Refrigerant Safety

The alternative refrigerants are as safe or safer than those they replace, but more care is needed with all refrigerants

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Dictionaries define safety as being free from harm or the risk of injury or loss. The concerns usually associated with refrigerants are toxicity, flammability and physical hazards. Are refrigerants completely safe? No, all pose one or more of these concerns. But can refrigerants, and especially the new refrigerants, be used safely? Yes, and generally more so than in the past.

Refrigerant history

The first practical refrigerating machine was built by Jacob Perkins in 1834; it used ether in a vapor compression cycle. The first absorption machine was developed by Edmond Carré in 1850, using water and sulfuric acid. His brother, Ferdinand Carré, demonstrated an ammonia/water refrigeration machine in 1859.[1]

A mixture called chemogene (consisting of petrol ether and naphtha) was patented as a refrigerant for vapor compression systems in 1866. Carbon dioxide was introduced as a refrigerant in the same year.[1-3]

Ammonia was first used in vapor compression systems in 1873, sulfur dioxide and methyl ether in 1875, and methyl chloride in 1878. Dichloroethene (dilene) was used in Willis Carrier's first centrifugal compressors, and was replaced with methylene chloride in 1926.[1-3]

Nearly all of the early refrigerants were flammable, toxic or both, and some also were highly reactive. Accidents were common.

The task of finding a nonflammable refrigerant with good stability was given to Thomas Midgley in 1926. He already had established himself by finding tetraethyl lead, to improve the octane rating of gasoline.

With his associates Henne and McNary, Midgley observed that the refrigerants then in use comprised relatively few chemical elements, clustered in an intersecting row and column of the periodic table of elements. The element at the intersection was fluorine, known to be toxic by itself. However, Midgley and his collaborators felt that compounds containing it should be both nontoxic and nonflammable.[4]

Their attention was drawn to organic fluorides by an error in the literature. It showed the boiling point for tetrafluoromethane (carbon tetrafluoride) to be high compared to those for other fluorinated compounds. The correct boiling temperature subsequently was found to be much lower. Nevertheless, the incorrect value was in the range sought and led to evaluation of organic fluorides as candidates.[5]

The shorthand convention later introduced to simplify identification of the organic fluorides, for a systematic search, is used today as the numbering system for refrigerants. The number designations unambiguously indicate both the chemical compositions and structures.

Within three days of starting, Midgley and his collaborators had identified and synthesized dichlorodifluoromethane, now known as R-12.[4]

The first toxicity test was performed by exposing a guinea pig to the new compound. Surprisingly, the animal was completely unaffected, but it died when the test was repeated with another sample.

Subsequent examination of the antimony trifluoride (used to prepare the dichlorodifluoromethane from carbon tetrachloride) showed that four of the five bottles available at the time contained water. This contaminant forms phosgene ($COCl_2$) during the reaction of antimony trifluoride with carbon tetrachloride. Had the initial test used one of the other samples, the discovery of organic fluoride refrigerants might well have been delayed for years.[2]

The development of fluorocarbon refrigerants was announced in April 1930.[5] To demonstrate the safety of the new compounds, at a meeting of the American Chemical Society, Midgley inhaled R-12 and blew out a candle with it.[6] While this demonstration was dramatic, it would be a clear violation of safe handling practices today.

CFC refrigerants

Commercial chlorofluorocarbon (CFC) production began with R-12 in early 1931, R-11 in 1932, R-114 in 1933, and R-113 in 1934. The first hydrochlorofluorocarbon (HCFC) refrigerant, R-22, was produced in 1936.

By 1963, these five products accounted for 98% of the total production of the organic fluorine industry. Annual sales had reached 372 million pounds, one-half of it R-12.[1] These chlorofluorochemicals were viewed as nearly nontoxic, nonflammable and highly stable, in addition to offering

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J. M. Calm, "Refrigerant Safety," *ASHRAE Journal*, 36(7):17-26, July 1994

good thermodynamic properties and materials compatibility at low cost.

Almost 50 years passed between the introduction of CFCs and recognition of their harm to the environment when released. Specific concerns relate to their depletion of stratospheric ozone and to possible global warming by their actions as greenhouse gases. Ironically, the high stability of CFCs enables them to deliver ozone-depleting chlorine to the stratosphere. The same stability prolongs their atmospheric lifetimes, and thus their persistence as greenhouse gases.

Ideal refrigerants

In addition to having the desired thermodynamic properties, an ideal refrigerant should be nontoxic, nonflammable, completely stable inside a system, environmentally benign even with respect to decomposition products, and abundantly available or easy to manufacture.

Also, it should be self-lubricating (or at least compatible with lubricants), compatible with other materials used to fabricate and service refrigeration systems, easy to handle and detect, and low in cost. It should not require extreme pressures, either high or low.

There are additional criteria, but no current refrigerants are ideal even based on this partial list. Furthermore, no ideal refrigerants are likely to be discovered in the future.

Toxicity

A fundamental tenet of toxicology, attributed to Paracelsus in the 16th Century, is *dosis solo facit venenum*, or *the dose makes the poison*.[7] All substances are poisons in sufficient amounts. For example, toxic effects have been observed for such common substances as water, table salt, oxygen and carbon dioxide in extreme quantities.

