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**NEW CHEMICAL ALTERNATIVE FOR OZONE-DEPLETING SUBSTANCES:  
HFC-236fa**

By:

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16. ABSTRACT The report gives results of a preliminary evaluation of a new hydrofluorocarbon (HFC)--HFC-236fa or 1, 1, 1, 3, 3, 3-hexafluoropropane--as a possible alternative for chlorofluorocarbon (CFC)-114 (1, 2-dichloro-1, 1, 2, 2-tetrafluoroethane) refrigerant for chillers and as a possible fire suppressant replacement for halon-1301 (bromotrifluoromethane). (NOTE: HFCs form a class of chemicals having the potential to replace stratospheric ozone depleting substances such as CFCs and hydrochlorofluorocarbons.) Evaluation tests included an examination of flammability, stability, atmospheric lifetime, thermophysical properties, lubricant miscibility and solubility, materials compatibility, inhalation toxicity, refrigeration performance, heat transfer characteristics, and flame suppression. Results of these evaluations indicate that HFC-236fa is a viable alternative for CFC-114 refrigerant and for halon-1301 or -1211 fire extinguishing agent. Its relatively long atmospheric lifetime may be a concern from a global warming perspective.			
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## FOREWORD

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E. Timothy Oppelt, Director  
National Risk Management Research Laboratory

## ABSTRACT

Hydrofluorocarbons (HFCs) form a class of chemicals having the potential to replace stratospheric ozone depleting substances such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). This report gives results of a preliminary evaluation of a new HFC (HFC-236fa or 1,1,1,3,3,3-hexafluoropropane) as a possible alternative for CFC-114 (1,2-dichloro-1,1,2,2-tetrafluoroethane) refrigerant for chillers and as a possible fire suppressant replacement for halon-1301 (bromotrifluoromethane). Evaluation tests included examinations of flammability, stability, atmospheric lifetime, thermophysical properties, lubricant miscibility and solubility, materials compatibility, inhalation toxicity, refrigeration performance, heat transfer characteristics, and flame suppression. Results of these examinations indicate that HFC-236fa is a viable alternative for CFC-114 refrigerant and for halon-1301 or halon-1211 fire extinguishing agents. Its relatively long atmospheric lifetime may be a concern from a global warming perspective.

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## SCIENTIFIC SYMBOLS AND ABBREVIATIONS

cP	centipoise
cSt	centistokes
$C_p$	ideal gas heat capacity at constant pressure
$C_v$	ideal gas heat capacity at constant volume
COP	coefficient of performance
fpi	fins per inch
$Ma_2$	Mach number
N	compressor speed (revolutions per minute)
NOAEL	no observable adverse effect level
$p_e$	evaporating pressure
$p_c$	condensing pressure
ppm	parts per million
$P_c$	critical pressure
$P_\sigma$	vapor pressure
$Q_E$	compressor refrigerating capacity
R	universal gas constant
RMS	root mean square
rpm	revolutions per minute
$T_c$	condensing temperature
$T_c$	critical temperature
$T_b$	boiling point
$u_2$	compressor impeller tip speed
$V_s$	volumetric flow rate, suction
$V_d$	volumetric flow rate, discharge
$\rho_c$	critical density
$\rho_L$	saturated liquid density
$\rho_v$	saturated vapor density

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## 1. INTRODUCTION

Fully halogenated chlorofluorocarbons (CFCs) and their bromine-containing relatives (halons) are recognized as primary contributors to depletion of the Earth's stratospheric ozone layer. As early as 1978, the United States, on the basis of what was then largely theoretical evidence for depletion of stratospheric ozone by CFCs, responded by promulgating restrictions on the use of CFCs as propellants in aerosol products. At that time, aerosol propellants represented the single largest commercial use of CFCs. Only Sweden, Norway, and Canada joined the United States in enacting measures to reduce CFC emissions at that time.

In the mid-1980's, as scientific evidence confirming stratospheric ozone depletion mounted, the U. S. Environmental Protection Agency (EPA) began considering additional regulatory restrictions on the use of CFCs and halons by weighing the environmental benefits against the economic and societal consequences of such action. In the course of this study, it became apparent that few, if any, alternative chemicals were readily available or had been proven applicable to the numerous CFC and halon uses which had grown dramatically in the short time span following the 1978 CFC aerosol propellant ban.

In the Spring of 1987, the EPA convened a panel of international experts to assess the likelihood of finding suitable alternative chemicals. Compounds in which one or more of the chlorine or bromine atoms of the CFCs and halons were replaced by hydrogen atoms appeared to offer a high probability of serving as successful alternatives. It was noted that the presence of hydrogen in the molecules would increase the probability that the molecules would degrade in the lower atmosphere and be dissipated before reaching the ozone layer. However, it was also noted that replacing halogen atoms with hydrogen atoms could lead to undesirable flammability, toxicity, and/or reduced efficacy of the compounds in certain applications. Among the findings of the expert panel was the conclusion that governments should sponsor research to enhance knowledge of chemical substitutes, particularly research into those chemicals that were not already under active consideration by chemical companies (Nelson, 1988).

Shortly after the landmark Montreal Protocol on Substances that Deplete the Ozone Layer was negotiated in September 1987 (UNEP, 1987), the EPA's Air and Energy Engineering Research Laboratory (AEERL)\* initiated a search for new chemical alternatives. This effort was undertaken to try to provide an expanded set of candidate alternatives in the event that the few chemicals which had then been proposed as alternatives fell short of expectations.

In 1988, AEERL and the Electric Power Research Institute (EPRI) formed a cooperative project with the chemistry departments of Clemson University and The University of Tennessee to synthesize a number of partially fluorinated propanes and butanes and fluoroethers which, on the basis of molecular structure and anticipated boiling points, were thought to be possible CFC or halon alternatives. These compounds also possessed structural features believed to enhance degradation of the compounds in the troposphere. Over a 3-year period, 37 compounds were prepared of sufficient stability and in sufficient yield and purity to obtain a limited set of relevant property measurements. Of the 37 chemicals synthesized, 15 were hydrofluoropropanes and butanes (HFCs), 8 were hydrofluoroethers (HFEs), 5 were fully fluorinated ethers (FEs), and 9 were hydrochlorofluoropropanes (HCFCs). These compounds and their normal boiling points are listed in Table 1.

AEERL selected for further study 12 of the 37 synthesized chemicals whose measured boiling points and critical temperatures most closely matched those of CFCs-11, -12, -114, and -115 or which might form mixtures having desirable properties. Alternatives for CFC-113, widely used as a solvent, were not emphasized since a number of chemicals and technologies appeared to already exist or be emerging to replace this compound. Also, compounds which possessed chlorine (HCFCs) were ruled out for further evaluation since such compounds had non-zero ozone depletion potentials and would also be subject to future phaseout. Table 2 presents the 12 compounds selected by AEERL for further examination.

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\* Recently redesignated the Air Pollution Prevention and Control Division of the National Risk Management Research Laboratory, Research Triangle Park (NRMRL - RTP), NC.

Table 1. Chemical codes, formulas, and boiling points of the 37 new chemicals synthesized.

Chemical Code	Chemical Formula	T <sub>b</sub> (°C)
HFC-227ca	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> H	-16.3
HFC-227ea	CF <sub>3</sub> -CHF-CF <sub>3</sub>	-18.3
HFC-236ca	CHF <sub>2</sub> -CF <sub>2</sub> -CHF <sub>2</sub>	12.6
HFC-236cb	CF <sub>3</sub> -CF <sub>2</sub> -CFH <sub>2</sub>	- 1.4
HFC-236ea	CF <sub>3</sub> -CHF-CF <sub>2</sub> H	6.5
HFC-236fa	CF <sub>3</sub> -CH <sub>2</sub> -CF <sub>3</sub>	- 1.1
HFC-245ca	CF <sub>2</sub> H-CF <sub>2</sub> -CFH <sub>2</sub>	25.0
HFC-245cb	CF <sub>3</sub> -CF <sub>2</sub> -CH <sub>3</sub>	-18.3
HFC-245fa	CF <sub>3</sub> -CH <sub>2</sub> -CF <sub>2</sub> H	15.3
HFC-254cb	CF <sub>2</sub> H-CF <sub>2</sub> -CH <sub>3</sub>	- 0.8
HFC-329mccp	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> H	15.1
HFC-338pccq	CHF <sub>2</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CH <sub>2</sub> F	42.5
HFC-338mccq	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CFH <sub>2</sub>	27.8
HFC-338meem	CF <sub>3</sub> -CHF-CHF-CF <sub>3</sub>	25.4
HFC-347mccs	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CH <sub>3</sub>	15.1
HCFC-225ba	CF <sub>3</sub> -CFCl-CFHCl	51.9
HCFC-225da	CF <sub>3</sub> -CHCl-CF <sub>2</sub> Cl	50.8
HCFC-226da	CF <sub>3</sub> -CHCl-CF <sub>3</sub>	14.1
HCFC-226ea	CF <sub>3</sub> -CHF-CF <sub>2</sub> Cl	17.1
HCFC-234da	CF <sub>3</sub> -CHCl-CFHCl	70.1
HCFC-235ca	CF <sub>3</sub> -CF <sub>2</sub> -CH <sub>2</sub> Cl	28.1
HCFC-243da	CF <sub>3</sub> -CHCl-CH <sub>2</sub> Cl	76.7
HCFC-244ca	CF <sub>2</sub> H-CF <sub>2</sub> -CH <sub>2</sub> Cl	54.8
cy-HCFC-326	cy-(CF <sub>2</sub> ) <sub>3</sub> -CHCl-	38.1

(continued)

Table 1. Continued

Chemical Code	Chemical Formula	T <sub>b</sub> (°C)
HFE-125	CF <sub>3</sub> -O-CF <sub>2</sub> H	-34.6
HFE-134	CF <sub>2</sub> H-O-CF <sub>2</sub> H	4.7
HFE-143	CF <sub>2</sub> H-O-CFH <sub>2</sub>	29.9d
HFE-143a	CF <sub>3</sub> -O-CH <sub>3</sub>	-24.1
HFE-227ca	CF <sub>3</sub> -O-CF <sub>2</sub> -CF <sub>2</sub> H	-3.1
HFE-124B1	CF <sub>2</sub> H-O-CF <sub>2</sub> Br	24.5
FE-115B1	CF <sub>3</sub> -O-CF <sub>2</sub> Br	-5.4
FE-116	CF <sub>3</sub> -O-CF <sub>3</sub>	-58.7
FEE-218	CF <sub>3</sub> -O-CF <sub>2</sub> -O-CF <sub>3</sub>	-9.8
cy-HFE-225	cy-CHF-CF <sub>2</sub> -O-CF <sub>2</sub> -	3.4
cy-HFE-234	cy-CH <sub>2</sub> -CF <sub>2</sub> -O-CF <sub>2</sub> -	21.2
cy-FE-216	cy-CF <sub>2</sub> -CF <sub>2</sub> -O-CF <sub>2</sub> -	-28.2
cy-FEE-216	cy-CF <sub>2</sub> -O-CF <sub>2</sub> -O-CF <sub>2</sub> -	-22.1

Note: Chemical codes for the ether compounds have not been standardized. The listed codes are AEERL designations. "d" = decomposes.

Table 2. Chemicals selected for further characterization.

Alternatives for:	Chemical Code	Chemical Formula	Chemical Name
CFC-11/HCFC-123	HFC-245ca	CF <sub>2</sub> H-CF <sub>2</sub> -CFH <sub>2</sub>	1,1,2,2,3-pentafluoropropane
	HFC-245fa	CF <sub>3</sub> -CH <sub>2</sub> -CF <sub>2</sub> H	1,1,1,3,3-pentafluoropropane
	HFC-338mccq	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> -CFH <sub>2</sub>	1,1,1,2,2,3,3,4-octafluorobutane
CFC-12	HFC-227ca	CF <sub>3</sub> -CF <sub>2</sub> -CF <sub>2</sub> H	1,1,1,2,2,3,3-heptafluoropropane
	HFC-227ea	CF <sub>3</sub> -CHF-CF <sub>3</sub>	1,1,1,2,3,3,3-heptafluoropropane
	HFC-245cb	CF <sub>3</sub> -CF <sub>2</sub> -CH <sub>3</sub>	1,1,1,2,2-pentafluoropropane
	HFE-143a	CF <sub>3</sub> -O-CH <sub>3</sub>	1,1,1-trifluorodimethyl ether
CFC-114	HFC-236cb	CF <sub>3</sub> -CF <sub>2</sub> -CFH <sub>2</sub>	1,1,1,2,2,3-hexafluoropropane
	HFC-236ea	CF <sub>3</sub> -CFH-CF <sub>2</sub> H	1,1,1,2,3,3-hexafluoropropane
	HFC-236fa	CF <sub>3</sub> -CH <sub>2</sub> -CF <sub>3</sub>	1,1,1,3,3,3-hexafluoropropane
	HFC-254cb	CF <sub>2</sub> H-CF <sub>2</sub> -CH <sub>3</sub>	1,1,2,2-tetrafluoropropane
CFC-115	HFE-125	CF <sub>3</sub> -O-CF <sub>2</sub> H	pentafluorodimethyl ether

Extended evaluation of these 12 candidates was undertaken by AEERL with emphasis on their potential use as refrigerants and as blowing agents for insulation foams. Expanded evaluation included

determination of atmospheric lifetimes, inhalation toxicities, chemical stabilities, material compatibilities, vapor thermal conductivities, lubricant miscibilities, and refrigeration performance.

This report summarizes results obtained for one of the candidates, HFC-236fa (1,1,1,3,3,3-hexafluoropropane), as a potential alternative refrigerant for CFC-114 in chillers and as a possible replacement for the halon fire extinguishing agents halon-1301 (bromotrifluoromethane) and halon-1211 (bromochlorodifluoromethane).

## 2. SUMMARY AND CONCLUSIONS

Theoretical analysis and experimental evaluations in a semihermetic compressor confirm that HFC-236fa should be considered as a replacement for CFC-114 in shipboard chillers. HFC-236fa has a higher refrigerating capacity and coefficient of performance (COP) than CFC-114 at shipboard chiller conditions because of its higher volumetric efficiency in the semihermetic compressor and is, therefore, not an exact drop-in replacement. The HFC-236fa volumetric capacity and the measured compressor capacity with HFC-236fa are higher than with CFC-114 at condensing temperatures below about 80°C. Although the theoretical HFC-236fa COP is lower than that of CFC-114, the experimental COP is higher than or equal to that of CFC-114 at condensing temperatures up to 70°C. There is some drop-off in performance of HFC-236fa at higher condensing temperatures.

HFC-236fa contains no chlorine or bromine and therefore has zero potential to deplete stratospheric ozone. Its measured reaction rate at 298 K with hydroxyl (OH) radical was  $1.1 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> as determined by the National Institute of Standards and Technology (NIST), and  $0.034 \times 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> sec<sup>-1</sup> as determined by the Jet Propulsion Laboratory (JPL) of the National Aeronautics and Space Administration (NASA) (JPL, 1994). The favored value is that of JPL due to small amounts of impurities present in the material examined by NIST which may have contributed to a higher than expected rate constant. Accepting the JPL measured rate constant gives an atmospheric lifetime due solely to reaction with an OH radical of 192 years relative to an OH atmospheric lifetime for methyl chloroform of 6.6 years. A lifetime of this duration gives cause for concern from a global warming perspective. The Intergovernmental Panel on Climate Change (IPCC, 1995) has assigned a global warming potential (GWP) of 6300 to HFC-236fa (100-year horizon, GWP of CO<sub>2</sub> = 1).

Considerable toxicity testing has been completed for HFC-236fa due in large part to the U. S. Navy's interest in retrofitting its shipboard CFC-114 chillers with HFC-236fa. Toxicity tests included



acute inhalation, cardiac sensitization, genetic toxicity, developmental inhalation, and 90-day subchronic inhalation. Maximum concentration of the chemical administered to rats and rabbits for the inhalation toxicity evaluations was 50000 ppm. The one notable compound-related effect was a diminished response or lack of response by the test animals to an alerting stimulus during exposure. Although rats exposed to 50000 ppm were generally non-responsive and rats exposed to 20000 ppm have a diminished response during the first week of exposure of the 2-week study, most animals exhibited normal alerting responses during the second week. Any diminished response effect was completely reversible upon cessation of exposure. A maximum concentration of 200000 ppm of HFC-236fa in air was used for the cardiac sensitization tests using male beagle dogs as the subjects where half of the dogs indicated positive responses. There were no positive responses when the concentration was at 100000 ppm or less. Based on all toxicity tests performed, it is concluded that HFC-236fa should pose no significant toxicity problems.

