201-455-2052

24-Hour Emergency Number: 201-455-2000

DATE OF CURRENT ISSUE: December 1990

NOTE: HFC-32 is a development chemical and it is on the TSCA inventory, however this material should be used under the supervision of a technically qualified person.

FIRST AID MEASURES:

INHALATION: Immediately remove to fresh air. If breathing has stopped give artificial respiration. Use oxygen as required, provided a qualified operator is available. Call a physician. Do not give epinephrine (adrenaline).

EYES: Immediately flush eyes with large amounts of water for at least 15 minutes [in case of frostbite, water should be lukewarm (not hot)] water, lifting eyelids occasionally to facilitate irrigation. Get medical attention if symptoms persist.

SKIN: Promptly flush skin with water until all chemical is removed. If there is evidence of frostbite, bathe (do not rub) with lukewarm (not hot) water. In the absence of water, cover with soft wool or similar covering. Call a physician.

INGESTION: Ingestion is unlikely because of the physical properties of HFC-32. If conscious, immediately give 2 to 4 glasses of water and induce vomiting by touching finger to back of throat. Call a physician.

HAZARDS INFORMATION:

INHALATION: Very little is known about the toxicity of HFC-32. All information is derived from data on similar compounds. When oxygen levels in air are reduced to 12-14% by displacement symptoms of asphyxiation, loss of coordination, increased pulse rate and deeper respiration will occur. At high levels, cardiac arrhythmia may occur (by analogy with animal studies made with related fluorocarbons).

HAZARDS INFORMATION: (cont'd)

INGESTION: Discomfort in the gastrointestinal tract would results from the rapid evaporation (perhaps boiling) of the material, as liquid, and consequent evolution of gas. In addition, some of the effects of inhalation would be expected. Necrosis from freezing of tissue could occur.

SKIN: Irritation would result from a defatting action on tissue, and frostbite may result from contact with liquid.

EYES: Liquid contact can cause irritation, which may be severe. Mist may irritate.

PERMISSIBLE CONCENTRATION: AIR. No OSHA/PEL or ACGIH/TLV established.

FIRE AND EXPLOSION:

	FLASH POINT:	N.A. - No flash point.
	AUTO IGNITION:	Unknown, probably not applicable.
	FLAME LIMITS:	(In air (% by vol.) Lower : 14.7 Upper : 25.3

UNUSUAL FIRE AND EXPLOSION HAZARDS:

Contact with certain reactive metals (See Section G) may result in formation of explosive or exothermic reactions under specific conditions (e.g., very high temperatures and/or appropriate pressures).

PRECAUTIONS/PROCEDURES:

FIRE EXTINGUISHING AGENTS RECOMMENDED:
Use any standard agent--choose the one most appropriate for type of surrounding fire.

FIRE EXTINGUISHING AGENTS TO AVOID:
None known.

SPECIAL FIRE FIGHTING PRECAUTIONS:

Firefighters should wear self-contained, NIOSH-approved breathing apparatus for protection against possible toxic decomposition products. Proper eye and skin protection should also be provided. Use water spray to keep fire-exposed containers cool and to suppress vapors.

VENTILATION:

Provide local exhaust at filling zones and areas where leakage is probable. Mechanical (general) ventilation may be adequate for other operating and storage areas.

NORMAL HANDLING:

Avoid breathing vapors and liquid contact with eyes, skin or clothing. Do not puncture or drop cylinders or expose them to open flame or excessive heat. Use authorized cylinders only. Follow standard safety precautions for handling and use of cylinders of compressed gases/

STORAGE:

Store in a cool, well-ventilated area of low fire risk. Protect cylinder and its fittings from physical damage. Storage in subsurface locations should be avoided. Close valve tightly after use and when empty.

SPILL OR LEAK (Always wear personal protective equipment)

Evacuate unprotected personnel. Protected personnel should remove any flames and shut off leak, if without risk, and provide ventilation. Unprotected personnel should not return until air has been tested and determined safe, including low-lying areas.

SPECIAL PRECAUTIONS/procedures/LABEL INSTRUCTIONS:

Signal Word - Warning : Observe all labeled precautions.

This product could cause death by inhalation or other personal injury if not handled properly.

PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY PROTECTION:

None generally required for adequately ventilated work situations. For accidental or nonventilated situations, use a self-contained, NIOSH-approved breathing apparatus or supplied air respirator. For escape: use the former or a NIOSH-approved gas mask with organic vapor canister.

