BAM
Bundesanstalt für Materialforschung und -prüfung

FINAL TEST REPORT
Ignition behaviour of HFO1234yf

BAM reference	II-2318/2009 I
Copy	1st copy of 2 copies
Customer	Umweltbundesamt Wörlitzer Platz 1 06844 Dessau-Roßlau
Order date	8 October 2009
Reference	54353-5/1 (Förderkennzeichen: 363 01 262)
Receipt of order	12 October 2009
Test samples	• HFO1234yf (2,3,3,3-Tetrafluoroprop-1-ene), supplied by Apollo Scientific • Ethane, purity > 99.5 %, supplied by Air Liquide Germany GmbH • Oil for refrigerant compressor G 052 154 A2, batch no. 17048 • R134a (1,1,1,2-Tetrafluoroethane) purity > 99.5 % • Compressed air, free of moisture and oil both supplied by BAM
Receipt of samples	7 October 2009
Test date	Begin: 12 October 2009 End: 10 June 2010
Test location	BAM, Unter den Eichen 87, 12205 Berlin Building 40, Room 413 Building 42, Room 044 and 083 BAM Test Side Technical Safety, Baruth/Mark
Test procedure according to	• DIN 51649 "Determination of explosion limits of gases and vapours" • Enclosed Space Ignition Test; Section 31 "Classification Procedures, Test Methods and Criteria relating to Flammable Aerosols of Class 2" of the Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria

This test report consists of page 1 to 31.

TEST REPORT

0 Table of Contents

1 Scope

BAM was commissioned by the Federal Environment Agency in German (UBA) to examine the reaction behaviour of 2,3,3,3-Tetrafluoroprop-1-ene (HFO-1234yf) when exposed to ignition sources like sparks or hot surfaces. The focus of the examinations was not only to the determination of the flammability in different realistic scenarios and the formation of HF due to the hazards caused by the toxicity of HF. Therefore lab scale tests as well as tests with a car were carried out and are described in the following report.

2 Safety characteristics, terms and definitions

The safety characteristics and terms used in this report are defined as follows:

LEL, UEL	Lower and upper explosion (flammability) limit (LEL, UEL), lower and upper limiting value of the flammable gas concentration in a gaseous fuel/air mixture, at which just no more flame propagation (explosion) takes place after an ignition.
Explosion range	Concentration range between LEL and UEL, which is called the explosion range. Fuel/air mixtures within the explosion range can be ignited by an ignition source.
Explosion region	For a ternary gas mixture consisting of ethane, refrigerant and air the course of the LEL and UEL enclose the explosion region. For each refrigerant concentration one explosion range with LEL and UEL exists. The sum of all explosion ranges forms the explosion region.
p_0	Initial pressure in a closed vessel. Unit is bara (bar absolute).
p_{ex}	Explosion pressure, peak value of the pressure time curve, measured in a closed vessel upon deflagration of an explosive gas mixture.
p_{ex}/p_0	Explosion pressure ratio, explosion pressure divided by the initial pressure.
T_0	Initial gas temperature in the explosion vessel.
T_{ex}	Explosion temperature, peak value of the temperature time curve, measured in a closed vessel upon deflagration of an explosive gas mixture.
MIT	Minimum ignition temperature, lowest temperature of the hot surface at which a self ignition was observed at specified test conditions.
Self Ignition	Sudden pressure and/or temperature increase in a closed vessel.
IDT	Ignition Delay Time, time period between the start of filling the test mixture into the explosion vessel and the observed self ignition.
IC	Ion chromatography, analysis method for the determination of the HF-concentration in gas samples
MAC	Mobile air conditioning system

3 Work package 1: Explosion regions of ethane-refrigerant-air mixtures

3.1 Introduction

In a first work package the explosion region of the ternary gas system ethane-HFO1234yf-air was determined. The results were compared to literature values also determined in the past by BAM for the ternary system ethane-R134a-air. The explosion regions of the resulting mixture compositions in case of a leakage of HFO1234yf with small amounts of a hydrocarbon in air will be discussed regarding the flammability of these mixtures.

A detailed report [1] was already sent to the customer.

3.2 Test procedure

The tests have been carried out according to the former German standard DIN 51649 “Determination of explosion limits of gases and vapours” in a glass tube. Although this standard was replaced by the European standard EN 1839 the former German standard was applied due to comparability to the literature values. Furthermore studies of BAM already showed that the difference between the explosion regions determined according to the DIN 51649 and EN 1839 “T” (tube method; in EN 1839 two test methods are described, one in a glass tube and one in a closed bomb.) is negligible for the most fuels [2].

Details of the test method as well as the procedure were reported in a separate test report with the BAM reference number BAM-Az.: II-2318/2009 [1]. The test mixtures were prepared separately in a 14-dm^3-sphere with a mixing device inside. After the preparation the gas mixture was filled to the ignition tube, which was a vertical glass tube with an inner diameter of 60 mm and a height of 300 mm. This glass tube is an open system due to the non-fixed lid at the top. In case of strong reactions the overpressure is released by lifting the lid.

Prior to each ignition test, the tube was purged with the test mixture. The purging volume was at least ten times the volume of the tube. Subsequently the test mixture by-passes the glass tube and was supplied into the exhaust system; the inlet to the test vessel was sealed. After purging the ignition tube with the test mixture the gas flow was stopped. The induction spark igniter is fired when test mixture is quiescent (about 15 s after gas flow was stopped), and it is observed whether a flame detaches from the ignition source or not.

If an ignition is observed, the amount of ethane respectively HFO1234yf in the test mixture was iteratively varied until no further flame detachment occurred. The step size for the variation was fixed to 0.2 mol-%. The test mixture with which a further flame detachment just failed was used to carry out further four tests. The determination was terminated when all five tests have taken place without flame detachment. If this was not the case, the ethane content was varied again, i. e. for the determination of the LEL the ethane content was reduced by one step size; for the UEL, it was increased by one step size.

This procedure was carried out for different fixed amounts of HFO1234yf respectively ethane in order to determine the course of the lower and the upper explosion limits and therefore the complete explosion region of the ternary gas system.

3.3 Results

The resulting explosion region for the ternary gas system ethane-HFO1234yf-air as well as the one for ethane-R134a-air is shown in Fig. 1. The explosion regions are finally comparable large considering the whole region. But there is an important difference to the ethane-R134a-air mixtures which is caused by the flammability of HFO1234yf itself. The flammability of HFO1234yf leads to the fact that the course of the lower explosion limit of ethane hits the x-axis at the LEL respectively the UEL of HFO1234yf.