HFC-236fa was included in a matrix of four HFCs (HFCs-236fa, -236ea, -245ca, and -245fa), and one HFE (HFE-125) examined for thermal and hydrolytic stability and materials compatibility. These tests showed that, with and without a polyolester (POE) lubricant present, Buna-N<sup>TM</sup>, Buna-S<sup>TM</sup>, Geolast<sup>®</sup>, Hypalon<sup>®</sup>, silicone rubber, and EPDM elastomers gave acceptable overall performance. Fluoropolymers such as Viton<sup>®</sup>, Kalrez<sup>®</sup>, and Teflon<sup>®</sup> were especially susceptible to absorption of HFCs, including HFC-236fa, resulting in unacceptable swelling. Hydrogenated nitrile butyl rubber and natural rubber showed excessive swelling when the POE lubricant was present. Neoprene was deemed unsuitable due to shrinkage and embrittlement, with and without the lubricant present.

Aluminum, steel, cast iron, copper, brass, and bronze were compatible with HFC-236fa and the POE lubricant. Of the four molecular sieve bead desiccants tested, three were of 0.3 nm average pore diameter and exhibited no apparent reactivity with HFC-236fa. The fourth desiccant had an average pore diameter of 0.4 nm and showed some evidence of degradation of HFC-236fa based on the increased fluoride ion content of the desiccant after the aging test.

HFC-236fa was found to be completely miscible with ISO-68 polyolester lubricant over the temperature range of -30.1 to + 125°C. Lubricity tests indicated that the chemical is compatible with this type of lubricant and that the presence of the refrigerant in the oil improved the wear performance of the oil.

Heat transfer coefficients of HFC-236fa were determined in test rigs configured to investigate refrigerant-side coefficients in centrifugal chiller systems. Coefficients were measured for two conventional finned tubes and three performance-enhanced tubes during shell-side condensation and pool boiling on the outside of a single horizontal tube. As expected, the high-performance enhanced tubes were found to increase heat transfer and produce higher heat transfer coefficients than the conventional finned tubes. Comparison of shell-side heat transfer coefficients obtained for HFC-236fa with those obtained for CFC-114 under identical conditions showed HFC-236fa to have better heat transfer during condensation with a maximum increase of 40 percent relative to CFC-114. For pool boiling, HFC-236fa provided a maximum heat transfer increase of 80 percent relative to CFC-114.

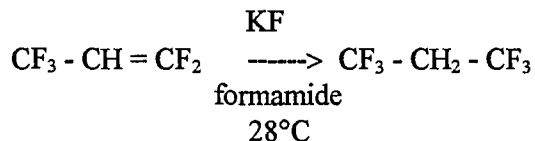
For pool boiling tests, a miscible POE lubricant was added to the HFC-236fa up to a lubricant concentration of 3 weight percent. With the exception of one of the high performance tubes, the oil caused the heat transfer coefficients to decrease by less than 10 percent from those obtained for the HFC-236fa alone.

HFC-236fa has received a safety classification of "A1" (low toxicity, nonflammable) by standards set forth by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE, 1992). A concentration of 5.6 volume percent HFC-236fa in air was found to extinguish an n-heptane flame in a standard cup burner test. This extinguishing concentration is equivalent (within experimental error) to that of a commercially available fire extinguishing agent (HFC-227ea, 1,1,1,2,3,3,3-heptafluoropropane).

### 3. THERMOPHYSICAL AND APPLICATION PROPERTIES OF HFC-236fa

#### SYNTHESIS OF HFC-236fa

HFC-236fa was prepared in laboratory quantities (ca. 100 g) by the reaction of 0.028 moles of 1,1,1,3,3-pentafluoropropene ( $\text{CF}_3\text{CH}=\text{CF}_2$ ) with a mixture of 3 g of potassium fluoride (KF) and 25 mL of formamide ( $\text{HCONH}_2$ ) at  $28^\circ\text{C}$ . Yield from this reaction was 86 percent.



The product obtained from this reaction was characterized by gas chromatography (GC), infrared (IR) spectrophotometry, mass spectrometry (MS), and  $^{19}\text{F}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrometry. Purity of the HFC-236fa thus prepared was 99.5 percent. Initial laboratory synthesis and preliminary thermophysical property measurements were performed by Clemson University under joint sponsorship of the EPA and EPRI.

Larger (kilogram) quantities of the compound needed for performance and stability/compatibility tests were procured from PCR, Inc. in Gainesville, FL. Individual lots of the compound delivered to AEERL for testing were subjected upon receipt to purity assay by combined GC/MS, and Fourier transform infrared spectroscopy (FTIR) and found to be 98.9 percent pure. Figures 1 and 2 present FTIR and mass spectra for HFC-236fa, respectively.

Quantities of several thousand kilograms of HFC-236fa required for extended duration toxicity tests were supplied by the DuPont and 3M companies.

#### THERMOPHYSICAL PROPERTIES

Table 3 gives thermophysical property data for HFC-236fa derived by the National Institute of Standards and Technology (NIST) from measured data correlated by the modified Benedict-Webb-Rubin (mBWR) equation of state.

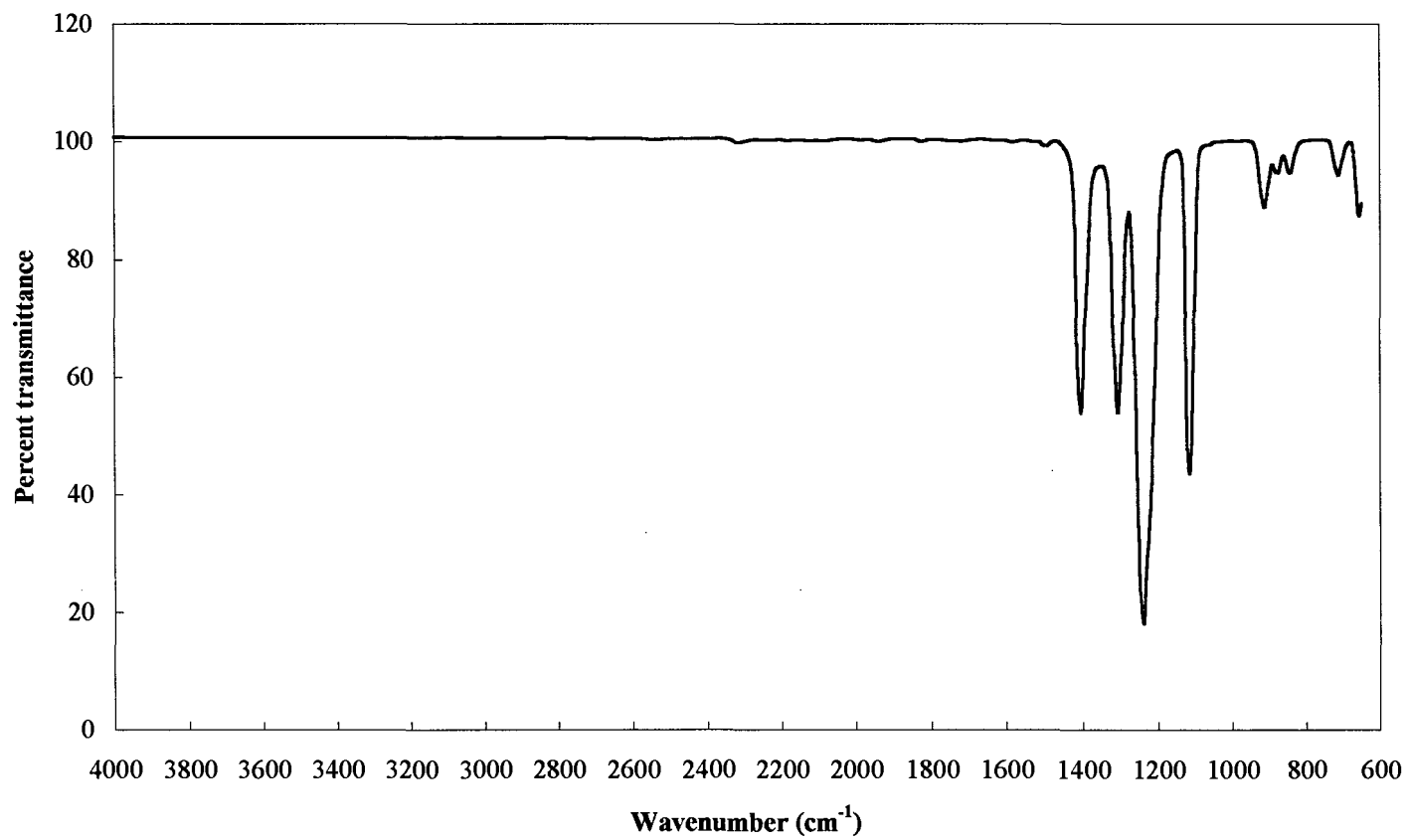


Figure 1. Fourier-transform infrared spectrum of HFC-236fa

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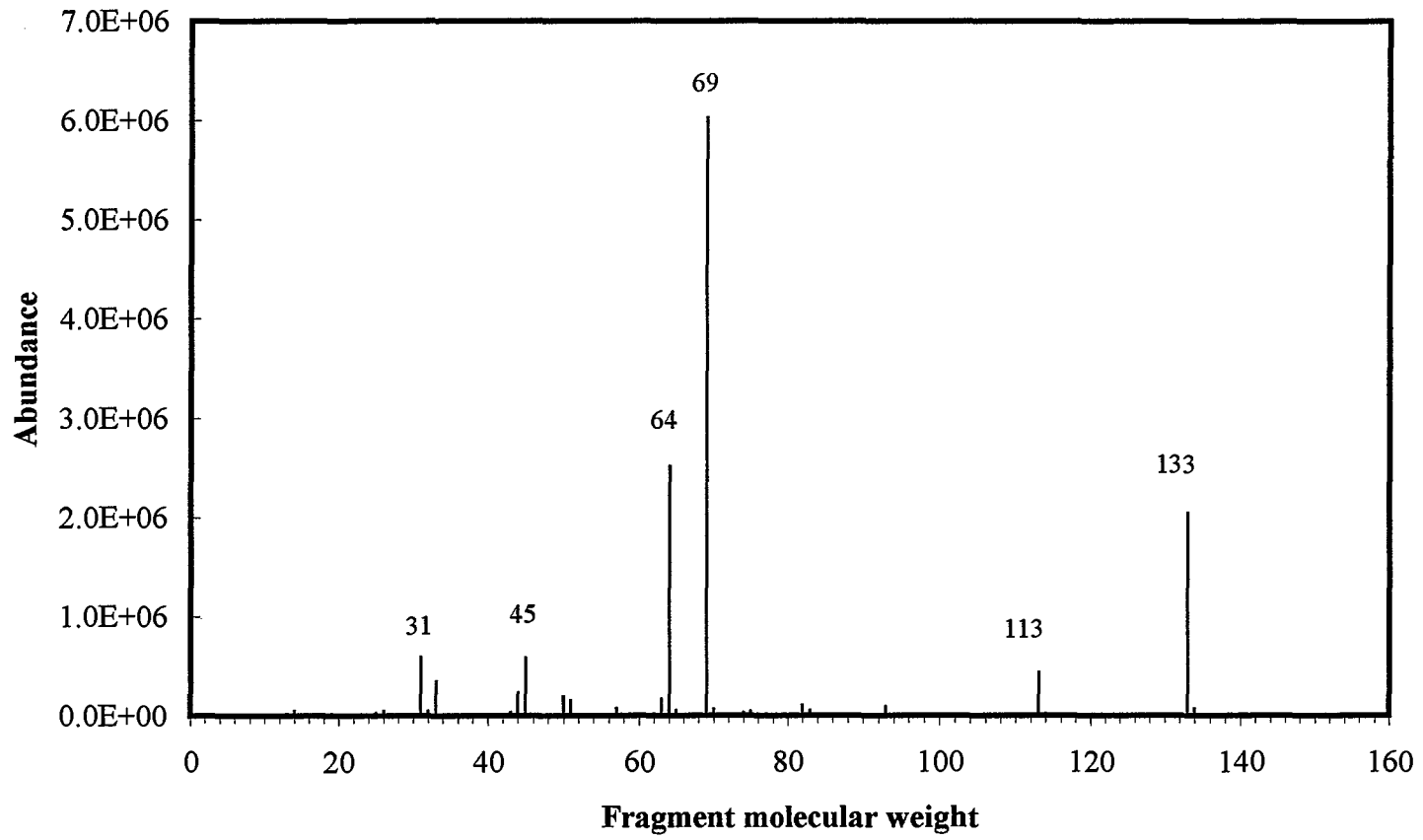


Figure 2. Mass spectrum of HFC-236fa

Table 3. Thermophysical properties of liquid and vapor HFC-236fa

T(°C)	P(kPa)	Density (kg/m <sup>3</sup> )		Volume (m <sup>3</sup> /kg)		Entropy (kJ/kg K)		Enthalpy (kJ/kg K)		Cv (kJ/kg K)		Cp (kJ/kg K)	
		vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid
-50	7.623	0.6292	1590	1.589	6.29E-04	0.5924	-0.2274	126.7	-56.2	0.6469	0.7998	0.7041	1.113
-45	10.60	0.8571	1575	1.167	6.35E-04	0.5896	-0.2027	130.1	-50.6	0.6558	0.8031	0.7137	1.122
-40	14.48	1.149	1560	0.8705	6.41E-04	0.5876	-0.1782	133.5	-45.0	0.6648	0.8072	0.7235	1.130
-35	19.47	1.517	1546	0.6594	6.47E-04	0.5862	-0.1542	137.0	-39.3	0.6740	0.8120	0.7336	1.139
-30	25.80	1.974	1531	0.5065	6.53E-04	0.5854	-0.1304	140.4	-33.6	0.6833	0.8174	0.7440	1.148
-25	33.71	2.537	1516	0.3942	6.60E-04	0.5852	-0.1070	143.9	-27.8	0.6928	0.8233	0.7547	1.158
-20	43.48	3.222	1501	0.3104	6.66E-04	0.5854	-0.0838	147.4	-22.0	0.7025	0.8296	0.7658	1.167
-15	55.42	4.046	1486	0.2472	6.73E-04	0.5861	-0.0609	150.9	-16.2	0.7123	0.8363	0.7772	1.177
-10	69.84	5.029	1471	0.1988	6.80E-04	0.5873	-0.0382	154.3	-10.2	0.7222	0.8434	0.7890	1.187
-5	87.10	6.193	1456	0.1615	6.87E-04	0.5888	-0.0158	157.8	-4.30	0.7323	0.8507	0.8012	1.197
0	107.6	7.560	1440	0.1323	6.94E-04	0.5906	0.0064	161.3	1.70	0.7426	0.8581	0.8138	1.208
5	131.6	9.155	1425	0.1092	7.02E-04	0.5928	0.0284	164.8	7.80	0.7529	0.8657	0.8269	1.218
10	159.7	11.00	1409	0.0909	7.10E-04	0.5952	0.0501	168.3	13.9	0.7635	0.8734	0.8405	1.229
15	192.2	13.14	1393	0.0761	7.18E-04	0.5978	0.0717	171.7	20.1	0.7741	0.8812	0.8546	1.240
20	229.6	15.58	1376	0.0642	7.27E-04	0.6007	0.0931	175.2	26.4	0.7849	0.8890	0.8694	1.252
25	272.4	18.38	1360	0.0544	7.35E-04	0.6037	0.1143	178.6	32.7	0.7959	0.8968	0.8849	1.264
30	321.0	21.57	1343	0.0464	7.45E-04	0.6068	0.1353	182	39.0	0.8070	0.9047	0.9013	1.277
35	376.0	25.19	1325	0.0397	7.55E-04	0.6101	0.1562	185.3	45.4	0.8182	0.9125	0.9186	1.291
40	437.8	29.30	1308	0.0341	7.65E-04	0.6135	0.1770	188.6	51.9	0.8297	0.9203	0.9371	1.305
45	507.0	33.95	1289	0.0295	7.76E-04	0.6169	0.1976	191.9	58.5	0.8413	0.9282	0.9569	1.321
50	584.2	39.21	1270	0.0255	7.87E-04	0.6203	0.2181	195.1	65.2	0.8531	0.9360	0.9785	1.338
55	669.9	45.15	1251	0.0222	8.00E-04	0.6237	0.2386	198.3	71.9	0.8652	0.9439	1.0020	1.356
60	764.7	51.87	1230	0.0193	8.13E-04	0.6270	0.2590	201.3	78.7	0.8775	0.9519	1.0280	1.377
65	869.4	59.49	1209	0.0168	8.27E-04	0.6303	0.2794	204.3	85.6	0.8902	0.9600	1.0580	1.400
70	984.5	68.15	1187	0.0147	8.43E-04	0.6333	0.2997	207.1	92.7	0.9033	0.9682	1.0920	1.427

