DTIC FILE COPY

SDI

SYSTEM DYNAMICS, INT'L., INC.

AD-A232 118

TECHNOLOGY ASSESSMENT OF GASSES USEFUL AS COOLANTS IN OPEN CYCLE JOULE-THOMSON CYROSTAT COOLERS

Report Number:
H-89-38

Prepared by:
James E. English, P.E.
Cherie Banks

Prepared for:
U.S. Army Missile Command
Redstone Arsenal, AL 35898

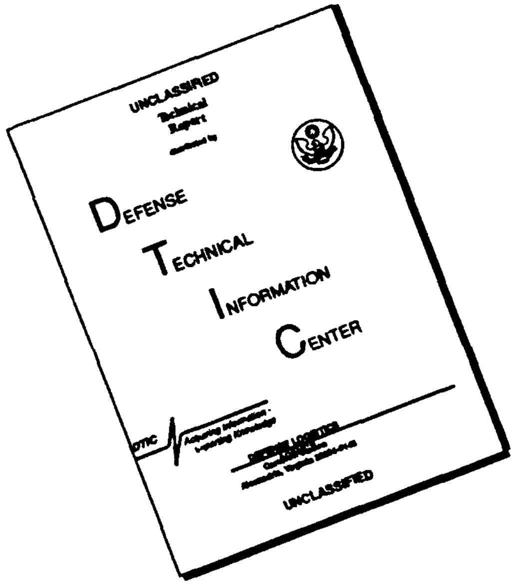
Under:
Contract No. DAAH01-87-D-A005, D.O. 0055

September 1989

91 3 12 154

4940 CORPORATE DRIVE, SUITE C • HUNTSVILLE, ALABAMA 35805
PHONE (205) 837-6813 • FAX (205) 895-0321

DISCLAIMER NOTICE



THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

TECHNOLOGY ASSESSMENT OF GASSES USEFUL AS COOLANTS IN OPEN CYCLE JOULE-THOMSON CYROSTAT COOLERS

Report Number:
H-89-38

Prepared by:
James E. English, P.E.
Cherie Banks

Prepared for:
U.S. Army Missile Command
Redstone Arsenal, AL 35898

Under:
Contract No. DAAH01-87-D-A005, D.O. 0055

September 1989

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY n/a	3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE n/a	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) H-89-38	5. MONITORING ORGANIZATION REPORT NUMBER(S) n/a
6a. NAME OF PERFORMING ORGANIZATION Systems Dynamics Inc. (SDI) 6b. OFFICE SYMBOL (If applicable) SS	7a. NAME OF MONITORING ORGANIZATION See Block 8A
6c. ADDRESS (City, State, and ZIP Code) 4940 Corporate Dr., Suite C Huntsville, Al. 35805	7b. ADDRESS (City, State, and ZIP Code) See Block 8A
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army Missile CMD 8b. OFFICE SYMBOL (If applicable) AMSMI-RD-AS-OG	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAH01-87-D-A005
8c. ADDRESS (City, State, and ZIP Code) Redstone Arsenal Huntsville, Al. 35898-5253	10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. --- PROJECT NO. --- TASK NO. 055 WORK UNIT ACCESSION NO. ---

11. TITLE (Include Security Classification)
Technology Assessment of Gases Useful as a Coolant in Open Cycle Joule-Thomson Cryostat Coolers (U)

12. PERSONAL AUTHOR(S)
James E. English, Cherie Banks

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 6/28/89 TO 9/24/89	9/30/89	64

16. SUPPLEMENTARY NOTATION
n/a

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Open cycle J.T. Cooler, Cryogen, Refrigerant, Cryostat, I.R. Seeker, J-T Efficiency, Joule-Thomson

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report documents the results of a ten week effort to identify cryogenic candidate compounds, mixtures, and solids that can be used as a coolant or precoolant in Infrared (IR) Seekers to allow rapid cool down of the detector to be achieved.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL Ed Miller	22b. TELEPHONE (Include Area Code) (205)876-1094 22c. OFFICE SYMBOL AMSMI-RD-AS-OG

TABLE OF CONTENTS

LIST OF TABLES

SUMMARY

This report documents the results of a ten week effort to identify cryogenic candidate compounds, mixtures, and solids that can be used as a coolant or pre-coolant in Infrared (IR) seekers to allow rapid cool-down of the detector.

The approach taken is described and the major sources of information identified. One of the objectives of this task was to identify sources of information as well as information in the literature that can be used now and in the future. There is much work being done in cryogenics by various groups, in industry and government, but the effort is not coordinated. Finding the proper source of information can be a very time consuming task. The list of sources and documents in this report will make future tasks of finding information easier.

A five step evaluation approach was used to eliminate the list of candidate coolants. A large list of compounds (165) and a few mixtures (11) were evaluated against the criteria. A total of eleven (11) compounds and four (4) mixtures satisfied all the evaluation criteria and remained as viable candidates. From this list, the best candidates were selected. Four (4) compounds and all four (4) mixtures were identified as the best candidates. They are:

- Argon
- Nitrogen
- Air
- Krypton
- Ar/N_2
- Kr/N_2
- Kr/Ar
- $He/H_2/Ar/Ne$

There is very little information available on mixtures and information on solids is almost non-existent. There is a definite need for work in this area to create an information data base. Also, information on the solubility of solids in liquid nitrogen is very scarce. Information on references and sources used is included in Appendix A.

1. INTRODUCTION

The primary purpose of this task was to identify cryogenic candidate compounds, mixtures, and solids that can be used as a coolant in Infrared (IR) Seekers to allow rapid cooldown of the detector to be achieved. The cryogens can be used in conjunction with or as an alternative to high pressure nitrogen. The secondary purpose of this task was to identify useful information that may be openly available in literature and/or from manufacturers; areas in which more information is needed; and identify companies that are pursuing work internally in this area, from which useful information might be obtained.

It is worthy to note that this report was not and is not intended to provide a detailed discussion of cryogenic thermodynamic principles or the design aspects of Joule-Thomson (J-T) open cycle cryostats; however, there are a few basic properties that must be defined in order to understand the information provided and the recommendations made. Therefore, a brief discussion of these properties and brief description of a Joule-Thomson open cycle cryostat is provided in the appropriate sections of this report.

This report is organized into 5 sections. Section 1 is the introduction. Section 2 discusses the task objectives; System Dynamics Incorporated (SDI) approach; background information; and a brief synopsis of the problem. Section 3 presents the data in essentially a tabular format, and provides a discussion on the five step evaluation criteria used to obtain viable candidates. Section 4 presents the SDI conclusions and Section 5 presents our recommendations. Finally, a list of people and companies contacted along with other pertinent information obtained in performing this task is provided in Appendix 1.

2. BACKGROUND

The goal of this analysis is the discovery of a pre-coolant as good as methane, but which does not absorb the infrared signal in the 3-5 and 8-12 micron wavelength regions. In addition, it is desirous that this substance have a cooldown time of less than 10 seconds and can maintain cooling for up to 1 hour.

The SDI approach to performing this task was to review available documentation, perform a literature search, and contact specialists, both individuals and companies, in the field of cryogenics. Next, this data was evaluated against evaluation criteria SDI established which included the criteria stated in the task statement of work (SOW). The evaluation criteria consisted of six steps as follows:

1. The boiling point at one atmosphere pressure must be less than - 100 degrees Centigrade, (°C) although less than - 170 °C degrees is desired.

2. Safety and long term stability

3. Infrared Transmission in the 3-5 and 8-12 micron regions

4. Two Phase Characteristics

5. Affordability/Availability

6. J-T cooling efficiency; i.e., it must achieve a maximum temperature drop upon free expansion from a high pressure.

All potential candidates were evaluated against criterion one (1), boiling point, and candidates that met this criterion were then evaluated against the next, second, set of criteria. This was progressively done through step 6 to eliminate all but the most viable candidates. This was done for both compounds and mixtures, although information regarding mixtures was not readily available or easily obtained. As for solids, very little information was available and information on solubility in liquid nitrogen was essentially non-existent. Before discussing the details of this research effort, a brief description of a J-T cryostat would be appropriate at this point and is provided in the next section.

2.1 JOULE-THOMSON CRYOSTAT

The Joule-Thomson cryostat is a method that is widely used to cool IR detectors and it is based on the fact that a cooling effect can be achieved from a gas or liquid that is passed through a restriction, such as a throttle valve. The gas pressure is reduced; and there is essentially no change in enthalpy (adiabatic process) since it occurs so rapidly in a relatively small area. Under normal pressure and temperature conditions, a perfect gas does not produce a cooling effect during a throttling process (throttling is a method of cooling through expansion without doing work). In actuality, when a gas undergoes a throttling process at high pressures and/or low temperatures, there is a change in internal energy which results in cooling of the gas. The J-T effect involves the ratio of temperature change to pressure change of a gas during the throttling process. This ratio is called the J-T coefficient, μ, and is defined as:

$$(1)\quad \mu = \frac{dT}{dP}$$

A positive coefficient means that a temperature drop occurs during throttling and a negative coefficient means that a temperature increase results during throttling. This coefficient is, of course, dependent upon the gas properties and for every gas, there is one temperature at which no temperature change occurs during expansion; this is called the inversion temperature. Therefore, one must be certain that the operating temperature and pressure result in a positive J-T coefficient or heating instead of cooling will occur. There are several other important characteristics which must be considered, but they are identified, and discussed, in the appropriate areas in Section 3.

The typical open cycle J-T cryostat cooler consists of a high pressure gas bottle, a filter, finned tube in the shape of a coil, a fixed or variable orifice (throttle valve), and a vacumn dewar. A picture of a typical open cycle J-T cooler was provided by ADP Cryogenics and is included in Appendix A.

2.2 DISCUSSION OF PROBLEM

Open Cycle Joule-Thomson cryostat coolers are a standard means of cooling infrared (IR) detectors used in military and space applications. They are used because they are generally cheaper than other types of coolers, can meet the space/weight requirements of a tactical missile system and they are reliable. These types of coolers do have problems. They have limited operating time, require a complex dewar design, have long term storage problems, have a tendency to clog, and have phase separation problems (which can result in solids forming, resulting in a clogged line). Problems in designing the open cycle cooler are further enhanced because the system has certain performance specifications which directly or indirectly affect the design of the J-T cooler. The cryostat design itself, is dependant upon the coolant used. The heat load (detector and possibly cold filter and cold shield) and operating temperature of the detector needed to meet the sensitivity requirement also impacts the cooler design and selection of the cryogen. The input pressure must also be considered and certain gases, if selected, would require precooling in order to achieve the required operating temperature. Finally, all of the above factors affect cool down time, which is the time it takes for the system (in this case, the detector) to reach the required operating temperature. And this, in turn, determines if the system can meet the specified performance requirements.

Unfortunately, it is often difficult to achieve an optimum design and tradeoffs must be made. For some weapon systems, these tradeoffs have not been satisfactory. This has resulted in efforts to improve the J-T design and identify cryogens other than the standard, nitrogen, that can be used in place of, or in conjunction with nitrogen as a precoolant. Previous efforts to identify an alternate coolant resulted in selecting a gas that absorbed (poor transmission of the signal) the IR signal in the 3-5 and 8-12 micron regions of interest. This is a severe problem for an open cycle J-T cooler because the heat load (detector) is inside the seeker head covered by a dome which is normally pressurized to one (1) atmosphere and as the gas flows to cool the detector, the gas fills the seeker head cavity where it then becomes part of the optical path that the IR signal must pass through to reach the detector; consequently, if the gas absorbs at the wavelength of interest, the sensitivity of the system can be so severely degraded that the weapon system becomes ineffective.

The problem then, is to identify candidate cryogens that have transmission "windows" at the wavelengths of interest (3-5 and 8-12) and that will satisfy all the other requirements specified in the previous paragraphs. To accomplish this, certain thermodynamic characteristics of the candidate cryogens must be known. These characteristics include the following:

- Normal Boiling Point at One Atmosphere
- Melting Point
- Enthalpy/Entrophy
- Inversion Temperature/J-T Coefficient
- Pressure/Temperature/Volume (PVT) Behavior
- Stability of the Compound Alone and in Mixtures
- Safety Hazards/By Products of Mixtures
- Short/Long Term Storage Capability
- I.R. Transmission Characteristics for the Optical Path Length and Pressure Specified
- J-T Cooling Efficiency
- Affordability/Availability

Section 3 presents the results of this effort and discusses the above characteristics in the appropriate evaluation step to which they apply. A synopsis of our approach for obtaining the required information is presented in the next section.

2.3 SYNOPSIS OF APPROACH

The initial approach taken by SDI was to obtain as much information as possible concerning compounds, mixtures and solids. Therefore, SDI reviewed open literature and requested both Redstone Scientific Information Center (RSIC) and the Infrared Information Analysis Center (IRIAC) to conduct a bibliographic literature search. They were very helpful. Research was also conducted by SDI personnel at RSIC and several useful texts/articles were found. The purpose of this effort was to ascertain if previous work had been done or how much of what had been done in the past might be helpful in this task. At this point, we were also trying to identify any compounds or mixtures that may have been overlooked that might have potential as a useful cryogen. The results of this literature survey are documented in Appendix 1. At the same time, we called several companies, research centers, and laboratories. The National Bureau of Standards (NBS) Cryogenic Center, New England Research Center, Sadtler Research Laboratory, Chemical Research Development and Engineering Center, and Air Products Division were extremely helpful. In particular, NBS stated that they are inundated continually with calls concerning this subject, especially with regard to mixtures. NBS stated that very little information was available on mixtures. The results of our effort support that statement.

To obtain information on affordability and availability, several gas manufacturers were contacted. Sources such as EEM, Gold Book, Buyers Guides, and individual recommendations were used to find the best sources of information. Matheson Gas Company, Scott, and Air Products Division were very helpful.

Information on safety was requested of all sources, but, in particular, Dr. William Volz (Recon Optical) and Jim Ely (NBS) were very helpful.

Information on vapor phase spectra of gases, I.R. Transmission, and J-T cooling efficiency was difficult to obtain; especially since they are so dependent upon design parameters such as optical path length and cryostat design. However, Dr. Bob Kroutil (CRDE) provided useful I.R. transmission data and Dr. Ralph Longsworth (APD) provided useful information on J-T efficiency.

SDI reviewed all the available data and applied the evaluation criteria, explained previously in this report, to all viable candidates. The information was compiled into tables and is presented in Section 3.

3. EVALUATION RESULTS

This section presents the results of our evaluation and provides a brief description of the evaluation criteria.

3.1 ELIMINATION BASED ON BOILING POINT

Tables 3-1 and 3-2 contain a list of all possible candidate coolants. Those candidates that met the boiling point (BP) criteria or point (BP) criteria or were (173.16°K) and the desired temperature of -170°C (103.16°K) at one (1) atmosphere are shown in Table 3-2. Candidates with a boiling point (BP $\geq$ -78°C) within +22°C of the -100°C threshold were allowed to remain on the list because they might be viable candidates for use in mixtures, provided that they satisfied the other criteria.