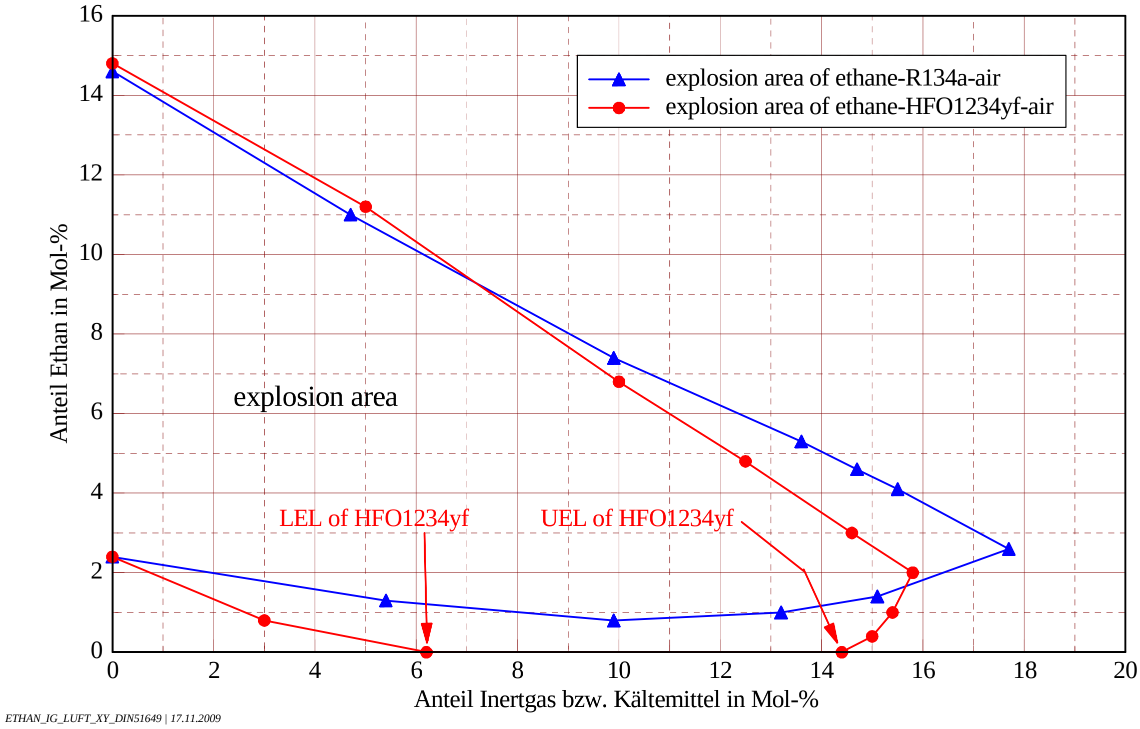


Fig. 1: Explosion regions of ethane-R134a-air and ethane-HFO1234yf-air, determined at atmospheric pressure and a temperature of 25 °C according to DIN 51649

The presence of hydrocarbons depends on the use of the refrigerant. In many cases there are hydrocarbons present e. g. oil. Oils are hydrocarbons with long C-chains which can be cracked at hot surfaces. Smaller molecules are formed which can also react with the refrigerant. Therefore the influence of hydrocarbons on the explosion region is shown by the example of ethane addition.

That leads to the fact that in case of HFO1234yf leakages the probability to produce explosive atmospheres in presence of hydrocarbons is larger compared to R134a.

Especially in the range of the lower explosion limit curves a number of mixtures exists, where HFO1234yf becomes flammable by addition of low fractions of hydrocarbons (see difference between the LEL curves of HFO1234yf and R134a in Fig. 1).

4 Work package 2: HF formation at hot surfaces

4.1 Introduction

It was well known that HF is formed when fluorinated hydrocarbons are exposed to ignition sources and especially to hot surfaces. This effect is also mentioned for HFO1234yf in the Material Safety Data Sheet (MSDS) [5] from the supplier Honeywell. In Section 2 “Hazards Identification”, Section 5 “Fire-fighting measures” and Section 10 “Stability and Reactivity” of the MSDS information regarding decomposition products are given. One of these products is HF.

In the past many discussions arose what amounts of HF can be formed when the refrigerant is released from the MAC. Gas sampling after realistic scenarios is not easy. Very often the results reflects only the HF-amount at the places where the gas samples were taken. If a model test is carried out discussions about the plausibility arose very often as well as doubts regarding the applicability.

In this work package the HF formation was determined away from any scenario to get an impression about the amounts of HF which can occur in principle after exposure of defined HFO1234yf-air mixtures to hot surfaces.

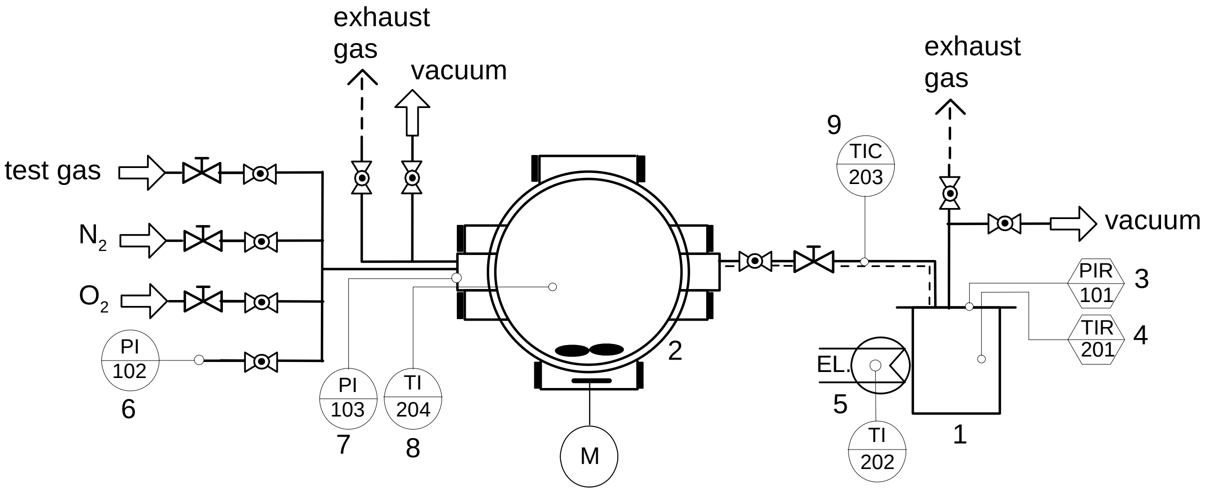
4.2 Test equipment

The test equipment is shown schematically in Fig. 2. Fig. 3 shows a picture of the set-up which was used for the determination of the HF-concentration after defined mixtures of refrigerant-air have been exposed to the vessel hot surface for ten minutes.

The equipment was installed in a fume hood and consists of a mixing vessel ($V = 14\ dm^3$) and a heated explosion vessel ($V = 3\ dm^3$). Both vessels could be evacuated, filled and vented separately.

The explosion vessel was an autoclave made from stainless, creep resistant steel (German steel code: 1.4122; composition in units of %-w/w: C = 0.4, Si = 1, Mn = 1.5, P = 0.04, S = 0.015, Cr = 16.5, Mo = 1, Ni $\leq$ 1, Fe = 78.5) with an inner diameter of 150 mm and a height of 188 mm. Sealing was made from graphite. All connectors for gas inlets and outlets as well as an air cooled pressure transducer and a 1.5-mm-NiCr/Ni-coated thermo couple were installed in the lid of the vessel. The explosion vessel was heated by a heating sleeve with integrated electrical temperature controller and insulator from the company HORST GmbH (Inner-∅ 175 mm; length 280 mm, 2800 W heating capacity, max. temperature 850 °C). Bottom and top of the vessel were insulated by mineral fibrous insulating material. This set-up guarantees temperature gradients < 10 K in the explosion vessel.

Gas sampling after the tests was realized by adding two wash bottles - each of them filled with a defined NaOH-solution - to the vacuum pipe. The volume taken out of the test vessel was controlled by a volume metering device.



