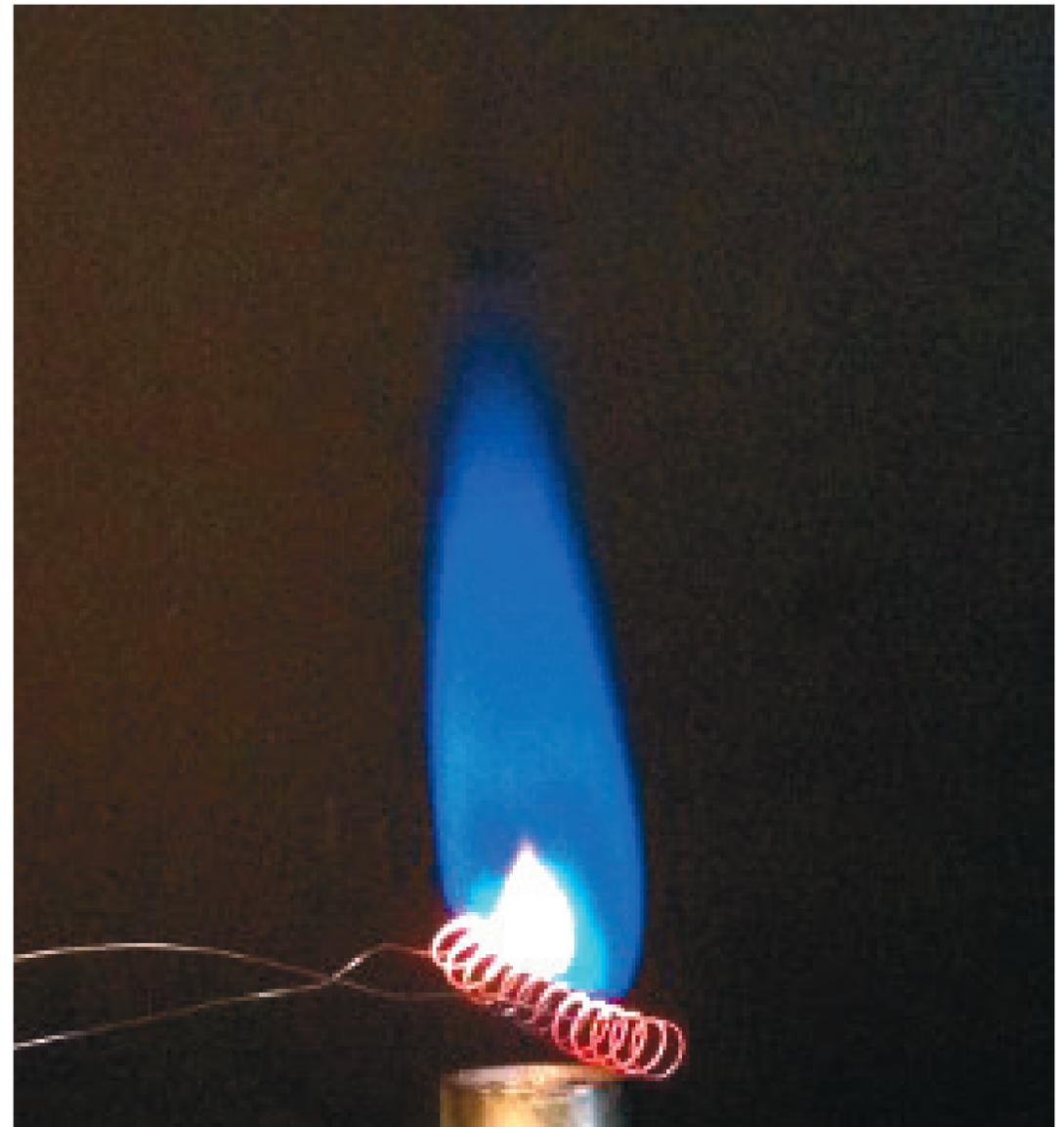




# Identification and brief toxicological assessment of combustion products of the refrigerant HFO-1234yf

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FOI-R--4285--SE  
ISSN 1650-1942

June 2016

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Titel	Gasanalys vid brand av freonen HFO-1234yf
Title	Identification and brief toxicological assessment of combustion products of the refrigerant HFO-1234yf
Rapportnr/Report no	FOI-R--4285--SE
Månad/Month	June
Utgivningsår/Year	2016
Antal sidor/Pages	20 p
ISSN	1650-1942
Kund/Customer	Umeå Universitet
Forskningsområde	2. CBRN-frågor och icke-spridning
FoT-område	
Projektnr/Project no	E4250
Godkänd av/Approved by	Åsa Scott
Ansvarig avdelning	CBRN-skydd och säkerhet

Bild/Cover: FOI/Lars Hägglund

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## Sammanfattning

Denna studie syftar till att påvisa vilka kemiska ämnen som bildas vid antändning av det nya kylmediet HFO-1234yf samt att kort beskriva vilka eventuella negativa hälsoeffekter dessa ämnen kan medföra vid en exponering. Försöket utfördes genom kontrollerad förbränning i luft med ett dynamiskt system vid två olika luft/freon-förhållanden. De kemiska ämnena identifierades med GC-MS, FT-IR och Drägerorr.