Table 3-1. List of Refrigerants Not Acceptable - B.P. > -78 C at 1 Atmosphere Pressure

REFRIGERANT	BOILING POINT (°C)
Propane (C_3H_8)	- 42.
Butane (C_4H_{10})	- 2.
Pentane (C_5H_{12})	35.
Hexane (C_6H_{14})	69.
Heptane (C_7H_{16})	97.
Octane (C_8H_{18})	124.
Propylene (C_3H_6)	- 48.
Butene (C_4H_8)	- 5.
Pentene (C_5H_{10})	30.
Butadiene (C_4H_6)	- 4.
Isoprene (C_5H_8)	33.
Benzene (C_6H_6)	80.
Toluene (C_7H_8)	114.
Ethyl-Ether (C_4H_{10})	35.
Methylene Chloride (CH_2Cl_2)	40.
Freon 113 - Trichlorotrifluoroethane (CCl_2F-$CClF_2$)	48.
Azeotrope of R12 and R152a (R500)	- 30.
Azeotrope of R22 and R115 (R502)	- 53.
Azeotrope of R32 and R115 (R504)	- 57.
n-Butane	- 10.
Water (H_2O, R718)	100.
Diethyl Ether ($C_2H_5OC_2H_5$)	35.
Ammonia (NH_3)	- 34.
Chlorine (Cl_2)	- 34.
Ethyl Chloride (C_2H_5Cl)	13.
Freon 12 - Dichlorodifluoromethane (CCl_2F_2)	- 30.
Hydrogen Sulfide (H_2S)	- 60.

Table 3-1 (Continued).

REFRIGERANT	BOILING POINT (°C)
Isobutane (C_4H_{10})	- 12.
Methyl Chloride (CH_3Cl)	- 24.
Sulfur Dioxide (SO_2)	- 10.
Freon 11 - Trichlorofluoromethane (CCl_3F)	24.
Freon 22 - Chlorodifluoromethane ($CHClF_2$)	- 41.
Freon 21 - Dichloromonofluoromethane ($CHCl_2F$)	9.
Freon C318 - Octafluorocyclobutane (C_4F_8)	- 6.
Di-Isopropyl Ether	68.
Carbonyl Sulfide (COS)	- 50.
Vinyl Fluoride (CH_2=CHF)	- 72.
Arsine (AsH_3)	- 55.
Carbon Oxychloride ($COCl_2$)	8.
Chorine Monoxide (Cl_2O)	4.
Cyanogen (C_2N_2)	- 21.
Hydrogen Bromide (HBr)	- 69.
Hydrogen Fluoride (HF)	- 37.
Hydrogen Iodine (HI)	- 36.
Hydrogen Selenide (H_2Se)	- 42.
Hydrogen Sulfide (H_2S)	- 62.
Hydrogen Telluride (H_2Te)	- 2.
Methyl-Ether $(CH_3)_2O$	- 25.
Monomethylamine (CH_3NH_2)	- 7.
Nitrosyl Chloride (NOCl)	- 6.
Silicon Tetrafluoride (SiF_4)	- 68.
Freon 13B1 - Bromotrifluoromethane ($CBrF_3$)	- 58.
Freon 114 - Dichlorotetrafluoroethane ($C_2Cl_2F_4$)	4.
Gen' tron 115 - Chloropentafluoroethane (C_2ClF_5)	- 40.
R142b - Chlorodifluoroethane (C_2ClF_2)	- 62.
R152a - Difluoroethane ($C_2H_4F_2$)	- 25.
R216 - Dichlorohexafluoropropane	- 46.

Table 3-2. List of Refrigerants Acceptable - B.P. < -78° C at 1 Atmosphere Pressure.

REFRIGERANT	BOILING POINT (° C)
Compounds	
Methane (CH_4)	-162.*
Ethane (C_2H_6)	- 89.
Ethylene (C_2H_4)	-104.
Acetylene (C_2H_2)	- 84.
Argon (Ar)	-186.*
Carbon Dioxide (CO_2)	- 80.
Helium (He)	-268.*
Hydrogen (H_2)	-253.*
Hydrogen Chloride (HCl)	- 85.
Natural Gas (representative)	-151.*
Neon (Ne)	-246.*
Nitric Oxide (NO)	-151.*
Nitrogen (N_2)	-196.*
Nitrous Oxide (N_2O)	- 91.
Oxygen (O_2)	-183.*
Air (Mixture of Ne, He, Kr, H, Xe, Ar, Ra N_2, O_2, CO_2)	-194.*
Freon 14 - Carbon Tetrafluoride (CF_4)	-128.
Freon 13 - Monochlorotrifluoromethane ($CClF_3$)	- 81.
Deuterium (D_2)	-249.*
Fluorine (F_2)	-188.*
Xenon (Xe)	-109.
Krypton (Kr)	-152.*
Carbon Monoxide (CO)	-192.*
Methyl Fluoride (CH_3F)	- 78.
Deuterium Chloride (DCl)	- 82.
Trifluoromethylene Ester	- 95.
Freon 23 - Trifluoromethane (CF_3)	- 82.
R503 - Azeotrope of R13 and R23	- 90.
n-Hydrogen (R702)	-253.*
p-Hydrogen (R702a)	-253.*
n-Helium (R704)	-268.*
Carbonyl Fluoride (COF_2)	- 83.
Boron Fluoride (BF_3)	-100.
Boron Hydride (B_2H_6)	- 93.
Hexafluoroethane (C_2F_6)	- 80.
Chorine Monofluoride (ClF)	-101.
Phosphine	- 87.
Ozone (O_3)	-111.9

Table 3-2. List of Refrigerants Acceptable - B.P. < -78° C at 1 Atmosphere Pressure. (Continued)

REFRIGERANT	BOILING POINT (°C)
Mixtures	
Phosphorous Trifluoride (PF_3)	-102.
5% N_2 in CH_4 **	--170.*
2 1/2% N_2 in CH_4	--168.*
$.25CH_4/.25N_2/.25H_2/.25He$	--217.*
$.25He/.25H_2/.25Ar/.25Ne$	--238.*
$.5Ar/.5N_2$	--191.*
$.5CH_4/.5N_2$	--179.*
$.5N_2/.25CH_4/.25Ar$	--181.*
$.5CH_4/.5Ne$	--204.*
$.5Ar/.5CO_2$	--133.
$.5Kr/.5N_2$	--174.*
$.5Kr/.5Ar$	--169.*

* Meets desired criteria or is close enough
** Temperatures of mixtures have been estimated on the Basis of the substances which make them up.

3.2 Elimination Based on Safety

Candidate refrigerants not eliminated on the basis of boiling point are now evaluated on the basis of safety. This information has been obtained from Matheson Gas Data Handbook, CRC Handbook of Chemistry and Physics, and Air Products Specialty Gases. Those coolants which are toxic, flammable, highly reactive or a strong oxidant are considered to be unsafe and appear in Table 3-3 while those which seem to be safe are in Table 3-4. Mixtures which may be acceptable on the basis of safety are listed in Table 3-5. For some of these, it might be possible, according to Dr. Longsworth, to use injection orifices to vent the undesired gas to eliminate the unsafe conditions; but this requires further evaluation.[1] This would add to the cost of the cryostat; however, for mixtures which do not satisfy the safety criteria, but offer quick cooldown and long run time, this may be desirrable.

It is important to note that methane failed this criterion , but was kept because if it were used in low enough concentrations, it might be a viable candidate. Therefore, we decided to keep methaneon the list to determine its characteristics against the the remaining criteria.

---

1 Longsworth, Ralph C., APD Cryogenics, Inc.

Table 3-3. Refrigerants Unacceptable on the Basis of Safety

REFRIGERANTS	REASON UNACCEPTABLE
Methane (CH_4)	Simple asphyxiant with flammability limits of 5-15%; auto ignition temperature of 580 °C; explosion hazard with oxygen or air; overpressure hazard if liquid or cold gas is trapped; combustible; highly flammable.
Ethane (C_2H_6)	Highly flammable with limits of 0.3-12.4%; asphyxiant; explosion hazard with oxygen or air; overpressure hazard if liquid or cold gas is trapped; combustible.
Ethylene (C_2H_4)	Simple asphyxiant; highly flammable with limits of 2.7-36%; Combustible; overpressure hazard if liquid or cold gas is trapped; explosion hazard with oxygen or air.
Acetylene (C_2H_2)	Simple asphyxiant, irritant,and anesthetic; extremely flammable with limits of 2.5-100%; may decompose violently and explode under pressure.
Hydrogen (H_2)	Explosion hazard with oxygen or air; overpressure hazard if liquid or cold gas trapped; combustible; flammable with limits of 4-75%.
Hydrogen Chloride (HCl)	Highly toxic; extremely irritating and destructive to tissues; contact with skin causes severe burns; 1300-2000 ppm lethal to humans on brief exposure.
Natural Gas (representative)	Fire hazard.
Nitric Oxide (NO)	Toxic; 25 ppm can cause pulmonary signs in 8 hours; Class "A" poison gas.

Table 3-3. (Refrigerants Unacceptable on the Basis of Safety)

REFRIGERANT	REASON UNACCEPTABLE
Oxygen (O_2)	Explosion hazard with combustible materials; strong oxidizer; over-pressure hazard if liquid or cold gas trapped.
Deuterium (D_2)	Simple asphyxiant; flammable with limits of 4.9-75%.
Fluorine (F_2)	Highly toxic; extremely irritating and corrosive to tissues; strong oxidizer; very reactive with brass, iron, aluminum, copper and certain alloys.
Carbon Monoxide (CO)	Toxic without warning properties; flammable with limits of 12.5-74%; may react with steel.
Methyl Fluoride (CH_3F)	Flammable at room temperature and atmospheric pressure; 'Red Gas Label'.
Deuterium Chloride (DCl)	Very toxic and corrosive.
Phosphine (PH_3)	Flammable; highly toxic; 2000 ppm is lethal to man in a few minutes.
n-Hydrogen (R702)	Explosion hazard; combustible; flammable.
p-Hydrogen (R702a)	Explosion hazard; combustible; flammable.
Carbonyl Fluoride (COF_2)	Toxic; threshold limit = 2 ppm; 50 ppm fatal for 30-60 minutes; temperature > 125 °F can create dangerous hydrostatic pressure.
Vinyl Fluoride (CH_2=CHF)	Extremely flammable; high concentrations may cause dizziness or frostbite.
Boron Fluoride (BF_3)	Highly irritating; highly toxic; 50 ppm may be fatal in 30-60 minutes.

Table 3-3. (Refrigerants Unacceptable on the Basis of Safety) (Continued)

REFRIGERANTS	REASON UNACCEPTABLE
Boron Hydride (B_2H_6)	In presence of water decomposes to H_3BO_3 and Hydrogen; stability and flammability problem.
Chlorine Monofluoride (ClF)	Good oxidizer; more toxic than Chlorine; corrosive.
Phosphorous Trifluoride (PF_3)	Highly poisonous; threshold limit below 1 ppm.
Ozone (O_3)	Toxic, unstable, potentially explosive, nasty to handle and transport.

Table 3-4. Refrigerants Acceptable on the Basis of Safety

REFRIGERANT	SAFETY DATA
Argon (Ar)	Overpressure hazard if liquid or cold gas trapped; nontoxic; nonflammable; tissue damage can result from exposure to liquid or vapors.
Carbon Dioxide (CO_2)	Simple asphyxiant; short term exposure is 15000 ppm; dry ice used in refrigeration; nonflammable; slightly acidic; inerting agent in fire extinguishers to prevent oxidation; avoid use of carbon steel and other materials which become brittle at low temperatures; heavy gas which will remain in low spots if not well ventilated.
Helium (He)	Overpressure hazard if liquid or cold gas is trapped; will condense air and give oxygen enrichment; nontoxic; nonflammable.
Neon (Ne)	Nonflammable; simple asphyxiant; overpressure hazard if liquid or cold gas trapped; will condense air and give oxygen enrichment.
Nitrogen (N_2)	Simple asphyxiant; nonflammable; extensive tissue damage can result from exposure to liquid or vapor; overpressure hazard if liquid or cold gas trapped; will condense and give oxygen enrichment.
Nitrous Oxide (N_2O)	Nontoxic; nonflammable; weak anesthetic; simple asphyxiant when mixed with oxygen; supports and accelerates combustion of flammables; noncorrosive.

Table 3-4. (Refrigerants Acceptable on the Basis of Safety) (Continued)

REFRIGERANT	SAFETY DATA
*Air (Mixture of N_2, O_2, Ne, He, Kr, H, Xe, Ra, Ar, CO_2)	Nontoxic; nonflammable; avoid use of oil in systems at full cylinder pressure; compressed air can accelerate burning of materials which are comustible at atmospheric pressure.
Carbon Tetrafluoride (CF_4)	Essentially nontoxic; skin frostbite may occur; nonflammable.
Monochlorotrifluoromethane (R-13, $CClF_3$)	Relatively nontoxic;nonflammable; noncorrosive; may cause frostbite
Xenon (Xe)	Nonflammable; noncorrosive; simple asphyxiant; overpressure hazard if liquid or cold gas trapped.
Krypton (Kr)	Overpressure hazard if liquid or cold gas trapped; simple asphyxiant; noncorrosive.
Trifluoromethane (Freon 23, CHF_3)	Nontoxic; nonflammable; may cause frostbite.
Azeotrope of R13 and R23 (R503)	Nontoxic; nonflammable.
n-Helium	Nontoxic; nonflammable.
Hexafluoroethane (C_2F_6)	Nonflammable; nontoxic at room temperature.

* Air is a mixture which varies with the altitude at which the sample is taken.

Table 3-5. Mixtures Which May Be Acceptable on the Basis of Safety

MIXTURE	COMMENTS
5% N_2 in CH_4 2 1/2% N_2 in CH_4	Flammability problem still exists but may be able to solve the problem by using an orifice to vent air.
$CH_4/N_2/H_2/He$	May be able to use low enough concentrations of CH_4 and H_2 so that it is not explosive or flammable.
$He/H_2/Ar/Ne$	A low enough concentration of H_2 may be used so that explosion and flammability hazards are minimal.
Ar/N_2	No safety problems here.
$.5CH_4/.5N_2$	Flammability limits should become smaller with smaller concentrations of CH_4. More analysis needs to be done.
$.5N_2/.25CH_4/.25Ar$	Flammability may not be as much a concern here.
$.5CH_4/.5Ne$	Would probably need orifice to vent air to meet safety conditions.
$.5Ar/.5CO_2$	Probably no safety problems; must be well ventilated.
$.5Kr/.5N_2$	Probably excellent mixture as far as safety is concerned.
$.5Kr/.5Ar$	Probably excellent mixture as far as safety is concerned.