EYES AND FACE:

For normal conditions, wear safety glasses. Where there is reasonable probability of liquid contact, wear chemical safety goggles. Contact lenses should not be worn under such conditions.

HANDS, ARMS, AND BODY:

Wear protective, impervious gloves and clothing with an outer layer of MYLAR®-coated Durafab (2nd choices: PVA and neoprene), if prolonged or repeated contact with liquid is anticipated. Remove and wash clothing promptly, if wet. Any nonimpervious clothing should also be promptly removed when contaminated and washed before reuse.

OTHER CLOTHING AND EQUIPMENT:

Impervious boots in case of spillage or leakage, or if there is the probability of repeated or prolonged contact with liquid product. High dose-level warning signs are recommended for areas of principal exposure. Provide eyewash stations and quick-drench shower facilities at convenient locations. For tank cleaning operations, see OSHA regulations.

PHYSICAL DATA:

HFC-32 is a gas at normal temperatures.

Appearance: Clear colorless liquid and vapor with a faint ethereal odor.
Boiling Point: -61°F (-51.7°C)
Vapor Pressure: 220.9 psia @ 70°F
506.3 psia @ 130°F
Vapor Density: (Air = 1) 1.8
% Volatiles by volume @ 20°C (68°F) = 100
Solubility in Water : Unknown
Liquid Density: 60.9#/CF @ 80°F

REACTIVITY DATA

The product is stable.

CONDITIONS TO AVOID

Any source of high temperature, such as lighted cigarettes, flames, hot spots, welding.

May yield toxic and/or corrosive decomposition products.

INCOMPATIBILITY (MATERIALS TO AVOID)

(Under specific conditions: e.g., very high temperatures and/or appropriate pressures.)

Freshly abraded aluminum surfaces (may cause strong exothermic reaction).
Chemically active metals: sodium, potassium, calcium - ibid.
Powdered aluminum, magnesium and zinc ibid.

HAZARDOUS DECOMPOSITION PRODUCTS

Halogens, halogen acids, and possibly carbonyl halides, such as phosgene. These are toxic and corrosive.

HAZARDOUS POLYMERIZATION

Will not occur.

CONDITIONS TO AVOID

None known.

ENVIRONMENTAL

DEGRADABILITY/AQUATIC TOXICITY:

Degradability (BOD): Not pertinent.

OCTANOL WATER PARTITION COEFFICIENT: Unknown

EPA HAZARDOUS SUBSTANCE: No

CLEAN WATER ACT SECT. 311: No

WASTE DISPOSAL METHODS (Disposer must comply with federal, state and local disposal or discharge laws.)

Disposal of waste HFC-32 difluoromethane may be subject to federal regulations. Users should review their operations, then consult with appropriate regulatory agencies before discharging or disposing of waste material. Disposal by a licensed waste disposal company may be necessary.

RCRA STATUS OF UNUSED MATERIAL IF DISCARDED:

Not a hazardous waste.

REGULATORY STANDARDS:

DOT Classification per 49 CFR 172.101. I.D. No.: UN 1954
(1) OSHA regulations for compressed gases: 29 CFR 1910.101.

DOT Classification: Flammable gas

GENERAL:

(a) CGA Pamphlet P-1, "Safe Handling of Compressed Gases in Containers," 1974, Compressed Gas Association (1980 printing)
(b) Bretherick, L., "Handbook of Reactive Chemical Hazards," 2nd ed., 1979, Butterworths, Boston.

Immediate and Pressure

HMIS Classification 1-2-0

ADDITIONAL HAZARDS INFORMATION

Non-mutagenic to salmonella strains TA100 and DTA1535 with and without S-9 mix.

Negative in styles assay with BHF-21 in presence of S-9 mix (1984).

4-hour ACL (rats) at 200,000 ppm (v/v) (1978)

Two week exposure (rats) at 200,000 ppm (v/v):

No observed treatment-related effects (1979).

THIS PRODUCT SAFETY DATA SHEET IS OFFERED SOLELY FOR YOUR INFORMATION, CONSIDERATION AND INVESTIGATION.