Tjugofem ämnen identifierades och emissionsfaktorer togs fram som massa emissionsprodukt per massa tillförd HFO-1234yf. De kemiska ämnen som uppmättes i högst halt var icke-förbränd HFO-1234yf (220-480 mg/g), karbonyldifluorid (170-360 mg/g), koldioxid (120-320 mg/g) och vätefluorid (70-240 mg/g). Både karbonyldifluorid och vätefluorid är starkt frätande för vävnad såsom hud, ögon och luftvägar. Karbonylfluorid är reaktiv med vatten och vid kontakt med fuktig luft, mukus i luftvägarna, och ögon sönderdelas karbonylfluorid till vätefluorid och koldioxid. Vätefluorid kan tränga in i vävnader såsom luftvägar och hud. Vid exponering för vätefluorid kan hypokalcemi uppstå genom att vätefluorid binder till kalcium. Även kolmonoxid (5-80 mg/g) kunde detekteras i brandgasen. Inandning av kolmonoxid leder till syrebrist, detta i och med att kolmonoxid jämfört med syre binder starkare till hemoglobin. Även flera fluorerade kolväten uppmättes i rökgasen men i avsevärt lägre halter. Majoriteten av dessa anses inte vara akuttoxiska för människa.

Vid genomförandet av studien påvisades det att HFO-1234yf är svårantändligt och behöver en het yta för att bibehålla en låga. Sannolikheten för brand av HFO-1234yf och därmed bildandet av giftiga gaser ser vi som mycket låg. Likväl, vid fordonsbrand kan temperaturer tänkas uppnås som kan riskera att antända kylmediet. Avsikten med denna rapport är att ge information till bilindustri, räddningstjänst och andra intressenter vid implementeringen av nya kylmedier samt att belysa konsekvenserna om brand av HFO-1234yf ändå skulle inträffa. Rapporten avser inte att kartlägga brandbenägenhet eller exponeringsnivån av giftig brandgas vid t.ex. trafikskadehändelser, för detta krävs ytterligare studier.

## Summary

This study aims to identify chemical reaction products upon combustion of the new freon HFO-1234yf intended for mobile air-conditioning systems. It also summarize possible negative health effects of the identified gases. The experiment was performed with controlled combustion of HFO-1234yf in a dynamic laboratory setup at two different air-to-freon mixtures. The chemicals were detected by means of GC-MS, FT-IR, and Draeger tubes.

Twenty-five chemicals were identified and emission factors were determined as mass of the emission product per supplied HFO-1234yf. The major detected components were unburned HFO-1234yf (220-480 mg/g), carbonyl difluoride (170-360 mg/g), carbon dioxide (120-320 mg/g) and hydrogen fluoride (70-240 mg/g).

Both carbonyl difluoride and hydrogen fluoride are strongly corrosive to tissues such as skin, eyes and the respiratory tract. Carbonyl difluoride is highly reactive with water and decomposes into hydrogen fluoride and carbon dioxide upon contact with humid air, eyes or mucus in the respiratory tract. Hydrogen fluoride can penetrate tissues and exposure to hydrogen fluoride may induce hypocalcaemia by binding to calcium. At lower levels, carbon monoxide (5-80 mg/g) was detected. Inhalation may lead to cellular hypoxia since carbon monoxide has a higher affinity to haemoglobin as compared to oxygen. In addition, a number of fluorinated hydrocarbons were detected at considerably lower levels. The majority of these are not acutely toxic to humans.

In this study, we found that HFO-1234yf required a hot surface to sustain fire. We consider the risk of fire of HFO-1234yf to be low. However, in situations with burning vehicles the temperature will possibly reach levels that ignite HFO-1234yf. The intended use for this report is to serve for automotive industry, rescue services, and other stakeholders to take the correct choices when implementing new technology of the refrigerant and to increase awareness for those who may come into contact with fire products.

## Content

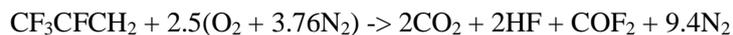
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# 1 Introduction

In response to the Kyoto protocol to reduce the anthropogenic sources of greenhouse gases the European Parliament adopted on the 17th of May 2006 a directive phasing out refrigerants of global warming potential (GWP) higher than 150 (where CO<sub>2</sub> has GWP=1)<sup>1</sup>. Because of leaks and improperly recycling of cooling systems the commonly used refrigerant hydrofluorocarbon-134a (R134a) with GWP=1300 still has a negative impact on climate change. HFO-1234yf, which presents a considerably lower GWP (less than one)<sup>2</sup>, was chosen by the automotive industry to replace R134a. However, in 2012, Daimler concluded that ignition and flammability of the new refrigerant was of concern<sup>3</sup>. Not only was HFO-1234yf (with chemical name 2,3,3,3 – Tetrafluoropropene, also known as R1234yf) considered a fire hazard, it was also shown that hydrogen fluoride (HF), which is a highly toxic acidic gas, was formed already in contact with hot surfaces. The German authority for motor vehicle safety, KBA (Kraftfahrt Bundesamt), took action and conducted a series of independent crash tests to study the risk of fire and levels of particularly HF at different positions in the car<sup>4</sup>. At moderate speeds (40 km/h) no rupture or fire was confirmed, however when higher speeds were simulated there was an assumption of rupture and significant levels of HF. This led KBA to conclude that a general safety-problem cannot be ruled out and further tests are necessary. Nevertheless, as late as March 7th of 2014 the European Commission conducted a scientific review stating that “there is no evidence of a serious risk in the use of this refrigerant in MAC (note: mobile air conditioning systems) systems under normal and foreseeable conditions of use” and pushes back the responsibility of cars catching fire to the manufacturers<sup>5</sup>. HFO-1234yf is indeed classified to the lowest flammability class A2L<sup>6,7</sup> and in the U.S. it has been excluded from control as a volatile organic compound<sup>8</sup>.