3.3 INFRARED TRANSMISSION

The candidates that satisfied the evaluation criteria up to this point are shown in Table 3-6. These candidates were then evaluated to determine their I.R. signature. A description of how the data was obtained is presented in the following paragraphs.

It was evident from our efforts that very little information was available on I.R. signatures for cryogens, compounds or mixtures. The Matheson Gas Book (see reference list in Appendix 1) did (does) have I.R. spectra on a variety of gases, which was obtained from Sadtler Research Laboratory. Sadtler does a lot of work in spectroscopy and has tabulated about 9200 compounds. Generally, they perform the tests in an 8-10 centimeter (cm) cell filled with Helium at one (1) atmosphere. They vaporize the sample which is then injected into the cell and the transmission at the desired wavelength is determined. The problem that exists on using this available data is that the pressure and the concentration of the sample is unknown. Large concentrations could cause excitations which could excite the gas into the next higher region (wavelength) where the gas absorbance increases. Therefore, the I.R. transmission cannot be accurately determined from this data. However, the data is representative of what one can expect at one atmosphere, and 10-20 cm path length, which is a representative pressure and optical path length for many I.R. seekers. The conditions, then, under which the I.R. signature is obtained is very important. If, as is the case in much of the data in the Matheson Gas Book, the I.R. signature is obtained at a pressure much different than 1 atmosphere (760 mm Hg), the data may not be representative of what would happen at 1 atmosphere.

Sadtler markets both a hard copy (books) and computer program of the 9200 compounds, which is P.C. compatible (no McIntosch) in either 3 1/2 or 5 1/4 floppy disks for about $12,000. They also have a smaller version of 3300 compounds for about $1500. It was contractually impossible to purchase this data under this contract. Sadtler was very helpful, however, and put us in contact with Dr. Bob Kroutil at the Chemical Research Development and Engineering Center in Maryland.

Much of the information on IR transmission was obtained through CRDEC (Chemical Research Development and Engineering Center) via Sadtler Software and Database and Dow Chemical Company. A visit was made to CRDEC in which the following substances were identified as having no significant absorbance in the 3-5 and 8-12 micron (3300-2000 and 1250-833 wave numbers respectively) regions. (Wavenumber number is the reciprocal of wavelength expressed in cm^{-1}.)

ARGON (Ar)
HELIUM (He)
NEON (Ne)
NITROGEN (N_2)
AIR (Mixture of Ne, He, Kr, H, Xe, Ra)
XENON (Xe)
KRYPTON (Kr)
n-HELIUM (R704)
He/H_2/Ar/Ne
Ar/N_2
Kr/N_2
Kr/Ar

A description of the IR transmission in the specified bands for each of the candidates which passed the safety criteria is given in Table 3-6.

Table 3-6. I-R Transmission of Candidate

Candidate	Percent Transmission 3-5 µm	Percent Transmission 8-12 µm	Reference
Argon (Ar)	95-100	95-100	CRDEC
Helium (He)	95-100	95-100	CRDEC
Neon (Ne)	95-100	95-100	CRDEC
Nitrogen (N_2)	95-100	95-100	CRDEC
Air (Mixture of Ne, He, Kr, H, Xe, Ra)	95-100	95-100	CRDEC
Xenon (Xe)	95-100	95-100	CRDEC
Krypton (Kr)	95-100	95-100	CRDEC
n-Helium (R704)	95-100	95-100	CRDEC
He/H_2/Ar/Ne	95-100	95-100	Matheson Gas Data Book
Ar/N_2	95-100	95-100	CRDEC, APD Cryogenics
Kr/N_2	95-100	95-100	CRDEC, APD Cryogenics
Kr/Ar	95-100	95-100	CRDEC, APD Cryogenics
Carbon Dioxide (CO_2)	3-4.2: 96-100% 4.2-4.35: sharp drop to 3.2% 4.35-4.55: sharp rise to 96% 4.55-5.0: 96-100%	96-100	CRDEC, DOW Chemical Co.

Table 3-6 (Continued)

Candidate	Percent Transmission 3-5 μm	Percent Transmission 8-12 μm	Reference
Nitrous Oxide (N_2O)	3-3.7: 96-99% 3.7-4.35: 84.7-100% 4.35-4.45: sharp drop to 3.2% 4.45-4.55: sharp rise to 17.9% 4.55-4.57: sharp drop to 6.6% 4.57-5.0: sharp rise to 96%	96-100	CRDEC, DOW Chemical Co.
Carbon Tetrafluoride (CF_4) (FREON 14)	3-3.8: slight increase from 80 to 86% 3.8-3.92: decrease to 76% 3.92-4.55: increase to 90% 4.55-4.6: decrease to 43% 4.6-4.65: increase to 89% 4.65-5.0: 87-90%	8.0-8.1: sharp increase from 20-73% 8.1-8-2: sharp decrease to 20% 8.2-8.3: sharp increase to 92% 8.3-12: 90-96%	CRDEC DOW CHEM. CO. MATHESON GAS DATA BOOK
MONOCHLOROTRIFLUOROMETHANE ($CClF_3$, FREON13)	3-5μm: 78-90%	8-8.2: decrease from 80-0% 8.2-8.35 -- 0% 8.35-8.6: increase to 92% 8.6-8.9: decrease to 0% 8.9-9.2 -- 0% 9.2-9.5: increase to 94% 9.5 - 12.0: 90-97%	CRDEC MATHESON GAS DATA BOOK DOW CHEMICAL CO.

Table 3-6 (Continued)

Candidate	Percent Transmission 3-5 μm	Percent Transmission 8-12 μm	Reference
TRIFLUOROMETHANE (CHF_3) (FREON 23)	3-3.2: decrease from 90% - 33% 3.2-3.35: increase to 85% 3.35-3.7: 85-91% 3.7-3.75: drop to 84% 3.75-3.8: rise to 90% 3.8-4.35: rise to 93% 4.35-4.4: drop to 77% 4.4-5.0: rise to 90%	8-8.2: decrease from 86% to 77% 8.2-8.3: increase to 85% then decrease to 26% 8.3-8.4: increase to 78% 8.4-8.8: decrease to 0% 8.8-9.1: increase to 87% 9.1-12.0: increase to 91%	CRDEC, DOW CHEM. CO.
HEXAFLUOROETHANE (C_2F_6)	3-5μm: 80-91%	8-8.15 -- 0% 8.15-8.25: increase to 81% 8.25-8.35: decrease to 60% 8.35-8.6: increase to 93% 8.6-8.8: decrease to 0% 8.8-9.1 -- 0% 9.1-9.3: increase to 94% 9.3-12: 92-97%	CRDEC SADTLEF RESEARCH LABS, INC.
METHANE (CH_4)	3-3.13: 80% 3.13-3.6: many peaks fluctuating between 8% and 80% 3.6-5.0: increase to 91%	8.0-8.3 many peaks between 71% and 93% 8.3-12.0 rise to 96%	CRDEC DOW CHEM. CO.

A few of the candidates shown in Table 3.6 do not have a flat response at the wavelengths of interest. A review of this table will show that Carbon Dioxide, Nitrous Oxide, Monochlorotrifluoromethane, and Methane all absorb in both the 3-5 and 8-12 micron regions. Monochlorotrifluoromethane has almost no absorption[2] in the 3-5 micron region while Methane appears to absorb only in the first 0.5 of each region.

If operation can be limited to certain portions of the IR spectrum, all candidates in Table 3-6 are viable; consequently, they have not been eliminated. IR transmission curves for those candiates that do not have a flat response at the desired wavelengths are included in Appendix A. Review of these curves will show that Carbon Tetrafluoride absorbs mainly in the 3-5 micon region while Trifluoromethane and Hexafluoroethane also have absorbance, in both the 3-5 and 8-12 micron regions. The following section of this report takes a look at the two-phase possibilities of the remaining candidates.

3.4 TWO PHASE CHARACTERISTICS

Cryostat openings are so small that water droplets or solid particles can block the coolant flow. Many substances change state at low ambient temperatures which can cause solids and/or liquids to form in the storage container (dewar). This could easily cause clogging of the gas line and/or container.

In order to eliminate substances which have state changes (two phase possibilities), the following properties were tabulated in Table 3.7:

1. boiling point (B.P.)
2. melting point (M.P.)
3. critical temperature (C.T.)
4. triple point (T.P.)
5. freezing point (F.P.)

This data was obtained from Matheson Gas Data Book and the CRC Handbook of Chemistry and Physics, 68th edition.

The critical temperature is the temperature above which a substance cannot exist in the liquid state, regardless of the pressure. At this temperature, materials may change phase thus causing appreciable changes in the properties of the materials. The triple point is the thermo-dynamic state at which three phases of a substance exist in equilibrium.

---

2 Absorption = $\text{Log}_{10} \frac{100}{\%T}$ where T = Transmission

Table 3-7 shows that two phase problems for most substances can be eliminated by controlling the temperature. Substances such as neon and nitrous oxide which have boiling points very close to their triple points should be approached with caution as possible candidates. The refrigerants which are known to condense at low ambient temperatures and cause two phase problems in the gas bottle are Freon 13, Freon 23, xenon, and nitrous oxide. For this reason they are no longer viable candidates in this analysis. The next section of this report looks at the affordability of the remaining candidates.

TABLE 3-7. TWO PHASE CHARACTERISTICS

REFRIGERANT	B.P. (°C)	M.P. (°C)	C.T. (°C)	T.P. (°C)	F.P. (°C)	TWO-PHASE POSSIBILITIES
ARGON (Ar)	-185.7	-189.2	-122.4	-189.4@ 68.8 KPa		NO PROBLEM IN GAS BOTTLE; TWO PHASE PROBLEMS BELOW -185.7 DEG. C.
HELIUM (He)	-268.9	-272.0@ 2555 KPa	-268.0			NO PROBLEM IN GAS BOTTLE; TWO PHASE PROBLEM BELOW -268.9 DEG. C.
NEON (Ne)	-246.1	-248.7	-228.7	-248.6@ 43.3 KPa		NO PROBLEM IN GAS BOTTLE; TWO PHASE PROBLEM BELOW -246.1 DEG.. C. T.P. CLOSE TO B.P.
NITROGEN (N_2)	-195.8	-209.86	-146.9	-210.0@ 12.5 KPa		NO PROBLEM IN GAS BOTTLE; NO TWO PHASE CONCERN UNLESS TEMPERATURE IS LESS THAN -209 DEG. C.
AIR (MIXTURE OF Ne, Kr, He, H, Xe, Ra)	-194.35		-140.6			NO PROBLEMS
XENON (Xe)	-108.1	-111.9	16.6	-111.9@ 82 KPa		TEMPERATURE IN GAS BOTTLE SHOULD BE ABOVE 16.6 DEG. C. TWO PHASE PROBLEM BELOW -108.1 DEG. C.
KRYPTON (Kr)	-153.4	-156.6	-63.8	-157.4@ 73.2 KPa		NO PROBLEM IN GAS BOTTLE. TWO PHASE PROBLEM BELOW -153.4 DEG. C.
n-HELIUM (R704)	-268.9	-272.0@ 2555 KPa	-268.0			NO PROBLEMS UNLESS TEMPERATURE IS BELOW -268.0 DEG. C.
CARBON DIOXIDE (CO_2)	-78.6	-56.6	31.0	-56.6		GAS BOTTLE TEMPERATURE SHOULD BE ABOVE 31.0 DEG. C; TWO PHASE PROBLEM AT -56.6.

TABLE 3-7. TWO PHASE CHARACTERISTICS

REFRIGERANT	B.P.(°C)	M.P.(°C)	C.T.(°C)	T.P.(°C)	F.P.(°C)	TWO-PHASE POSSIBILITIES
NITROUS OXIDE (N_2O)	-88.5	-90.8	36.4	-90.8	--	GAS BOTTLE TEMPERATURE SHOULD BE ABOVE 36.4 DEG. C.; TWO PHASE PROBLEM BELOW -88.5; T.P. VERY CLOSE TO B.P.**
CARBON TETRAFLUORIDE (CF_4) (FREON 14)	-129.0	-150.0	-45.6	--	-186.8	NO PROBLEM IN GAS BOTTLE FOR TEMPERATURE ABOVE -45.6 DEG. C.; NO TWO PHASE PROBLEMS
MONOCHLOROTRIFLUOROMETHANE ($CClF_3$, FREON 13)	-81.1	-181.0	28.8	--	181.0	GAS BOTTLE TEMPERATURE SHOULD BE ABOVE 28.8 DEG. C. BUT THIS GAS MAY CONDENSE IN GAS BOTTLE NO TWO PHASE PROBLEMS IN LINES.*
TRIFLUOROMETHANE (FREON 23-CHF_3)	-82.2	-160.0	25.9	--	-155.2	GAS BOTTLE TEMPERATURE SHOULD BE ABOVE 19.7 DEG. C.; NO TWO PHASE PROBLEMS.**
HEXAFLUOROTHANE (C_2F_6)	-78.2	-94.0	19.7	-100.0	-100.6	GAS BOTTLE TEMPERATURE SHOULD BE ABOVE 19.7 DEG. C.; NO TWO PHASE PROBLEMS.
METHANE (CH_4)	-161.5	-182.0	-82.1	−182.5@ 11.69 K.P.	---	NO PROBLEMS.
HE/H /Ar/Ne	~-238.0	~-242.0	~-215.0	---	---	NO APPARENT TWO PHASE PROBLEMS.
Ar/N_2	~-191.0	~-199.5	~-134.7	-199.7	--	NO TWO PHASE PROBLEMS.
Kr/N_2	~-174.6	~-183.2	~-105.4	-183.7	---	NO TWO PHASE PROBLEMS.
Kr/Ar	~-169.6	~-172.9	~-93.1	-173.4	---	NO TWO PHASE PROBLEMS.

*LONGSWORTH, RALPH, APD CRYOGENICS INC., PRIVATE CONVERSATION

** POSSIBLE CONDENSATION IN CONTAINER

3.5 AFFORDABILITY

The affordability of potential refrigerants appears to be dependent on availability, purity and cost. These factors are tabulated for the various refrigerants in Table 3-8. Prices were obtained from Matheson Gas Products. There is a shortage of some of the rare gases due chiefly to lack of demand. However, most of the gases can be obtained from the atmosphere by air separation plants and a greater demand might increase the supply, which may in turn lower the cost. Also, a high purity substance will help lower the cost since an extensive effort to remove water and contaminants will not be required. Furthermore, Scott Speciality Gases will guarantee stability of all the possible refrigerants for at least one year and claims stability could be much longer if the cylinders are properly maintained.

From Table 3-8 it can be seen that the most expensive refrigerant is Freon 14. Krypton goes from expensive to very inexpensive when the quantity purchased at one time is increased from 100 liters (l) to 5000 liters (l). The expensive refrigerants may still be viable candidates, however, since the amount required for one fast cool-down may be less than 10 liters. It should be noted that the cost data is based on different units and one must be careful in making cost comparisons. Cost comparisons should be made on calories of heat removed (cost/calorie) for each of the candidates. As stated, this is very dependent on cooler design. Consequently, when all factors are considered, the cost of the coolant may decrease for large production buys and may be cost effective when performance versus cost trade studies are done. The next section of this report examines the J-T efficiency of the refrigerants.