(continued)

Table 3. Continued

T(°C)	P(kPa)	Density (kg/m <sup>3</sup> )		Volume (m <sup>3</sup> / kg)		Entropy (kJ/kg K)		Enthalpy (kJ/kg)		Cv (kJ/kg K)		Cp (kJ/kg K)	
		vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid	vapor	liquid
75	1111	78.02	1163	0.0128	8.60E-04	0.6362	0.3201	209.9	99.80	0.9169	0.9767	1.132	1.458
80	1249	89.33	1138	0.0112	8.79E-04	0.6387	0.3406	212.4	107.1	0.9311	0.9856	1.181	1.494
85	1400	102.4	1111	0.0098	9.00E-04	0.6409	0.3612	214.7	114.6	0.946	0.9949	1.241	1.538
90	1565	117.6	1081	0.0085	9.25E-04	0.6425	0.3820	216.8	122.2	0.9619	1.005	1.319	1.593
95	1744	135.6	1049	0.0074	9.53E-04	0.6434	0.4030	218.6	130.1	0.9791	1.016	1.424	1.664
100	1940	157.1	1013	0.0064	9.87E-04	0.6434	0.4245	219.9	138.2	0.9981	1.028	1.576	1.760
105	2152	183.7	972.7	0.0054	1.03E-03	0.6421	0.4465	220.7	146.7	1.019	1.042	1.814	1.902
110	2383	117.5	924.6	0.0046	1.08E-03	0.6388	0.4695	220.6	155.7	1.044	1.058	2.229	2.136
115	2634	263.2	865.1	0.0038	1.16E-03	0.6326	0.4941	219.2	165.5	1.074	1.079	3.107	2.615
120	2907	332.7	782.4	0.0030	1.28E-03	0.6206	0.5221	215.5	176.8	1.111	1.107	5.896	4.199

Measurements were made using HFC-236fa which had been repurified by preparative gas chromatography to a purity of 99.98 percent. The normal boiling point of the repurified chemical was -1.1°C. Table 4 lists the types and ranges of experimental data used in the mBWR correlation. Due to a lack of data in some regions, predictions from an extended corresponding states (ECS) model for HFC-236fa were used. These “data” were used to ensure that extrapolation of the mBWR equation beyond the range of the experimental data would not result in physically unreasonable behavior.

Table 4. Summary of experimental data used in mBWR correlation of HFC-236fa

Source	No. of Data Points	Temp. Range (K)	Pressure Range (MPa)	Density (mol/L)
Vapor pressure	28	306 - 358	0.35 - 1.4	----
	18	266 - 334	0.08 - 0.8	----
	7	180 - 240	2E-04 - 0.02	----
Sat'd liquid density	28	248 - 372	---	6.7 - 9.8
	3	370 - 390	---	5.4 - 6.7
Sat'd vapor density	11	180 - 310	---	1E-04 - 0.17
	5	350 - 390	---	0.54 - 1.8
Ideal gas heat capacity	6	276 - 380	---	----
Pressure-Volume-Temperature	325	248 - 372	1.0 - 6.5	7.1 - 10.1
	842	274 - 345	1.0 - 35	8.2 - 9.5
	202	276 - 400	0.01 - 0.36	0.003 - 0.156
	41	370 - 450	0.01 - 10	0.003 - 7.8
Isochoric heat capacity	117	274 - 343	---	----
	78	183 - 327	---	----
	40	210 - 450	---	----
Speed of sound	108	276 - 400	---	----
Second & third virials	7	276 - 400	---	----

As part of the fitting routine, vapor pressure, saturated liquid and saturated vapor density, and ideal gas heat capacity data were fit to ancillary equations. These equations were then used by the mBWR fitting routine to calculate other derived thermodynamic properties. Ancillary equations used for vapor pressure ( $P_v$ ), saturated liquid density ( $\rho_L$ ), saturated vapor density ( $\rho_V$ ), and ideal gas heat capacity ( $C_p$ ) are:



$$\ln \left[ \frac{P_\sigma}{P_c} \right] = \frac{\alpha_0 \tau + \alpha_1 \tau^{1.5} + \alpha_2 \tau^2 + \alpha_3 \tau^4 + \alpha_4 \tau^{6.5}}{1 - \tau} \quad (1)$$

$$\rho_L = \rho_c [1 + d_0 \tau^\beta + d_1 \tau^{2/3} + d_2 \tau + d_3 \tau^{4/3} + d_4 \tau^2 + d_5 \tau^3] \quad (2)$$

$$\rho_v = P_\sigma \left[ \left[ \frac{1 + f_0 \tau^\beta + f_1 \tau^{2\beta} + f_2 \tau + f_3 \tau^2 + f_4 \tau^4}{1 + f_5 \tau} \right] \frac{P_\sigma (Z_c - 1)}{P_c T_r^8} + 1 \right]^{-1} \quad (3)$$

$$C_p^\circ = c_0 + c_1 T + c_2 T^2 \quad (4)$$

where: T = temperature (in kelvin)

$T_c$  = critical temperature

$T_r = T/T_c$

$\tau = 1 - T_r$

$P_c$  = critical pressure

$\rho_c$  = critical density

$\beta = 0.325$

$Z_c = P_c / (\rho_c R T_c)$

Coefficients for the ancillary equations are listed in Table 5.

Table 5. Coefficients for ancillary equations (1) - (4)

i	0	1	2	3	4	5	RMS (%)
$\alpha_i$	-8.034525	2.784457	-2.548348	-4.719707	0.586451	0	0.041
$d_i$	0.782372	6.233671	-9.692730	5.808706	0	0	0.160
$f_i$	-0.284461	-2.986825	2.361121	1.588164	-1.577292	0	0.251
$c_i$	53.466256	0.228092	0.000353	0	0	-0.663588	0.111

Critical constants used in the fit are:

$T_c = 398.07$  K

$P_c = 3.200$  MPa

$\rho_c = 3.626$  mol/L (551 kg/m<sup>3</sup>)

and  $R = 0.008314 \text{ L}\cdot\text{MPa}/(\text{mol}\cdot\text{K})$

The mBWR equation used was that proposed by Jacobsen [Jacobsen and Stewart, 1973] and is of the form:

$$P = \sum_{i=1}^9 a_i(T)\rho^i + \exp(-\delta^2) \sum_{i=10}^{15} b_i(T)\rho^{2i-17} \quad (5)$$

where  $\delta = \rho/\rho_c$ , the temperature dependence of the  $a_i$  coefficients are:

$$\begin{aligned} a_1 &= RT & a_9 &= b_{19}/T^2 \\ a_2 &= b_1T + b_2T^{0.5} + b_3 + b_4/T + b_5/T^2 & a_{10} &= b_{20}/T^2 + b_{21}/T^3 \\ a_3 &= b_6T + b_7 + b_8/T + b_9/T^2 & a_{11} &= b_{22}/T^2 + b_{23}/T^4 \\ a_4 &= b_{10}T + b_{11} + b_{12}/T & a_{12} &= b_{24}/T^2 + b_{25}/T^3 \\ a_5 &= b_{13} & a_{13} &= b_{26}/T^2 + b_{27}/T^4 \\ a_6 &= b_{14}/T + b_{15}/T^2 & a_{14} &= b_{28}/T^2 + b_{29}/T^3 \\ a_7 &= b_{16}/T & a_{15} &= b_{30}/T^2 + b_{31}/T^3 + b_{32}/T^4 \\ a_8 &= b_{17}/T + b_{18}/T^2 \end{aligned}$$

and the values for the  $b_i$  coefficients are:

$$\begin{aligned} b_1 &= -0.6611218748\text{E-}01 & b_{12} &= -0.1112078439\text{E+}04 & b_{23} &= 0.3194201231\text{E+}10 \\ b_2 &= 0.8617639027\text{E+}01 & b_{13} &= -0.2637100515\text{E+}00 & b_{24} &= 0.7929461073\text{E+}04 \\ b_3 &= -0.2337322560\text{E+}03 & b_{14} &= 0.4775211631\text{E+}02 & b_{25} &= -0.6936062956\text{E+}06 \\ b_4 &= 0.4374862328\text{E+}05 & b_{15} &= 0.1978040351\text{E+}04 & b_{26} &= 0.8498362591\text{E+}02 \\ b_5 &= -0.5396777615\text{E+}07 & b_{16} &= -0.4857108989\text{E+}01 & b_{27} &= 0.2097020511\text{E+}07 \\ b_6 &= -0.7575885520\text{E-}02 & b_{17} &= 0.1448211964\text{E+}00 & b_{28} &= 0.1106003692\text{E+}01 \\ b_7 &= 0.1073795635\text{E+}02 & b_{18} &= -0.2210593229\text{E+}02 & b_{29} &= 0.9537147118\text{E+}02 \\ b_8 &= -0.1066265886\text{E+}05 & b_{19} &= 0.9262701699\text{E+}00 & b_{30} &= -0.8818152066\text{E-}02 \\ b_9 &= -0.1030474554\text{E+}06 & b_{20} &= 0.5779206662\text{E+}07 & b_{31} &= 0.9731949088\text{E+}01 \end{aligned}$$

$$b_{10} = -0.1948680916E-02 \quad b_{21} = -0.9855110656E+09 \quad b_{32} = -0.9355169222E+03$$

$$b_{11} = 0.4383652281E+01 \quad b_{22} = 0.1971998080E+06$$

The mBWR equation for HFC-236fa was shown to exhibit reasonable behavior upon extrapolation to temperatures down to the triple point (180 K) and up to 500 K and pressures up to 40 MPa.

Thermophysical properties for HFC-236fa are also available from the NIST database REFPROP Version 5.0 (NIST, 1996).

#### ATMOSPHERIC LIFETIME

Compounds such as HFC-236fa which do not contain chlorine or bromine atoms are not capable of destroying stratospheric ozone. However, the presence of carbon-fluorine (C-F) bonds in the molecule can render the chemical a strong absorber of infrared radiation thereby posing global warming concerns if the atmospheric lifetime of the compound is sufficiently long. The presence of hydrogen (H) atoms in the molecule subjects the chemical to degradation by reaction with atmospheric hydroxyl (OH) radicals. Therefore, atmospheric stability of a chemical containing C-H bonds is usually determined by measuring the reaction rate of the chemical with the OH radical. Atmospheric lifetimes are then calculated by comparing the measured rate constant with that of methyl chloroform ( $9.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ ) whose atmospheric lifetime due to OH removal alone (6.6 years) is independently known.

Kinetic experiments for the HFC-236fa/OH reaction were performed for the EPA by NIST using the technique of resonance fluorescence spectrometry. This technique is based on the rate of disappearance of OH radical in the presence of a great excess of the stable substrate. While the method has some advantages over other approaches, it is very sensitive to the presence of even trace amounts of reactive impurities. By this method, the reaction rate constant for abstraction of a H atom from HFC-

236fa with OH was determined to be  $1.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at 298 K leading to an OH atmospheric lifetime of 59 years. However, a plot of the logarithm of the rate constant vs.  $1/T$  was non-linear which is not consistent with the well-established temperature behavior of HFCs and which suggested the presence of a small amount of a highly reactive impurity. A GC analysis of the material indicated that the sample vapor was 99.6 percent pure. It is therefore possible that this measured rate constant is too large and the corresponding atmospheric lifetime too short.

Subsequent to the NIST determination of the HFC-236fa/OH rate constant, researchers at the Jet Propulsion Laboratory (JPL) of the National Aeronautics and Space Administration (NASA) measured the rate constant to be  $0.34 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at 298 K (JPL, 1994). The JPL method differed from the NIST method by measuring the simultaneous rate of disappearance of the unknown and a known reference chemical. By obtaining the ratio of the two rate constants determined simultaneously, any effect due to any impurities cancels out. The JPL rate constant is more in line with what is predicted based on the molecular structure of the chemical. Adopting this rate constant gives an OH atmospheric lifetime of 192 years for HFC-236fa.

An atmospheric lifetime of 192 years raises concerns about the global warming potential of the HFC-236fa. The Intergovernmental Panel on Climate Change (IPCC) has assigned a Global Warming Potential (GWP) of 6300 to HFC-236fa (100-year horizon, GWP of  $\text{CO}_2 = 1$ ) as compared to a GWP of 9300 for CFC-114 (IPCC, 1995).

#### INHALATION TOXICITY

With U. S. Navy co-sponsorship, the EPA undertook a rigorous evaluation of the inhalation toxicity of HFC-236fa. Included in this battery of toxicity tests were a 5-day acute inhalation test, a genetic toxicity screening, a cardiac sensitization test, a 2-week inhalation test, a 90-day subchronic test, and developmental toxicity tests. A brief synopsis of test protocols and results follows.

### Mutagenicity Testing of HFC-236ea in the Salmonella typhimurium and Escherichia coli Plate Incorporation Assay

HFC-236fa was evaluated for mutagenicity in Salmonella typhimurium strains TA100, TA1535, TA97, and TA98 and in Escherichia coli WP2uvrA (pKM101) with and without an exogenous metabolic activation system (S9). The maximum concentration tested was an atmosphere of 100 percent of HFC-236fa. Additional lower concentrations of 0, 20, 40, 60, 70, and 80 volume percent HFC-236fa in air were also evaluated. No evidence of mutagenic activity was detected in two independent trials.

### In-vitro Assay of HFC-236fa for Chromosome Aberrations in Human Lymphocytes

HFC-236fa was evaluated for clastogenic (chromosome damaging) activity in human lymphocytes in-vitro following 3-hr treatments with and without metabolic activation (S9). Two independent trials were conducted. In Trials 1 and 2, concentrations of approximately 0, 20, 30, 40, and 100 volume percent and 0, 40, 60, 80 and 100 volume percent HFC-236fa in air were evaluated, respectively. No statistically significant increases in the percent of chromosomally abnormal cells occurred at any HFC-236fa concentration evaluated, and no concentration-related trends in chromosome aberration induction were observed. HFC-236fa was not clastogenic in this assay.

### Mouse Bone Marrow Micronucleus Assay of HFC-236ea by Inhalation

This test was conducted to determine whether HFC-236fa induces an increase in the frequency of micronucleated polychromatic erythrocytes in bone marrow. In this study, groups of male and female Crl:CD<sup>®</sup>-1(ICR)BR mice were placed in inhalation exposure chambers and exposed whole body to HFC-236fa at target concentrations of 0, 5000, 20000, and 50000 ppm for 6 hours/day for 2 consecutive days. Bone marrow smears were prepared approximately 24 and 48 hours after the second exposure, and 2000 polychromatic erythrocytes per animal were evaluated for the presence of micronuclei.

No statistically significant increases in micronucleated polychromatic erythrocytes were observed in the animals at any HFC-236fa concentration tested. In addition, no significant decreases in the ratio of young polychromatic erythrocytes to mature normochromatic erythrocytes were observed. Under the conditions of this study, HFC-236fa was negative; i. e., HFC-236fa did not induce micronuclei in bone marrow cells.