1 3 dm^3 explosion vessel

2 14 dm^3 vessel with mixing device

3 measurement chain for pressure (piezoresistive pressure transducer, measuring range 0 bara up to 5 bara; amplifier; A/D-converter; computer)

4 measurement chain for temperature (1.5-mm-NiCr/Ni-coated thermo couple, amplifier; A/D-converter; computer) for the determination of the initial temperature and the temperature-time-history inside the explosion vessel

5 Heating device with integrated controller

6 vacuum indication

7 piezoresistive pressure transducer, measuring range 0 bara up to 5 bara for the mixture preparation

8 1.5-mm-NiCr/Ni-coated thermo couple with digital indicator

9 Heating device with temperature controller for heating the gas inlet pipe

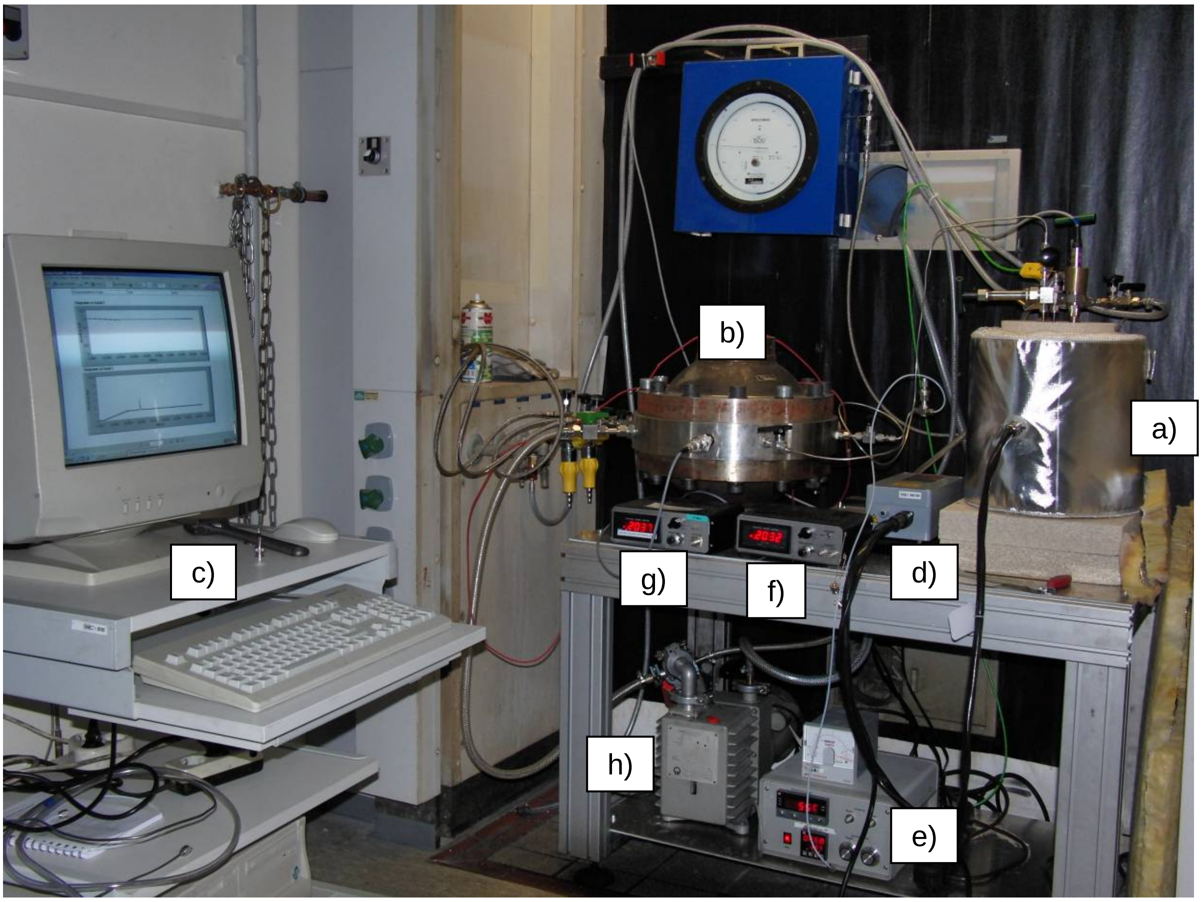
Fig. 2: Schematically view of the set-up for the determination of HF after exposure of refrigerant-air-mixtures to hot surfaces

4.3 Data acquisition

In order to determine partial pressures during the mixture preparation, the initial pressures and the pressure-time-histories in the test vessel piezoresistive pressure transducers from the company Keller (explosion and mixing vessel: type PAA-10, measuring range 0 bara up to 5 bara; both pressure transducers with a limiting frequency f > 30 kHz) were used. The transducers had a resolution of 0.0002 bara with a linearity better than 0.5 %. All pressure transducer were calibrated over the complete measuring range by means of a digital pressure controller DPI 515 from the company Druck (uncertainty of measurement < 0.01 % full scale).

The initial temperatures and the temperature-time-histories inside the explosion vessel were measured with a digital thermometer from the company Greisinger (type GTH 1200 A) with a 1.5 mm coated thermocouple.

The pressure recording equipment and the temperature recording equipment in the test vessel were connected to an A/D-converter (company Jet Systemtechnik GmbH, Typ MCL-USB, 16 channels 12 Bit A/D, sampling frequency 500 kHz) in a computer. All pressure-time- and temperature-time-histories in the explosion vessel were measured and stored digitally.



a) explosion vessel
b) mixing vessel
c) data acquisition system
d) heating device for the explosion vessel
e) heating device for the pipes
f) pressure gauge for the explosion vessel
g) pressure gauge for the mixing vessel
h) vacuum pump

Fig. 3: Set-up for the determination of minimum ignition temperature (MIT) of process gases at atmospheric and non-atmospheric conditions

4.4 Test procedure

Defined gas mixtures consisting of 5 mol-%. 10 mol-% and 20 mol-% of HFO1234yf respectively R134a in air have been prepared separately in the 14 dm^3 spherical vessel with mixing device. Afterwards the homogeneous mixtures were filled into the evacuated, pre-heated explosion vessel of 3 dm^3. For a time period of ten minutes the pressure-time- as well as the temperature-time-histories were recorded to detect possible ignition phenomena inside the vessel. The tests were carried out at three different initial temperatures of 200 °C, 350 °C and 500 °C.

After ten minutes a 500 ml gas sample was taken out of the ignition vessel in order to analyse it regarding HF concentration. As analysis method mainly ion chromatography was used.

Further tests have been carried out with mixtures where 3 % oil was added to the HFO1234yf or R134a before mixed with air. By that procedure the influence of oil on the HF formation could be detected at these specified conditions.

4.5 Combustion of fluorinated hydrocarbons

During the combustion of a fluorinated hydrocarbons like HFO1234yf the formation of HF is possible according to:

$CH_2 = CF\text{-}CF_3 + 2.5\ O_2 \rightarrow 2\ HF + 0.5\ CF_4 + 2.5\ CO_2$

Of course further products can occur like COF_2 (carbonyl fluoride) which is also highly toxic.