The difference between those substances regarded as *safe* and those viewed as *toxic* is the quantity or concentration needed to cause harm and, in some cases, the duration or repetition of exposures. Substances that pose high risks with small quantities, even with short exposures, are regarded as highly toxic. Those for which practical exposures cause no harm are viewed as safer.

There are several reasons that toxicity concerns have surfaced with the introduction of new refrigerants. First, they are less familiar. Second, public consciousness of health hazards is growing. Manufacturer concerns with liability also have increased. Third, few refrigerant users fully understand the measures and terminology used to report the extensive toxicity data being gathered.[8] And finally, the new chemicals are somewhat less stable when released and exposed to air, water vapor, other atmospheric chemicals and sunlight. This increased reactivity is desired to reduce atmospheric longevity, and thereby to reduce the fraction of emissions that reaches the stratospheric ozone layer or that persists in the atmosphere as a greenhouse gas.

While toxicity often increases with higher reactivity, atmospheric reactivity is not necessarily pertinent. The most toxic compounds are those with sufficient stability to enter the body and then decompose or destructively metabolize in a critical organ. For example, most CFCs are very stable in the atmosphere, generally less stable than either HCFCs or hydrofluorocarbons (HFCs) in refrigeration systems, and generally have comparable or greater acute toxicity than HCFCs or HFCs.

Concerns with refrigerant safety have been heightened by negative marketing by competing equipment vendors. Frequent overstatement, to influence customer perceptions, coupled with contradictions have fueled discomfort in refrigerant choices for all of the alternative refrigerants.

Acute versus chronic risks. Acute toxicity refers to the impacts of single exposures, often at high concentrations. It suggests the possible risk levels for the consequences of accidental releases, such as from a spill or rupture. It also is a gauge for service operations in which high exposures may be experienced for brief periods, such as upon opening a compressor or removing a gasket that may have refrigerant trapped under it.

Chronic toxicity refers to the effects of repeated or sustained exposures over a long period, such as that experienced in a lifetime of working in machinery rooms. Few technicians actually spend their full day in machinery rooms and concentrations may fluctuate. Therefore, most chronic exposure indices are expressed as time-weighted average (TWA) values.

The nature of chronic effects is such that most can be anticipated and/or monitored, and occupational safety measures can be taken to minimize their impacts. For example, refrigerant concentrations can be lowered by designing equipment with reduced leakage and promptly repairing leaks that do occur. Refrigerant sensors can also be used to sense and warn technicians of concentration increases. Further measures are identified below, in the discussion of safety standards.

From a safety perspective, the goal is to reduce both acute and chronic risks.

PAFT tests. The Programme for Alternative Fluorocarbon Toxicity Testing (PAFT) is a cooperative effort sponsored by the major CFC producers from nine countries. PAFT was designed to accelerate the development of toxicology data for fluorocarbon substitutes, as refrigerants and for other purposes. Examples of the other uses include as blowing agents, aerosol propellants and solvents.

The PAFT research entails more than 100 individual toxicology tests by more than a dozen laboratories in Europe, Japan and the United States. The first tests were launched in 1987, to address R-123 and R-134a (PAFT I). Subsequent programs were initiated for R-141b (PAFT II), R-124 and R-125 (PAFT III), R-225ca and R-225cb (PAFT IV), and R-32 (PAFT V).[9] The cost of testing for each compound is $1 million to $5 million, and the duration is two to six years, depending on the specific tests deemed necessary or indicated by initial findings.[10]

These PAFT studies investigate acute toxicity (short-term exposures to high concentrations, such as from accidental releases), subchronic toxicity (repeated exposure to determine any overall toxicological effect), and chronic toxicity and carcinogicity (lifetime testing to assess late-in-life toxicity or potential to cause cancer).[10]

The experiments also gauge genotoxicity (effects on genetic material, an early screen for possible cancer-inducing activity), reproductive and developmental toxicity (teratology, assessment of the effects on the reproductive system and of the potential for causing birth defects), and ecotoxicity (assessment of potential to affect living organisms in the environment).[10]

A new program initiated in 1994, PAFT M, is addressing the mechanistic causes of tumors and other effects observed in other programs. PAFT M was spurred by findings of benign tumors in earlier tests of R-123, R-134a and R-141b. Although the tumors occurred late in life and were

neither cancerous nor life threatening, a better understanding of causal effects is being sought.

Table 1 explains key toxicity and safety terminology to assist readers in understanding the following summaries.

R-123 toxicology.[10] Tests of R-123 indicate that it has very low acute inhalation toxicity, as measured by the concentration that causes 50% mortality in experimental animals: a 4-hour LC_{50} of 32,000 ppm in rats.

A cardiac sensitization response was observed at approximately 20,000 ppm. This response was measured in experimental screening with dogs, with simultaneous injection of epinephrine to simulate human stress reactions. Anesthetic-like effects (weakness, disorientation or incoordination) were observed at concentrations greater than 5,000 ppm, or 0.5%. R-123 has very low dermal toxicity (by skin application) and is only a mild eye irritant.

Long-term inhalation of R-123 caused an increase in the incidence of benign tumors in the liver, pancreas and testis of rats. None of the tumors attributable to the exposures were malignant or life-threatening; all occurred near the end of the study, late in the lives of the test specimens. The exposed animals actually exhibited higher survival rates at the end of testing than those in the control group.