Table 3.8. AFFORDABILITY OF POTENTIAL REFRIGERANTS

REFRIGERANT	PURITY	AVAILABILITY	COST ($/1)	QUANTITY(1)*
ARGON (Ar)	99.9995	Readily available	2.30	100
HELIUM (He)	99.9999	Readily available	2.13	100
NEON (Ne)	99.999	Readily available (limited quantities)	2.56	100
NITROGEN (N_2)	99.9995	Readily available	2.13	100
AIR	ULTRA ZERO	Readily available	0.02	8745
KRYPTON (Kr)	99.995	Readily available (limited quantities)	1.32 6.61	5000 100
n-HELIUM (R704)	**			
CARBON DIOXIDE (CO_2)	99.9995	Readily available	2.13	100
CARBON TETRAFLUORIDE (CF_4 FREON 14)	99.999	Readily available	0.28	8716
HEXAFLUOXOETHANE (C_2F_6)	**	Readily available		
METHANE (CH_7)***	99.99	Readily available	2.12	125
Ar/N_2 (50-999 ppm)		Readily available	0.03	7160
Kr/N_2		No data available		
Kr/Ar		No data available		
He/H_2/Ar/Ne		No data available		

*This is the quantity that must be bought in order to get the best price.
**Price information not currently available.
***Methane included as it might be acceptable in low concentrations.

3.6 J-T EFFECTIVENESS

The J-T cooling efficiency of a cryogen is a measure of how much refrigeration is available for cooling. A cryogen with a high J-T efficiency has a maximum temperature drop upon free expansion from a high pressure. The temperature drop of a refrigerant can be found by inspection of the temperature-entropy (T-S) charts. Charts used to obtain the data in Table 3-9 are included in Appendix A. From Table 3-9, it is seen that the cryogens with the highest J-T cooling efficiency are Methane, Carbon Tetrafluoride, and Argon. There are some blanks in the table due to difficulty in locating temperature entropy charts. Bob McCarty of NBS has said, however, that this information can be obtained from National Standard Reference Data Service of the USSR, Volumes 8, 9, and 10.

TABLE 3-9. Temperature Drops of Various Cryogens

Refrigerant	Ambient Temperature (°K)	Temperature Drop (°K)
NITROGEN (N_2)	340 (298)	26 (40)
METHANE (CH_4)*	340 (298)	83 (108)
AIR	300	35
HELIUM	--	--
CARBON DIOXIDE	298	60
ARGON	340	65
CARBON TETRAFLUORIDE	340	75
KRYPTON (Kr)	300 (350)	50 (100)
n-HELIUM		--
HEXAFLUOROETHANE		--
NEON		--
Ar/N_2 (50-999ppm)		--
Kr/N_2		--
Kr/Ar		--
He/H_2/Ar/Ne		--

*Methane included as it might be acceptable in low concentrations.

These candidates must be evaluated in J-T coolers to evaluate the J-T cryostat efficiency for each coolant. J-T cryostat efficiency is a useful measure of the way an actual machine measures up to the thermodynamic ideal machine. The J-T cryostat efficiency is the ratio of actual coefficient of performance (COP) to the Carnot coefficient and is represented by

J-T efficiency = Actual COP/Carnot COP

It would be very beneficial to develop a model(s) for a J-T cryostat so that J-T efficiencies for various heat loads and cryogens can be determined. The equations already exist from which a model could be developed. The subsequent section of this report presents SDI conclusions and recommendations.

4. CONCLUSION

The results of this effort show that there is much work being performed in this area by individual companies and organizations such as NBS and the Environmental Protection Agency (EPA). However, it is not an easy task to identify the proper source for obtaining information because there is no coordinated effort. There is not much information available on mixtures or about solids that are soluble in liquid nitrogen. Also, there is not much information readily available on determining the J-T efficiency of various cryogens in J-T coolers since this is very dependent upon the J-T cooler design. Information, however, about the cryogen J-T efficiency can be obtained from the Temperature/Entropy (T-S) characteristics of the cryogen which will provide an indication of how well the cryogen might perform in a J-T cooler. Three companies, Carlton Technology, APD Cryogenics, and MMR Technologies (brochure included in appendix), are actively doing research in this area and all consider their work to be proprietary.

I.R. signature data is available from the Matheson Gas book and from Sadtler Research Laboratory which also markets I.R. signature data computer programs and data books in some 9000 compounds (smaller 3000 version available). Also, Sprouse, Inc. will do analysis for a fee on any gas or mixture under conditions established by the customer.

The viable candidate coolants are shown in Table 4-1. Of these candidates, the cryogen with the best potential is krypton. Dr. Bob McCarty (NBS) recommended both xeon and/or krypton. Xeon was eliminated, however, because it would condense in the gas bottle at low ambient temperatures. Krypton is more expensive than other gases, but it is affordable (see Table 3.8). A cost versus performance trade-off study would provide the information needed to make a proper assessment. Also, if krypton became more widely used, the price may drop.

Review of Table 4-1 will show that two compounds which met all the criteria have been dropped from the list of best candidates. These compounds are helium and neon, both of which have a small operating temperature range compared to other coolants in Table 4-1. A review of the thermodynamic characteristics for both of these compounds will show that at one atmopshere pressure, the boiling point termperatures are low, but the inversion temperatures do not provide a large cooling region. Neon has an inversion temperature of +27°F which is much better than helium at

Table 4-1A. SUMMARY OF BEST CANDIDATE KEY CHARACTERISTICS

COOLANT	BOILING POINT °C	IR TRANSMISSION 3-5μm	8-12μm	J-T EFFICIENCY TEMP DROP°K	AMBIENT TEMP°K
Argon (Ar)	-186	95-100	95-100	65	340
Nitrogen (N_2)	-196	95-100	95-100	26 40	340 298
Air (Mixture of Ne, O_2, N_2, He, Kr, H, Xe, Ar, Ra)		95-100	95-100	--	--
Krypton (Kr)		95-100	95-100	--	--
He/H_2/Ar/Ne		95-100	95-100	--	--
Ar/N_2		95-100	95-100	--	--
Kr/N_2		95-100	95-100	--	--
Kr/Ar		95-100	95-100	--	--

Note: Four compounds dropped out as best candiates because they have extreme fluctuations in IR Transmission in the 3-5 μm and 8-12 μm regions. The four are:

- o Hexaflouroethane (C_2Fc)
- o Carbon Tetrafluoride (CF_4)
- o Carbon Dioxide (CO_2)
- o Trifluoromethane (CHF_2) - Freon 27

TABLE 4-1B. SUMMARY OF BEST CANDIDATES KEY CHARACTERISTICS

COOLANT	SAFETY	TWO PHASE CHARACTERISTICS	COST PRICE	COST QTY
Argon (Ar)	OVERPRESSURE HAZARD IF LIQUID OR COLD GAS TRAPPED; NONTOXIC; NON-FLAMMABLE; TISSUE DAMAGE CAN RESULT FROM EXPOSURE TO LIQUID OR VAPORS.	NO PROBLEM IN GAS BOTTLE; TWO PHASE PROBLEMS BELOW -185.7 DEG. C.	2.30/l	100 l
Nitrogen (N2)	SIMPLE ASPHYXIANT; NONFLAMMABLE; EXTENSIVE TISSUE DAMAGE CAN RESULT FROM OVEREXPOSURE TO LIQUID OR VAPOR; OVERPRESSURE HAZARD IF LIQUID OR COLD GAS TRAPPED; WILL CONDENSE AND GIVE OXYGEN ENRICHMENT.	NO PROBLEM IN GAS BOTTLE; NO TWO PHASE CONCERNS UNLESS TEMPERATURE IS LESS THAN -209 DEG. C.	2.13/l	100 l
Air (Mixture of N2, O2, Ne, He, Kr, H, Xe, Ra, CO2, and Ar)	NON-TOXIC; NONFLAMMABLE; AVOID USE OF OIL IN SYSTEMS AT FULL CYLINDER PRESSURE; COMPRESSED AIR CAN ACCELERATE BURNING OF MATERIALS WHICH ARE COMBUSTIBLE AT ATMOSPHERIC PRESSURE.	NO PROBLEMS	0.02/l	8745 l
Krypton (Kr)	OVERPRESSURE HAZARD IF LIQUID OR COLD GAS TRAPPED; SIMPLE ASPHYXIANT; NONCORROSIVE	NO PROBLEM IN GAS BOTTLE; TWO PHASE PROBLEM BELOW -153.4 DEG. C	1.32/l	5000 l
MIXTURES				
He/H2/Ar/Ne	A LOW ENOUGH CONCENTRATION OF H2 MAY BE USED SO THAT EXPLOSION AND FLAMMABILITY HAZARDS ARE MINIMAL.	NO APPARENT TWO PHASE PROBLEMS	------	------
Ar/N2	NO SAFETY PROBLEMS HERE.	NO TWO PHASE PROBLEMS.	0.03/l	7160 l
.5Kr/.5N2	PROBABLY EXCELLENT MIXTURE AS FAR AS SAFETY IS CONCERNED.	NO TWO PHASE PROBLEMS.	------	------
.5Kr/.5Ar	PROBABLY EXCELLENT MIXTURE AS FAR AS SAFETY IS CONCERNED.	NO TWO PHASE PROBLEMS.	------	l

-367°F. However, the critical pressures for both are very low which results in a very small cooling region. Consequently, operation of these compounds at very low pressures can result in a "heating" instead of a "cooling" effect. And, in the case of helium, a two phase problem can occur in which solidification takes place. These compounds would be good candidates for use in two stage coolers. However, one must be very careful in establishing the operating conditions when using these compounds alone or in a mixture.

Argon is a gas that is commonly used and appears to be the choice of many people working in this field. The Non-Line-of-Sight (NLOS) contractor uses argon as a pre-coolant, then switches in a mixture of nitrogen/neon as the sustained coolant. Another contractor uses argon as a pre-coolant at a high flow rate, then switches to nitrogen at a low flow rate, to achieve a 3-4 second cool-down time. Therefore, argon is also high on the list of best candidates. It is interesting to note that of the mixtures that survived the evaluation criteria, argon or krypton appear to always be present in the mixture.

APD Cryogenics has performed tests on a variety of mixtures in J-T open cycle cryostats. A list of some of these mixtures along with their cooldown time appears in Table 4-2.

Table 4-2. MIXTURES TESTED BY APD CRYOGENICS, INC.

MIXTURE	AMBIENT (°C) TEMPERATURE	COOLDOWN TIME (SEC)
CF_4/N_2	21	1.8
CF_4/n_2	70	2.1
Ar/N_2	21	3.3
Ar/N_2	70	4.7
$CF_4/N_2/Ne$	---	2.3

These mixtures have achieved a cooldown temperature of 77 - 82°K in a small amount of time. All of the mixtures, with the exception of $CF_4/N_2/Ne$, have equal concentrations of compounds and are tested at the same flow rate. In the $CF_4/N_2/Ne$, however, CF_4 is used as a precoolant and then a $.7N_2/.3Ne$ mixture is added. MMR Technologies has also been testing mixtures. In particular, they have been testing some of the mixtures the USSR has tested. They have found that a small percentage of halon can be used in order to reduce flammability and that control mechanisms can be used to lower flow rate and thus drop the temperature.

It is clear from the research results and efforts mentioned above, that much more work must be done in the area of mixtures. Namely, testing and analysis needs to be done for various concentrations and flowrates in mixtures. Also, more analysis should be done on control mechanisms used to monitor flowrates.

Based on our analysis, the list of candidates was narrowed down to eleven (11) compounds and four (4) mixtures as follows:

- Argon
- Helium
- Neon
- Nitrogen
- Air
- Krypton
- n-Helium (R704)
- Carbon Dioxide (CO_2)
- Carbon Tetrafluoride (CF_4, Freon 14)
- Hexafluoxoethane (C_2F_6)
- Methane (CH_7) (possibly in low concentrations)
- Ar/N_2 (59 - 999 ppm)
- Kr/N_2
- Kr/Ar
- $He/H_2/Ar/Ne$

Methane was retained since it might be acceptable in mixtures if low concentrations are used. None of these candidates were identified as having long term storage problems as long as the container is properly maintained.

The list of candidates was narrowed down to the best candidates which consisted of four (4) compounds and four (4) mixtures as shown in Table 4-1. Of these, krypton and argon appear to be the best candidates to use as a coolant or pre-coolant with nitrogen.

5. RECOMMENDATIONS

The NBS Cryogenic Center would like to establish a program to develop a data base on cryogenic compounds, mixtures, and solids. MICOM should consider helping in the development of such a program because there are many unanswered questions and a data base is needed both now and in the future.

MICOM should also consider a program for developing a data base for the compounds and mixtures identified in this report as having the best potential as a pre-coolant. They should consider a variety of temperatures, pressures, and mixture concentrations. In addition, the program should consider determining what concentrations of coolants like methane are acceptable in mixtures.

MICOM should consider purchasing some of the existing software programs that exist and develop two standard open-cycle J-T models (two different designs) which can be used to obtain/compare information on J-T efficiency for various mixtures, and cryogens against different heat loads. Two designs are needed to compare single versus two line designs and/or conventional to more advanced open cycle J-T cooler designs. This would provide MICOM with the ability to respond quickly to problems/questions which may arise in the future, and to design coolers for future missile systems.

APPENDIX A

REFERENCES AND SOURCES OF INFORMATION

REFERENCES

1. S.S. Erler Bitt. Blake, IR Spectra of Gases and Vapors - Vol. I- Prism Spectra, 10M. eell, The Dow Chemical Co., Midland, Mich, March 1964.