How much HF is finally formed is dependent on many factors influencing the pathway of reaction, e. g. is there a flame propagation (explosion) in the system, is pure refrigerant released and got in contact to a hot surface etc. The amount of the refrigerant which is heated up to high temperatures, like they can occur in flames, is influencing the amount of HF. In case of an explosion usually a flame propagates through that volume in which a flammable mixture is available. Therefore the HF amount found after those “explosions” are in the range of percentages according to the above mentioned reaction. The maximum amount of HF is 13.9 mol-% for a stochiometric reaction according to the formula:

$1\ \text{mol HFO1234yf} + 11.9\ \text{mol air} \rightarrow 2\ \text{mol HF} + 0.5\ \text{mol}\ CF_4 + 2.5\ \text{mol}\ CO_2 + 9.4\ \text{mol}\ N_2$

This theoretical value will not be reached in most of the cases because a flame propagation through a complete volume is not often observed. In case the refrigerant is released usually not the full amount of the released substance gets into contact to hot surfaces or open flames e. g. the flame of a match. Nevertheless high amounts of HF can never be excluded.

4.6 Results

The explosions and the HF concentrations determined for HFO1234yf-air mixtures without and with oil are summarized in Tab. 1, for R134a-air mixtures without and with oil in Tab. 2.

Tab. 1: HF concentrations of HFO1234yf-air mixtures after exposure to hot surfaces for a time period of ten minutes

Test no.	Mixture composition [mol-%]		Vessel temperature [°C]	Explosion yes / no	HF concentration [mol-% ± 0.01 mol-%] **
	HFO1234yf	air			
UBA 04	5.0	95.0	200	no	0.01
UBA 05	10.0	90.0	200	no	0.01
UBA 06	20.0	80.0	200	no	0.01
UBA 07	5.0	95.0	350	no	2.04
UBA 08	10.0	90.0	350	yes	15.9
UBA 09	20.0	80.0	350	yes	45.9
UBA 16	5.0	95.0	500	no	0.71
UBA 17	10.0	90.0	500	yes	5.58
UBA 18	20.0	80.0	500	yes	6.90
UBA 26	5.0 *	95.0	350	no	1.74
UBA 27	10.0 *	90.0	350	no	1.07
UBA 28	20.0 *	80.0	350	no	0.11
UBA 30	5.0 *	95.0	500	no	0.62
UBA 31	10.0 *	90.0	500	yes	1.81
UBA 32	20.0 *	80.0	500	yes	7.27

* mixture of 97 % HFO1234yf and 3 % oil

** 1.0 mol-% = 10,000 ppm

Tab. 2: HF concentrations of R134a-air mixtures after exposure to hot surfaces for a time period of ten minutes

Test no.	Mixture composition [mol-%]		Vessel temperature [°C]	Explosion yes / no	HF concentration [mol-% ± 0.01 mol-%] **
	R134a	air			
UBA 01	5.0	95.0	200	no	0.03
UBA 02	10.0	90.0	200	no	0.01
UBA 03	20.0	80.0	200	no	0.01
UBA 10	5.0	95.0	350	no	0.24
UBA 11	10.0	90.0	350	no	0.60
UBA 12	20.0	80.0	350	yes	12.07
UBA 13	5.0	95.0	500	no	0.36
UBA 14	10.0	90.0	500	no	0.21
UBA 15	20.0	80.0	500	no	0.33
UBA 20	5.0 *	95.0	350	no	0.03
UBA 21	10.0 *	90.0	350	no	0.04
UBA 22	20.0 *	80.0	350	yes	5.35
UBA 33	5.0 *	95.0	500	no	0.15
UBA 24	10.0 *	90.0	500	no	0.28
UBA 25	20.0 *	80.0	500	no	0.61

* mixture of 97 % R134a and 3 % oil

** 1.0 mol-% = 10,000 ppm

It turned out that high amounts of HF were detected at temperature of 350 °C and 500 °C after exposing the defined mixtures to a hot surface for a time period of ten minutes. The higher the amount of refrigerant was in the mixture the higher the amount of HF detected. In some cases the analysed HF concentrations were higher than those occurring for the stochiometric combustion reaction. Such high fractions are possible by fuel rich combustion and forming of COF_2, which can hydrolyse with water to HF during the analysis process. Small amounts of oil in the mixtures decrease the amount of HF, but nevertheless several percent of HF were analyzed.

At various test conditions ignition phenomena were observed. In this test series it was not the intention to determine these phenomena in detail, but familiar behaviour is already known for other hydrocarbons [6]. In Fig. 4 to Fig. 6 pressure-time- and temperature-time-histories are shown as example for these ignition phenomena.

In test no. UBA 08 (10 mol% HFO1234yf in air at 350°C, Fig. 4) and in test no. UBA 09 (20 mol% HFO1234yf in air at 350°C, Fig. 5) clear explosions were detected visible as short pressure and temperature peaks. The difference is to find in the ignition delay time (IDT) which decreased with increasing amount of HFO1234yf in the mixture. In test no. UBA 12 (20 mol% R134af in air at 350°C, Fig. 6) also a pressure and temperature increase was observed. It was also defined as “explosion” although it is an exothermic reaction not that fast as detected in the two tests with HFO1234yf shown in Fig. 4 and Fig. 5. In all three tests very high amounts in the range of percentages of HF have been analyzed.

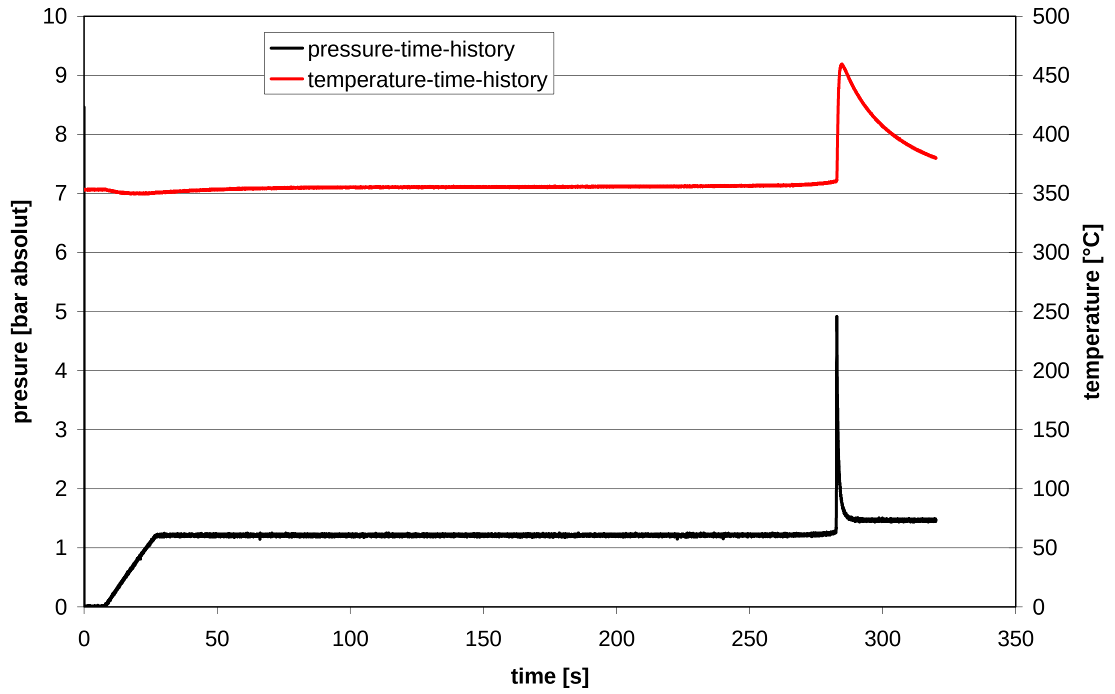


Fig. 4: Pressure-time- and temperature-time-histories of test no. UBA 08 (10 mol-% HFO1234yf in air at 350 °C initial temperature)