Although the difference of opinion in fire tendency, HFO-1234yf may burn also when it is not the cause of fire. Alarming voices were heard when the combustion resulted not only in a high exchange of HF, but also in carbonyl difluoride (COF<sub>2</sub>), which is about three times as potent as chemical warfare agent phosgene used in World War I<sup>9</sup>. These results stemmed however from stoichiometric combustion of HFO-1234yf in air<sup>9,10</sup>:



At a mass basis this corresponds to 772 mg CO<sub>2</sub>, 351 mg HF, and 570 mg COF<sub>2</sub> per 1 g HFO-1234yf. In reality, combustion processes are never perfect or complete and other products such as unburned carbon (soot), carbon monoxide and incompletely combusted fuel will be formed. Factors such as temperature, pressure, availability of oxygen and presence of catalysts also influence the actual combustion products. Here we have used a dynamic small-scale open-flow system in air with a laminary premixed flame propagating from a hot surface to investigate the combustion of HFO-1234yf. This setup mimics a real scenario while allowing determination of emission factors defined as mass of the emission product per supplied HFO-1234yf.

On behalf of Umeå Universitet and Ulf Björnstig the Swedish Defense Research Agency has conducted this laboratory study to identify further combustion products of HFO-1234yf. The request is an action to influence the debate over the by-law forced introduction of refrigerants of GWP less than 150 in all new vehicles from January 1<sup>st</sup> 2017, as set out in directive 2006/40/EC of the European Union. Another substance with GWP < 150 considered for MAC systems is CO<sub>2</sub> (GWP=1 by definition). From a toxicological point of view CO<sub>2</sub> is much less harmful than HFO-1234yf, but the latter is proposed by the car industry due to its physical and technical advantages.

The presented compounds in terms of amount combustion product per amount HFO-1234yf are accompanied with a toxicological evaluation and exposure limit values. No scenario or any kind of data of exposure in the event of a real and accidental fire is given,

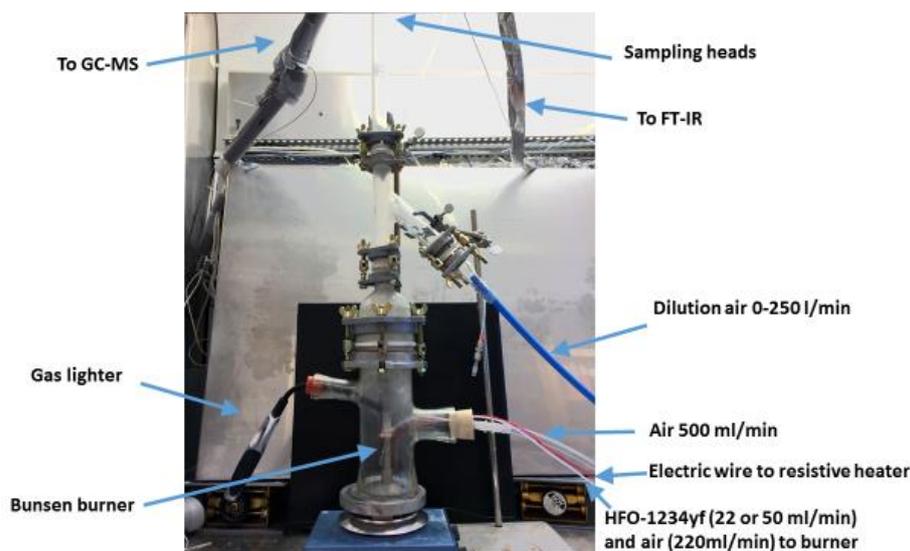
thus the results from this study shall be used only to gain insights in potential health where HFO-1234yf is indeed on fire.

## 2 Experimental

### 2.1 Setup

The combustion chamber designed for dynamic small-scale generation, dilution, and measurement of combustion gases produced from HFO-1234yf is shown in Figure 1. Controlled flows of dry filtered air ( $T = 19^{\circ}\text{C}$ , R.H.  $<1.5\%$ ) and HFO-1234yf (DuPont™ Opteon® YF gas cylinder, Linde AG, Germany) was achieved by mass flow controllers, mixed and delivered to a Bunsen burner (i.d. = 7 mm, height = 106 mm) placed inside a cylindrical borosilicate glass vessel (i.d. = 75 mm, height = 330 mm, QVF®, De Dietrich Process Systems GmbH, Germany) to produce a laminar premixed flame. To sustain fire, a coiled resistance wire ( $\text{Ø} = 0.236$  mm, Kanthal iron-chromium-aluminium alloy) was mounted a few mm above the tip of the Bunsen burner and set to glow by a voltage of  $\sim 14$  V DC (current  $\sim 1.4$  A). The fuel/air mixture was ignited with a gas lighter (it was not possible to ignite the mixture by the glowing wire alone).

To keep the flame from self-suffocation, an air atmosphere was produced inside the glass vessel by leading a laminar co-flow of dry filtered air (535 ml/min) into the glass vessel delivered by a mass flow controller. Combustion gases and air added were led out from the top of the glass vessel through a vertical borosilicate glass chimney (i.d. = 19 mm, length = 700 mm, QVF®, De Dietrich Process Systems GmbH, Germany) into which additional dry filtered air was added, by means of two additional mass flow controllers (0-5 l/min and 0-250 l/min), for further dilution of the combustion gases. This experimental set-up offered the possibility to vary the fuel/air-ratio and total flow of fuel/air mixture delivered to the Bunsen burner within a wide range. Furthermore, the system offered great flexibility regarding dilution of the combustion gases. Actual dilution settings differed depending on combustion conditions and measurement technique used. All flows was verified/calibrated by means of a primary flow meter (DC-Lite, Bios International, NJ, USA) or mass flowmeters (TSI 4100 Series, model 4143 D and model 4043 F, TSI Inc., MN, USA). Sampling probes for gas analysis (GC-MS, FTIR, Gas detection tubes) were mounted inside the chimney placed  $\sim 5$  cm below the outlet and sampled diluted combustion gas ( $19$ - $21^{\circ}\text{C}$ ) was led through heated Teflon lines ( $90^{\circ}\text{C}$ ) to respective analysis technique.