The rats exposed to higher concentrations also experienced slight reductions in body weight and decreases in cholesterol and triglyceride levels. Studies are continuing to investigate the biological relevance of the tumors to humans. The tests completed to date indicate that R-123 is neither a developmental toxicant nor a genotoxin.

Based on the findings of extensive testing, R-123 has been deemed to have low toxicity.[10] Refrigerant manufacturers recommend that long-term, occupational exposures not exceed limits of 10 and 30 ppm, on 8-hour time-weighted average (TWA) bases. One manufacturer suggests a TWA limit of 100 ppm, but is expected to revise this recommendation to somewhere in the 10 to 30 ppm range.

The differences in recommended limits stem from conservative interpretations of the data. As discussed below,

Table 1. Glossary of Safety Terminology

acute toxicity	The effect of a single, short-term exposure, as might occur during an accidental release
Ames assay	A test for mutagenicity on bacteria, designed as a screen for possible carcinogens
benign	Not malignant; not likely to cause death or deterioration
carcinogen	A substance that causes cancer
cardiac sensitization	An effect in which the heart is rendered more sensitive to the action of adrenalin and similar drugs, possibly resulting in cardiac arrythmia and arrest (heart attack)
Ceiling	An exposure level (as in PEL-C, REL-C or TLV-C) that should not be exceeded during any part of the day, assessed as a 15-minute TWA unless otherwise specified
chronic toxicity	Long-term toxicity effects, generally assessed over the lifetime of test animals to gauge late-in-life signs of toxicity
dermal	Of or relating to the skin
genotoxicity	Effects on genes or chromosomes, an early screen for possible cancer-inducing activity
IDLH	*Immediately Dangerous to Life and Health:* The maximum concentration of airborne contaminants, normally expressed as parts per million (ppm), from which one could escape within 30 minutes without a respirator and without experiencing any escape impairing (severe eye irritation) or irreversible health effects. Set by the US National Institute of Occupational Safety and Health (NIOSH).
ingestion	Taken into the body by mouth or swallowing
inhalation	Taken into the body by breathing
LC_{50}	A measure of acute, inhalation toxicity representing a lethal concentration for 50% of exposed test animals
LFL	*Lower Flammability Limit:* The minimum concentration in air at which flame propagation occurs
mouse micronucleus assay	A test for changes in chromosomes in a mouse, designed as a screen for possible mutagens and carcinogens
NOEL	*No Observed Effect Level:* The maximum dose at which no signs of harm are observed
mutagen	A substance that causes a change in the amount or structure of genetic material
PAFT	*Programme for Alternative Fluorocarbon Toxicity Testing:* A cooperative effort to accelerate the development of toxicology data for fluorocarbon substitutes
PEL	*Permissible Exposure Level:* The TWA concentration that must not be exceeded during any eight-hour workshift of a 40-hour work week. Set by the US Occupational Safety and Health Administration (OSHA). Chemical manufacturers publish similar recommendations (acceptable exposure level, AEL; industrial exposure limit, IEL; or occupational exposure limit, OEL, depending on the company), generally for substances for which a PEL has not been established.
ppm	parts per million (generally in air at 25°C, 77°F, and 1 atmosphere of pressure, 14.7 psia); may be converted to percentages by dividing by 10,000
REL	*Recommended Exposure Limit:* A recommended occupational exposure limit generally on a TWA basis for up to 10 hour/day during a 40 hour work week; may also be on a STEL or Ceiling basis; set by NIOSH
STEL	*Short-Term Exposure Limit*
TLV	*Threshold Limit Value:* The airborne concentration of a substance to which nearly all workers may be exposed without adverse health effects; set by the American Conference of Government Industrial Hygienists (ACGIH).
TWA	*Time-Weighted Average* for concentrations
subchronic toxicity	The effects obtained after repeated exposures to a chemical, usually for 90 days
UFL	*Upper Flammability Limit:* The maximum concentration in air at which flame propagation occurs
WEEL	*Workplace Environmental Exposure Limit.* Set by the American Industrial Hygiene Association (AIHA).

occupational exposures can be held well below even the most stringent of these recommendations.

The exposure limits are based on chronic rather than acute toxicity, and are below the levels at which toxic effects were observed in the laboratory tests. Higher concentrations are allowable for short periods, but exposures still should be kept to the minimum practicable, as for all chemicals.

R-134a toxicology.[10] R-134a also has very low acute inhalation toxicity. The lowest concentration that causes mortality in rats, the 4-hour Approximate Lethal Concentration (ALC), exceeds 500,000 ppm. The cardiac sensitization response level for R-134a is approximately 75,000 ppm. Anesthetic-like effects are observed at concentrations greater than 200,000 ppm, or 20%.

Long-term exposures with very high concentrations (50,000 ppm) caused an increased incidence of benign tumors in the testis of rats. Again, none of the observed tumors were life threatening, and all occurred near the end of the study. The evidence from all tests in cultured cells or organisms, as well as in laboratory animals, indicates that R-134a is not genotoxic and that the increased incidence in benign tumors is not due to an effect on genetic material.

The test findings indicate that R-134a has very low acute and subchronic inhalation toxicity, is not a developmental toxicant, and is not genotoxic.[10] Most refrigerant manufacturers recommend that TWA occupational exposures not exceed 1,000 ppm; this also is the level recommended by the American Industrial Hygiene Association, Workplace Environmental Exposure Limit (WEEL) Committee.[11] Again, exposures still should be kept to the practicable minimum. (A WEEL guide has not been published for R-123 at this time.)