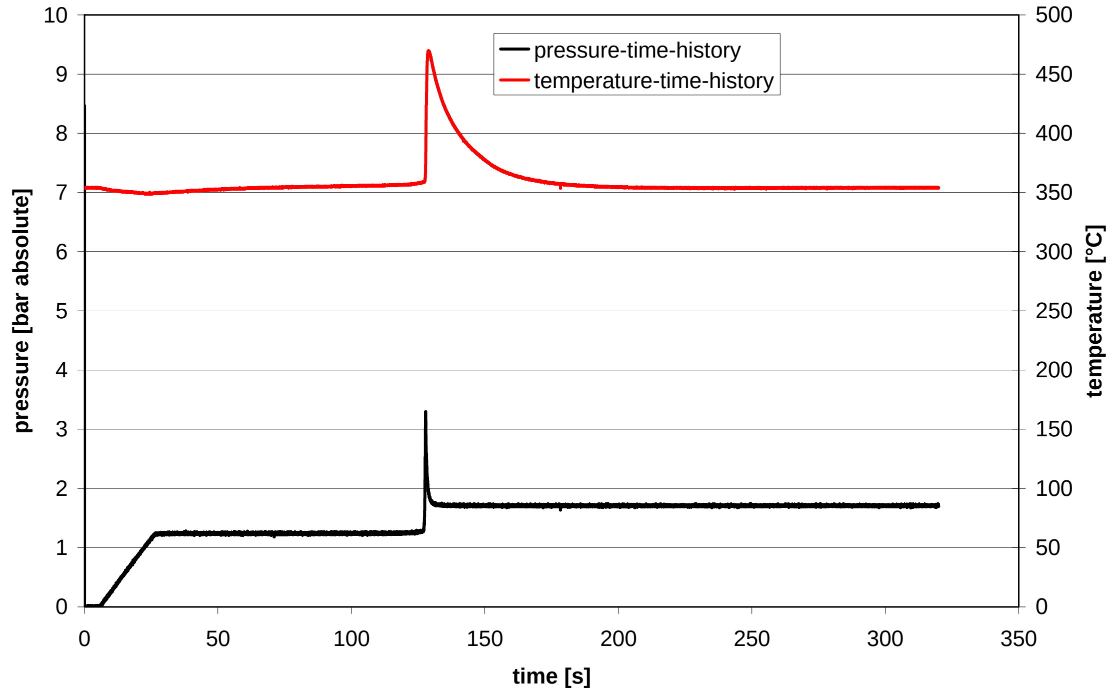


Fig. 5: Pressure-time- and temperature-time-histories of test no. UBA 09 (20 mol-% HFO1234yf in air at 350 °C initial temperature)

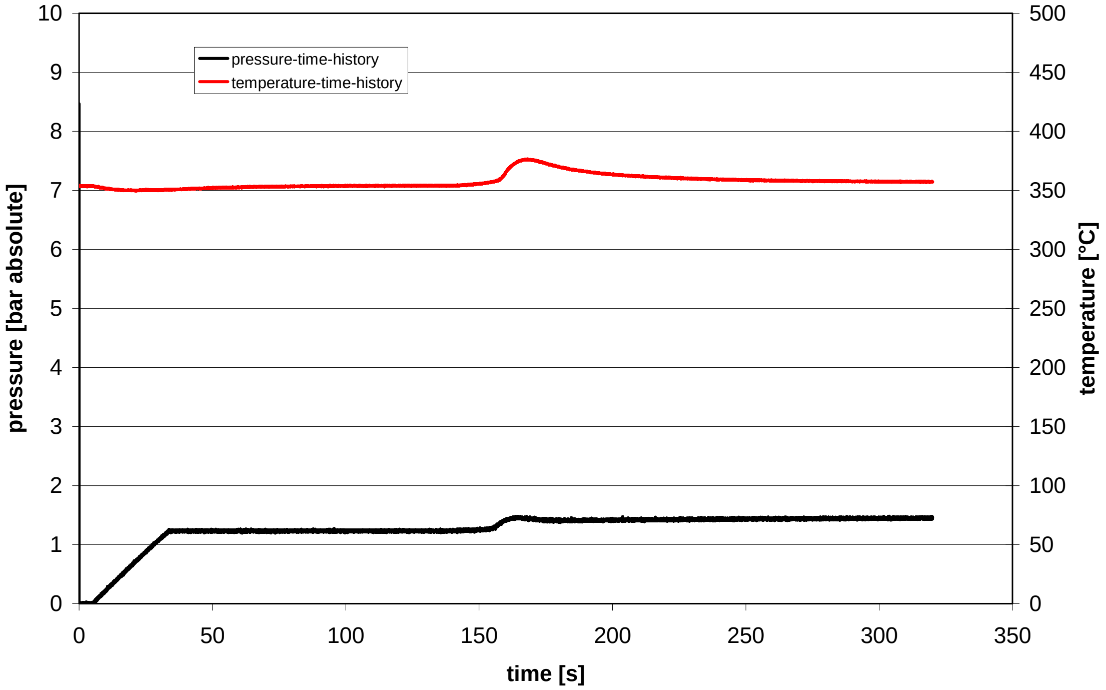


Fig. 6: Pressure-time- and temperature-time-histories of test no. UBA 12 (20 mol-% R134a in air at 350 °C initial temperature)

5 Work package 3: Ignition behaviour at hot surfaces

5.1 Introduction

The tests in work package 2 (chapter 4) were carried out without any scenario in the background. Maximum amounts of HF were determined after exposing specified mixtures from HFO1234yf in air respectively R134a in air to a pre-heated vessel.

A real scenario in a car would be that a part of the MAC is leaky or ruptured and the refrigerant is released to the motor compartment. Hot surfaces are always available as far as the car was moving. On the one hand the ignition behaviour of HFO1234yf and R134a was examined. Although the minimum ignition temperature (MIT) of HFO1234yf is well known (MIT = 405 °C [5]) no information exists about possible ignition of the refrigerant in a flowing state. The minimum ignition temperature is always determined according to standards like EN 14522 [7] where inhomogeneous and quiescent mixtures are examined. The only forced flow is slow buoyancy.

On the other hand the amounts of HF after the release and the contact to a hot surface was of great interest as not the complete released substance got in contact the hot metal surface.

5.2 Test equipment

For this test series a model volume of 200 dm^3 was constructed. One side of this box was made from Plexiglas®(Fig. 7). A metal block was pre-heated in a ceramic oven up to temperatures of 1100 °C. After the block was taken out it was installed on a mesh wire to protect the walls of the volume against the high temperatures. The temperature of the metal block was determined in a small hole with a diameter of 2 mm and 2 mm depth. The temperature measurement itself was realized by use of a digital thermometer from the company Greisinger (type GTH 1200 A) with a 1.5 mm coated thermocouple.