**Figure 1.** Combustion chamber for measuring the combustion gases produced from HFO-1234yf.

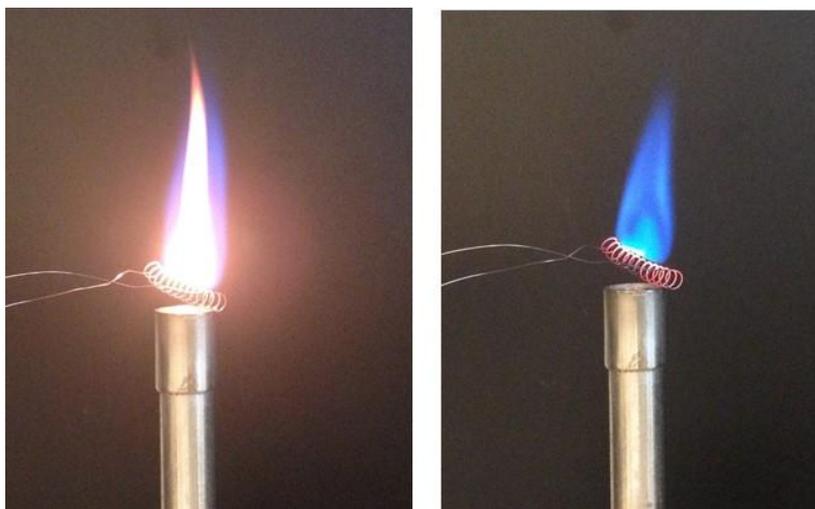
## 2.2 Combustion conditions

Airflow to the Bunsen burner was kept constant at 220 ml/min and the flow of HFO-1234yf was investigated at two levels, 22 ml/min and 50 ml/min, both corresponding to rich flames (air-fuel equivalence ratios,  $\lambda$ , of 0.84 and 0.37, respectively). Repeated experiments for each air/fuel mixture were performed. In general, lean combustion will result in a more complete combustion and produce a hotter blue flame, while rich combustion will result in incomplete combustion and produce a colder luminous yellow and sootier flame. This evidenced in figure 2, the leaner mixture burned with homogenous blue flame and the richer mixture produced a flame with yellow inner core and blue outer core.

The combination of premixed and diffusion flame from the Bunsen burner has been illustrated before by Williams et.al.<sup>11</sup>. The inner core is the reaction zone of a premixed flame, but the flame is fuel-rich, so the products of incomplete combustion burn in the outer core as a diffusion flame with the surrounding air. With this setup no leaner air/fuel mixture was possible to achieve avoiding flame extinction, however, the color of the flames indicated that the actual combustion conditions were leaner than that of the premixed flame. Furthermore, the fact that the flame propagated from the heated wire located a few millimeters above the Bunsen burner (no flame at the Bunsen burner exit) potentially allowed additional mixing with sheath air.

HFO-1234yf has been reported to have mild flammability properties characterized by low burning velocity ( $1.2 \pm 0.3$  cm/s), lower and upper flammability limits of 6.8% and 12.0%, respectively, and a remarkably high activation energy required for ignition<sup>10</sup>.

In accordance with the mild flammability reported for HFO-1234yf, the experiences from the present combustion tests were that it was not possible to achieve a self-sustainable premixed flame in air without the presence of a hot surface from which the flame could propagate. Furthermore, the flame was very sensitive to turbulence, which easily extinguished the flame. In addition, combustion pre-tests in a closed vessel showed difficulties to set a stoichiometric mixture of HFO-1234yf with *air* on fire, while a stoichiometric mixture with *oxygen* very easily ignite and combust rapidly.



**Figure 2.** Flame corresponding to richer (*left*) and leaner (*right*) air-fuel mixture burning conditions.

## 2.3 Sampling and analysis protocol

Analysis was performed using three different techniques; Gas Chromatography-Mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FT-IR), and gas

detection tubes. The latter were used for the analysis of hydrogen fluoride, one of the three main combustion products according to the stoichiometric reaction formula and previously reported as a main combustion product from HFO-1234yf<sup>9</sup> and other HFC's<sup>12</sup>. COF<sub>2</sub>, another reported main product<sup>9,12</sup> was analyzed by FT-IR. GC-MS was used for detection of a number of other combustion products. Neither HF nor COF<sub>2</sub> were possible to analyze with GC-MS, in the case of COF<sub>2</sub> possibly because of hydrolysis to CO<sub>2</sub> and HF in contact with water in the column and for HF because of its high reactivity. At each air/fuel mixture tested, three or more measurements were performed with each analytical technique.

## 2.4 GC-MS

Diluted combustion gases were sampled through a heated polytetrafluoroethylene (PTFE) tube at 90°C and 200 ml/min, filtered through a heated PTFE filter (Ø=25 mm, Zefluor, PALL, USA), and led into a 100 µl injection loop mounted in a 10-port valve connected to the GC (Agilent 7890B GC system, USA). The GC conditions were as follows: valve temperature 90 °C, inlet temperature 175 °C, split ratio of 10, GC held at 25 °C for 1 min then ramped at 10 °C/min to 160°C, then ramped at 30 °C/min to 250 °C and held for 2 minutes. Helium was used as the carrier gas at 2 ml/min on a PLOT column (GS-GAPRO, 30 m length, 0.32 mm i.d., Agilent J&W Scientific, USA) connected to the MS (Agilent 5977A MSD, USA) via a short DB-5MS column (0.3 m length, i.d. = 0.25 mm, Agilent J&W Scientific, USA). The GS-GASPRO PLOT column is ideal for GC-MS and show good performance for separation of low molecular weight hydrocarbons as well as volatile inorganic gases. The MS was operated in synchronous SIM/scan mode with a scan range of 12-250 a.m.u. and m/z for SIM-mode: 20, 28, 33, 44, 47, 66, 69, and 114. The full-scan mode allowed compound identification, while the SIM-mode allowed enhanced sensitivity for selected compounds. Full-scan data was analyzed using the software AMDIS (Automatic Mass Spectral Deconvolution and Identification Software, National Institute of Standards and Technology, NIST, Gaithersburg, Md.) and matched against the NIST Mass Spectral Library for compound identification. The selection criteria for positive identification was a net match factor above 90 (maximum match factor=100). Amounts of detected compounds were semi-quantitatively determined from a 12-point calibration curve (TIC area versus concentration, µg/l) generated for HFO-1234yf at different concentrations by dilution. Verification of this quantification method by analysis of reference concentrations of propane and CO<sub>2</sub> showed a relative error < 15%.