It is important to note that the tumors attributable to the R-123 and R-134a exposures were not cancerous. The findings reflect an increase in tumor incidence compared to rats in the experimental control group, those not exposed to the refrigerants. Some tumors also were observed in this control group, but not as many.

Also, the recommended occupational exposure limit for each refrigerant is below the level at which toxic effects were observed in laboratory animals. The use of rats, dogs and other animals is based on accepted scientific procedures and sensitivities to specific concerns by species. The lower exposure limit affords both a margin of safety and a conservative reflection of potential differences, between responses in individual humans and between humans and test animals.

Other refrigerants. Information on the toxicity of other refrigerants is available from chemical manufacturers, published literature, and chemical and safety databases. The toxicology findings for other refrigerants covered by PAFT are also available.[10]

Table 2. Safety Indicators for Common Chiller Refrigerants[a]

	R-11	R-123	R-12	R-134a	R-22	R-717
Acute (Short-Term) Toxicity						
LC_{50}, 4 hr rat (ppm)	26,200	32,000	760,000	>500,000	220,000	2,000[b]
cardiac sensitization, dog (ppm)	5,000[c]	20,000	50,000	75,000	50,000	5,000
NIOSH IDLH (ppm)	10,000[d]	4,000[e]	50,000	50,000[e]	50,000[e]	500
short-term exposure limit (ppm)	1,000 card sens	1,000[f]	50,000 card sens	75,000 card sens	50,000 card sens	35 TLV-STEL
Subchronic Toxicity						
NOEL, rat(ppm)	10,000	1,000	10,000	50,000	10,000	<50
Mutagenicity or Carcinogicity						
Ames assay	negative	negative	negative	negative	negative	unknown
mouse micronucleus assay	negative	negative	negative	negative	negative	g
carcinogenic	no	no[h]	no	no[h]	weak[i]	unknown
Teratogenicity						
rats or rabbits	none	none	none	none	none	unknown
Chronic (Long-Term) Toxicity						
occupational exposure limit (ppm)	C1000 PEL, TLV-C	10-30 manu-facturers	1,000 PEL, TLV-TWA	1,000 manu-facturers	1,000 PEL, TLV-TWA	50 PEL i
Flammability						
LFL-UFL ($\%_{vol}$ in air)[31]	none[k]	none[k]	none[k]	none[k]	none[k]	15-25[l]
heat of combustion (MJ/kg)	0.9	2.1	-0.8	4.2	2.2	22.5
Safety Classification[m]	A1	B1	A1	A1	A1	B2

[a]*These data are taken from material safety data sheets (MSDSs) and other sources believed to be reliable,[10,32-36] but are not warranted by the sources or the author. The data are subject to change and must be verified before use.*

[b]*From 4 hour tests at 1,000, 2,000 and 4,000 ppm; published 1 hour LC_{50} are 7,338-19,770 ppm*

[c]*One manufacturer reports sensitization levels as low as 3,500 ppm.*

[d]*ARI recommends 5,000 ppm based on the cardiac sensitization potential.[35]*

[e]*NIOSH has not set an IDLH for this compound; the value shown is the ARI recommendation determined in a consistent manner.*

[f]*One manufacturer suggests a 60 minute limit of 1,000 ppm with a 1 minute ceiling of 2,500 ppm.*

[g]*Limited data suggest possible mutagenic effects.[36]*

[h]*increased incidence of benign (noncancerous) tumors was observed at concentrations of 5,000 and 20,000 ppm for R-123 and 50,000 ppm for R-134a*

[i]*Late-in-life, malignant tumors were found in the salivary glands of male rats exposed at 50,000 ppm. The European Chemical Industry Ecology and Toxicology Centre (ECETOC) assessment concluded that R-22 presents no carcinogenic hazard to man at exposure levels anticipated to occur in industry or from use in consumer products.[32]*

[j]*OSHA PEL is 50 ppm; ACGIH TLV-TWA is 25 ppm.*

[k]*Not flammable by ASTM E681-85 as modified by ANSI/ASHRAE Standard 34-1992 §6.1.3.[13]*

[l]*Varies by data source with LFL and UFL ranges of 14.8% to 16% and 25% to 33.4% respectively.*

[m]*ANSI/ASHRAE Standard 34-1992[13] and Addendum 34a-1993[29]*

R-123 and R-134a were summarized here as the newest of the widely used refrigerants for chillers. Other chiller refrigerants are addressed in less detail below, and a survey of toxicity data is underway, by the author, on alternative refrigerants for additional applications.[12]

Relative impacts

Table 2 summarizes safety data (including acute, subchronic and chronic toxicity indicators) for the refrigerants most commonly used in chillers. It also presents the lower and upper flammability limits (LFL and UFL) of refrigerants in air, calculated heats of combustion, and the safety classifications assigned by *ASHRAE Standard 34*.[13, 29] The table enables comparison of data for the alternative refrigerants with corresponding information for R-11 and R-12, which are being phased out to protect the environment.

Safety specialists (including toxicologists, industrial hygienists and fire prevention authorities) should be consulted for interpretations, because other data and specific conditions may be pertinent for individual applications. Also, chemical manufacturers provide frequently updated Material Safety Data Sheets (MSDSs) that summarize risks, recommend first-aid measures, and give other safety guidance. Individuals who work with refrigerants should be familiar with these documents and have access to them for reference.