#### Acute Inhalation Toxicity of HFC-236fa in Rats

Acute inhalation toxicity of HFC-236fa in male rats was investigated and found to be very low. Lethal concentrations in air were not determined since no rats died during or after exposure. The highest concentration tested for HFC-236fa was approximately 189000 ppm for 4 hours. HFC-236fa caused symptoms of narcosis (sleep induction) at a concentration of 189000 ppm, but not at 134000 ppm. Rats recovered quickly (within an hour) after cessation of exposure, and no delayed effects were seen in a 1 to 4 day recovery period.

#### 2-Week Inhalation Toxicity Study with HFC-236fa in Rats

Four groups of five male and five female Crl:CD<sup>®</sup>BR rats were exposed by inhalation for 6 hours a day, 5 days a week for 2 weeks to concentrations targeted at 0, 5000, 20000, or 50000 ppm HFC-236fa (one concentration per group). The rats were weighed prior to exposure each day and were observed for clinical signs both prior to and following each exposure. The response to an alerting stimulus (response to sound stimulus during exposure) was determined during exposures. Clinical pathology evaluations were conducted prior to the end of the study. Immediately following the last exposure, rats were sacrificed and necropsied. All rats were examined for gross and microscopic pathological changes, and liver tissue was evaluated for peroxisomal  $\beta$ -oxidation activity.

Rats exposed to HFC-236fa had no body weight effects and no abnormal clinical observations either prior to or following exposures. The one notable compound-related effect was a diminished response or lack of response to an alerting stimulus during exposure. Although rats in the 50000 ppm group were generally non-responsive and rats in the 20000 ppm group had a diminished response during

the first week of exposure, most of these rats exhibited normal alerting responses during the second week. All rats exposed to 5000 ppm behaved normally during exposure and were responsive to a stimulus following exposure.

No compound-related effects were noted during clinical pathology evaluations. No organ weight differences or gross abnormalities were seen during necropsy and no histopathologic changes were observed upon microscopic evaluation of tissues.

Although HFC-236fa did not induce peroxisome proliferation, a slight but statistically significant decrease in hepatic  $\beta$ -oxidation activity occurred in the 50000 ppm rats that were sacrificed after the tenth exposure. This decrease was considered compound-related but not biologically adverse since the change was not accompanied by relevant clinical pathologic, organ weight, or liver histopathologic changes.

Under the conditions of this study, the no-observable-adverse-effect level (NOAEL) was 5000 ppm, based on the transient, reduced responsiveness to an alerting stimulus during exposure to concentrations of 20000 ppm or greater. This effect was completely reversible upon cessation of exposure.

#### 90-Day Inhalation Toxicity Study with HFC-236fa in Rats

Four groups of 10 male and 10 female CrI:CD<sup>®</sup>BR rats were exposed by inhalation for 6 hours a day, 5 days a week, over a 14-week period (65 exposures) to concentrations targeted at 0, 5000, 20000, and 50000 ppm (one concentration per group). All rats were weighed weekly and were also individually observed for clinical signs of toxicity following each exposure. The response to an alerting stimulus was determined during the exposures. Ophthalmological examinations were performed prior to commencement of the study and at the end of the study. Clinical pathology evaluations were conducted near the midpoint and at the end of the study. The day following the last exposure, the rats were sacrificed and necropsied. All rats were examined for gross and microscopic pathological changes, and liver tissue was evaluated for peroxisomal  $\beta$ -oxidation activity.

HFC-236fa had no effect on body weights, no abnormal clinical observations were seen in rats either prior to or following exposures, and no effect on food consumption or food efficiency was observed. The one notable compound-related effect was a diminished response to an alerting stimulus during exposure in the 50000 ppm male and female rats during the first 2 weeks of the study. A diminished alerting response was noted in some rats, primarily during the last 2 hours of the exposure. The number of rats affected generally decreased with successive exposures such that by study day 18 all rats from this group had a normal alerting response. All rats exhibited normal alerting response during the evaluation period immediately after exposure.

No compound-related effects were detected during the ophthalmological and clinical pathology evaluations. No organ weight differences or gross abnormalities were seen during necropsy and no histopathologic changes were observed upon microscopic evaluation of tissues. No biologically significant alterations in hepatic peroxisomal  $\beta$ -oxidation activity were seen in any group.

The assigned NOAEL was 20000 ppm, based on the transient, reduced responsiveness to an alerting stimulus during exposure to 50000 ppm. This effect was not seen in all rats from the 50000 ppm group and was completely reversible upon cessation of exposure.

#### Inhalation Developmental Toxicity Study of HFC-236fa in Rats

A pilot study was conducted at 0, 5000, 20000, and 50000 ppm HFC-236fa in rats. Results indicated a diminished to absent alerting response (response to sound stimulus during exposure at 50000 ppm). Some of the rats exposed to 20000 ppm also had diminished responses. No changes in alerting response were seen after test day 4 in the 20000 ppm exposed rats. Normal reactions occurred in rats in the 5000 ppm groups each day and in rats from all groups when they were tested 10 - 20 minutes after the generation of the test material ceased. The abnormal alerting responses were reversible, compound related effects, since they occurred only during exposures. Under the conditions of this pilot study, maternal toxicity characterized by diminished alerting response during exposure, was detected at concentrations of 20000 and 50000 ppm. There was no other evidence of maternal toxicity. No



fetotoxicity was observed at any concentration level. Based on these results, exposure levels of 0, 5000, 20000, and 50000 ppm HFC-236fa were chosen for the main developmental study in rats.

HFC-236fa was administered by inhalation to four groups of 25 CrI:CD<sup>®</sup>BR female rats on days 7 - 16 of gestation at a daily concentration of 0, 5000, 20000, or 50000 ppm (one concentration per group). At 20000 and 50000 ppm, there were significant dose related decreases in maternal body weight gain over the first 2 days of inhalation exposures. At 50000 ppm, this reduction in weight gain was accompanied by a significant reduction in maternal food consumption and occasional instances of diminished alerting responses during the inhalation exposures. No evidence of maternal toxicity was detected at 5000 ppm. There was no evidence of developmental toxicity at any level tested.

Fetal findings showed that there were no compound-related effects on the incidence of early, late, or total resorptions detected. There were no dead fetuses. No compound-related effects for mean fetal weight were detected. The values for mean fetal weight were comparable across the control and exposure.

Under the conditions of this study, significant maternal toxicity was demonstrated at daily exposure levels of 20000 and 50000 ppm. The maternal NOAEL was 5000 ppm. Developmental toxicity was not detected at any exposure level. The developmental NOAEL was 50000 ppm. Thus, HFC-236fa is not considered to be uniquely toxic to the rat conceptus.

#### Extended Acute Inhalation Toxicity of HFC-236fa in Rats

This study was carried out to assess the toxicity of HFC-236fa following the extension of the normal single 4-hour exposure period employed in acute inhalation studies to exposure for 5 consecutive days. The target concentration used in this study was 50000 ppm as selected by the EPA.

A group of five male and five female Alpk:APFSD<sup>®</sup> rats (approximately 7 weeks old) supplied from a colony maintained at Alderly Park, Cheshire, UK, was exposed nose-only to a target atmospheric concentration of 50000 ppm, for 6 hours per day, for 5 consecutive days. These rats were then retained for a period of 14 days for observation following the last exposure.

Test animals were observed for gross clinical abnormalities during each exposure period and were checked daily thereafter. In addition, animals were given a detailed examination after exposure on days 1-5 and then daily during the 14-day observation period up to and including day 19.

HFC-236fa was generated close to target concentration. The only finding possibly attributable to exposure of HFC-236fa was associated with slight respiratory tract irritation. However, in the absence of any effects on body weight, and lung appearance and weight, this is considered to be of little significance at the concentration tested.

On the basis of this test, HFC-236fa is considered to have low acute inhalation toxicity at concentrations of 50000 ppm and lower.

#### Inhalation Developmental Toxicity Study of HFC-236fa in Rabbits

HFC-236fa was administered to groups of 20 Hra:(NZW)SPF female time-mated rabbits on days 7-19 of gestation at daily exposure levels of 0, 5000, 20000, and 50000 ppm. The highest level, 50000 ppm, was the highest concentration which could be attained without supplementing chamber oxygen.

There was no evidence of any maternal or developmental toxicity at any exposure concentration tested. There were no compound-related effects on maternal body weights, weight changes, food consumption, clinical observations, or post-mortem findings. There were no compound-related developmental or reproductive effects; the endpoints evaluated included mean fetal weight, mean litter size, measures of pre- and post-implantation embryo lethality, and the incidences of fetal malformations and variations. Thus, the maternal and developmental no-observed-effect-level (NOEL) was 50000 ppm. Therefore, the results of this study indicate that HFC-236fa was not uniquely toxic to the rabbit conceptus.

#### Cardiac Sensitization

The potential of HFC-236fa to cause cardiac sensitization by inhalation in beagle dogs was determined. Cardiac sensitization to adrenaline is a phenomenon associated with the inhalation of a

number of unsubstituted and halogenated hydrocarbons. After inhalation of the sensitizing agent, challenge with adrenaline causes cardiac arrhythmias. The technique used in this study involved the intravenous injection of adrenaline before and during the inhalation of the test gas. The effect of adrenaline on an electrocardiogram was examined in both cases and compared to assess any positive response to the test gas.

Six male beagle dogs were selected for the test. These dogs had been acclimatized to laboratory conditions and handling procedures and trained to accept restraint procedures during the course of previous studies. The cardiac response of the dogs to adrenaline alone was first monitored. The dogs were then exposed to the HFC-236fa by a snout-only delivery system. Concentrations of HFC-236fa examined were 5, 10, 15, 25, and 30 volume percent in air. At least 1 calendar day was allowed between exposure sessions to allow the dogs to recover.

The criterion for a positive effect was the appearance of a burst of multifocal ventricular ectopic activity (MVEA) or ventricular fibrillation (VF). Ventricular tachycardia alone was not necessarily considered definitive evidence of a positive response. At 5 and 10 percent (50,000 and 100,000 ppm) HFC-236fa all responses were negative. There were no clinical signs of any toxicological significance.

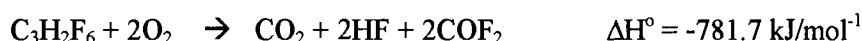
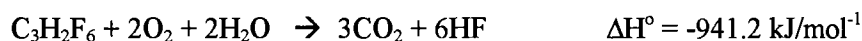
At 15 percent (150,000 ppm) HFC-236fa, 33 percent of responses were positive. One dog of the six responded with MVEA and one dog responded with VF: both responses were fatal. A third dog was observed to be unsteady in gait after removal from the restraint.

At 20 percent (200,000 ppm) HFC-236fa, 50 percent of responses were positive; i.e., two of the remaining four dogs responded with MVEA but survived. All dogs exposed at this concentration were observed to be unsteady in gait after removal from the restraints.

Exposures at 25 and 30 percent HFC-236fa were prematurely terminated because the dogs either struggled significantly during exposure or were anaesthetized. Overall, half of the dogs gave positive responses at 20 percent HFC-236fa in air. There were no positive responses at 10 percent or less HFC-236fa.

## FLAMMABILITY AND FIRE SUPPRESSION CHARACTERISTICS

Flammability of HFC-236fa was evaluated by means of the American Society for Testing and Materials E681-94 standard method for determination of flammability limits (ASTM, 1994). Tests were conducted at room temperature (27°C or 300 K) and at 100°C (373K) at atmospheric pressure (ca. 754 torr or 100.5 kPa) using a 5-L glass test vessel and a 0.1 second alternating current (ac) spark generated by a 15 kV, 30 mA power supply as the ignition source. Air mixed with the HFC-236fa had a relative humidity of 50 percent. HFC-236fa/air mixtures were prepared by individually metering the HFC and air into the evacuated (ca. 1.7 torr or 0.23 kPa) flask equipped with a pressure transducer accurate to  $\pm 1.5$  torr or 0.2 kPa. At room temperature, tested concentrations of HFC-236fa in air were 5.1, 8.1, 11.0, and 15.0 volume percent. At 100°C, tested concentrations were 8.0, 12.0, 15.9, and 20.0 volume percent. No flame was generated or propagated in these tests, indicating that the material was nonflammable. This is in agreement with the axiom that fluorocarbons having a C-F/(C-H + C-C) bond ratio  $>1$  are not flammable. Calculated standard enthalpies of combustion (298.15 K, 101.3 kPa) for the two possible overall combustion reactions for HFC-236fa (with all reactants and products in the vapor state) are (Smith and Tufts, 1996):



Because of its nonreactivity, HFC-236fa was among several chemicals examined by the EPA as possible alternatives for ozone depleting fire extinguishing agents such as the halons. This work was conducted by the New Mexico Engineering Research Institute (NMERI) under EPA Cooperative Agreement No. CR817774. Laboratory scale suppression of a n-heptane flame was measured using the cup-burner technique (Skaggs et al., 1995). The concentration of HFC-236fa in air found to just extinguish the flame was 5.6 volume percent. This is nearly twice the concentration of halon-1301 (CF<sub>3</sub>Br) to extinguish the same flame under the same conditions (3.0 volume percent). Taking into account the difference in the liquid densities of HFC-236fa and halon-1301, the volume of liquefied

HFC-236fa which would have to be available to extinguish a fire is 2.16 times the volume of liquefied halon-1301. The greater fire extinguishment effectiveness of halon-1301 is due to the presence of bromine atoms in the molecule. Bromine atoms have been found to be very effective scavengers of reactive combustion radicals, thereby allowing combustion chain reactions to be terminated. It would appear, however, that HFC-236fa would be as effective in fire suppression as HFC-227ea (1,1,1,2,2,3,3-heptafluoropropane), a commercial streaming fire extinguishing agent.

#### HFC-236fa/POE LUBRICITY

A wear test based on ASTM Method D2670-88, "Standard Test Method for Measuring Wear Properties of Fluid Lubricants (Falex Pin and Vee Block Method)" (ASTM, 1988) was carried out. This ASTM method was modified to accommodate testing the lubricant/refrigerant combinations by substituting the standard oil test cup with a glass cup with an internal glass frit in the bottom and a side arm. Lubricant was added to this glass cup and the test gas added through the side arm. The test gas would then bubble up through the oil.

The Falex test machine rotates a metal journal between two metal stationary vee blocks immersed in an oil bath. Load is applied to the system through lever arms (load arms) to the vee blocks. An analog, dial-type gauge measures the applied load, and an electronic load cell measures the torque transferred by the friction between the rotating pin and the vee blocks. The load is generated by a screw-drive clamp mounted across the ends of the load arms. The amount of wear of the test pieces is measured as the amount of rotation of a toothed wheel attached to the screw-drive (200 teeth equal one full rotation).

The wear test uses a 5 minute break-in period at fixed load. Following the break-in period, the wear test consists of operating the machine at a fixed load for 15 minutes; the total number of teeth passing a reference point is reported as the result.

The extreme pressure test used the step test procedure described in ASTM D3233-92, "Standard Test Methods for Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin and Vee

Block Methods)" (ASTM, 1992). The pressure test also involves a 5 minute break-in period at fixed load. Following the break-in period, the load is increased in 250-lb increments and maintained for 1 minute at each increment. The extreme pressure test is complete when a brass shear pin breaks (at approximately 100 in-lb torque) or when the maximum system load (2885 lb) is reached without failure of the shear pin. The load at failure (or maximum load) is reported as the result. Results of the step tests are in "pounds" of load applied to the test pieces at failure. In this case, a larger number indicates better performance. A value "2885+" indicates that the test piece did not seize or break after the completion of the maximum load of the test machine.

A combined test matrix was developed using a mineral oil-sulfur mixture (ASTM D 2670-88 Blend B) and argon gas as controls. The order of the tests was randomized to remove possible bias as a result of test order. Argon was chosen as an inert control gas since nitrogen might react with the hot test pieces during testing. A gas flow rate of 0.1 L per minute was maintained in all tests. The cylinder, valve, flow meter, and lines were kept at ambient temperature. The mass flow rate for HFC-236fa was approximately 1 g per minute.