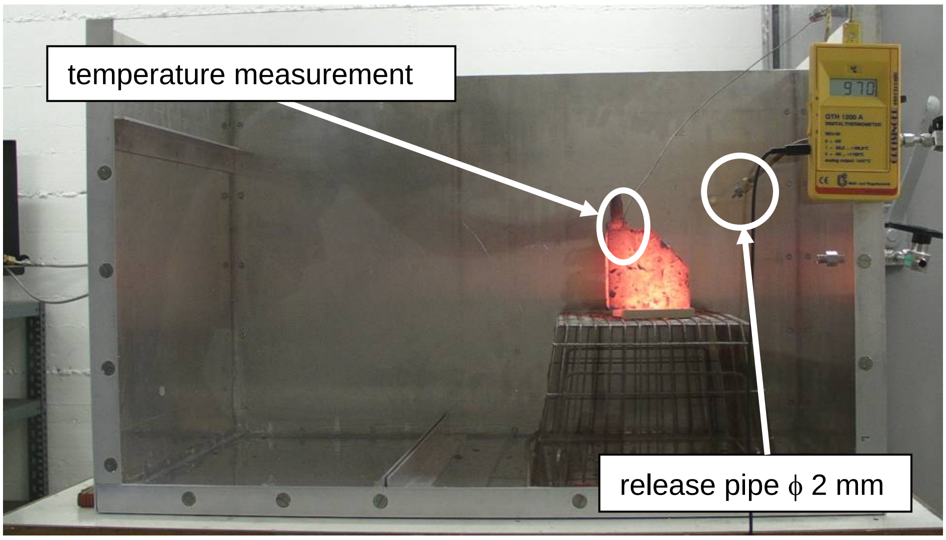


Fig. 7: Model volume for release of refrigerants to a hot metal surface

The release of refrigerant was performed by use of a ¼`` pipe with a reduction to 2 mm diameter at its end. The released mass of refrigerant was determined with a balance from the company Sartorius (type 3808 MP, measuring range up to 30,000 g, resolution: 1 g).

In a few tests the amounts of HF in the model volume were determined by use of detector tube of the company Dräger (type Hydrogen fluoride 0.5/a, measuring range 0.5 to 15 ppm respectively 10 to 90 ppm). Gas sampling was done after the release test by lifting the lid of the volume slightly and applying the measuring system manually.

Data acquisition for ignition behaviour and temperature observation was realized by video recording. The weight of released refrigerant was noted and the amount of HF was detected by the detector tubes.

5.3 Test procedure

The pre-heated metal block was taken out from the oven and installed on the mesh wire. When the surface temperature dropped down to the initial temperature approximately 50 g/min of pure HFO1234yf or R134a were released and directed towards the metal block. Possible reactions were documented by video. Further tests have been carried out with mixtures where 3 % oil was added to the refrigerants.

After two tests gas samples were taken as already described in chapter 4.2 in order to determine the HF amount by IC. In four other tests the HF amount was determined with the detector tubes.

5.4 Results

In Tab. 3 the results of the tests regarding the ignition behaviour at hot surfaces are summarized.

Tab. 3: Results/observations during leakages of R134a and HFO1234yf to a model volume with a hot metal surface

Test no.	Refrigerant and released mass	Temperature of metal [°C]	Explosion yes / no	HF concentration [ppm]
Box 01	R134a; 56 g	700	no	no analysis
Box 02	R134a; 53 g	800	no	no analysis
Box 03	R134a;52 g	900	no	no analysis
Box 04	HFO1234yf; 54 g	900	yes	no analysis
Box 05	HFO1234yf; 52 g	800	no	no analysis
Box 06	HFO1234yf; 55 g	700	no	no analysis
Box 07	HFO1234yf; 54 g	500	no	700 (0.07 mol-%)
Box 08	HFO1234yf; 52 g *	500	no	500 (0.05 mol-%)
Box 09	HFO1234yf; 51 g *	600	yes	no analysis
Box 10	R134a;52 g	500	no	0.5 ***
Box 11	HFO1234yf; 50 g	500	no	5.0 ***
Box 12	R134a; 51 g *	500	no	> 90 ***
Box 13	HFO1234yf; 50 g *	500	no	> 90 ***
Box 14	R134a;52 g *	600	no	no analysis
Box 15	R134a;51 g *	700	no	no analysis
Box 16	R134a;51 g *	800	no ****	no analysis
Box 17	R134a;50 g *	900	no ****	no analysis

* mixture of refrigerant and 3 % oil

** 1.0 mol-% = 10,000 ppm

*** detector tube

**** small flame on hot surface due to oil

In this test for HFO1234yf a minimum temperature for ignition was determined at 900 °C (pure substance, test no. Box 04, Fig. 8) respectively 600 °C (refrigerant + 3 % oil, test no. Box 09, Fig. 9). In both test a blue flame propagation was visible. In the test where the mixture with oil was released a white fog was produced at first. In this step the hydrocarbons in the oil were cracked and the intermediately formed species led to a lower ignition temperature than determined for the pure HFO1234yf. For R134a at temperatures up to 900 °C no ignition were observed (pure substance as well as for mixture with 3 % oil).

The gas samples taken after test no. Box 07 and 08 were analyzed by IC for HF. In order to compare these values to those achieved in work package 2 (chapter 4.6) the tests were carried out at temperatures of 500 °C. HF concentrations determined in these tests in work package 3 were lower compared to those in work package 2 due to lower contact times of the HFO1234yf to the hot surface.

Further analysis were carried out with the detector tubes (test no. Box 10 to 13). The initial temperature of the metal block was always set to 500 °C. At first repetition tests with the pure substances were carried out to get a reference to the more precise analysis by IC. It turned out that the HF analysis with detector tubes (test no. Box 10 and 11) is not that sensitive as IC. The HF amounts were below the values determined by IC. Nevertheless in test no. Box 12 and 13 HF amounts of more than 90 ppm were detected, when the refrigerants were mixed with low amounts of oil.

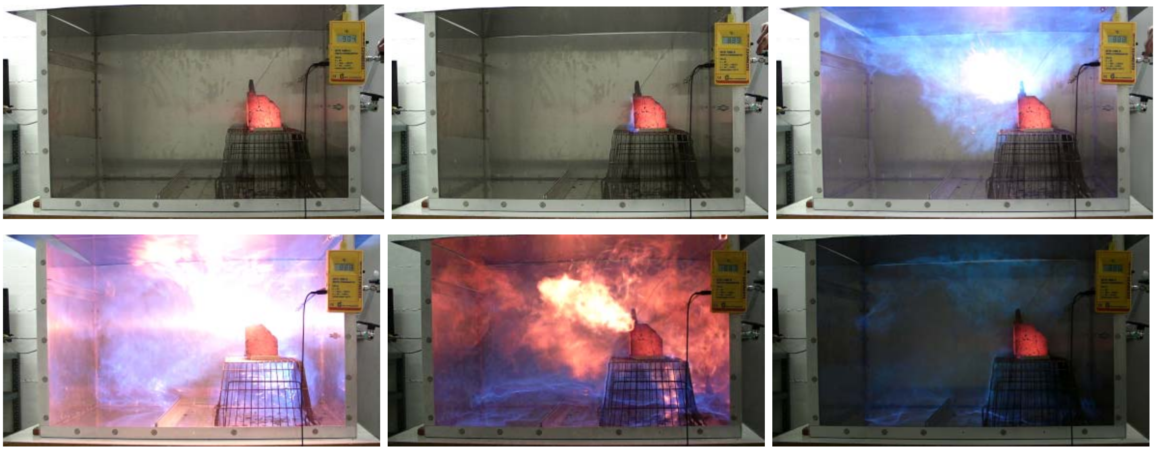


Fig. 8: Picture sequence from the video record of test no. Box 04: Release of pure HFO1234yf on a hot metal surface with 900 °C initial temperature