R-11 and R-12 have been in wide use for more than 60 years. While some accidents have occurred with them, both are regarded as fairly safe substances. Both have been used as aerosol propellants for consumer products, including cosmetics likely to be inhaled or sprayed on exposed skin. Both are used as propellants in metered dose inhalers, intended for inhalation with medications.

As indicated in *Table 2* and further discussed below, the alternative refrigerants introduced to replace R-11 and R-12 are safer in many respects, especially those involving acute toxicity concerns.

R-717 (ammonia) poses higher acute toxicity and flammability concerns than the fluorochemicals listed. It still can be safely used with proper installation, service and handling procedures, especially in industrial applications. While not suited for all applications, there is opportunity for broader use of ammonia.[14] Technicians who work with it quickly point to an advantage: the pungent odor of ammonia gives warning of a leak.

Direct comparison of relative safety is complicated because no single refrigerant is the safest in every category. All of those listed in *Table 2* can be used safely, but each requires appropriate safety measures.

Many other refrigerant candidates, some with excellent thermodynamic properties, have been rejected from consideration to avoid their higher risk levels. Likewise, R-505 and R-506 were withdrawn from commercial use after discovery that one of their components, R-31, was a probable carcinogen.

R-22, R-123, R-134a and R-717 have all been approved as substitute refrigerants under the Significant New Alternatives

Program (SNAP).[15] The SNAP assessment, by the US Environmental Protection Agency (EPA), was required by the Clean Air Act Amendments of 1990 and includes consideration not only of environmental implications, but also of safety.

Other refrigerant hazards

The discussion of physical hazards will be limited because there is no real change with the new refrigerants. Most physical hazards are associated with accidents, failures or incidents of short duration.

Exposures to refrigerants, or other substances, at very low temperatures can cause frostbite. Likewise, prolonged contact, splashing into the eyes, or release of pressurized gases or liquids pose occupational hazards. Several preventive measures are recommended, including use of appropriate eye protection and gloves when there is a possibility of occupational contact.

No examination of refrigerant safety would be complete without discussion of the potential for asphyxiation. All of the fluorocarbon refrigerants are heavier than air and can displace it, thereby creating the possibility of *suffocation* with a major leak or spill. Fatal accidents have occurred with the familiar refrigerants, including a well-publicized incident involving an R-22 leak in a mall skating rink.[16]

Most refrigerant vapors cannot be seen, tasted or smelled, so there is no natural warning. *ASHRAE Standard 15* now requires leak or oxygen depletion sensors to provide a hazard indication in machinery rooms.[17] A revision to broaden the requirement for leak detectors is under consideration.

Ammonia is lighter than air, but still can pose an asphyxiation hazard if workers are incapacitated during an accident or are unable to exit for other reasons. While it will disperse fairly rapidly outdoors, ammonia can be trapped in a machinery room with ventilation at floor level, and again displace air.

Ammonia also can be corrosive to the skin and eyes in high concentrations. Its irritation level is such that workers will vacate the area quickly, if they can, when a significant leak occurs. Most people can detect its odor at concentrations far below those at which it causes harm. For this reason, ammonia sometimes is referred to as the self-warning refrigerant.

Most flammability concerns also involve acute or emergency conditions. To avoid misunderstanding of the data presented in *Table 2*, flammability increases with temperature and pressure, especially in the presence of combustible lubricants.

Accidents have occurred with refrigerants that once were viewed as completely nonflammable. For example, R-22 can ignite in air mixtures at elevated temperatures and pressures.[18] This is why mixtures of R-22 with air should never be used for leak testing; most manufacturers recommend that mixtures of R-22 with dry nitrogen be used instead.

Recognition is growing that all refrigerants containing hydrogen (including HCFCs and HFCs) are potentially combustible under some conditions.[19,20] For perspective, the required conditions are not ordinary and some of these compounds also are in use or proposed for use as fire suppressants, based on their behavior at typical conditions. Research is underway to develop tests that better characterize flammability limits and conditions.[20]

Application considerations

Boiling point differences. An argument can be made that low pressure, high boiling point refrigerants are inherently safer than high pressure fluids. The reasoning arises from two factors.

First, most of the refrigerant will remain a liquid or condense into a liquid at temperatures below the boiling point. As a