Results for the wear tests given in Table 6 show the number of teeth advanced on the screw drive (higher number equals more wear) or that the test pieces seized during the test. Using the POE oil in the absence of argon or HFC-236fa resulted in seizure of the test pieces in six of the eight trials, while the other two trials gave less wear than did operation with Blend B. This binodal distribution of results (either seizure or superior performance compared to Blend B) was observed in all tests with HFC-236fa. It was observed that fine metal particulate generated during the wear tests remained suspended in the Blend B oil but agglomerated in the POE oil and frequently accumulated in the test piece interfaces causing seizure. Agglomeration of the metal particulate in the POE oil may be related to an additive in the oil which was not present in Blend B. Overall, addition of argon to the POE oil gave significant improvement in wear resistance, as did addition of HFC-236fa. Still, even with the addition of these gases, seizure of the test pieces occasionally occurred. It is postulated that the decrease in the

amount of wear upon adding argon or HFC-236fa may be due to a reduction in the oil temperature caused by the flow of gas through the oil and/or to gas bubbles flushing metal particles from the journal/vee-block interfaces. For some tests, it was observed that all of the wear occurred in the last 5 minutes of the test when the oil had reached a temperature of 90 to 100°C.

Table 6. Wear tests results (unit is teeth of wear)

Blend B		POE Lubricant		
w/o Argon	w/Argon	w/o Argon	w/Argon	w/HFC-236fa
114	162	seized	56	0
117	140	seized	135	9
109	165	seized	90	42
111		seized	45	74
128		seized	43	118
131		seized	seized	seized
117		41	106	
118		73		

Results for the extreme pressure (step) tests are given in Table 7. Results are tabulated as either the load (in pounds) at which the rotating journal seized or “2885+” to indicate that the lubricant was tested to the limits of the machine without failing. Again, the standard Blend B oil outperformed the POE oil in all tests except for those in which HFC-236fa was added to the POE oil. Addition of argon slightly enhanced the lubricity of both the Blend B and POE oils in the step test, possibly due to a cooling effect. Addition of HFC-236fa to the POE oil improved its performance by a factor of about 2.5 in the step test. In general, it was found that the presence of HFC-236fa in the POE oil significantly improved the lubricity of the oil as measured in the ASTM wear and extreme pressure tests.

Table 7. Extreme pressure (step test) results (lb)

Blend B		POE Lubricant		
w/o Argon	w/Argon	w/o Argon	w/Argon	w/HFC-236fa
2600	2885+	765	1100	2885+
2600	2885	930	1100	2885+
2450	2885+	765	1100	2885+
2450		765	2885+	
2885+		930	765	
2885+		1100	765	
2600				
2600				

## HEAT TRANSFER CHARACTERISTICS

The shell-side heat transfer performance of HFC-236fa was evaluated for both conventional finned tubes (26 and 40 fins per inch [fpi] tubes) and high performance-enhanced Turbo-CII, Turbo-B, and Turbo-BII tubes.

Condensation of pure HFC-236fa was conducted on a 26 fpi, a 40 fpi, and a Turbo-CII tube. Pool boiling on four tube types (26 fpi, 40 fpi, Turbo-B, and Turbo-BII) was tested for pure HFC-236fa and for HFC-236fa mixed with 1 and 3 weight percent ISO68 POE lubricant. These tubes had nominal outer diameters of 19.1 mm (1/4 in) and were evaluated at a saturation temperature of 40°C for condensation and 2°C for pool boiling over the heat flux range of 15 to 40 kW m<sup>-2</sup>.

Heat transfer was improved for HFC-236fa by using the high-performance enhanced tubes. Specifically, the Turbo-CII tube performed better than the two conventional finned tubes in the condensation tests, while the performances of the Turbo-B and Turbo-BII tubes were superior to those of the two conventional finned tubes in the pool boiling tests.

The maximum increase in heat transfer coefficients for the Turbo-CII tube was 80 percent relative to the 26 fpi tube and 70 percent relative to the 40 fpi tube, while for the Turbo-B it was 1.7 and 2.2 times greater than for the 26 and 40 fpi tubes, respectively. In addition, the Turbo-BII tube gave boiling heat transfer coefficients up to 80 percent larger than those of the Turbo-B tube.

The heat transfer performance of HFC-236fa was compared with that of CFC-114 determined in the same facility under the same conditions. For all the tubes tested, except the Turbo-CII tube, the heat



transfer results showed that HFC-236fa outperformed CFC-114 for both shell-side condensation and pool boiling. The heat transfer coefficients for HFC-236fa during condensation were up to 40 percent larger than those for CFC-114 and during pool boiling were up to 80 percent larger.

Effects of compressor oil on heat transfer performance during pool boiling were also investigated. The presence of up to 3 weight percent ISO68 POE lubricant in HFC-236fa decreased the boiling performance of pure HFC-236fa by less than 10 percent for all but one of the tubes tested. The Turbo-BII tube, the only exception, showed an increase in boiling coefficients of up to 30 percent over the pure refrigerant values for tests with 1 percent lubricant, and up to 15 percent with 3 percent lubricant present.

#### STABILITY AND MATERIALS COMPATIBILITY

Thermal and hydrolytic stability of HFC-236fa in the presence of metal catalysts was evaluated by placing the chemical (0.7 g) in evacuated sealed glass tubes in contact with copper, steel, and aluminum coupons and heating the tubes at 175°C for 14 days in accordance with the methods described in ANSI/ASHRAE Standard 97-1989 (American Society of Heating, Refrigerating and Air-Conditioning Engineers) (ASHRAE, 1989). These tests were repeated with added POE lubricant (0.7 g) and with added moisture (0.07  $\mu$ L). Chemical to lubricant content was based on the mass rather than the volume ratio. At the end of the 14-day aging period, the contents of the tubes were visually inspected and the vapor and liquid phases analyzed by a combination of GC and FTIR. There was no evidence of copper plating on the steel and no evidence of either refrigerant or lubricant breakdown indicating excellent thermal and hydrolytic stability of the HFC-236fa both alone and in combination with lubricant.

Another matrix of sealed tube samples was prepared combining HFC-236fa with various desiccants, plastics, and elastomers with and without lubricant to test for compatibility of the HFC-236fa with these

materials. These samples were aged in an oven at 125°C for 14 days. All tests were run in duplicate. Table 8 gives the sample matrix for the compatibility tests. Table 9 describes the elastomers and plastics.

Table 8. Compatibility test matrix

Sample Number	Material(s)	Sample Number	Material(s)
1 a,b	HFC-236fa/Buna™-N	22 a,b	HFC-236fa/Geolast®/POE
2 a,b	HFC-236fa/E-70	23 a,b	HFC-236fa/Mylar™
3 a,b	HFC-236fa/HNBR	24 a,b	HFC-236fa/Nomex®
4 a,b	HFC-236fa/Hypalon®	25 a,b	HFC-236fa/Nylon 6,6
5 a,b	HFC-236fa/Kalrez® C	26 a,b	HFC-236fa/Mylar®/POE
6 a,b	HFC-236fa/Natural rubber	27 a,b	HFC-236fa/Nomex®/POE
7 a,b	HFC-236fa/NBRS	28 a,b	HFC-236fa/Nylon 6,6/POE
8 a,b	HFC-236fa/Neoprene 3229	29 a,b	HFC-236fa/Brass, Bronze
9 a,b	HFC-236fa/S-70	30 a,b	HFC-236fa/Cast iron
10 a,b	HFC-236fa/Teflon®	31 a,b	HFC-236fa/Brass, Bronze/POE
11 a,b	HFC-236fa/Geolast®	32 a,b	HFC-236fa/Cast iron/POE
12 a,b	HFC-236fa/Buna™-N/POE	33 a,b	HFC-236fa/Activated desiccant H-5
13 a,b	HFC-236fa/E-70/POE	34 a,b	HFC-236fa/Activated desiccant H-6
14 a,b	HFC-236fa/HNBR/POE	35 a,b	HFC-236fa/Activated desiccant H-7
15 a,b	HFC-236fa/Hypalon®/POE	36 a,b	HFC-236fa/Activated desiccant H-9
16 a,b	HFC-236fa/Kalrez®-C/POE	37 a,b	HFC-236fa/Activated desiccant H-5/POE
17 a,b	HFC-236fa/Natural rubber/POE	38 a,b	HFC-236fa/Activated desiccant H-6/POE
18 a,b	HFC-236fa/NBRS/POE	39 a,b	HFC-236fa/Activated desiccant H-7/POE
19 a,b	HFC-236fa/Neoprene 3229™/POE	40 a,b	HFC-236fa/Activated desiccant H-9/POE
20 a,b	HFC-236fa/S-70/POE	41 a,b	HFC-236fa/Viton® A
21 a,b	HFC-236fa/Teflon®/POE	42 a,b	HFC-236fa/Viton® A/POE

Table 9. Tested elastomers and plastics

Polymers	Descriptions
Buna™-N	Copolymer of 1,3-butadiene (70 percent) and acrylonitrile (30 percent)
HNBR	Hydrogenated nitrile butyl rubber
Hypalon®	Chlorosulfonated high density polyethylene
Geolast®	Nitrile polypropylene
NBRS or Buna™-S	Copolymer of 1,3-butadiene (70-75 percent) and styrene (25-30 percent)
Neoprene	Polychloroprene
Kalrez®-C	Perfluoropolymer of tetrafluoroethylene and perfluoromethyl vinyl ether
E-70 or EPDM	Ethylene propylene diene methylene rubber
S-70 or SI	Silicone rubber
Viton®-A	Copolymer of vinylidene fluoride and hexafluoropropylene
Teflon®	Polymer of tetrafluoroethylene
Nomex®	Polymer of m-phenylenediamine and isophthalic acid chloride
Mylar®	Polyethylene terephthalate
Nylon 6,6	Polymer of adipic acid and hexamethylenediamine

Figures 3 through 6 graphically display the results of the changes in volume, weight, linear swell, and hardness for the elastomeric materials with HFC-236fa with and without the lubricant. Values represent averages of the duplicate samples for each material. Some swelling of elastomeric materials is desired for gaskets and O-rings to form a good seal in equipment. However, volume increases of greater than 20 percent or linear swell of greater than 5 percent may be considered excessive and detrimental. Also, any shrinkage of the material is not desired. A change of hardness of  $\pm 10$  percent may indicate excessive softening or embrittlement and may be considered unacceptable. Depending on where in the equipment the O-ring and gasket materials are placed, they may experience contact primarily with HFC-236fa or with a combination of HFC-236fa and lubricant. Therefore, a given elastomer or plastic may be suitable for use in one section of the equipment and not in another.

In common with three other HFCs and one HFE tested for material compatibility, results of the HFC-236fa tests showed that with and without a polyolester (POE) lubricant present, Buna-N™, Buna-S™, Geolast®, Hypalon®, silicone rubber, and EPDM elastomers gave acceptable overall performance.