## 2.5 FT-IR

Diluted combustion gas was sampled through a heated PTFE tube (90°C) at 2.3 l/min for gas measurements using a portable Fourier transform infrared (FT-IR) spectroscopic gas analyzer (Gasmeter model DX-4030 FTIR Gas Analyser, Gasmeter Technologies Oy, Helsinki, Finland). The instrument was calibrated at the manufacturer except for HF and COF<sub>2</sub> for which calibration was done in-house with gas cylinders of certified reference gas (55±5.5 ppm HF in nitrogen, 50±2.5 ppm COF<sub>2</sub> in nitrogen, AGA, Sweden). Due to the incomplete combustion of HFO-1234yf some of the peaks in the spectra of the sample were interfering with spectra from the carbon difluoride, for quantification of carbonyl difluoride the adsorption at 1019 cm<sup>-1</sup> used to estimate the concentration.

## 2.6 Gas detection Tubes

Diluted combustion gas was sampled through a PTFE tube into colorimetric gas detection tubes for detection of hydrogen (Dräger-Tube 81 03 251, Drägerwerk AG & Co. KGaA, Lübeck, Germany) using an accuro Dräger-Tube pump. The relative standard deviation (RSD) using this technique is reported to be 15-20%<sup>13</sup>. Verification tests with certified HF reference resulted in a relative error below 20%.

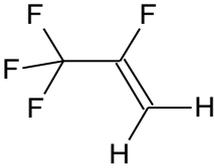
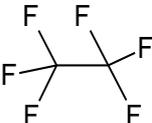
## 3 Results

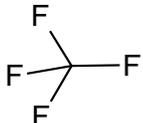
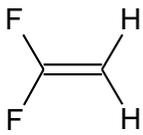
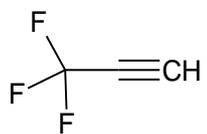
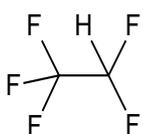
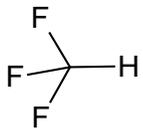
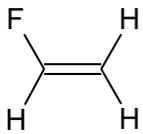
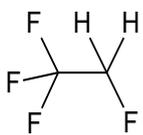
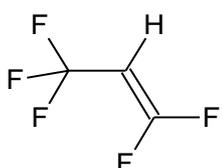
### 3.1 Chemical analysis

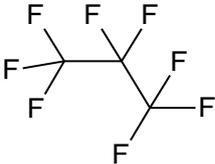
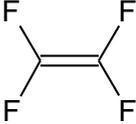
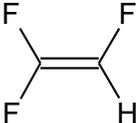
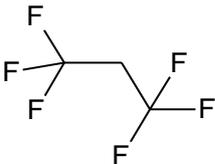
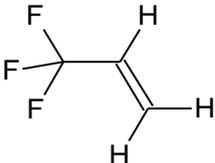
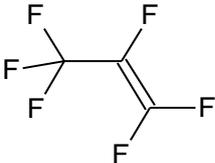
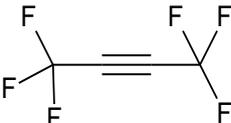
Twenty-five substances summarized in Table 1 were identified in the diluted combustion gases by means of GC-MS, FT-IR, and Dräger tubes. Emission factors in terms of mg per gram supplied HFO-1234yf are presented for each identified compound and given as a range over all performed experiments at the two different air/fuel mixtures. Selection criteria for positive identification with GC-MS was a match factor above 90.

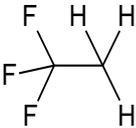
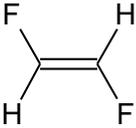
About one quarter to half of the refrigerant HFO-1234yf remained unburned through the flame (emission factor 220-480 mg/g). The rest of the refrigerant formed COF<sub>2</sub>, carbon dioxide (CO<sub>2</sub>), HF, and water as major combustion products, with emission factors ranging from 60 to 360 mg/g. Water is the only compound of these that is not expected from the combustion reaction formula. At lower concentration, GC-MS identified several fluorinated hydrocarbons, both saturated and unsaturated, with the number of carbons in the span of one to three. Within this group, hexafluoroethane (15-33 mg/g), tetrafluoromethane (6-24 mg/g), and 1,1-difluoroethene (2.4-6.6 mg/g), while lower emission factors (0.03-2 mg/g) were seen for the remaining compounds. Six compounds remained unidentified but characteristic ions in the mass-spectra indicated that these compounds also belonged to the group of fluorinated hydrocarbons.