2. Downing, Ralph C., Gluoocarbon Refrigerants Hdbk., Prentice Hall, Englewood Cliffs, New Jersey, 1988.

3. Giacique, William F., Scientific Papers, Vol. I Dover Publications, Inc., New York, 1969.

4. Kays/Londeon, Compact Heat Exchanges, 3rd ed., McGraw Hill Book Co., 1984.

5. Hogan, Walter H. & Mass, Dr. Trevor S. Cryogenics and IR Detection, 1970, Boston Technical Publishers, Inc., Central Square, Cambridge, Mass.,

6. LS Ingale, Entropy and Low Temperatures Physics, Hutchinson Univ. Library, London, 1966.

7. J.H. Vander Maas, Basic IR Spectroscopy, 2nd ed., Heyden and Son LTD., 1972.

8. Pinchas, Laulicht, Infrared Spectra of Labelled Compounds, cl, Academic Press, London & New York, 1971.

9. Rowlinson, Liquids and Liquid Mixtures, 2nd ed., London Butterworth, 1969.

10. J.W. Robinson, CRC Handbook of Spectroscopy, Vol II, CRC Press, 1974.

11. Z. Sterbacek, B. Biskup, P. Tauet, Calculation of Properties Using Corresponding State Methods, New York, 1979.

12. J. Taborek, G. F. Hewitt, N. Afgan, Heat Exchanges - Theory and Practice, 1983, Hemisphere Publishing Corp.

13. Temperley & Trevena, Liquids and Their Properties, Hatsted Press, New York, 1978.

14. Ed. by Timmerhouse; Advances in Cryogenic Engineering, Vol. 15, Plenum Press, New York-London, 1970.

15. Brian Thompson, Hazardous Gases and Vapors: IR Spectra & Phys. Constants, Beckman Instruments 1974.

16. Walker G., Cryocoolers I&II, 1983 Plenum Press, New York.

17. Weast, Robert CRC Handbook of Chemistry and Physics, Ph.D. CRC Press Inc., Boca Raton, Fla., 68th ed., 1987-1988.

18. K.D. Williamson, Jr., Frederick J. Esesruty, Liquid Cryogenics Vol I, Theory and Equipment, CRC Press, 1983.

19. R.D. Williamson, Jr., Frederick J. Esesruty, Liquid Cryogenics Vol II, Theory and Equipment,CRC Press, 1983.

20. Lang London Butterworhts, Absorption Spectra in the IR Region, Great Britian, 1976.

21. American Society for Testing and Materials, Cryogens and Gases: Testing Mehtods, and Stancaros Dev, 1973.

22. Cryogencis Safety Manual, A Guide to Good Practice, Mech. Eng., Pubs., Ltd, 1970.

23. Matheson Gas Products, Gas Data Book, 6th Ed. 1980, Seracuse, N.J.

24. 1976 American Society of Heating and Refrigerating and Air Cond. Eng. Inc., New York. Thermophysical Props. of Refrigerants,

25. Gibbs, Charles W., Compressed Air and Gas Data, 2nd ed., Ingersoll-Rand Co., 1962, Broadway, New York, N.Y. 10004.

26. Gibbons, R.M. and Kuebler, G.P. of Air Products and Chemicals Inc., "Research on Materials Essential to Cryocooler Technology", Quarterly Progress Report I, VII, and IX, April 1968, under contract number AF33(615)-2191.

27. Walker, G., Fauvel, O.R. and Reader, G., "Commercial Applications for Stirling Refrigerators", Department of Mechanical Engineering, University of Calgary, Alberta, Canada.

28. Wu, M.F., Rest, A.J. and Scurlock, R.G., "The Solubility of Solutes in Cryogenic Liquids", Department of Chemical Engineering, Loughborough University of Technology, Loughborough, LE11 3TU, UK, 1986.

29. Benedict, B.A., Bruel, J.D., Lester, J.M., and Pearson, R.J. of Ball Aerospace Systems Group, "Joule-Thomson Cryocooler", Air Force Wright Aeronautical Laboratories, June 1988, report number AFWAL-TR-88-3018.

30. Wapato, P.G. et al, Allied-Signal Aerospace Company, "Prototype Flight Cryocooler Design and Component Demonstration", December 1988, report AFSTC-TR-87-14.

31. Sherman, N.I. et al., Hughes Aircraft Company, "Component Development for a Five-Year Vuilleumier (VM) Cryocooler", Part XII., January 1985, report number AFFDL-TR-79-3092.

32. Smith, J.L.Jr., Robinson, G.Y.Jr., and Iwasa, Y., Massachusetts Institute of Technology, Department of Mechanical Engineering, Cryogenic Engineering Lab., Cambridge, Massachusetts 01239, "Survey of the State-of-the-Art of Miniature Cryocoolers for Superconductive Devices."

33. Walker, G., "Classification of Cryocoolers", Proceedings of the Third Cryocooler Conference, National Bureau of Standards, September 1984.

SOURCES OF INFORMATION

Cincinnati Electronics - Fred Steel, Jim Walker - 513-573-6265

Santa Barbara Research Center - Art Cockrum - 805-562-2352

* New England Research Center - Ralph Rotolante - 508-443-9561

* Carlton Technology - Danny Mascaritello, Paddy Cawdery - 716-662-0006 ext. 276

* APD Cryogenics, Inc. - Ralph Longsworth - 215-791-6708
- Rodger Hern - 215-481-8215

* Air Products and Chemicals, Inc. - Terry Monick - 717-467-2981

Texas Instruments - Jim Horton - 817-381-2748
- Val Herrera - 817-381-2723

CTI Cryogenics - Peter Kerney - 617-622-5391

Union Carbide - Chris Gottzman - 716-879-2633

Jet Propulsion Labs - 818-354-4321

AiResearch - O. Buchanon - 213-512-3393

* National Bureau of Standards (Colorado) - Bob McCarty, 303-497-3386 - Jim Ely, 303-497-3710

* Sadtler Research Lab - Mike Boruta, Wayne Liss - 215-382-7800

National Bureau of Standards (Maryland) - Joan Sauerwein - 301-975-2208
NOTE: Information on computer program DDMIX for calculating thermodynamical properties.

* IRIS Center - Toney LaRocca - 313-994-1200 ext. 2302

Chemical Research Development and Engineering Center - Bob Kroutil, 301-671-3021 - Lynn Hoffland, 301-671-2437 - Roger Combs, 671-3021

Redstone Scientific Information Center - Nancy Stillson - 205-876-5195

* Scott Specialty Gases - Glenn Sanford - 215-766-8861

  Andonian Cryogenics, Inc. - 617-969-8010

  Rogers and Clarke Mfg. Co. - 815-877-1484

  Allied Signal Cryogenics - Ned Pennelton, 602-893-4430 - Mike McCollum, 602-893-5117

* Sprouse Scientific - James F. Sprouse, Phd., Jack Carroll - 215-251-0316

  Nicholais Industry Co. - Bill Herget/Terry Grim - 608-271-3333

* Matheson Gas - Tom Pletzke - 201-867-4100

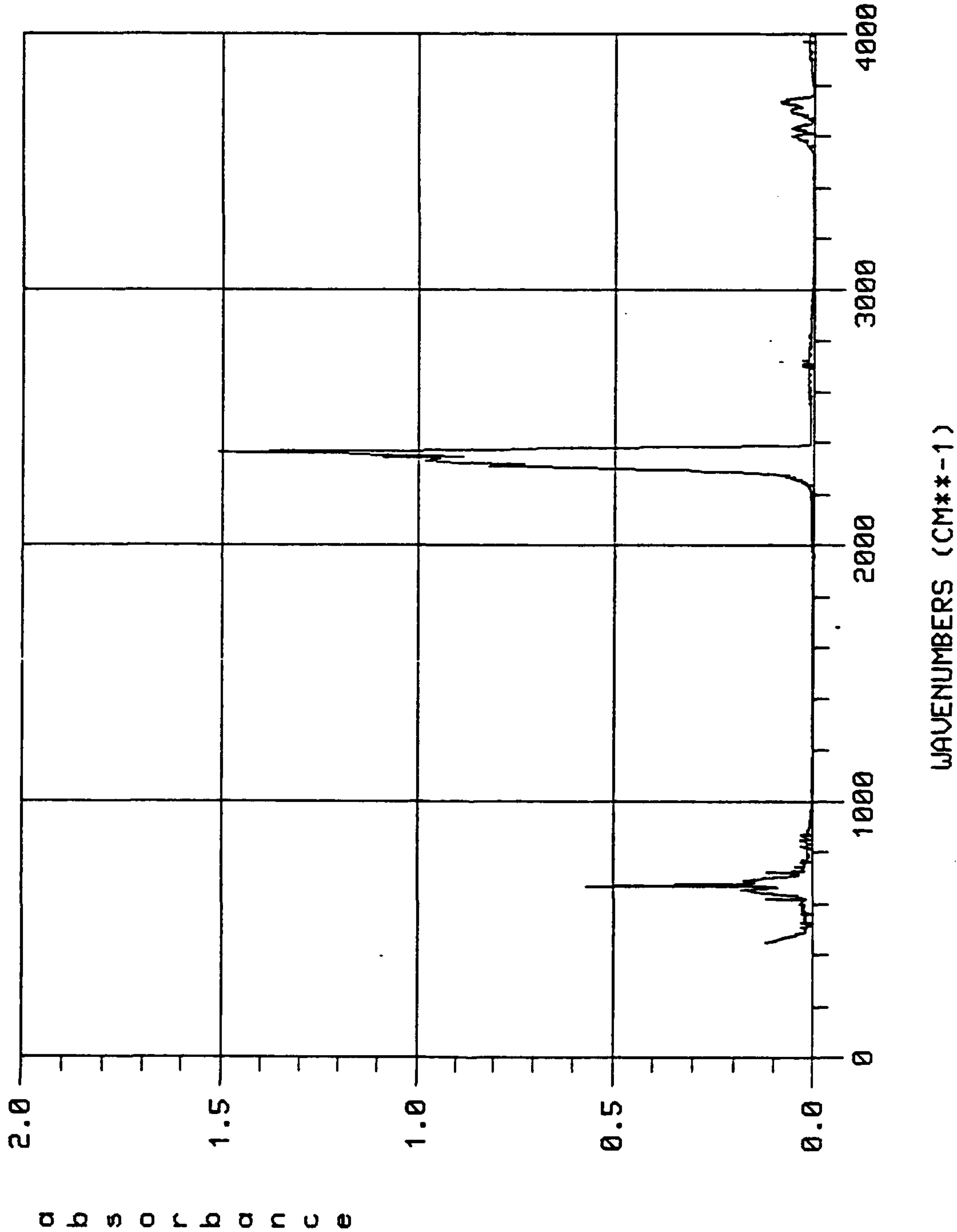
  Coblentz Society, CHEMIR Labs - St. Louis, MO

* Recon Optical - Bill Volz - 312-381-2400

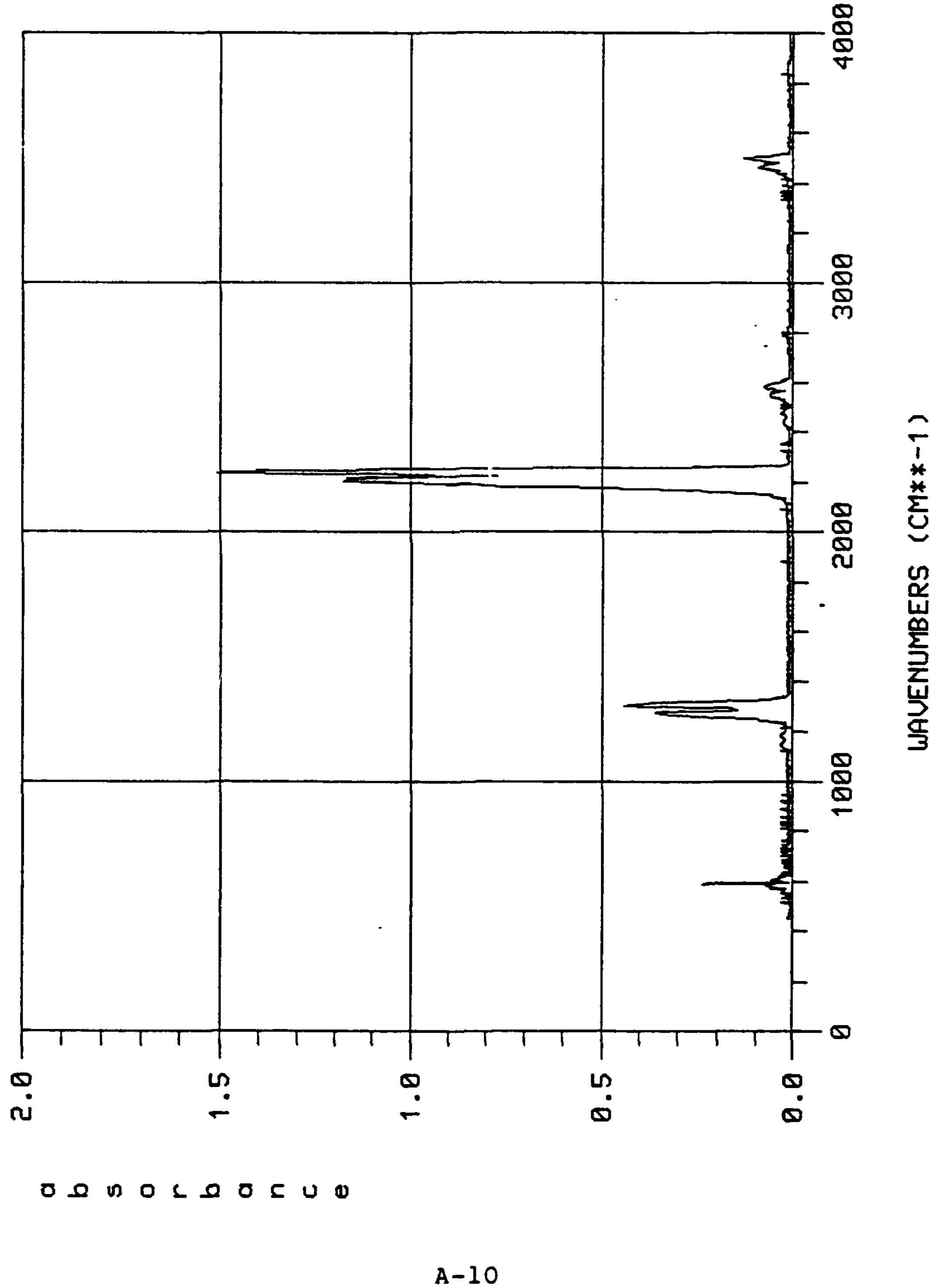
* Extremely helpful and provided valuable information.