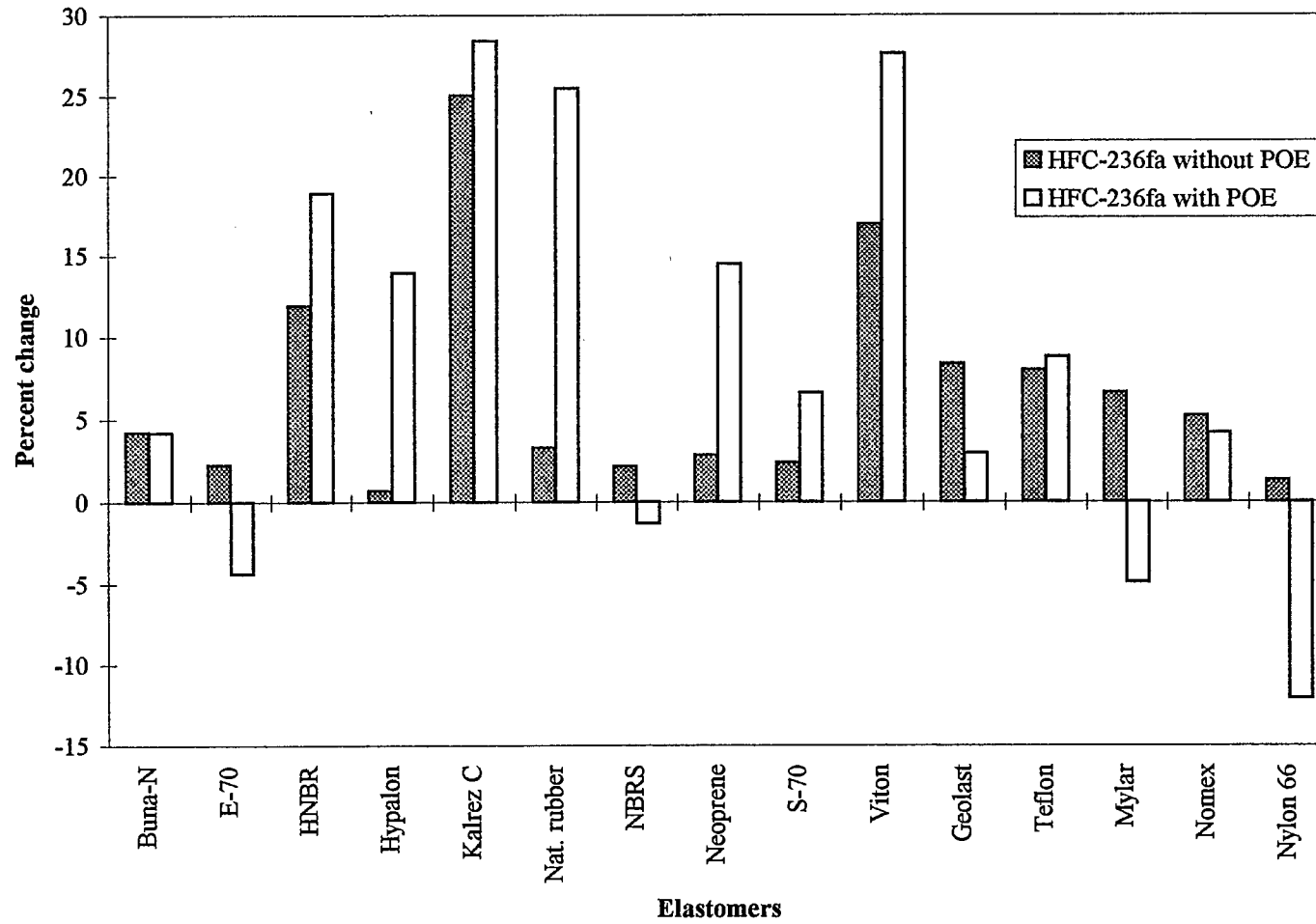


Figure 3. Volume change of elastomers with HFC-236fa

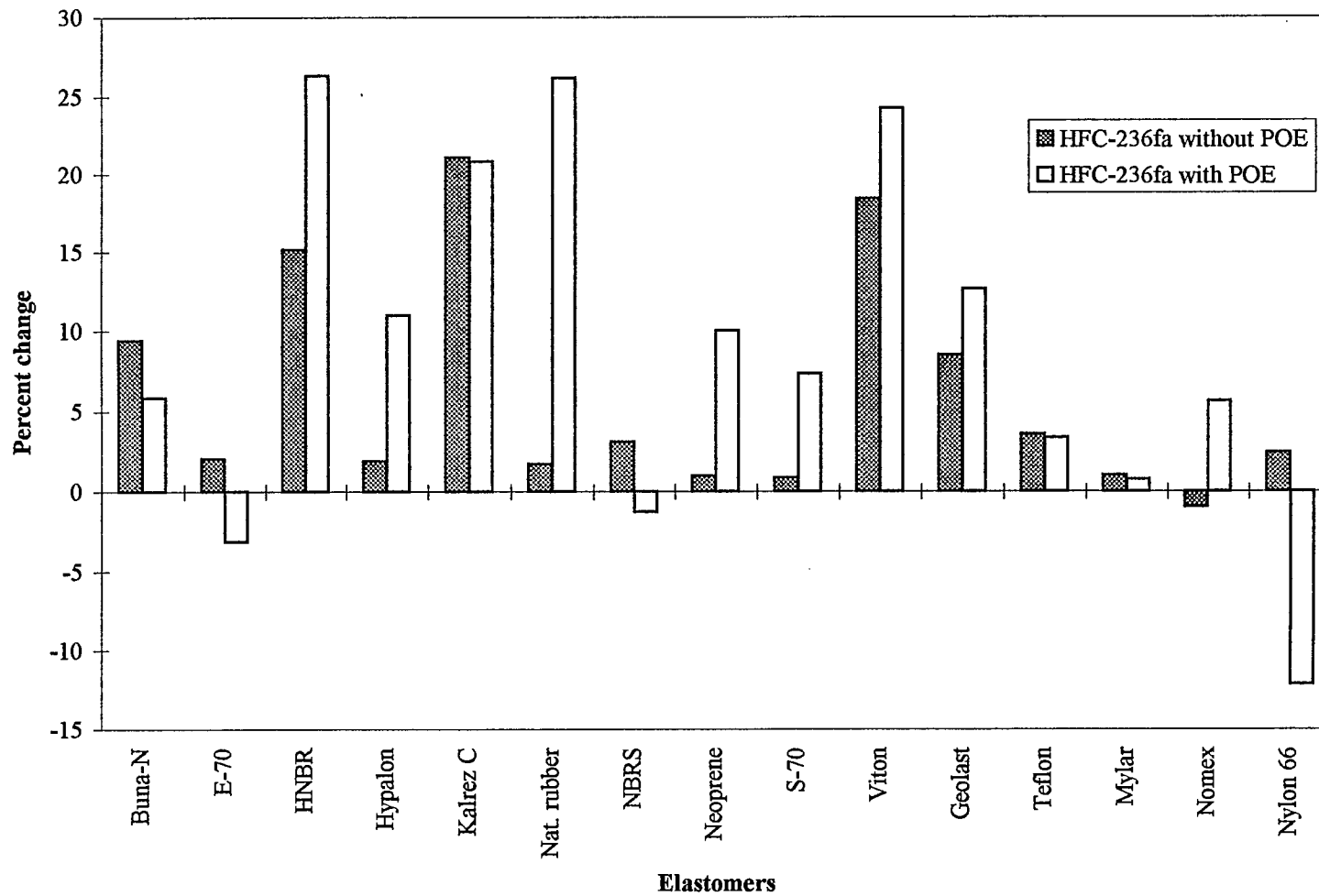


Figure 4. Weight change of elastomers in HFC-236fa

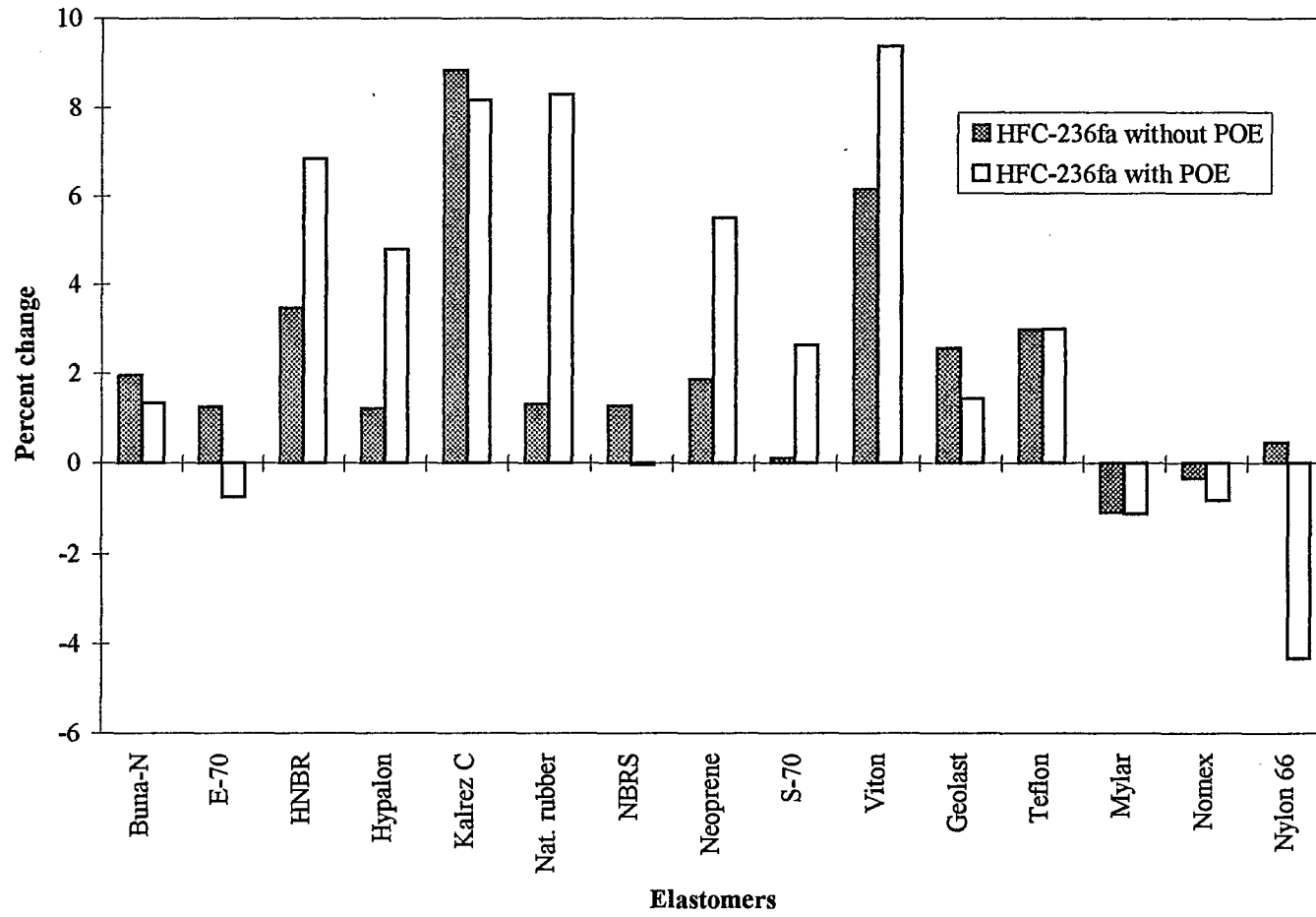


Figure 5. Linear swell of elastomers in HFC-236fa

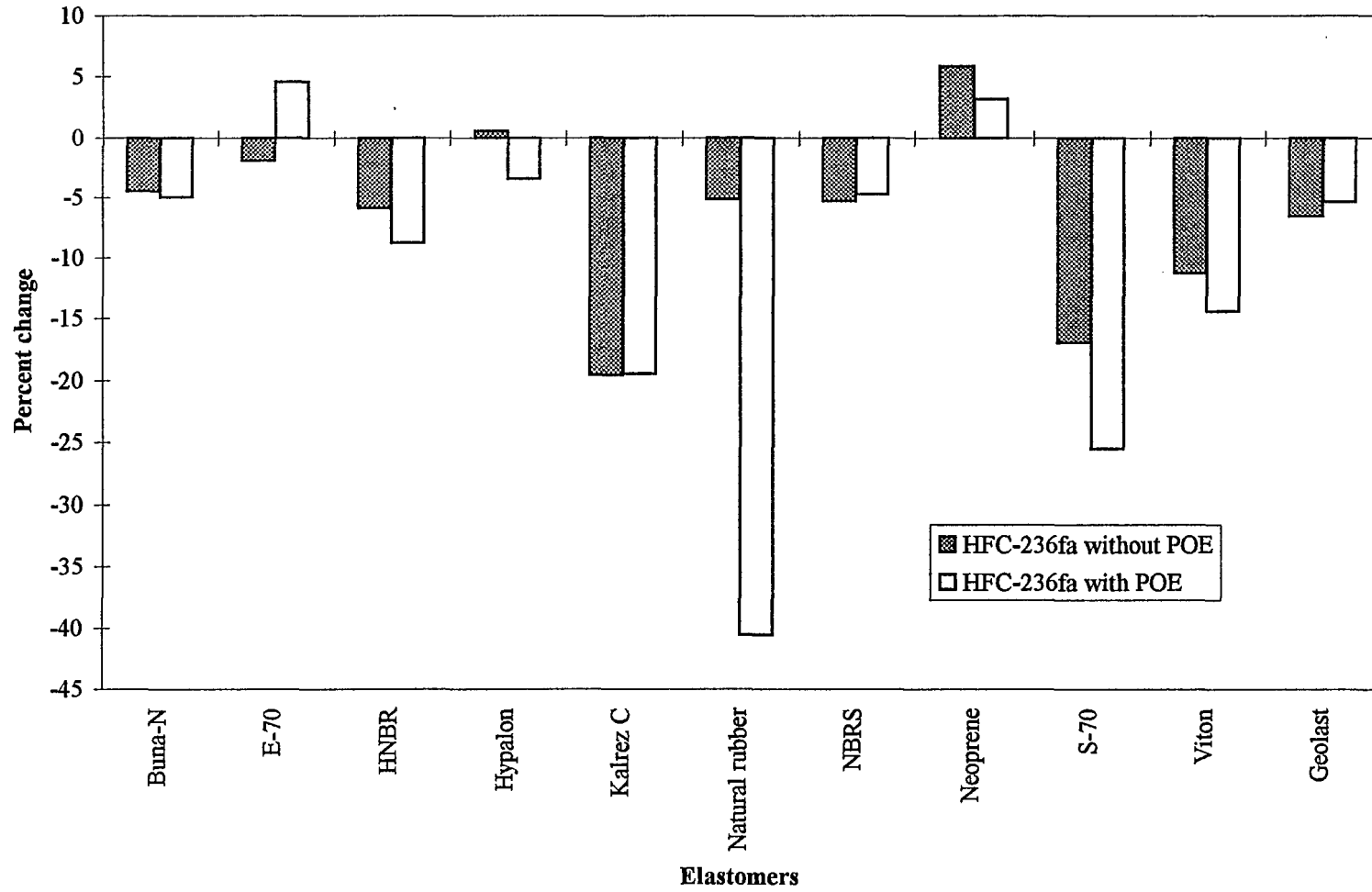


Figure 6. Hardness change of elastomers in HFC-236fa

Fluoropolymers such as Viton<sup>®</sup>, Kalrez<sup>®</sup>, and Teflon<sup>®</sup> were especially susceptible to absorption of HFCs, including HFC-236fa, resulting in unacceptable swelling. Hydrogenated butyl nitrile rubber and natural rubber showed excessive swelling in the presence of the HFC/lubricant mixtures. Neoprene was deemed unsuitable due to shrinkage and embrittlement with the HFCs, with and without the lubricant present.

Evidence for degradation of HFC-236fa was sought by comparison of the infrared spectra and gas chromatograms of the vapor phase from each of the 42 aged samples against the corresponding spectrum and chromatogram of unaged HFC-236fa. Degradation of the lubricant in aged samples was also checked by infrared spectral comparison with the unaged lubricant.

Neither HFC-236fa nor the lubricant showed any evidence of degradation in the presence of the various metals after the 2-week heating period. Some IR spectral changes were observed in the liquid (lubricant) phase for some of the samples containing the elastomers/plastics, but these features could not be attributed unambiguously to degradation of the elastomers/plastics or the lubricant or both. The most likely source of the new IR absorption features seemed to be leaching of some components of the elastomers such as fillers, accelerators, or plasticizers included in the formulations.

Desiccant compatibility with the refrigerant was checked by fluoride analysis of the condensate collected by passing steam over a bed of desiccant mixed with vanadium pentoxide ( $V_2O_5$ ) in a nickel tube furnace at 975°C. Fluoride analysis in desiccants was based on industry procedures (UOP, 1978; Association of Florida Phosphate Chemists, 1991). Four molecular sieve desiccants in the aluminosilicate family were aged along with HFC-236fa and the HFC-236fa/POE mixture. All types of unaged and aged desiccants were analyzed for fluoride. The original (unaged) desiccants did not show any fluoride content. However, one desiccant type in the aged group showed a small amount of fluoride deposition (<2 percent); see Table 10.



Table 10. Desiccant results with HFC-236fa

Desiccant and Refrigerant Combinations	Percent Fluoride	
	without POE	with POE
HX-5 <sup>1</sup> & HFC-236fa	1.66	0.12
HX-6 <sup>2</sup> & HFC-236fa	0.30	0.00
HX-7 <sup>2</sup> & HFC-236fa	0.00	0.00
HX-9 <sup>2</sup> & HFC-236fa	0.00	0.00

<sup>1</sup> pore size = 0.4 nm

<sup>2</sup> pore size = 0.3 nm

## 4. REFRIGERANT PERFORMANCE

### HFC-236fa AS A CFC-114 REPLACEMENT IN CHILLERS

CFC-114 has been used as the refrigerant of choice in centrifugal chillers with capacities ranging from 440 to more than 1200 kW. The U. S. Navy has been a major user of this type of equipment to supply comfort air conditioning and critical cooling needs on board its ships. Another application for this refrigerant has been high temperature heat pumps employed in waste heat recovery and utilization. HFC-236fa is one of several alternatives with normal boiling points near that of CFC-114. Table 11 presents a list of some CFC-114 alternatives in the order of their normal boiling points along with their critical properties.

### THEORETICAL PERFORMANCE EVALUATION

Both theoretical thermodynamic and experimental analyses were performed comparing the performance of HFC-236fa with CFC-114 under shipboard chiller conditions (2 to 13°C evaporating temperature and 40 to 65°C condensing temperature) and high temperature heat pump conditions (0 to 35°C evaporating and 40 to 110°C condensing temperatures) (Kazachki et al. 1995 and 1994). Important parameters for centrifugal compressors were compared for HFC-236fa and CFC-114 (Kazachki and Gage, 1993).

Table 11. Properties of HFC-236fa and other CFC-114 alternatives

Kazachki and Gage (1993)

Refrigerant	Name	Chemical Formula	T <sub>C</sub> (°C)	P <sub>C</sub> (kPa)	T <sub>b</sub> (°C)
HCFC-124	2-chloro-1,1,1,2-tetrafluoroethane	CF <sub>3</sub> CFCIH	122.5	3660	-13.2
HC-600a	isobutane	C <sub>4</sub> H <sub>10</sub>	135.0	3648	-11.7
HCFC-142b	1-chloro-1,1,-difluoroethane	CCIF <sub>2</sub> CH <sub>3</sub>	137.2	4120	-9.2
HFC-236cb	1,1,2,2,3-pentafluoropropane	CF <sub>3</sub> CF <sub>2</sub> CFH <sub>2</sub>	130.2	3118	-1.4
<b>HFC-236fa</b>	<b>1,1,1,3,3,3-hexafluoropropane</b>	<b>CF<sub>3</sub>CH<sub>2</sub>CF<sub>3</sub></b>	<b>130.7</b>	<b>3177</b>	<b>-1.1</b>
HFC-254cb	1,1,2,2-tetrafluoropropane	HCF <sub>2</sub> CF <sub>2</sub> CH <sub>3</sub>	146.2	3753	-0.8
HC-600	n-butane	C <sub>4</sub> H <sub>10</sub>	152.0	3797	-0.4
CFC-114	Dichlorotetrafluoroethane	CCIF <sub>2</sub> CCIF <sub>2</sub>	145.7	3248	3.6
HFE-134	1,1,2,2-tetrafluorodimethylether	HCF <sub>2</sub> OCF <sub>2</sub> H	147.1	4228	4.7
HFC-236ea	1,1,1,2,3,3-hexafluoropropane	CF <sub>3</sub> CHF <sub>2</sub> CF <sub>2</sub> H	141.2	3533	6.5
HFC-236ca	1,1,2,2,3,3-hexafluoropropane	HCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> H	155.2	3405	12.6

A theoretical thermodynamic analysis was performed using a computer model based on the thermodynamic properties of HFC-236fa predicted by REFPROP (NIST, 1996). Volumetric refrigerating capacity and coefficient of performance (COP) of the vapor compression cycle were the two main criteria used to evaluate performance. Since both CFC-114 and HFC-236fa have wet isentropic vapor compression, a vapor compression cycle with throttling and dry compression was used. Dry compression is defined as isentropic compression of refrigerant vapor with sufficient superheat for the compression process to end on the vapor saturation curve. Since the goal was to evaluate the performance of HFC-236fa relative to CFC-114, the results are presented as ratios of the particular characteristics of HFC-236fa to CFC-114.