**Table 1.** Identified combustion products of HFO-1234yf. GC-MS match factors ranged from 90 to 98.

Chemical compound	Structure	CAS#	Analytical technique	Emission factor [mg/g Fuel]
2,3,3,3-Tetrafluoropropene (HFO-1234yf)		754-12-1	GC-MS/FTIR	220-480
Carbonyl fluoride	COF <sub>2</sub>	353-50-4	FTIR	170-360
Carbon dioxide	CO <sub>2</sub>	124-38-9	GC-MS/FTIR	120-320
Hydrogen fluoride	HF	7664-39-3	Dräger	70-240
Water	H <sub>2</sub> O	7732-18-5	GC-MS	60-170
Carbon monoxide	CO	630-08-0	FTIR	5-80
Hexafluoroethane		76-16-4	GC-MS	15-33

Chemical compound	Structure	CAS#	Analytical technique	Emission factor [mg/g Fuel]
Tetrafluoromethane		75-73-0	GC-MS	6-24
1,1-Difluoroethene		75-38-7	GC-MS	2.4-6.6
Trifluoromethyl acetylene		661-54-1	GC-MS	0.2-2
Pentafluoroethane		354-33-6	GC-MS	0.6-1.6
Trifluoromethane		75-46-7	GC-MS	0.6-1.4
Fluoroethene		75-02-05	GC-MS	0.5-1.2
1,1,1,2-Tetrafluoroethane		811-97-2	GC-MS	0.7-1.1
1,1,3,3,3-Pentafluoro-1-propene		690-27-7	GC-MS	0.2-1

Chemical compound	Structure	CAS#	Analytical technique	Emission factor [mg/g Fuel]
Octafluoropropane		76-19-7	GC-MS	0.3-0.9
Tetrafluoroethene		116-14-3	GC-MS	0.2-0.8
Trifluoroethene		359-11-5	GC-MS	0.2-0.5
1,1,1,3,3,3-Hexafluoropropane		690-39-1	GC-MS	0.2-0.4
3,3,3-Trifluoropropene		677-21-4	GC-MS	0.1-0.4
Hexafluoropropene		116-15-4	GC-MS	0.04-0.3
Acetylene	$\text{HC}\equiv\text{CH}$	74-86-2	GC-MS	0.08-0.27
Bis(trifluoromethyl)acetylene		692-50-2	GC-MS	0.03-0.2

Chemical compound	Structure	CAS#	Analytical technique	Emission factor [mg/g Fuel]
1,1,1-Trifluoroethane		420-46-2	GC-MS	0.04-0.08
1,2-Difluoroethene		1691-13-0	GC-MS	<0.06
Non identified compounds (n=6, related structures)				2.5-3.9

### 3.2 Brief toxicological assessment

The present experiments have detected a complex mixture of different fluorinated hydrocarbons as well as COF<sub>2</sub>, HF and CO. The following summary gives a first indication of potential hazards related to single exposures via air, but does not take into account the possible hazards related to mixed exposures.

Amongst the detected chemicals with relatively high emission factors, COF<sub>2</sub>, HF and CO are of greatest health concern. COF<sub>2</sub> reacts immediately with water to form HF. This will take place in the airways upon contact with the lung lining fluid; mucus and surfactants. HF is highly toxic and corrosive. HF may induce pulmonary edema upon inhalation, and may cause severe burns following skin exposure. It can be adsorbed and penetrate tissues, and by binding to calcium HF may cause hypocalcemia. Damage in the form of hypocalcemia can be treated with an antidote. CO binds to haemoglobin and forms carboxyhaemoglobin which inhibits the transport of oxygen in the body resulting in hypoxia in many tissues of organs.

All the measured fluorinated hydrocarbons are considered to have low toxicity. Also, HFO-1234yf itself is considered to have low toxicity. Results from inhalation of HFO-1234yf in mice and rats showed no lethality following exposure to 101 850 and 405 800 ppm/4 hr respectively<sup>14</sup>. Schuster et al. showed that the amount of HFO-1234yf taken up in the lungs is very low, also at high exposure levels (50 000 ppm). The authors ascribed that most of the HFO-1234yf is exhaled due to the low boiling point of the substance. The absence of toxicity to this chemical is may also be related to its rapid biotransformation and elimination within the body<sup>15</sup>.

The full collection of toxicological data for the combustion products are found in table 2. In this overview we have used several databases. For several chemicals the data in these databases are based upon limited information, and, for instance the for fluorinated hydrocarbons only a general description is given.

**Table 2:** Exposure limit values, toxicological profiles and reaction to heat and fire of the combustion products of HFO-1234yf detected here. The different exposure limit values have different intended uses and different levels of certainty that must be taken into account when interpreting the data. The toxicological profiles given here are general descriptions and cannot be used for triage or medical treatment.

Chemical compound	CAS# <sup>1</sup>	AV# <sup>2</sup> mg/m <sup>3</sup>	PAC-1# <sup>3</sup> 1 hr mg/m <sup>3</sup>	PAC-2# <sup>3</sup> 1 hr mg/m <sup>3</sup>	Toxicity HSDB and Haz-Map# <sup>4</sup>	Effects of exposure to heat, fire or water HSDB# <sup>4</sup>
2,3,3,3-Tetrafluoropropene (HFO-1234yf)	754-12-1	---	10 000 <sup>T</sup> (2 200 ppm <sup>T</sup> )	110 000 <sup>E</sup> (24 000 ppm <sup>E</sup> )	---	
Carbonyl difluoride	353-50-4	---	(0.025 ppm)	0.76 <sup>A</sup> (0.28 ppm <sup>A</sup> )	HSDB: Corrosive substance. Extremely irritating to the mucous membranes of eyes, nose, throat, and mouth. Chest pain, shortness of breath respiratory irritation, bronchitis, and pulmonary oedema may occur.	Reacts with water and moist to form HF.
Hydrogen fluoride (HF)	7664-39-3	Limits (2015) LLV 1.5 mg/m <sup>3</sup> STV 1.7 mg/m <sup>3</sup>  For exposure to a mixture of fluorides and hydrogen fluorides, the level limit value for fluorides shall be applied.	0.82 <sup>A</sup> (1 ppm <sup>A</sup> )	20 <sup>A</sup> (24 ppm <sup>A</sup> )	HSDB: Highly toxic and highly corrosive. May induce skin burns and can be adsorbed through skin. Inhalation can lead to pulmonary edema and toxic pneumonia. Skin exposure or inhalation may provide risk of systemic hypocalcemia at severe intoxication. At mild to moderate intoxication: Dermal exposure can result in delayed severe pain without visible signs of injury. Ocular exposure can cause mucosal irritation. Inhalation may cause prompt mucosal irritation, dyspnea, cough and wheezing.	
Carbon monoxide	630-08-0	Limits (1990) LLV 25 mg/m <sup>3</sup>			HSDB: Binds to hemoglobin stronger than that of oxygen. Exposure may lead to cellular hypoxia and ischemia. Mild to moderate intoxication may cause headache, nausea, dizziness, vomiting, weakness, and confusion.	Flammable
Hexafluoroethane (R 116)	76-16-4	---	580 <sup>T</sup> (100 ppm <sup>T</sup> )	6 400 <sup>T</sup> (1 100 ppm <sup>T</sup> )	HSDB: (α) Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	Fire may produce irritating, corrosive and/or toxic gases.
Tetrafluoromethane (R 14)	75-73-0	---	330 <sup>T</sup> (92 ppm <sup>T</sup> )	3 600 <sup>T</sup> (1 000 ppm <sup>T</sup> )	HSDB: (α) Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	At hot surfaces above 52 °C or open flame, toxic fumes of HF are formed.