INFRARED TRANSMISSION
AND
ABSORBANCE CHARTS

CARBON DIOXIDE



NITROUS OXIDE

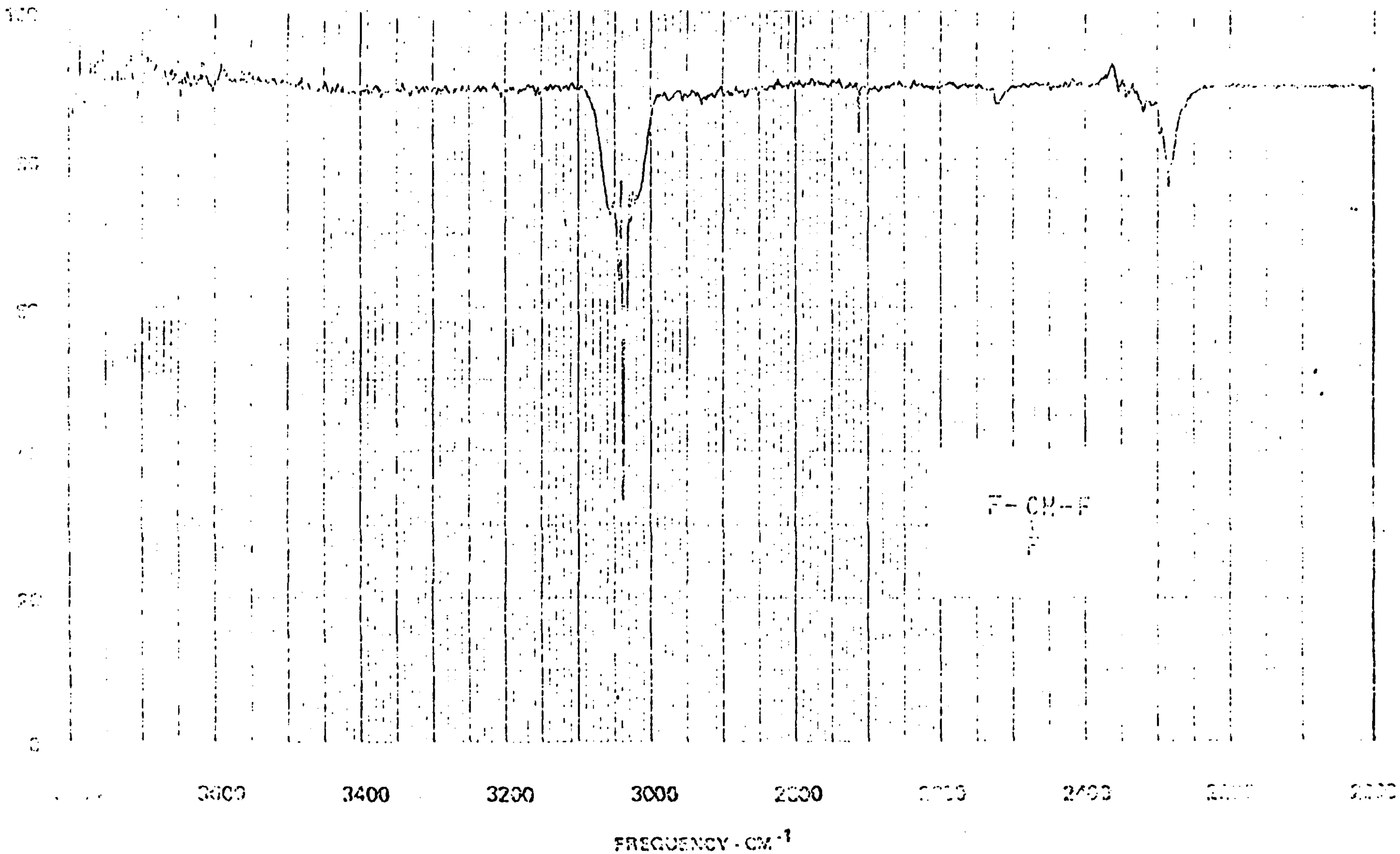


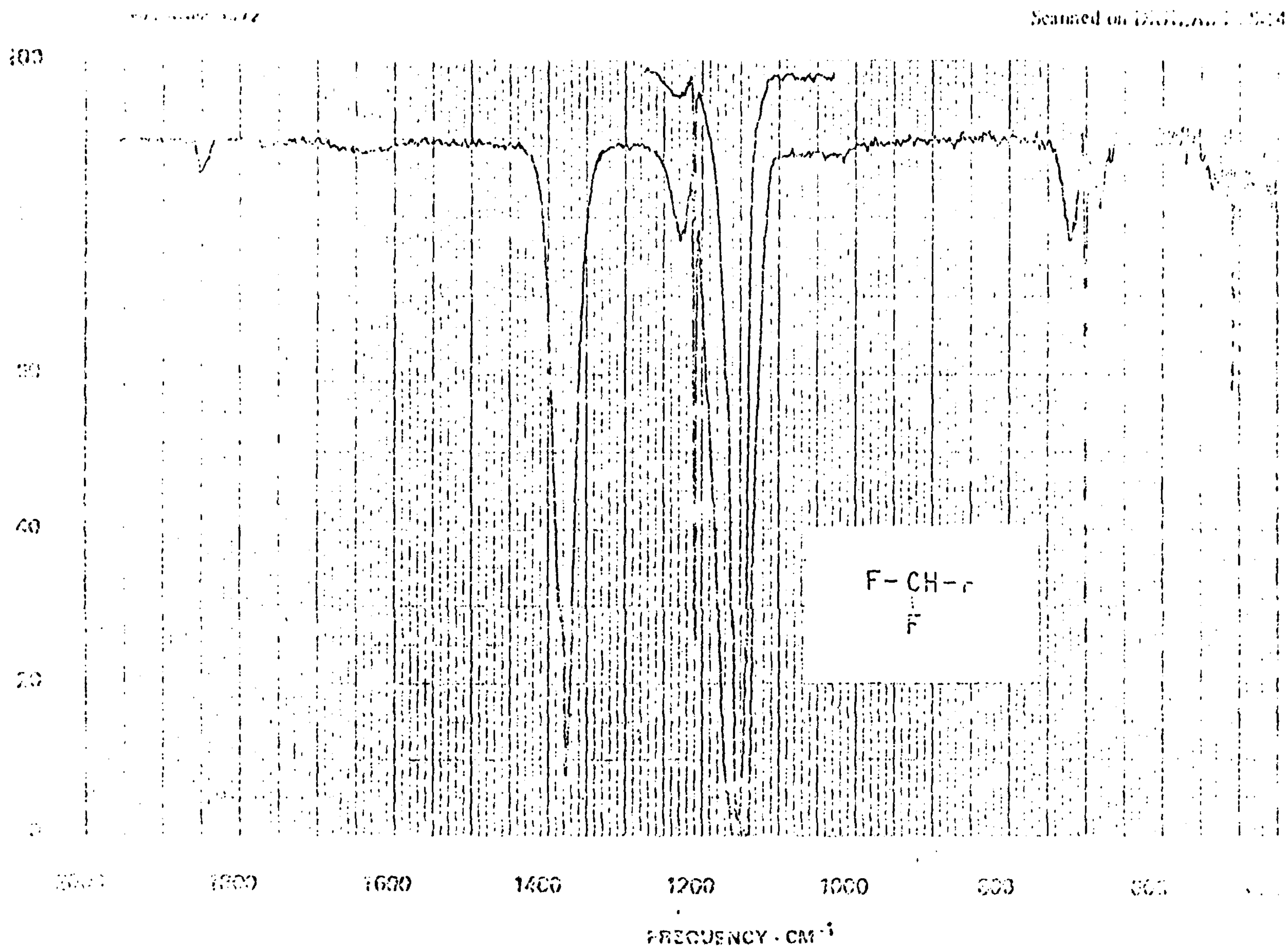
FREON 23

TRIFLUOROMETHANE

Subsidiary of Block Engineering, Inc.

Scanned on





OPERATING CONDITIONS
Path Length: 10 cm.

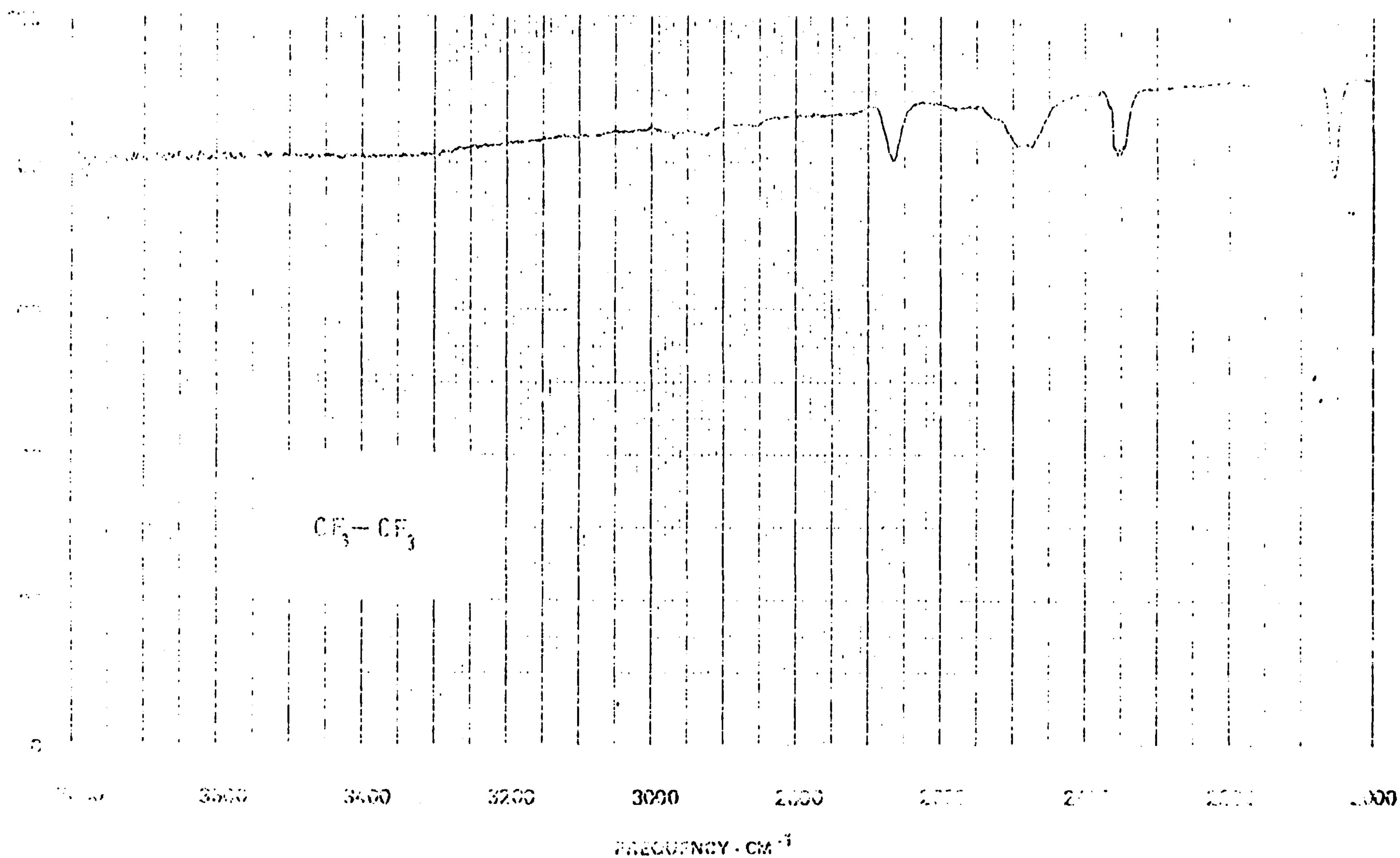
Complete Scan: 20 mm. Hg
Partial Scan: 0.5 mm.

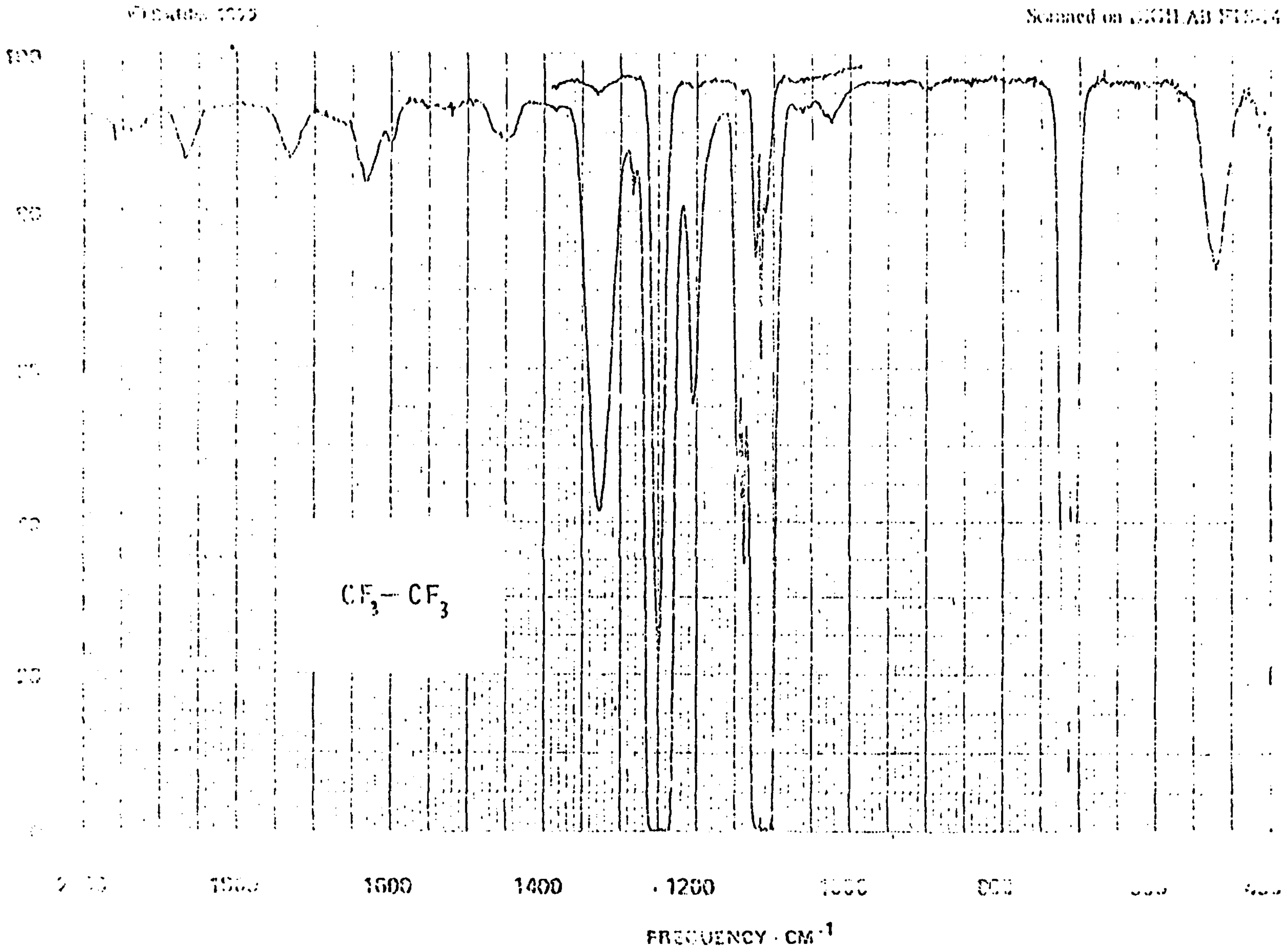
Mol. Form. CHF_3

Mol. Wt. 70.01
B.P. -115.7°F

HEXAFLUOROETHANE

Subsidiary of ... Engineering, Inc. © 1972



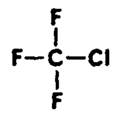


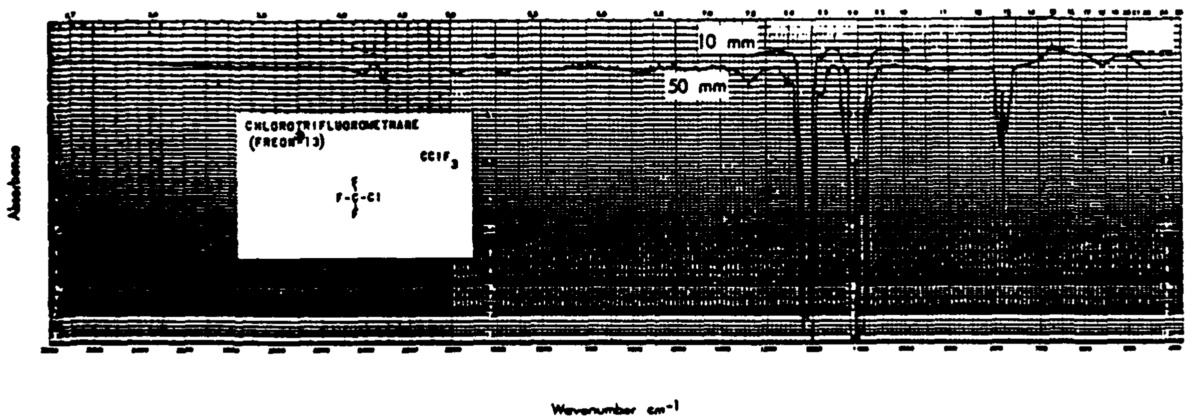
OPERATING CONDITIONS
[illegible]: 10 cm.