The COP ratio of HFC-236fa to CFC-114 is shown in Figure 7. At all conditions, the ratio is <1, and as much as 30 percent lower at the lowest evaporating temperature and highest condensing temperature for which the COP is calculated. The lower critical temperature of HFC-236fa compared to CFC-114 affects its performance in a negative way.

The volumetric capacity ratio of HFC-236fa to CFC-114 is presented in Figure 8 for five condensing temperatures. For up to 80°C the HFC-236fa volumetric capacity is 0 to 20 percent higher than CFC-114, probably because of the lower normal boiling point of HFC-236fa (-1.10 vs. 3.68°C). Due to the lower critical temperature of HFC-236fa (130.65 vs. 145.88°C), its volumetric capacity at 93.3°C condensing temperature is lower than that of CFC-114.

#### CENTRIFUGAL COMPRESSOR EVALUATIONS

The majority of compressors used in air-conditioning chillers are centrifugal. Important parameters for centrifugal compressors have been evaluated for HFC-236fa and compared to CFC-114. Table 12 presents some of these parameters for a compressor with an impeller diameter of 0.5 m and a tip width of 0.025 m for these refrigerants. In developing this table, the following values were used for the compressor coefficients: a compressor head coefficient of 0.6, a tip flow coefficient of 0.3, and a compressor volume flow coefficient of 0.053. This analysis shows that HFC-236fa has slightly higher discharge pressures. The compressor's refrigerating capacity,  $Q_E$ , with HFC-236fa is about 26 percent higher, indicating that a smaller impeller (or compressor) can be used.

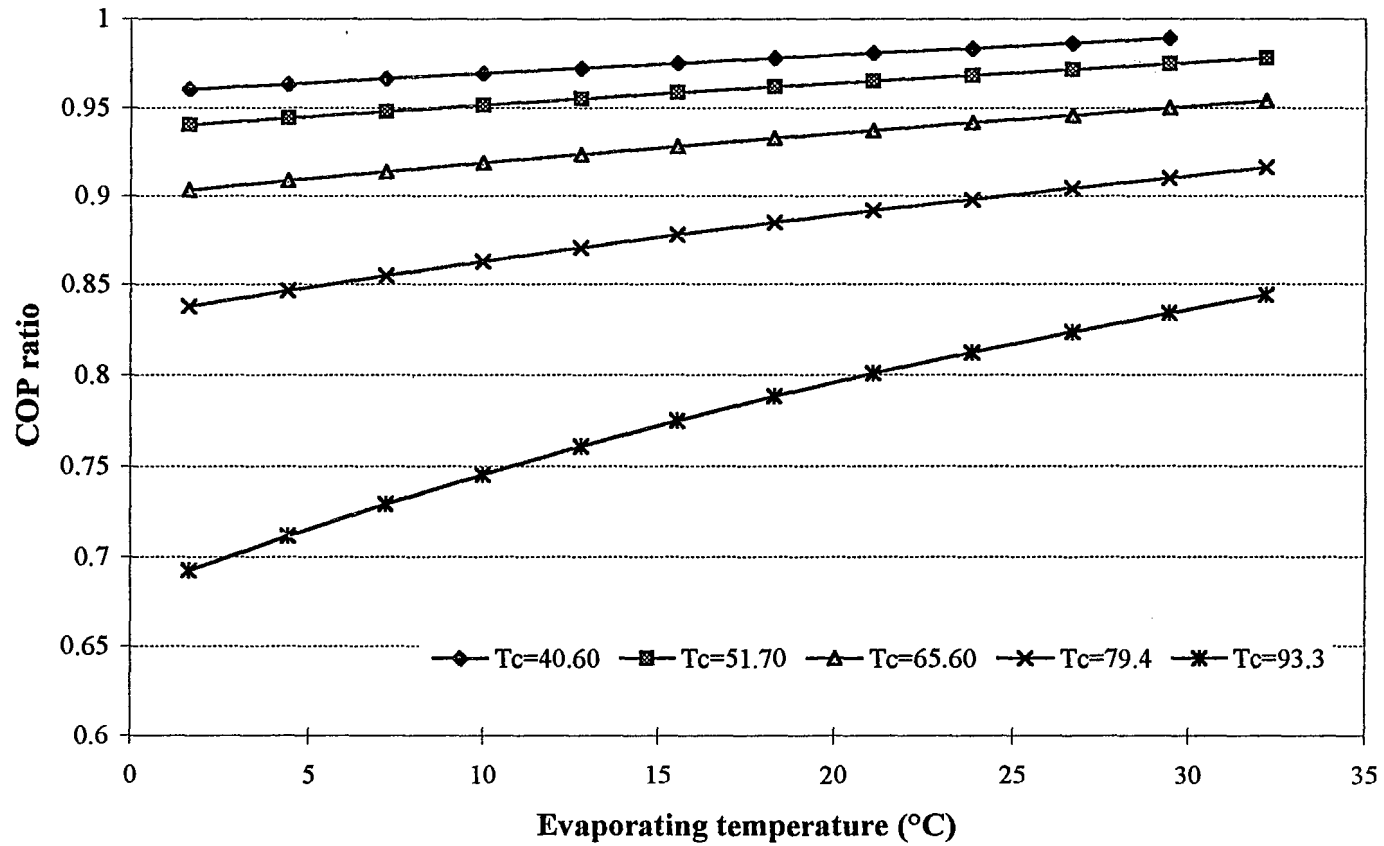


Figure 7. Coefficient of performance (theoretical) ratio of HFC-236fa relative to CFC-114

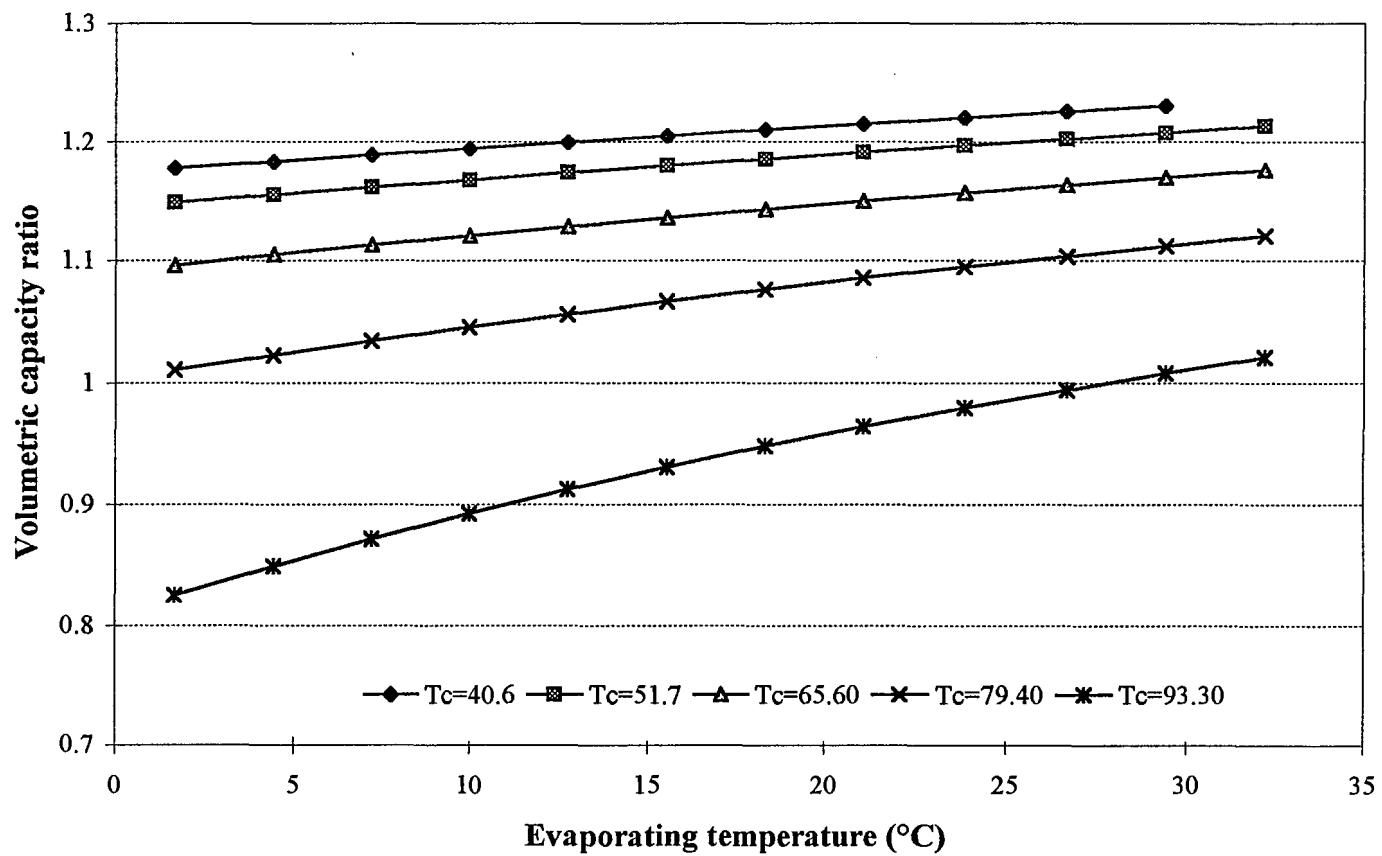


Figure 8. Volumetric capacity ratio of HFC-236fa relative to CFC-114

Table 12. Centrifugal compressor characteristics at 4°C evaporating and 40°C condensing temperatures

(From Kazachki and Gage, 1993)

Refrigerant	$P_e$ (kPa)	$P_c$ (kPa)	$u_2$ (m/s)	$Ma_2$ -	N (rpm)	$V_s$ (m <sup>3</sup> /s)	$V_D$ (m <sup>3</sup> /s)	$Q_E$ (kW)
HFC-236fa	123.1	416.2	174	1.43	6654	2.30	2.05	2076
CFC-114	102.7	336.3	163	1.41	6214	2.15	1.92	1653

### COMPRESSOR CALORIMETRY RESULTS OF CENTRIFUGAL CHILLER SIMULATION

One technique for additional evaluation of an alternative refrigerant is a calorimeter test of both the original refrigerant and the proposed alternative refrigerant. This calorimeter test suggests how the alternative refrigerant will perform in a certain compressor under actual operating conditions. Information on capacity and efficiency characteristics of the tested compressor is the output of such a test. A calorimeter evaluation was made of HFC-236fa as a potential alternative to CFC-114 under chiller operating conditions.

Comparative evaluations of CFC-114 and HFC-236fa were conducted in a compressor calorimeter test rig with a semi-hermetic compressor. The compressor was designed for use with HFC refrigerants, was lubricated with ISO68 POE lubricant, and included an air-cooled 0.56 kW (3/4 hp) motor. Its volumetric flow rate was 1.329 L/sec (169.2 ft<sup>3</sup>/hr) at a 1750 rpm motor speed. The evaluations were made over a wide range of evaporating and condensing temperatures representing both shipboard chiller and high temperature heat pump conditions. Some limitations on these conditions were imposed by the calorimeter's capacity rather than by the refrigerant's properties or compressor characteristics. The tests were performed according to ASHRAE Standard 23-1993 (ASHRAE, 1993).

Experimental cooling capacities are presented in Figure 9 as the ratio of HFC-236fa to CFC-114. The cooling capacities of HFC-236fa are higher than those of CFC-114, except at the higher condensing temperatures and lower evaporating temperatures. This is consistent with the theoretical results. The compressor volumetric efficiency with HFC-236fa is essentially the same as with CFC-114 (Figure 10).

The ratios of measured coefficients of performance (COP) for HFC-236fa relative to CFC-114 are presented in Figure 11. At condensing temperatures up to about 65°C, the HFC-236fa COP is greater than the CFC-114 COP. At higher condensing temperatures, it drops somewhat below that of CFC-114 but generally increases with increasing evaporating temperatures. The compressor isentropic efficiency with HFC-236fa (Figure 12) is about 10 percent better than with CFC-114, resulting in 10 percent higher COP compared to theoretically predicted values.

With the HFC-236fa refrigerant, the compressor ran for almost 1,800 hours without failure, excessive noise, vibration, or any other indication of abnormal operation. These test results indicate that HFC-236fa is a viable alternative refrigerant for CFC-114 in chillers.