Chemical compound	CAS# <sup>1</sup>	AV# <sup>2</sup> mg/m <sup>3</sup>	PAC-1# <sup>3</sup> 1 hr mg/m <sup>3</sup>	PAC-2# <sup>3</sup> 1 hr mg/m <sup>3</sup>	Toxicity HSDB and Haz-Map# <sup>4</sup>	Effects of exposure to heat, fire or water HSDB# <sup>4</sup>
1,1-Difluoroethene (R 1132a)	75-38-7	---	3 900 <sup>T</sup> (1 500 ppm <sup>T</sup> )	15 000 <sup>T</sup> (5 600 ppm <sup>T</sup> ) possible risk of explosion at this level	HSDB: (α) Haz-Map: CNS Solvent Syndrome	Extremely flammable, is easily ignited by heat, sparks or flames. May form explosive mixtures with air.
(Trifluoromethyl)- acetylene	661-54-1	---	---	---	Haz-Map: Simple Asphyxiant	
Pentafluoroethane (R 125)	354-33-6	Limits (2005) V: LLV 2 500 mg/m <sup>3</sup> STV 3 750 mg/m <sup>3</sup>	---	---	HSDB: (α) Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	Fire may produce irritating, corrosive and/or toxic gases.
Trifluoromethane (R 23)	75-46-7	---	1 000 <sup>T</sup> (350 ppm <sup>T</sup> )	11 000 <sup>T</sup> (3 800 ppm <sup>T</sup> )	HSDB: (α) Slightly irritating to the respiratory tract. Considered as non-toxic in low concentrations. Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	Fire may produce irritating, corrosive and/or toxic gases.
Fluoroethene	75-02-5	---	1 100 <sup>T</sup> (570 ppm <sup>T</sup> )	12 000 <sup>T</sup> (6 200 ppm <sup>T</sup> ) possible risk of explosion at this level	HSDB: The vapor may cause headache and dizziness. Probably carcinogenic to humans (Group 2A). Haz-Map: CNS Solvent Syndrome, Possible Carcinogen.	Extremely flammable. Easily ignited by heat, sparks or flames. Fire may produce irritating, corrosive and/or toxic fumes including HF.
1,1,1,2- Tetrafluoroethane (R134a)	811-97-2	Limits (1996) V: LLV 2 000 mg/m <sup>3</sup> STV 3 000 mg/m <sup>3</sup>	33 000 <sup>A</sup> (8 000 ppm <sup>A</sup> )	54 000 <sup>A</sup> (13 000 ppm <sup>A</sup> )	HSDB: (α) Considered to have a low toxicity. Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	
1,1,3,3,3 Pentafluoro- 1-propene	690-27-7	---	---	---	Haz-Map: CNS Solvent Syndrome	
Octafluoropropane (R 218)	76-19-7	---	---	---	Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	

Chemical compound	CAS#1	AV#2 mg/m <sup>3</sup>	PAC-1#3 1 hr mg/m <sup>3</sup>	PAC-2#3 1 hr mg/m <sup>3</sup>	Toxicity HSDB and Haz-Map#4	Effects of exposure to heat, fire or water HSDB#4
Tetrafluoroethene	116-14-3	---	90 <sup>A</sup> (22 ppm <sup>A</sup> )	220 <sup>A</sup> (55 ppm <sup>A</sup> )	HSDB: (π) Probably carcinogenic to humans (Group 2A). Haz-Map: Simple Asphyxiant, Nephrotic, Possible Carcinogen.	Extremely flammable. Easily ignited by heat, sparks or flames. Fire may produce irritating, corrosive and/or toxic gases.
Trifluoroethene	359-11-5	---	---	---	HSDB (π) Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	
1,1,1,3,3,3-Hexafluoropropane	690-39-1	---	---	---	Haz-Map: LCLo (rat) > 195 000 ppm/ 4hr. CNS Solvent Syndrome, Simple Asphyxiant	
3,3,3-Trifluoropropene	677-21-4	---	---	---	HSDB: (π) Haz-Map: Simple Asphyxiant.	Fire may produce irritating, corrosive and/or toxic gases.
Hexafluoropropene (R 1216)	116-15-4	---	250 <sup>A</sup> (40 ppm <sup>A</sup> )	560 <sup>A</sup> (91 ppm <sup>A</sup> )	HSDB: (π) Haz-Map: Simple Asphyxiant.	Fire may produce irritating, corrosive and/or toxic gases.
Acetylene	74-86-2	---	69 000 <sup>T</sup> (65 000 ppm <sup>T</sup> ) risk of explosion at this level	24 000 <sup>T</sup> (230 000 ppm <sup>T</sup> ) risk of explosion at this level	HSDB: Not acutely toxic below 25 000 ppm in humans. Haz-Map: CNS Solvent Syndrome, Simple Asphyxiant	Extremely flammable, is easily ignited by heat, sparks or flames.
Bis(trifluoromethyl)acetylene	692-50-2	---	0.36 <sup>T</sup> (0.054 ppm <sup>T</sup> )	3.9 <sup>T</sup> (0.6 ppm <sup>T</sup> )		
1,1,1-Trifluoroethane (R 143A)	420-46-2	Limits (2005) V: LLV 1 750 mg/m <sup>3</sup> STV 2 625 mg/m <sup>3</sup>	---	---	Haz-Map: CNS Solvent Syndrome. Simple Asphyxiant	
1,2-Difluoroethene	1691-13-0	---	---	---	Haz-Map: CNS Solvent Syndrome.	