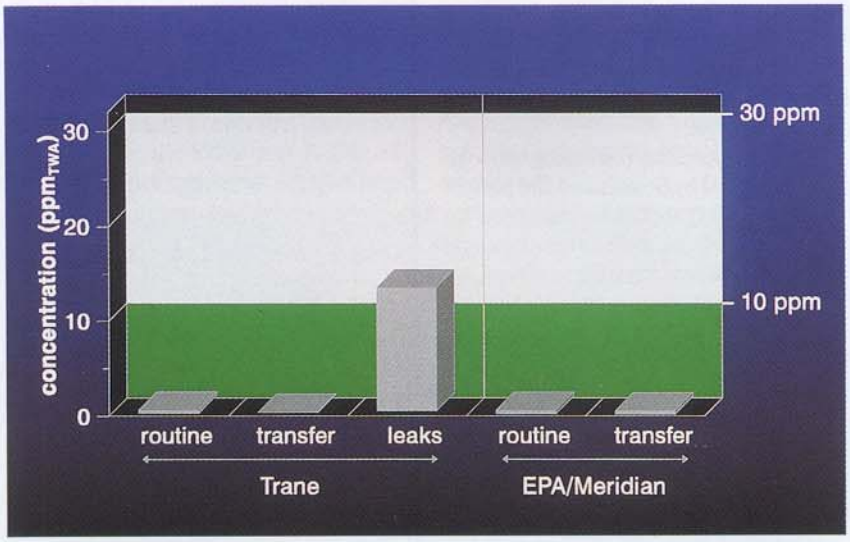

Figure 1. Measured machinery room concentrations for R-123 compared to recommended occupational exposure limits.[21,22] (The limits recommended by individual chemical manufacturers range from 10 to 30 ppm.) © James M. Calm, 1993.

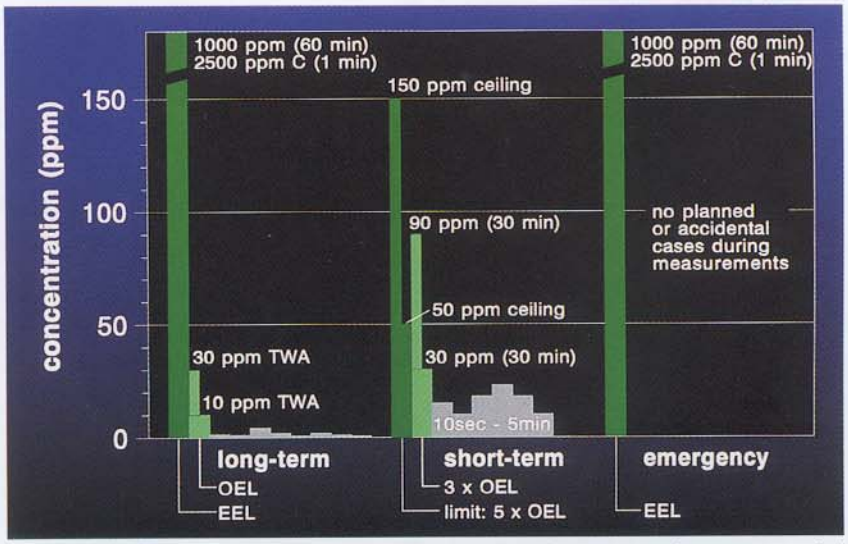

Figure 2. Measured worker exposures during internal service compared to recommended exposure limits.[23] © James M. Calm, 1993.

result, airborne concentrations impacting inhalation and flammability will be lower than for a high pressure, low boiling point fluid. The boiling temperatures at normal atmospheric pressure are 24 °C (75 °F) for R-11 and 28 °C (82 °F) for R-123, implying a small added margin for the latter.

Second, the probability of a rupture or rapid release when one occurs is lower, particularly if it occurs on the suction side of the compressor, which is below atmospheric pressure during normal operation.

Spills or leaks still pose a threat in a warm room or if the liquid refrigerant reaches a warm surface. Similarly, the slower vaporization may lead to prolonged occurrence of low concentrations, if not detected and corrected, whereas a high pressure fluid will vaporize and be removed more rapidly through ventilation. The simple answer is that neither low nor high pressure refrigerants are risk-free.

R-123 versus R-11. A more instructive comparison is between the alternative refrigerants and those they replace. Contrasting R-123 with R-11 shows the alternative refrigerant to be much safer in some respects, particularly for acute toxicity indicators.

The 4-hour LC_{50} (lethal concentration by inhalation) for rats is nearly 25% higher; the cardiac sensitization level is four times as high. As indicated in *Table 2*, these concentrations are 32,000 and 20,000 ppm for R-123, and 26,200 and 5,000 ppm for R-11. The concentrations at which anesthetic effects were observed in rats, for 10 minute exposures, were 40,000 ppm for R-123 as contrasted to 35,000 ppm for R-11.

The recommended exposure limit for chronic (long-term, repetitive or sustained) exposures to R-123 is much lower, 10 to 30 ppm time-weighted average (TWA), as discussed above. Actual concentrations were measured in two separate studies of 17 machinery rooms.[21,22] Both studies included some machinery rooms that do not satisfy minimum installation requirements.

The results of these studies are compared to the recommended exposure limits in *Figure 1*. The maximum measured concentrations are shown by the heights of bars labeled *routine, transfer* and *leaks*. They refer to concentrations during normal operation, during refrigerant transfer (charging and removal for two sites in one study and four in the other), and in the presence of identified leaks (discussed below).

The highest concentration measured (following recommended handling and service procedures) was 0.64 ppm on a TWA basis. The range of recommended limits, from 10 ppm (shown in green) to 30 ppm (in white), are 15 to 45 times higher.

Concentrations as high as 2.5 and 13.6 ppm were measured in two sites, in the vicinity of improperly sealed R-123 drums in one and with a leaking purge vent line and refrigerant drum in the other. The purge vent leak resulted from use of an incompatible material. Measurements repeated at the second site, after correction of the leaks, found a maximum of 0.56 ppm. These findings underscore the importance of proper installation, handling and storage procedures.