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genetron

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Allied-Signal Inc.
GENETRON Products
P.O. Box 1139R
Morristown, NJ 07960

PRODUCT SAFETY DATA SHEET

(DEVELOPMENTAL PRODUCT)

TRADE NAME: HFC-134a CAS.NO.: 811-97-2

CHEMICAL NAME: 1,1,1,2-Tetrafluoroethane

FORMULA: F_3CCH_2F

ADDRESS: Allied-Signal Inc.
Engineered Materials Sector
P. O. Box 1139R
Morristown, NJ 07960

CONTACT: Director, Product Safety Phone: 201-455-2052

DATE OF CURRENT ISSUE: April 1989

FIRST AID MEASURES:

INHALATION: Immediately remove to fresh air. If breathing has stopped give artificial respiration. Use oxygen as required, provided a qualified operator is available. Call a physician. Do not give epinephrine (adrenaline).

EYES: Immediately flush eyes with large amounts of water for at least 15 minutes [in case of frostbite, water should be lukewarm (not hot)], lifting eyelids occasionally to facilitate irrigation. Get medical attention if symptoms persist.

SKIN: Promptly flush skin with water until all chemical is removed. If there is evidence of frostbite, bathe (do not rub) with lukewarm (not hot) water. In the absence of water, cover with soft wool or similar covering. Call a physician.

HAZARDS INFORMATION:

INHALATION: **This material is low in toxicity. LC_{50} Rat >50% (4 hr.). Effects are primarily narcotic (drowsiness, loss of consciousness). When oxygen levels in air are reduced to 12-14%, symptoms of asphyxiation will occur; loss of coordination, increased pulse rate, cardiac sensitization, and deeper respiration are also possible. Also slight fetotoxicity noted at 50,000 ppm (rat).**

HAZARDS INFORMATION:

INHALATION: (continued)
Many refrigerant gases have been demonstrated to induce cardiac sensitization to epinephrine and to induce cardiac arrythmias. By analogy, HFC-134a may produce these effects at very high exposures or in the presence of injected epinephrine (see note on first aid). HFC-134a has been demonstrated to produce arrythmia at concentrations of 60% in the cat and monkey. (c)

INGESTION:	Not applicable, since material is a gas at normal temperatures and pressures.
SKIN:	Irritation would result from a defatting action on tissue.
EYES:	Liquid contact can cause irritation, which may be severe. Mist may irritate.

PERMISSIBLE CONCENTRATION: AIR No OSHA/PEL or ACGIH/TLV established.

BIOLOGICAL: None established.

FIRE AND EXPLOSION:

FLASH POINT: N.A - No flash point.

AUTO IGNITION: Unknown, probably not applicable.

FLAME LIMITS: (In air (% by vol.)
Lower : Not applicable
Upper : Not applicable

UNUSUAL FIRE AND EXPLOSION HAZARDS:

Contact with certain reactive metals may result in formation of explosive or exothermic reactions under specific conditions (e.g., very high temperatures and/or appropriate pressures).

PRECAUTIONS/PROCEDURES:

FIRE EXTINGUISHING AGENTS RECOMMENDED:

Use any standard agent--choose the one most approporiate for type of surrounding fire (material itself is not flammable).

PRECAUTIONS/PROCEDURES: (continued)

FIRE EXTINGUISHING AGENTS TO AVOID:

None known.

SPECIAL FIRE FIGHTING PRECAUTIONS:

Firefighters should wear self-contained, NIOSH-approved breathing apparatus for protection against possible toxic decomposition products. Proper eye and skin protection should also be provided. Use water spray to keep fire-exposed containers cool and to suppress.

VENTILATION:

Provide local exhaust at filling zones and areas where leakage is probable. Mechanical (general) ventilation may be adequate for other operating and storage areas.

NORMAL HANDLING:

Avoid breathing vapors and liquid contact with eyes, skin or clothing. Do not puncture or drop cylinders or expose them to open flame or excessive heat. Use authorized cylinders only. Follow standard safety precautions for handling and use of cylinders of compressed gases.

STORAGE:

Store in a cool, well-ventilated area of low fire risk. Protect cylinder and its fittings from physical damage. Storage in subsurface locations should be avoided. Close valve tightly after use and when empty.

SPILL OR LEAK (Always wear personal protective equipment)

Evacuate unprotected personnel. Protected personnel should remove any flames and shut off leak, if without risk, and provide ventilation. Unprotected personnel should not return until air has been tested and determined safe, including low-lying areas.