**Abbreviations:** CAS: Chemical number according to Chemical Abstract Service; LLV: Level limit value (working day, normally 8hr); STV: Short-term value (15 min reference period) used for toxic chemicals that do not have Ceiling limit values; V: Guiding short-term threshold; AEGL: Acute exposure guideline levels; ERPG: Emergency Response Planning Guideline; TEEL: Temporary Emergency Exposure Limits; LCLo: lowest concentration in air reported to have caused the death; ---: No data

<sup>#1</sup> Arbetsmiljöverket (**AV**). Occupational exposure limit values. Information from [www.av.se](http://www.av.se); AFS 2015:7 in Swedish.

<sup>#2</sup> Protective action criteria (**PAC**) Rev. 28A based on 1hr <sup>A</sup> AEGL, <sup>E</sup> ERPG, or <sup>T</sup> TEEL, see below and <http://orise.orau.gov/emi/scapa/chem-pacs-teels/default.htm> with a link to the current PAC workbook. <sup>A</sup>**AEGLs**: airborne concentration above which it is predicted that the general population, including susceptible individuals, could experience effects from a single exposure. AEGL-1: airborne concentration where notable but not disabling effects may occur that are reversible upon cessation of exposure. AEGL-2: airborne concentration above which irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape may occur. <sup>E</sup>**ERPG** values: estimates of concentrations where humans may experience effects. ERPG-1: airborne concentration below which nearly all individuals could be exposed for up to 1hr and only experience mild transient adverse health effects or perceiving a clearly defined, objectionable odor. ERPG-2: airborne concentration below which nearly all individuals could be exposed for up to 1hr without experiencing/ developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action. <sup>T</sup>**TEELs**: *approximated potential values* for exposure more than 1 hr. These can be changed with new/ better information and are developed to address human health effects in the general population, including susceptible individuals from a single exposure to airborne chemicals. TEEL-1: same definition as AEGL-1. TEEL-2: same definition as AEGL-2.

<sup>#3</sup> TOXNET: Toxicology data network at NIH (<http://toxnet.nlm.nih.gov/>). Summarized information from the Hazardous Substances Data Bank (HSDB) and the Haz-Map database. The information presented here focuses on toxicity after exposure via the skin, respiratory tract and eyes.

(α): A general description is given in HSDB for these fluorinated hydrocarbons and, in brief, they may act as simple asphyxiants by displacing oxygen and/ or may induce CNS solvent syndrome. Severe intoxication may induce respiratory depression, pulmonary edema, dizziness, cardiac dysrhythmias and unconsciousness and may for some agents induce hepatic or renal injury. Mild to moderate intoxication may irritate mucus membrane and eyes, and induce headache, nausea and vomiting.

## 4 Discussion

As noted, this work constitutes emission factor determination and a summary of toxicological data/effects of identified substances from combustion of HFO-1234yf. To evaluate the relation between concentrations in air and risk for toxic effects during rescue, a full scale experiment is necessary. Since the combustion conditions (specifically temperature and oxygen availability) in the case of a real fire diverges, the results from this controlled laboratory small-scale combustion experiment in terms of formed combustion products and their relative amounts must thus be regarded as indicative. One further limitation of this work is the lack of a comparison to alternative refrigerants such as R134a and CO<sub>2</sub>.

However, to put levels in some kind of relation, a SAAB 9-3 and a Volvo V70 has 680 g and 720 g of R134a respectively (and the required amount HFO-1234yf is approximately the same). This yields about 220 g of HF including transformed COF<sub>2</sub> to HF, calculated based on the average of measured emission factors. The 1 hr PAC1 value is 1 mg/m<sup>3</sup>, hence a volume of  $220 \text{ g} / 1 \text{ mg} \cdot \text{m}^{-3} = 220\,000 \text{ m}^3$  (which is for example a cube with sides 60 m) is required to dilute the gas to the PAC1 level. Now, such estimate does not include dilution, wind transport, or thermal rise of the hot gases. The interested reader may elaborate on dispersion in air with the dispersion tool "Spridning Luft"<sup>16</sup> issued by the Swedish Civil Contingencies Agency which soon will be updated with the "Dispersion Engine" concept<sup>17</sup>.

## 5 Conclusions

Emission factors have been determined for combustion byproducts from HFO-1234yf in a laboratory setup at varying burning conditions. Due to the low flammability a glowing metal surface was required to maintain a burning flame. Among twenty-five species identified; current data indicated that COF<sub>2</sub>, HF and CO pose the greatest health risk upon exposure to the combustion byproducts. COF<sub>2</sub> transform to HF which is corrosive and may induce pulmonary edema and cause severe burns on skin, whereas CO is suffocating. Should a fire develop in a vehicle air-conditioning system it is important to avoid contact with the gases. Although this study is not intended for exposure level and risk assessment of combustion products of HFO-1234yf, it is recommended that rescue personnel use proper protective measures during rescue at sites with burning MAC-systems. The source strength (i.d. the amount of HFO-1234yf available) and dilution of the source remains for others to determine – if or when taking HFO-1234yf in use.

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