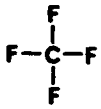
[illegible]: 20 mm. Hg
[illegible] Scan: 0.5 mm.

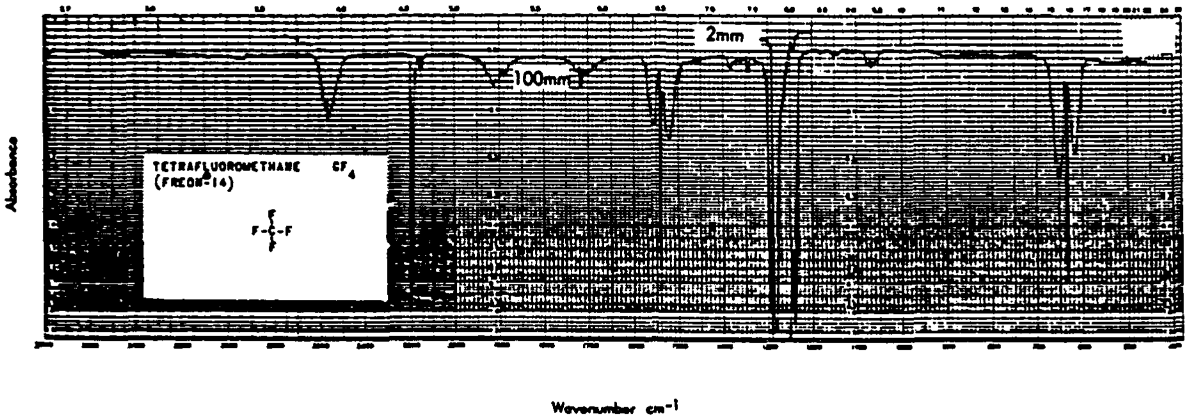
Mol. Form. C_2F_6

Mol. Wt. [illegible]
B.P. [illegible]

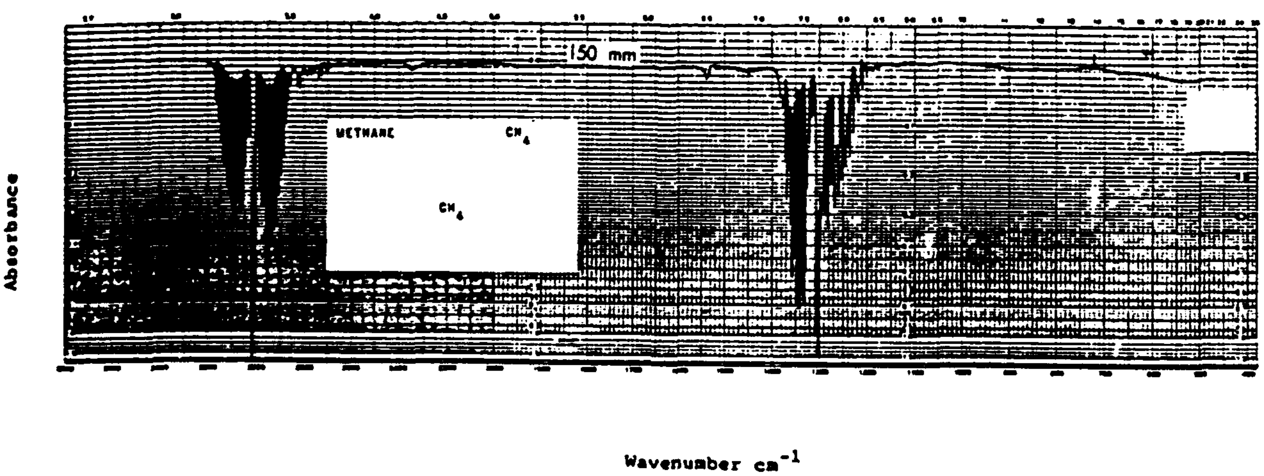
Chlorotrifluoromethane Freon® 13		CA# 18283-79-9	8825
$CClF_3$	SAMPLE PREP. N_2 added total pressure 600 mm PATH 5 cm	COBLENTZ STRUCTURE VERIFIED	
		STATE gas M.P. B.P.	
	SPECTROMETER MAKE + MODEL Dow KBr foreprism-grating: Changed 5.0, 7.5, 15.0μ	CONTRIBUTING LAB. Dow Chemical Company DATE RECORDED 1964	



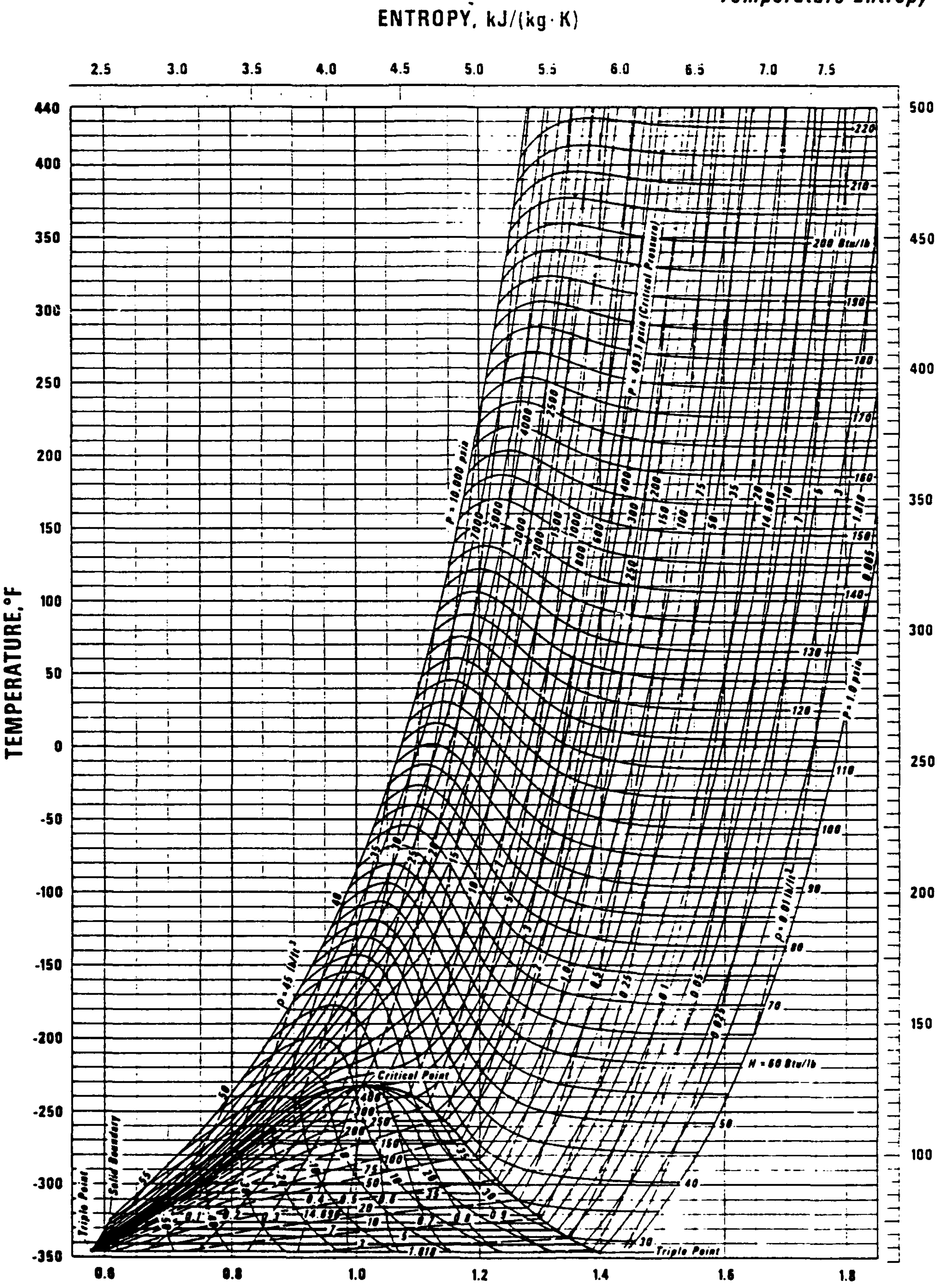
Tetrafluoromethane Freon® 14		C.A. #75-73-0	8850
CF_4	SAMPLE PREP. N_2 added total pressure 600 mm PATH 5 cm	COBLENTZ STRUCTURE VERIFIED	
		STATE gas M.P. B.P.	
	SPECTROMETER MAKE + MODEL Dow KBr foreprism-grating: Changed 5.0,7.5,15.0μ	CONTRIBUTING LAB. Dow Chemical Company DATE RECORDED 1964	



Methane		C.A. #74-82-8	8873
CH_4	SAMPLE PREP. N_2 added total pressure 600 mm PATH 5 cm	COBLENTZ STRUCTURE VERIFIED	
CH_4		STATE gas M.P. B.P.	
	SPECTROMETER MAKE + MODEL Dow KBr foreprism-grating: Changed 5.0,7.5,15.0μ	CONTRIBUTING LAB. Dow Chemical Company DATE RECORDED 1964	

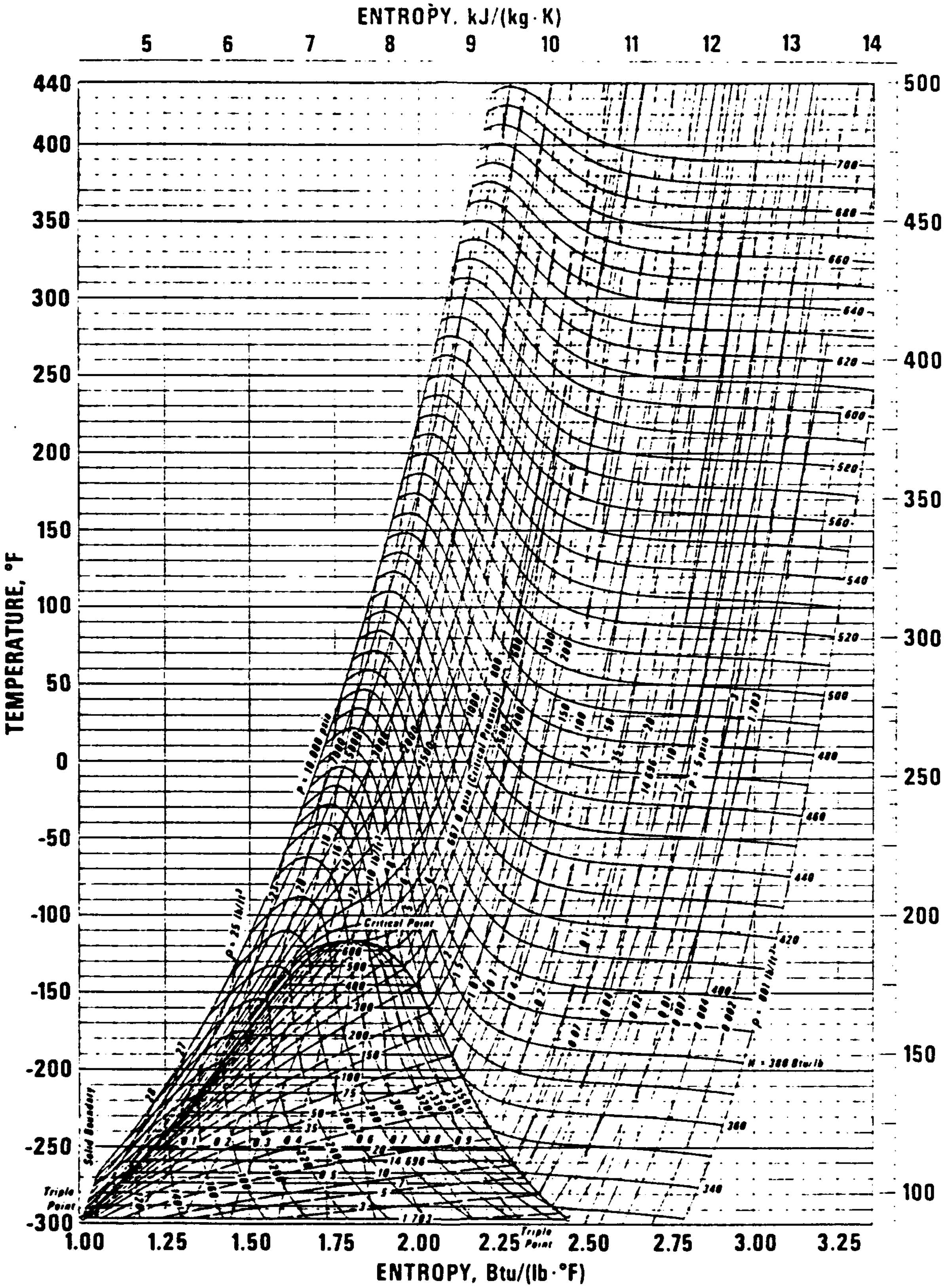


TEMPERATURE ENTROPY
CHARTS

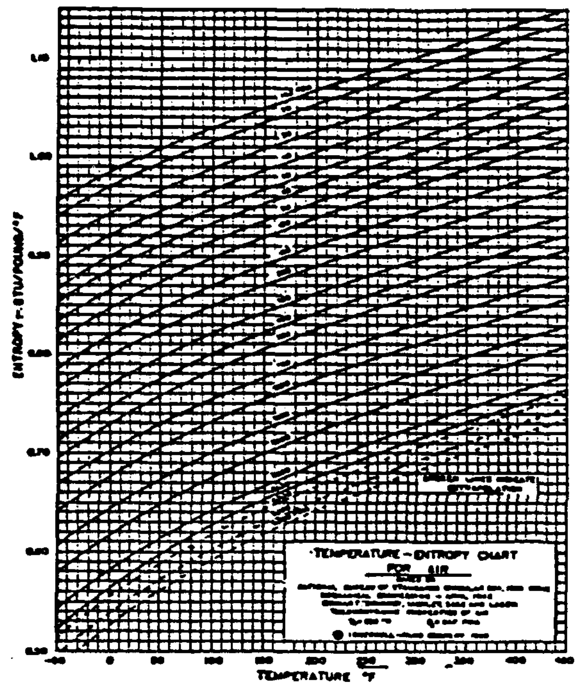


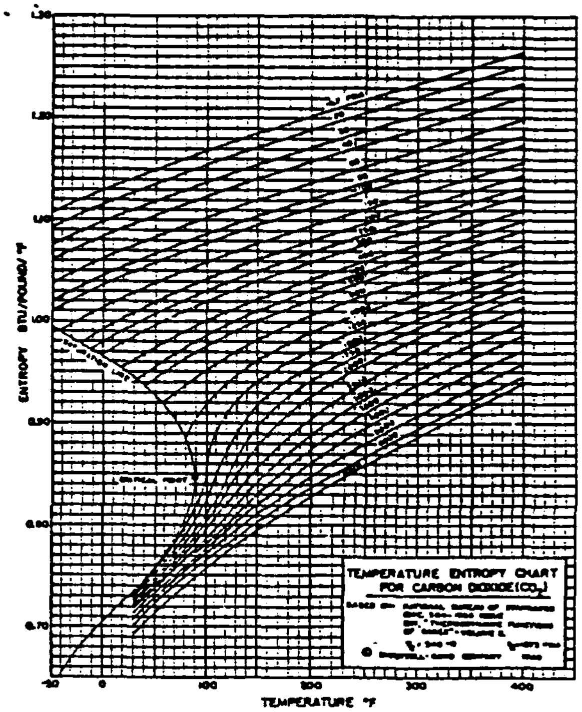
ENTROPY, Btu/(lbm·°F)