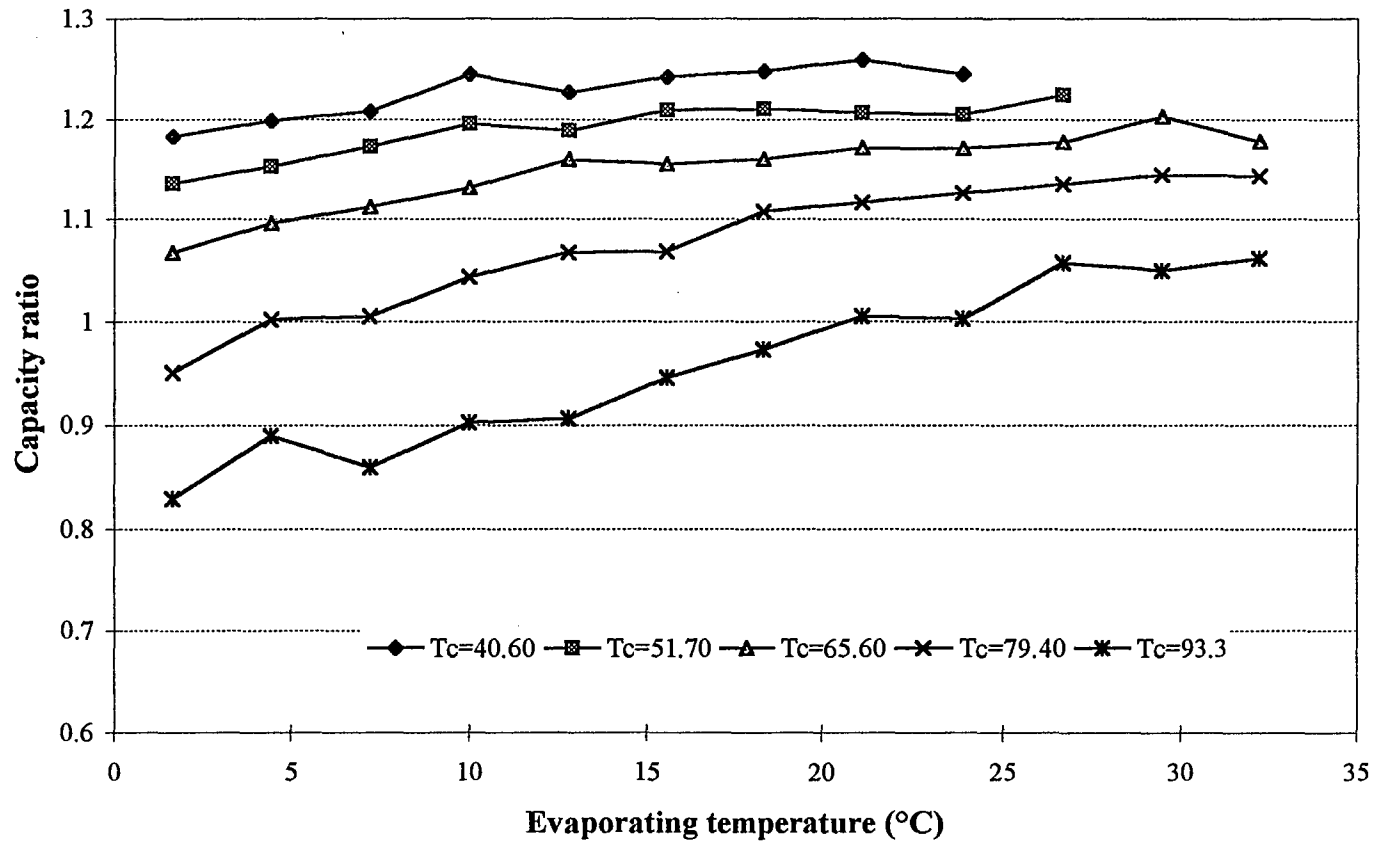


Figure 9. Experimental cooling capacity ratio of HFC-236fa relative to CFC-114

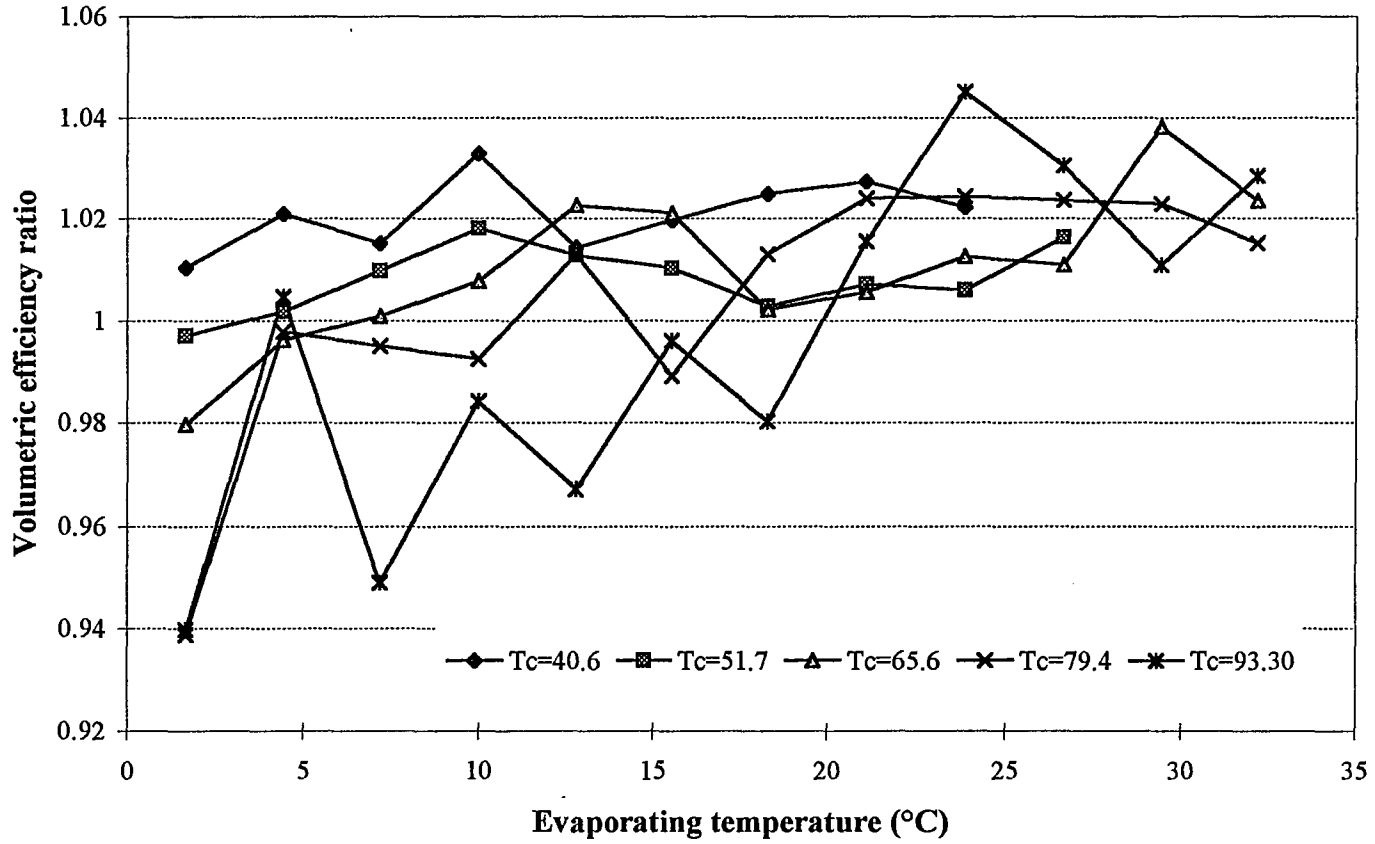


Figure 10. Volumetric efficiency ratio of HFC-236fa relative to CFC-114

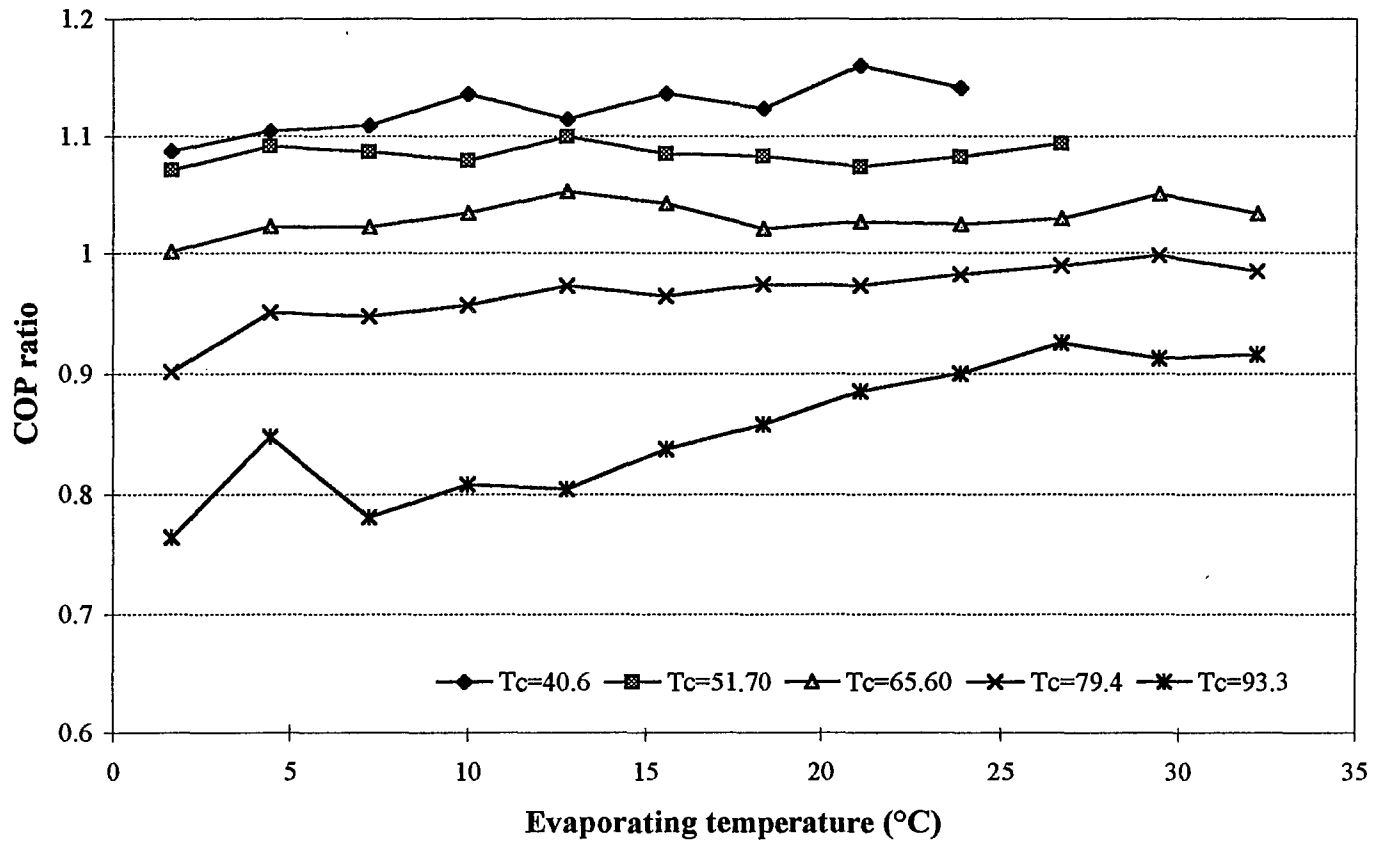


Figure 11. Coefficient of performance (experimental) ratio of HFC-236fa relative to CFC-114

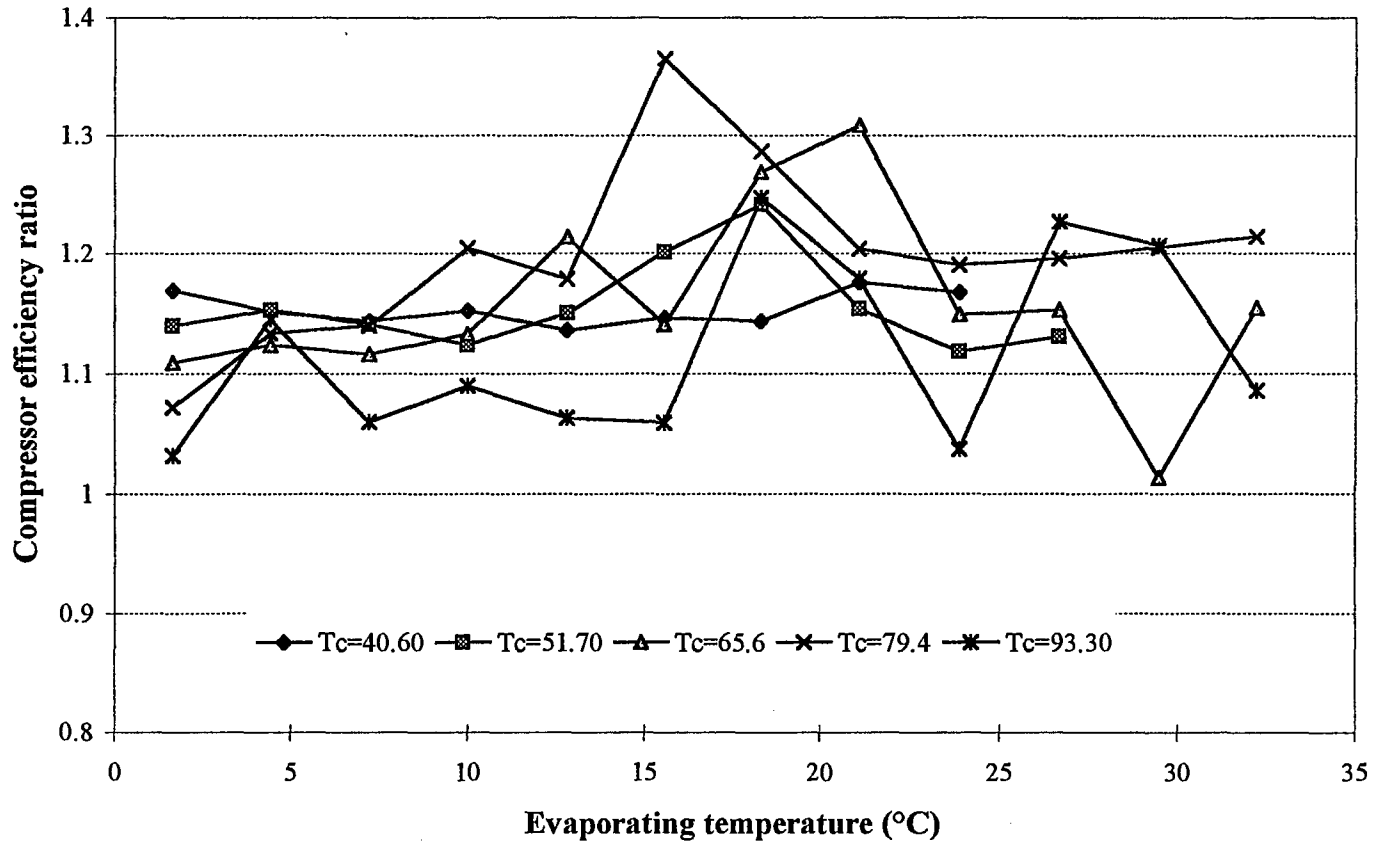


Figure 12. Compressor isentropic efficiency ratio of HFC-236fa relative to CFC-114

## 5. REFERENCES

ANSI/ASHRAE 97-1989, Sealed Glass Tube Method to Test the Chemical Stability of Material for Use Within Refrigerant Systems, American Society of Heating, Refrigerating and Air-Conditioning Engineers, 1791 Tullie Circle, NE, Atlanta, GA, 1989.

ASHRAE Standard 34-1992, Number Designation and Safety Classification of Refrigerants, American Society of Heating, Refrigerating and Air-Conditioning Engineers 1791 Tullie Circle, NE, Atlanta, GA, 1992.

ASHRAE Standard 23-1993, Methods of Testing for Rating Positive Displacement Refrigerant Compressors, American Society of Heating, Refrigerating and Air-Conditioning Engineers, 1791 Tullie Circle, NE, Atlanta, GA, 1993.

Association of Florida Phosphate Chemists, Methods of Analysis for Phosphate Rock; No.14 Fluoride-F in Methods Used and Adopted by the Association of Florida Phosphate Chemists, Seventh Edition, P. O. Box 1645, Bartow, FL, 1991.

ASTM (American Society for Testing and Materials), Standard Test Methods for Measuring Wear Properties of Fluid Lubricants (Falex Pin and Vee Block Methods), ASTM Designation: D2670-88, 1916 Race St., Philadelphia, PA, 1988.

ASTM (American Society for Testing and Materials), Standard Test Methods for Measurement of Extreme Pressure Properties of Fluid Lubricants (Falex Pin and Vee Block Methods), ASTM Designation: D3233-92, 1916 Race St., Philadelphia, PA, 1992.

ASTM (American Society for Testing and Materials), Standard Test Method for Concentration Limits of Flammability of Chemicals, ASTM Designation: E681-94, 1916 Race St., Philadelphia, PA, 1994.

EPA (U. S. Environmental Protection Agency) Health Effects Test Guidelines, Office of Toxic Substances, Federal Register, **50**, No. 188, Part 798.1150, September 1985.

IPCC (Intergovernmental Panel on Climate Change), Climate Change 1995, Cambridge University Press, UK, 1995.

Jacobsen, R. T. and R. B. Stewart, Thermodynamic Properties of Nitrogen Including Liquid and Vapor Phases from 63 K to 2000 K with Pressures to 10,000 Bar, J. Phys. Chem. Reference Data, **2**, 757, 1973.

JPL (Jet Propulsion Laboratory), Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation Number 11, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA December 15, 1994.

Kazachki, G. S., and C. L. Gage, Thermodynamic Evaluation and Compressor Characteristics of HFC-236ea and HFC-245ca as CFC-114 and CFC-11 Replacements in Chillers, Presented at the 1993 International CFC and Halon Alternative Conference, Washington, DC, October 20-22, 1993.

Kazachki, G. S., C. L. Gage, and R. V. Hendriks, Chlorine-Free Alternatives for CFC-114: Theoretical and Experimental Investigations, Presented at the 1995 International Congress of Refrigeration, the Netherlands, August 20, 1995.

Kazachki, G. S., C. L. Gage, R. V. Hendriks, and W. J. Rhodes, Investigation of HFC-236ea and HFC-236fa as CFC-114 Replacements in High Temperature Heat Pumps, Presented at

International Institute of Refrigeration Conference: CFCs, the Day After, Padua, Italy, September 21 - 23, 1994.

Nelson, T. P., Findings of the Chlorofluorocarbon Chemical Substitutes International Committee, EPA-600/9-88-009 (NTIS PB88-195664), April 1988.

NIST Standard Reference Database 23, Thermodynamic Properties of Refrigerants and Refrigerant Mixtures (REFPROP) Version 5.0, National Institute of Standards and Technology, Boulder, CO, 1996.

Skaggs, S. R., E. W. Heinonen, T. A. Moore, and J. A. Kirst, Low Ozone-Depleting Halocarbons as Total-Flood Agents: Volume 2 - Laboratory Scale Fire Suppression and Explosion Prevention Testing, EPA-600/R-95-150b (NTIS PB96-109079), September 1995.

Smith, N. D. and M. W. Tufts, Thermodynamic Properties of Selected HFC-Refrigerants, International Journal of Heating, Ventilating, Air-Conditioning and Refrigerating Research, 2:3, 257-261, July 1996.

UNEP (United Nations Environment Programme), Montreal Protocol on Substances that Deplete the Ozone Layer - Final Act, 1987.

UOP Tarrytown Analytical Laboratory Procedure, Determination of Fluoride in Aluminosilicates by Pyrohydrolysis/Ion Selective Electrode, UOP, 25 East Algonquin Road, Des Plaines, IL, June 1978.