Refrigerant Column, *Kyla & Värme* No. 1, 2022

Health Effects of Refrigerants

Halogenated hydrocarbons—**CFCs, HFCs and HCFCs**—were previously referred to as **"safety refrigerants."** This designation was based on the fact that they are **neither flammable nor acutely toxic**. This property was famously demonstrated shortly after they were proposed as refrigerants at a conference of the **American Chemical Society in 1930**.

During a lecture, one of the inventors, **Dr. Thomas Midgley**, demonstrated the safety of the new refrigerant by first filling his lungs with **R12** and then exhaling the gas over a lit candle, which immediately went out. The demonstration became legendary and showed that the gas was **neither poisonous nor flammable**.

Even today, **HFCs—and HFOs, which are a type of HFC derivative—are often preferred over hydrocarbons such as propane and isobutane** in many applications precisely because they are **non-flammable**.

PFAS and Refrigerants

A heated debate is currently underway concerning a large group of synthetic substances known as **PFAS**. This group consists of **more than four thousand compounds**, all characterized by **chains of carbon atoms with fluorine atoms attached**. According to the definition used by the **Swedish Chemicals Agency**, at least **one carbon atom must be bonded exclusively to fluorine atoms** for the substance to be classified as PFAS.

Under this definition, **many common refrigerants would also be considered PFAS**.

Sweden, together with several other countries, has proposed that the **entire PFAS group should be banned**. The reason is to avoid a situation in which banning one compound simply leads industry to substitute another similar substance that is not yet prohibited but may be **equally harmful**.

Already from **2023**, six PFAS substances will be banned within the EU. At the same time, work is ongoing on legislation that could **ban all PFAS substances**.

The reason for such proposals is that PFAS substances are **extremely persistent**, something that is familiar from the refrigerant debate. There is also evidence that **some PFAS compounds are harmful to human health in the long term**. For many others in the PFAS group, however, it remains unclear whether they pose a risk.

Health effects that have been observed for certain PFAS substances include:

- reduced fertility

- increased blood pressure
- developmental disorders
- low birth weight
- early puberty
- increased risk of certain cancers (including prostate, kidney and testicular cancer)
- weakened immune system
- hormonal disruption
- elevated cholesterol levels
- obesity

Because PFAS compounds are **very persistent**, they are already present throughout the **environment and even in human bodies**, and continued use may lead to **increasing concentrations over time**.

Should Refrigeration Technicians Be Concerned?

For those working with refrigerants, an important question arises: **should we be concerned about our health?** And should **HFC and HFO refrigerants really be classified as PFAS?**

A ban would have **major consequences for the refrigeration industry**.

On the **OECD website on chemical safety**, a list of PFAS substances is available (1). Both **HFCs and HFOs are listed as groups**, suggesting that they could potentially be included among substances subject to future bans.

However, this does **not automatically mean that refrigerants pose a health risk** for those working with them. The reason the proposed legislation includes all PFAS substances is mainly to prevent **dangerous substances from being replaced by similar compounds within the same group**.

The legislative proposal is still under development, and the Swedish Chemicals Agency is responsible for the work on the Swedish side. We contacted **Jenny Ivarsson**, project manager and spokesperson for the agency on these issues. She confirmed that the **OECD list is intended to define which substances could be banned**, and that it currently includes **R134a and R1234yf** (but **not R32**). At the same time, she emphasized that this is **ongoing work** and that the substances included are still under discussion. It is therefore possible that **some PFAS substances may ultimately be exempted**.

Toxicity Studies of Refrigerants

A very comprehensive article on the **flammability and toxicity of refrigerants** was published by **James Calm in 1994** (2). The article is still referenced on the website of the **U.S. Environmental Protection Agency (EPA)** (3). The EPA provides background information and refers to **ASHRAE Standard 34**, which classifies refrigerants into **Group A**

(lower toxicity) and **Group B (higher toxicity)**. The boundary between these groups is defined as the concentration at which **effects are observed at 400 ppm**.

HFC refrigerants belong to **Group A**, with the exception of **R123**, which is classified as **Group B**.

Calm's article describes work carried out under the **Program for Alternative Fluorocarbon Toxicity (PAFT)**, a collaborative research program conducted by refrigerant manufacturers during the **1990s**, when CFCs and HCFCs were being replaced by HFCs. One of the alternative refrigerants studied was **R134a**.

The PAFT studies investigated both **acute toxicity** and **long-term exposure toxicity**, including the risk of cancer.

At very high concentrations:

- **R123:** 5,000 ppm (0.5%)
- **R134a:** 200,000 ppm (20%)

anesthetic effects were observed in laboratory animals. With prolonged exposure at high concentrations, some animals developed **benign tumors**. Calm notes, however, that **occupational exposure limits are set well below the concentrations used in these experiments**.

Exposure Thresholds

The **U.S. Occupational Safety and Health Administration (OSHA)** has published a report on hazards associated with refrigerant work (4). Although the document is undated, it mentions that fluorinated hydrocarbons are expected to disappear by **2030**, suggesting that it is relatively recent.