A further study was performed to measure concentration excursions during internal maintenance on R-123 chillers, again following recommended installation and service practices. The maximum worker exposure, for short intervals, was found to be less than 2 ppm TWA; typical values were less than 1 ppm.[23]

The American Conference of Governmental Industrial Hygienists (ACGIH) recommends that worker exposure limits, for chemicals for which specific short-term exposure limits have not been set, exceed neither three times the TWA limit for 30 minutes nor five times the TWA limit instantaneously.[24]

For R-123, that translates to 30 or 90 ppm for 30 minutes, depending on which manufacturer's recommendation is used, and 50 or 150 ppm instantaneously. One manufacturer has set a short-term, emergency exposure limit for R-123 of 1,000 ppm for up to 60 minutes, with a ceiling (not to be exceeded) of 2,500 ppm for 1 minute.

Figure 2 contrasts the measured worker exposures[23] (in grey) to the recommended short-term limits (in green). The dark green bars labeled EEL show the emergency exposure limit recommended by the manufacturer producing the largest quantity of R-123. The split bar labeled OEL, in light green, reflects the range of occupational exposure limits recommended by different chemical manufacturers. The recommended short-term limits, also in light green, are those just discussed.

Once again, none of the exposures during service operations reached the recommended limits. Moreover, the highest exposures measured tended to be for much shorter durations than specified in the limits.

A separate study of a single chiller during servicing found TWA levels of 2 to 5 ppm, but with significant deviations. Floor-level concentrations reached 500 ppm for two intervals of several minutes during the most severe operations; corresponding excursions in the breathing zone were 80 and 100 ppm. One reason for the high concentrations is that the exhaust fans, which had been set to operate at 10 ppm, were reset to 500 ppm for this test.[25]

Additional concentration data have been reported by a refrigerant manufacturer, based on conversions of its own equipment from R-11 to R-123. The conversions and monitoring were performed with participation of the three original equipment manufacturers for the chillers involved. Typical concentrations of 1 to 2 ppm were measured, even during refrigerant removal and recharging. Spikes of 8 to 20 ppm occurred, notably when making or breaking hose connections.[26]

Based on these data, the margin of safety appears to be substantial, provided that recommended practices are followed. EPA summarized its assessment as follows:

> . . . EPA has conducted extensive industrial hygiene evaluations of typical industrial chiller installations and has found that chronic employee time weighted average exposures are below 1 ppm. The level [recommended occupational exposure limit] set by manufacturers is 10 ppm. By following the appropriate monitoring procedures and safe handling of refrigerant, EPA believes that HCFC-123 can be safely used in centrifugal chillers.[27]

R-134a versus R-12. R-134a is the primary replacement for R-12 in chillers and most other applications. It offers a 50% increase over the already high cardiac sensitization level of R-12, 75,000 and 50,000 ppm, respectively.

The concentrations at which anesthetic effects were observed in rats were 205,000 ppm for R-134a for 4-hour exposures, as contrasted to 254,000 ppm for R-12 for much shorter, 10-minute exposures. Both the cardiac sensitization response and anesthetic effect levels are far above concentrations normally encountered.

R-134a is being considered as a pharmaceutical propellant for metered dose inhalers, an application requiring extremely

low toxicity levels. Based on current toxicity data, R-134a is regarded as one of the safest refrigerants yet introduced.

Comparison findings. The primary conclusion from these comparisons is that the alternative refrigerants can be used with comparable or higher safety than those they replace, especially for the most life-threatening risks under emergency conditions.

After more than 50 years of wide use, with few incidents of injury or death, R-11 and R-12 have gained acceptance as being reasonably safe. The comparative data suggest that R-22, R-123 and R-134a can be as safe or safer. Ammonia also can be used safely, but requires additional precautions and has the advantage of being self-alarming.

ASHRAE Standards 15 and *34*

A key caveat to the stated findings—for both the older and newer refrigerants—is that safe use depends on adherence to proper installation, handling and service procedures. Such procedures and the added precautions for use of ammonia are outlined in *ASHRAE Standard 15* based on the safety classifications set in *ASHRAE Standard 34*.[13,17]

The current versions of both standards have been approved by the American National Standards Institute (ANSI) as voluntary, consensus standards. Both are widely recognized in building codes and are incorporated by reference or transcription in some.[28]

Standard 34 is the definitive source for assignment of the familiar refrigerant numbers, such as R-11 or R-22, and the new number designations for blends.[13,29] It also prescribes the accepted conventions for combining these numbers with tradenames and for distinguishing them with composition-designating prefixes, such as CFC-12, HCFC-123 and HFC-134a.

Additionally, *Standard 34* provides a safety classification system and is the source to find assigned classifications. The system is summarized in *Figure 3*, and the classifications assigned for common chiller refrigerants are presented in *Table 2*.

Assignments are recommended by a committee composed of qualified individuals with a balance of interests, based on a critical review of toxicity and flammability data. The proposed classifications then are subjected to a public review. Comments are carefully evaluated and may result in reconsideration if warranted. The resulting consensus classifications have been cited in building codes and safety regulations around the world.

Returning to *Figure 3*, the A1 safety group in the lower left corner (shown in green) includes fluids with lower toxicity that do not propagate a flame under prescribed tests. The B3 group in the upper right (shown in red) includes the refrigerants with higher toxicity that either ignite at low concentrations in air or have high heats of combustion.