Cryogenics Division, NBS/BS, Boulder, Colorado
Chart 2027 4.1.77



Cryogenics Division, NBS-IBS, Boulder, Colorado
Chart 2026 4-1-77


TEMPERATURE - ENTROPY CHART
FOR AIR
ENTROPY - BTU/POUND/°F
TEMPERATURE °F


TEMPERATURE ENTROPY CHART
FOR CARBON DIOXIDE (CO_2)
ENTROPY BTU/POUND/°F
CRITICAL POINT
TEMPERATURE °F

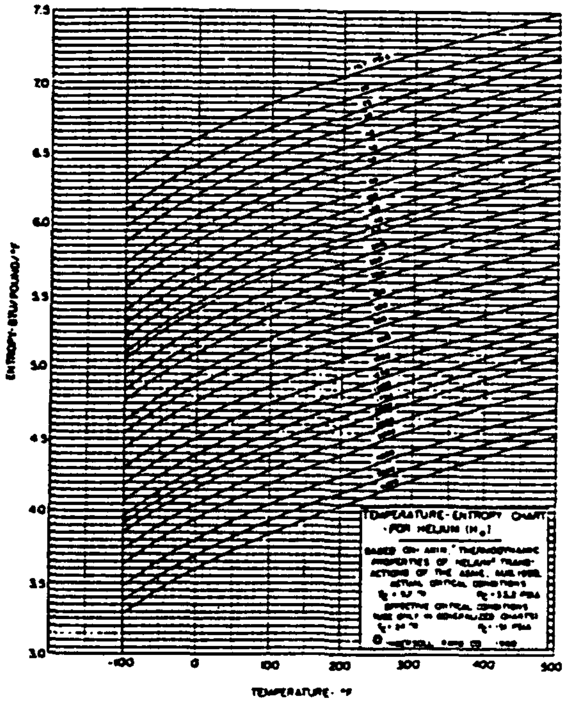
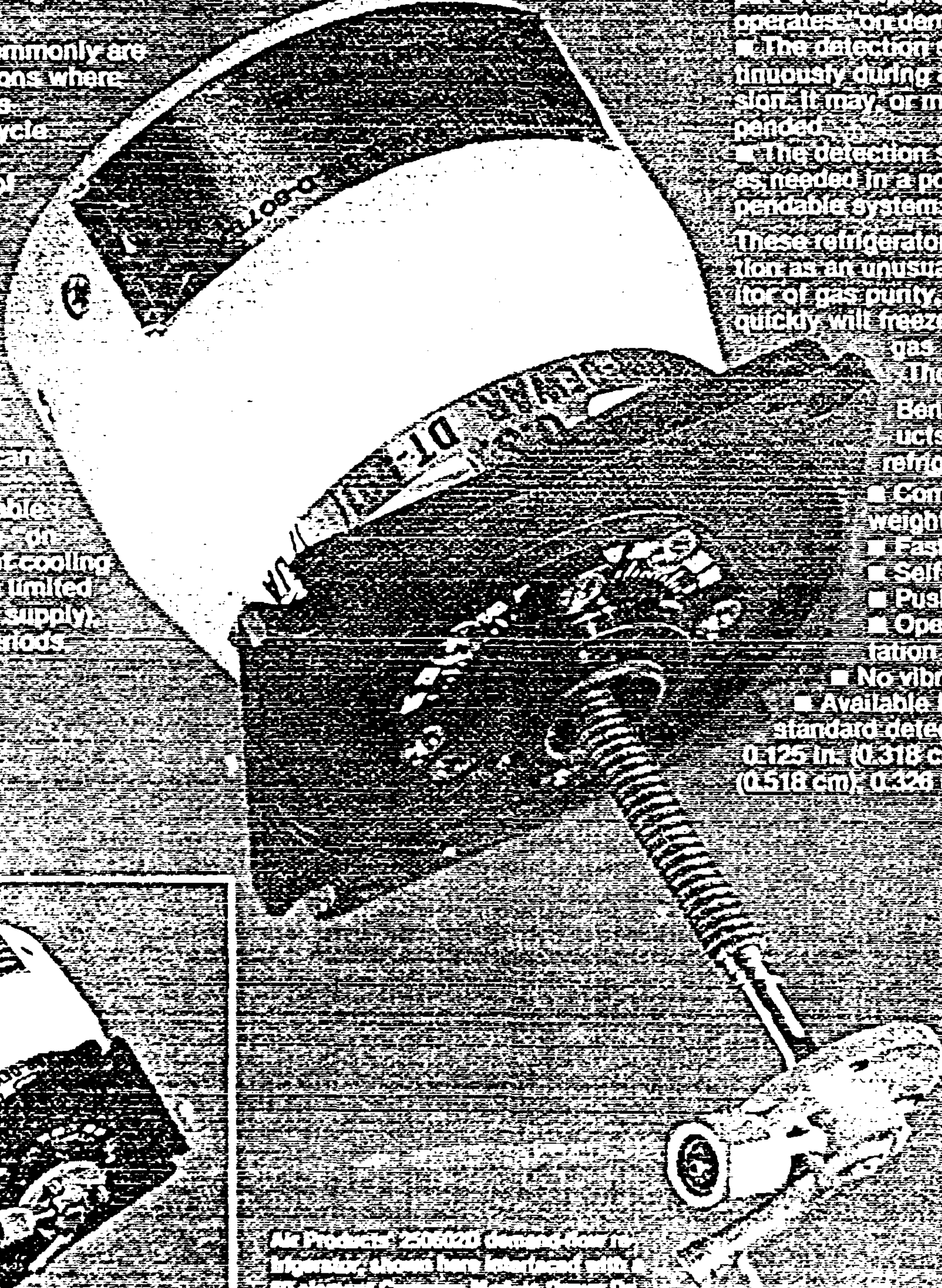

TEMPERATURE - ENTROPY CHART
FOR HELIUM (H_e)
BASED ON ... "THERMODYNAMIC PROPERTIES OF HELIUM" TRANSACTIONS OF THE ASME
ACTUAL CRITICAL CONDITIONS
EFFECTIVE CRITICAL CONDITIONS
ENTROPY - BTU/POUND/°F
TEMPERATURE - °F

ILLUSTRATION OF AN
AIR PRODUCT DEMAND
FLOW REFRIGERATOR

ir Products' miniature cryogenic oolers provide a quick-acting ource of refrigeration in the 77K ange by expanding a compressed as, typically air, argon, or itrogen.

hese coolers commonly are sed in applications where ulky, continuous unning closed-cycle efrigerators, or tored supplies of ryogens such s liquid air or iquid nitrogen, nay not be uitable.

oule-Thomson efrigerators end themselves deally to minia urization. They can e small, light in veight, and portable. They will operate "on lemand" for brief cooling nissions (with a limited compressed gas supply), or over longer periods either continuously or intermittently, with mission time limited only by gas availability.



Several types of infrared detection systems use Joule-Thomson refrigerators.

- The detector and its cooler are part of an expendable system that operates "on demand," only once.
- The detection system runs continuously during a complete mission. It may, or may not, be expended.
- The detection system operates as needed in a portable, non-expendable system. It can be reused.

These refrigerators also can function as an unusually sensitive monitor of gas purity, since impurities quickly will freeze out and plug the gas flow in a Joule-Thomson circuit.

Benefits of Air Products' Joule-Thomson refrigerators include:

- Compact, light weight
- Fast cooldown
- Self-regulating
- Pushbutton operation
- Operate in any orientation
- No vibration or noise
- Available in sizes to match standard detector Dewars: 0.125 in. (0.318 cm), 0.204 in. (0.518 cm), 0.326 in. (0.828 cm).

Air Products' 2506020 demand-flow refrigerator, shown here interfaced with a 60-element Common Module Dewar Detector Assembly. Inset shows refrigerator fully inserted and in place.

MMR TECHNOLOGIES BROCHURE

EXTRA

ɔlume 1, Number 1 May 10, 1988

MMR TECHNOLOGIES ANNOUNCES BREAKTHROUGH IN JOULE-THOMSON COOLING

MR Technologoes, Inc announced today a ɛakthrough in Joule-Thomson refrigeration ːhnology. The Mountain View company, ıich manufactures microminiature refrigrators r application in semiconductor materials R&D d University research, has developed a ɔprietary gas mixture, which when used with ɛir refrigerators gives them greatly enhanced rformance.

ɔoldown times from ambient to 80 K are amatically reduced. Using nitrogen gas at 00 psi the cooldown time of these refrigerators typically fifteen minutes. Using the new gas ixture at the same pressure, this time is reduced two to three minutes.

ˉ'geration capacity at all temperatures is ɛreased by a large factor. A Standard MMR ːigerator when operated with nitrogen gas at 00 psi has a refrigeration capacity of about 350 illiwatts. When used with the gas mixture, a frigeration capacity in excess of 2.5 Watts is served at 1800 psi ! The large refrigeration pacity makes it possible to operate the ːigerators without vacuum insulation, hieving a minimum temperature of 121 K thin five minutes of start-up. For the same ıson, operation of the refrigerators to the ʌwest temperatures is not hampered by poor ɛuum conditions, allowing the use of the ːigerators for cooling of medical specimens th high water content and of chemicals with ge vapor pressures.

The refrigerators can be operated at much lower pressures. Stable operation of the refrigerators can be had at pressures as low as 700 psi. At these low pressures the gas flow is reduced by a factor of two to three from that required for nitrogen. This, coupled with the larger fraction of the gas which can be used from a cylinder, gives very much longer runs without the need to change cylinders. Runs of 100 to 150 hours per cylinder are typical.

The special properties of the mixture make it much more tolerant of trace quantities of water or carbon dioxide contaminants. This allows clog-free operation of the refrigerators for time periods several orders of magnitude greater than for systems using nitrogen.

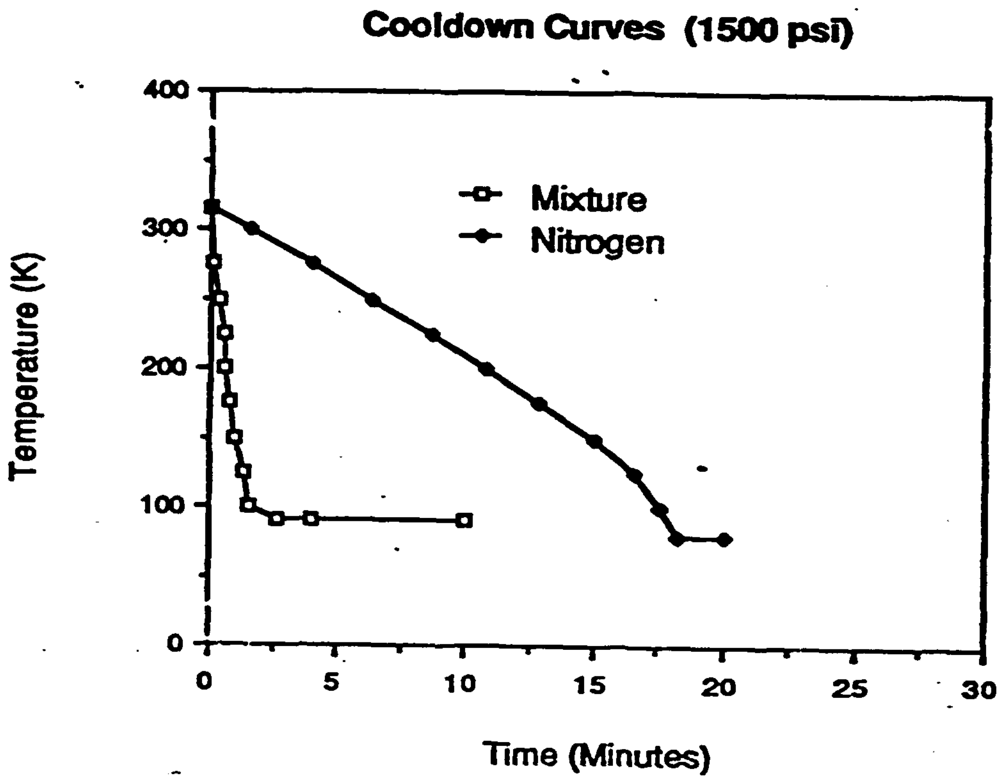
The gas mixture is safe and simple to use, but does require a special filter and monitoring system.

MMR Technologies is setting up distribution and licencing arrangements to make this technology available to its customers.

For more information contact:

Bill Asay, Sales Manager
MMR Technologies, Inc.
1400 Stierlin Road, Suite A-5
Mountain View, CA 94043

Telephone: (415) 962-9620



Cooldown Curves (1500 psi)
Mixture
Nitrogen
Temperature (K)
400
300
200
100
0
0
5
10
15
20
25
30
Time (Minutes)