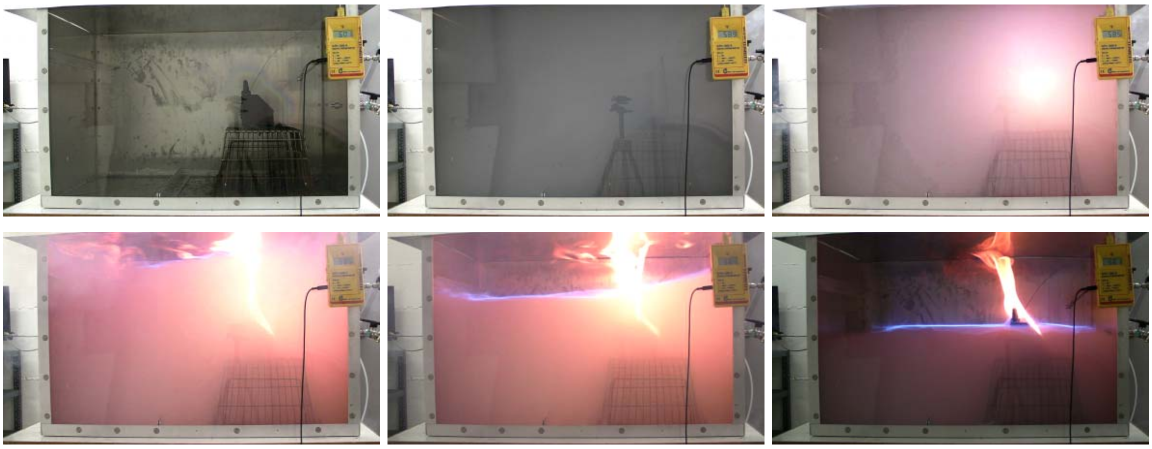


Fig. 9: Picture sequence from the video record of test no. Box 09: Release of HFO1234yf with 3 % oil on a hot metal surface with 600 °C initial temperature

6 Work package 4: Leakages to a model volume

6.1 Introduction

Chapter 5 described a scenario where high pressure leakages from a MAC were released and got in contact to a hot surface, e. g. a motor. Another scenario are small leakages, as they can occur e. g. from gas cylinders filled with refrigerant at a storage place. The densities of the refrigerants (HFO1234yf, R134a and CO_2) are bigger than the density of air. Therefore the substances “drop down” and accumulate at the bottom. The boundary of the refrigerant layer can get higher the longer the release takes place. Finally the height of the refrigerant can reach an ignition source, e. g. a burning candle. In this work package the ignition behaviour was looked at when HFO1234yf as well as R134a and CO_2 were slightly released into a model volume of 200 dm^3.

6.2 Test procedure

The same test box as described in chapter 5 was used. The mesh wire was removed and a candle was located in one edge of the volume (Fig. 10). Leakages with two different mass flows were generated. In a first test series the ¼`` pipe was extended with another pipe to direct the release to the bottom of the box. The released mass was determined with a balance from the company Sartorius (type 3808 MP, measuring range up to 30,000 g, resolution: 1 g). Approximately 50 g of the refrigerants were released. In a second test series this inner pipe was also removed and the mass flow reduced so that the flow directly “dropped down” to the bottom. The two test series were carried out with CO_2, R134a and HFO1234yf. All tests were recorded with a camcorder.

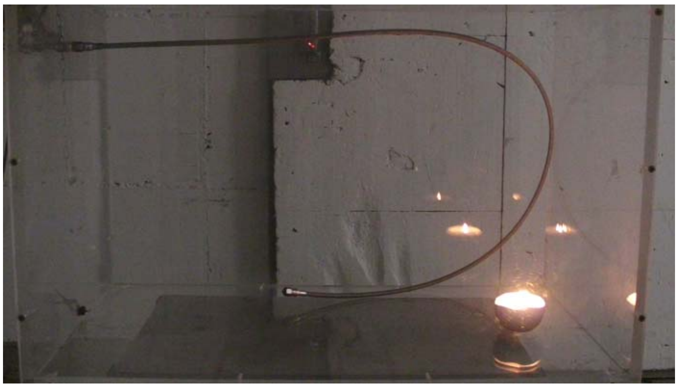


Fig. 10: Set-up for the refrigerant release to a volume of 200 dm^3.

After the tests with the fluorinated hydrocarbons the HF amount was determined by use of the detector tubes of the company Dräger (type Hydrogen fluoride 0.5/a, measuring range 0.5 to 15 ppm respectively 10 to 90 ppm).

6.3 Results

The tests are summarized in Tab. 4.

In the first test series (test no. V 01 to V03), the mass flows of the refrigerants were even high enough to cause slight turbulences during the release. In combination with that turbulences the flame was extinguished when the boundary layer reached the candle flame. During the release of the fluorinated hydrocarbons R134a and HFO1234yf a flame stretch was observed after 30 s.

For R134a the flame size remained constant for the duration of the test. Due to the non-flammability of R134a the flame was finally extinguished after 70 s. The same test with HFO1234yf led also to a flame stretch, but the flame size increased all the time (Fig. 11), but no flame propagation through the volume was observed. Finally the flame was extinguished after 70 s presumably due to lack of oxygen in the volume.

In a second test series (test no. V 04 to V06), the mass flow of the released refrigerants was reduced. In principle, the same observations were made. For R134a and HFO1234yf at first a flame stretch was observed after a certain time period. Finally the candle flame was always extinguished, but in case of the HFO1234yf release it took 18 min. In case of CO_2 and R134a the flame was extinguished after 360 s respectively 350 s.

Tab. 4: Release of refrigerants to a 200 dm^3 box with a burning candle at the bottom

Test no.	Refrigerant and released mass	Observation	HF concentration [ppm]
V 01	CO_2 (mass not determined) *	Flame extinguished after 50 s	no analysis
V 02	R134a; 52 g *	Flame got a bit larger after 30 s, but was extinguished after 70 s.	> 90
V 03	HFO1234yf, 46 g *	Blue flame at the top of the candle flame after 30 s. This flame got larger the more refrigerant was released. Flame extinction after 70 s (Fig. 11).	> 90
V 04	HFO1234yf (mass not determined)	Blue flame at the top of the candle flame after 500 s. Max. height of the blue flame during test was approx. 10 cm (Fig. 12).Flame extinguished after 18 min.	> 90
V 05	R134a (mass not determined)	Flame got a bit larger after 120 s, but was extinguished after 350 s.	> 90
V 06	CO_2 (mass not determined)	Flame extinguished after 360 s.	no analysis

* Release of refrigerant for approximately 60 s.