The level of implied risk increases as the safety classification moves from A1 to B3. Also, the divisions between lower and higher toxicity or increasing flammability are important distinctions for specific safety requirements.

	lower toxicity	higher toxicity	
higher flammability	A3	B3	LFL ≤0.10 kg/m³ or heat of combustion ≥19 000 kJ/kg
lower flammability	A2	B2	LFL >0.10 kg/m³ and heat of combustion <19 000 kJ/kg
no flame propagation	A1	B1	no LFL based on modified ASTM E681-85 test
	no identified toxicity at concentrations ≤400 ppm	evidence of toxicity below 400 ppm (based on data for TLV-TWA or consistent indices)	

Figure 3. Refrigerant safety classifications from *ASHRAE Standard 34*.[13] © James M. Calm, 1992.

When the classification system was conceived, the A1 refrigerants were those envisioned to be suitable for systems where a leak could readily enter an occupied space. Examples include those employing direct expansion, air-to-refrigerant or refrigerant-to-air heat exchangers, such as typical air conditioners.

The A1 and B1 fluids were those envisioned to be used where flammability was a high concern. The A1, B1, A2 and B2 refrigerants were those contemplated for use in indirect systems, such as those using chillers. This distinction involves an intermediate fluid, heated or cooled by the refrigerant, that in turn heats or cools air in an occupied area through a second heat exchanger or a spray. The probability of a refrigerant entering an occupied area is reduced in case of a leak. The A3 and B3 fluids were those foreseen primarily for industrial uses, when other refrigerants would not be suitable due to unique requirements.

The actual numerical criteria for classifications were determined based on both the conceptual scheme and consideration of historical practices, to afford some consistency.

The goal of classification into safety groups is to simplify safety guides and regulations, by allowing similar treatment of refrigerants with comparable risk levels. Both the toxicity and flammability criteria are being reviewed for refinement. Consideration also is being given to use of quantitative indicators of specific measures rather than discrete safety groupings.

ASHRAE Standard 15 prescribes safeguards for design, construction, installation and operation of refrigerating systems to improve safety.[17] Many specific requirements are based on the safety classifications from *Standard 34*.[13]

An effort is underway by the committees responsible for the two standards to move determination of consensus data needed for *Standard 15* into *Standard 34*, and to shift more of the interpretation of implications into *Standard 15*.

Standard 15 provides classification systems for building occupancies and refrigerating systems. Combined with the refrigerant safety classifications, it then recommends restrictions on refrigerant selection and allowed quantities by application. It identifies the maximum quantities allowed without a dedicated machinery room, for which access must be restricted to authorized personnel. The standard iden-

tifies specific safety measures with and without a machinery room.

For example, the standard requires that vessels containing refrigerants at design pressures exceeding 103 kPa gauge (15 psig) meet the design, fabrication, inspection and testing requirements of the *ASME Boiler and Pressure Vessel Code*.[30]

Standard 15 also specifies less stringent design requirements for low pressure refrigerants and alternative measures, such as listing by an approved testing laboratory, for small vessels. It explicitly requires that all refrigerating systems be protected by one or more pressure relief devices, or other means, designed to safely relieve pressure due to fire or other abnormal conditions.

A final section of *Standard 15* identifies general requirements for signs and labeling, charging and discharging of refrigerants, refrigerant storage, and responsibilities for operation and emergency shutdown.

Two of the requirements, introduced in the currently approved version, call for limiting machinery room access to authorized personnel and provision of at least one self-contained breathing apparatus (SCBA) for emergency use. The SCBA stipulation provides a recourse for corrective or recovery actions in an emergency, when an unsafe refrigerant concentration may be experienced. A second SCBA is recommended both as a backup and to enable two individuals to respond for added safety.

The committee members responsible for *Standard 15* have extensive experience in refrigerating equipment design and application. Some are involved in safety testing, building code development and insurance underwriting. Their recommendations to improve safety are again subjected to a consensus review process before final approval.

Conclusion

This article began by asking if refrigerants are completely safe and whether they can be used safely. The new, alternative refrigerants can be used with comparable or higher safety than those they replace, when applied following recommended selection, handling, installation and operating practices in equipment conforming to recognized safety standards.

The alternative refrigerants have been subjected to much more stringent qualification criteria and safety testing than in the past. There are no ideal refrigerants, and none are foreseen, but there are very good options.

None of the information in this article, in the cited standards and references, or in other guides will assure a completely safe system. The goal is to improve safety, but the most dangerous conditions occur when refrigerant users forget inherent risks. ■

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Acknowledgments

Because of the importance and sensitivities of the topic, a draft of this article was circulated to a large number of reviewers. The author appreciates comments provided by the following individuals: M. Kent Anderson (International Institute of Ammonia Refrigeration); William J. Brock (DuPont Fluoroproducts); James G. Crawford (American Standard); Lee W. Burgett, Robert G. Doerr and Eugene L. Smithart (The Trane Company); John J. Daly (consultant); Thomas W. Dekleva (ICI Klea); David A. Didion (National Institute of Standards and Technology); William Dietrich (York International Corp.); Glenn C. Hourahan (Air-Conditioning and Refrigeration Institute); Reva Rubenstein (US Environmental Protection Agency); George M. Rusch (Allied-Signal Inc.); Thomas E. Watson (Snyder-General Corp. and chairman of ASHRAE SSPC 15), and anonymous reviewers. All of the suggestions were carefully considered, but the final responsibility for the content and views in this paper is the author's.

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