SPECIAL PRECAUTIONS/PROCEDURES/LABEL INSTRUCTIONS:

Signal Word - Warning

This product could cause death by inhalation or other personal injury if not handled properly. Tank cleaning personnel should use only a formal entry procedure, based on recognized safety principles. Tanks cannot be effectively flushed of vapor if sumps contain liquid product. Observe all labeled precautions.

PERSONAL PROTECTIVE EQUIPMENT

RESPIRATORY PROTECTION:

None generally required for adequately ventilated work situations. For accidental or nonventilated situations, from estimated TLV to 5000 ppm, use a self-contained, NIOSH-approved breathing apparatus or supplied air respirator. For escape: use the former or a NIOSH-approved gas mask with organic vapor canister.

EYES AND FACE:

For normal conditions, wear safety glasses. Where there is reasonable probability of liquid contact, wear chemical safety goggles. Contact lenses should not be worn under such conditions.

HANDS, ARMS, AND BODY:

Wear protective, impervious gloves with PVA outer layer (2nd choice: neoprene) in situations where leakage or handling of liquid is a possibility. Impervious shoes and clothing should also be worn where leakage is probable. Gloves, clothing and shoes should be thermally insulated to prevent freezing.

OTHER CLOTHING AND EQUIPMENT:

Impervious boots in case of spillage or leakage, or if there is the probability of repeated or prolonged contact with liquid product. High dose-level warning signs are recommended for areas of principal exposure. Provide eyewash stations and quick-drench shower facilities at convenient locations. For tank cleaning operations, see OSHA regulations.

PHYSICAL DATA

Material is a gas at normal conditions.

Appearance: Clear colorless gas with a faint ethereal odor
(shipped as liquefied gas)
Boiling Point: - 26.2°C
Specific Gravity: (Water = 1) 1.222 @ 21.1°C (70°F)
Vapor Pressure: 71.1 psia @ 21.1°C
Vapor Density: (Air = 1) 3.6
% Volatiles by volume @ 68°F = 100
Solubility: Unknown

REACTIVITY DATA

The product is stable.

CONDITIONS TO AVOID

Any source of ignition, such as lighted cigarettes, flames, hot spots, welding.
Explosions may result if in the explosive range.
Nonexplosive conditions may yield toxic and/or corrosive decomposition products.

INCOMPATIBILITY (MATERIALS TO AVOID)

(Under specific conditions: e.g., very high temperatures and/or appropriate pressures.)

Freshly abraded aluminum surfaces (may cause strong exothermic reation).
Chemically active metals: sodium, potassium, calcium
Powdered aluminum, magnesium and zinc

HAZARDOUS DECOMPOSITION PRODUCTS

Halogens, halogen acids, and possibly carbonyl halides, such as phosgene. These are toxic and corrosive.

HAZARDOUS POLYMERIZATION

Will not occur.

CONDITIONS TO AVOID

ENVIRONMENTAL

DEGRADABILITY/AQUATIC TOXICITY:

Degradability (BOD): Not pertinent.

OCTANOL WATER PARTITION COEFFICIENT: Unknown

EPA HAZARDOUS SUBSTANCE: No

CLEAN WATER ACT SECT. 311: No

WASTE DISPOSAL METHODS (Disposer must comply with federal, state and local disposal or discharge laws.)

Disposal of waste HCFC-134a tetrafluoroethane may be subject to federal regulations. Users should review their operations, then consult with appropriate regulatory agencies before discharging or disposing of waste material. Disposal by a licensed waste disposal company may be necessary.

RCRA STATUS OF UNUSED MATERIAL IF DISCARDED:

Not a hazardous waste.

REGULATORY STANDARDS:

DOT Classification per 49 CFR 172.101. I.D. No.: UN 1078
(1) OSHA regulations for compressed gases: 29 CFR 1910.101.

DOT Classification: Nonflammable gas

GENERAL REFERENCES:

(a) CGA Pamphlet P-1, "Safe Handling of Compressed Gases in Containers," 1974, Compressed Gas Association (1980 printing)
(b) Bretherick, L., "Handbook of Reactive Chemical Hazards," 2nd ed., 1979, Butterworths, Boston.
(c) Shulman, M & Sandove, M.S. "1,1,1,2-Tetrafluoroethane - an inhalation anesthetic agent of intermediate potency," Anesthesia & Analgesia, 1967.

This product safety data sheet is offered for your information, consideration and investigation. Allied-Signal Inc. provides no warranties, either expressed or implied and assumes no responsibility for the accuracy or completeness of the data contained herein.

PSDS File 1082