However, the exposure thresholds provided refer only to older refrigerants such as **R12, R113 and R114**.

Table 1. Exposure thresholds for halocarbons (R12, R113, R114)(based on reference 4)

Concentration	Symptoms
1000 ppm (0.1%)	Detectable odor
75,000 – 100,000 ppm (7.5–10%)	Dizziness
200,000 ppm (20%)	Drowsiness, unconsciousness
300,000 ppm (30%)	Potentially fatal after only a few breaths

These values can be compared with the **Swedish occupational exposure limits for R134a**, which are:

- **500 ppm** for long-term exposure (8 hours)
- **750 ppm** for short-term exposure (15 minutes) (5)

Submarine Exposure Limits

Another study prepared for the **U.S. Navy** proposes exposure limits for refrigerants used in **submarines** (7). The study distinguishes between **long-term exposure (90 days)** and **short-term exposure (1 hour)**.

Table 2. Proposed exposure limits for refrigerants in U.S. Navy submarines

Refrigerant	Short-term limit (1 h)	Long-term limit (90 days)
R236fa	10,000 ppm	—
R23	20,000 ppm	350 ppm
R404A	12,900 ppm	800 ppm
R125	7,500 ppm	900 ppm
R143a	25,000 ppm	700 ppm
R134a	8,000 ppm	900 ppm

Short-term limits for **R236fa** were set at one-tenth of the concentration at which **cardiac effects were observed in dogs after five minutes of exposure**. Most other limits were also based on **animal experiments**.

The exception is the short-term exposure limit for **R134a**, which was based on **human tests**, where **no effects were observed after one hour of exposure at 8000 ppm**.

Studies on HFO Refrigerants

A search in scientific literature databases shows several studies examining **short- to medium-term exposure (up to several weeks)** of laboratory animals to various **HFC and HFO refrigerants**, with results similar to those described above.

In several cases, however, it is noted that **long-term studies examining cancer risk or genetic effects are lacking**.

It is worth remembering that **CFCs were previously used as propellants in asthma inhalers**, so any serious long-term health effects would likely have been noticed.

A useful overview of the scientific knowledge—although published in **1999**—was produced by **Occupational Medicine in Gothenburg** (8). The report notes that exposure to CFCs via inhalers has in some cases led to **increased airway resistance**.

The report also includes measurements of refrigerant concentrations in the working environment of refrigeration technicians using **personal monitoring equipment**. Four studies were summarized.

’The results showed:

- occasional **very high peaks up to 35,000 ppm**, lasting only seconds when pipes were cut
- several instances where the **short-term limit of 750 ppm was exceeded**
- however, the **8-hour average exposure never exceeded 500 ppm**

These measurements were mainly carried out during the **1980s**, and current requirements for refrigerant recovery likely mean that technicians today are exposed to **lower concentrations**.

Are HFO Refrigerants More Dangerous?

The studies cited above mainly concern **CFC and HFC refrigerants**. A relevant question is whether **HFO refrigerants**, which are chemically more reactive, might pose greater health risks.

In **2017**, the **Norwegian Environment Agency** published a report examining both **environmental and health effects of HFO refrigerants** (9). The report concluded that the **health risks of R1234yf—the most widely used HFO—appear to be low**.

However, the report also pointed out that increasing concentrations of the degradation product **TFA (trifluoroacetic acid)** in the environment may represent a **future risk to both ecosystems and human health**.

Another review was published by **Refolution Industriekälte** (10), an organization advocating greater use of **natural refrigerants**. This report also highlighted the potential environmental and health risks of **TFA**, but found little evidence suggesting that **HFO refrigerants themselves pose significant health risks**. Nevertheless, the authors emphasized that **further research is needed**.

Additional Risks

Because **HFC refrigerants have almost no odor**, there is a risk that workers may not realize they are being exposed to high concentrations. This can create a risk of **asphyxiation**. Such accidents have occurred on **fishing vessels**, where leaked refrigerant was not adequately ventilated.

Frostbite injuries are also a risk associated with all refrigerants and should not be overlooked.

The OSHA report (4) also highlights the danger of **hot work** in the presence of refrigerants. When **HFC or HFO refrigerants burn**, they may form **hydrogen fluoride (HF)**, **carbonyl difluoride**, and other highly toxic gases.

For **chlorine-containing refrigerants** (CFC, HCFC, HCFO), combustion can also produce **hydrochloric acid (HCl)** and small amounts of **phosgene ($COCl_2$)**. A short report from the **Swedish Defence Research Agency (FOI)** describes the health effects of these gases in more detail (6).

Conclusions

In summary, the risk of injury caused by inhalation of **pure HFC or HFO refrigerants** appears to be **low**. Nevertheless, additional research has been requested regarding **long-term exposure effects**, particularly for **HFO refrigerants**.

Most likely, the health risks associated with refrigerants themselves are **much smaller than the risks posed by toxic gases formed during combustion**, especially during hot work when refrigerant residues or oil decomposition products may still be present in the system.