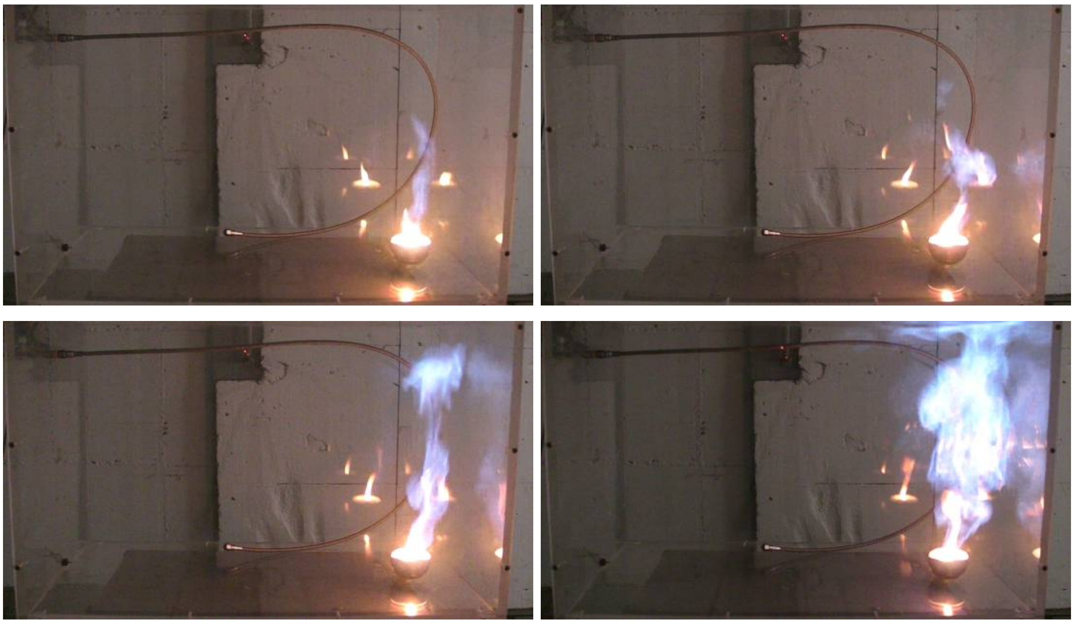


Fig. 11: Picture sequence from the video record of test no. V 03: Release of 46 g HFO1234yf within 70 s.

Fig. 12: Picture from the blue stagnant flame taken after 300 s from test no. V 04: release of HFO1234yf

7 Work package 5: Enclosed space ignition test

7.1 Introduction

The enclosed space ignition test is part of the classification procedure for aerosol dispenser. It is defined in Section 31 of the UN Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria [8]. In the enclosed space ignition test the flammability of aerosols is determined when they are released from the dispenser. The flammability is strongly dependent on the mass of the substance released to the air and this is dependend of the inside pressure of the dispenser as well as of the size of the aerosol droplets which are determined by specific parts of the dispenser.

Although there exist these dependencies the tests can give a very good impression of the flammability of substances when released as aerosol. This is possible when the refrigerants are released at higher pressures e. g. in MAC. Therefore the enclosed space ignition tests as defined in the UN Recommendations was carried out with HFO1234yf and R134a and for their mixtures with a compressor oil.

7.2 Test procedure

The test substance was released into an enclosed space with a defined geometry (inner volume: 200 dm^3, Fig. 13). Inside this volume a candle was located in the center in order to ignite the resulting aerosol-air mixtures (Fig. 14). The time period of observation was limited to 60 s. The candle flame and the possible ignitions were recorded with a camcorder through a window of the volume. After each test the volume was intensively flushed with pressurized air.

Two test series were carried out. In the first test series the mass flows of pure HFO1234yf and R134a as well as their mixtures with 3% oil were limited to a release of approximately 50 g in 60 s. In a second test series pure HFO1234yf was taken out of the cylinder from the gas phase and from the liquid phase and the mass flow realized by the full vapour pressure inside the cylinder, was not limited.

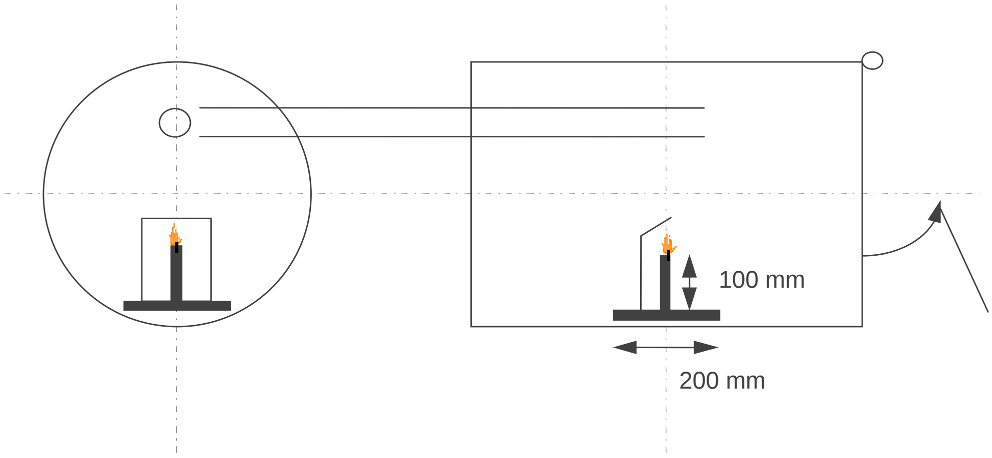


Fig. 13: Schematic view of the enclosed space for aerosol testing

Fig. 14: Pictures of the set-up for the enclosed space ignition test (left picture: full view of enclosed space with open lid for pressure release; right picture: burning candle as ignition source)

7.3 Results

Tab. 5 summarizes the enclosed space ignition tests carried out with the fluorinated hydrocarbons HFO1234yf and R134a respectively their mixtures with 3 % oil.

During the test ESI 01 to ESI 04 with R134a no special observations were made (Tab. 5).

he test with HFO1234yf was carried out with flow limitation. It turned out that The released amount of HFO1234yf during the test period of 60 s was to small to lead to an ignition. The typical flame stretch combined with a pale blue flame was observed. This confirmed again the test results reported in chapter 6.3 (Leckage to a test volume).

In tests with HFO1234yf ESI 09 and ESI 11 no flow limitation was used, so that the vapour pressure inside the storage cylinder led to higher release rates of the HFO1234yf. In test ESI 09 at first the substance was released from the gas phase of the cylinder. After 50 s an ignition was observed (Fig. 15). In test ESI 09 only the window view was recorded. Test ESI 09 was repeated (ESI 10) to report a complete view of the set-up. In this test ESI 10 it is visible that due to the explosion pressure the right lid opened (Fig. 16). Ignition always started with a stretch of the candle flame followed by pale blue flames propagating upwards due to buoyancy. When this flame was large enough ignition of the mixture at the top started.

Tab. 5: Enclosed space ignition tests carried out with HFO1234yf and R134a

Test no.	Refrigerant, aggregate state and released mass	Observation
ESI 01	R134a, gas phase, 56 g	No visible reaction
ESI 02	R134a, liquid phase, 50 g	No visible reaction
ESI 03	R134a + 3% oil, gas phase, 47 g	No visible reaction
ESI 04	R134a + 3% oil, liquid phase, 51 g	No visible reaction
ESI 05	HFO1234yf + 3% oil; gas phase; 55 g	Flame stretch, blue coloured
ESI 06	HFO1234yf + 3% oil; liquid phase; 52 g	Flame stretch, blue coloured
ESI 07	HFO1234yf; gas phase; 52 g	Flame stretch, blue coloured
ESI 08	HFO1234yf; liquid phase; 54 g	Flame stretch, blue coloured
ESI 09	HFO1234yf, gas phase, no flow limitation	Ignition after 50 s
ESI 10	HFO1234yf, gas phase, no flow limitation (repetition of ESI 09)	Ignition after 50 s
ESI 11	HFO1234yf, liquid phase, no flow limitation	Ignition after 15 s

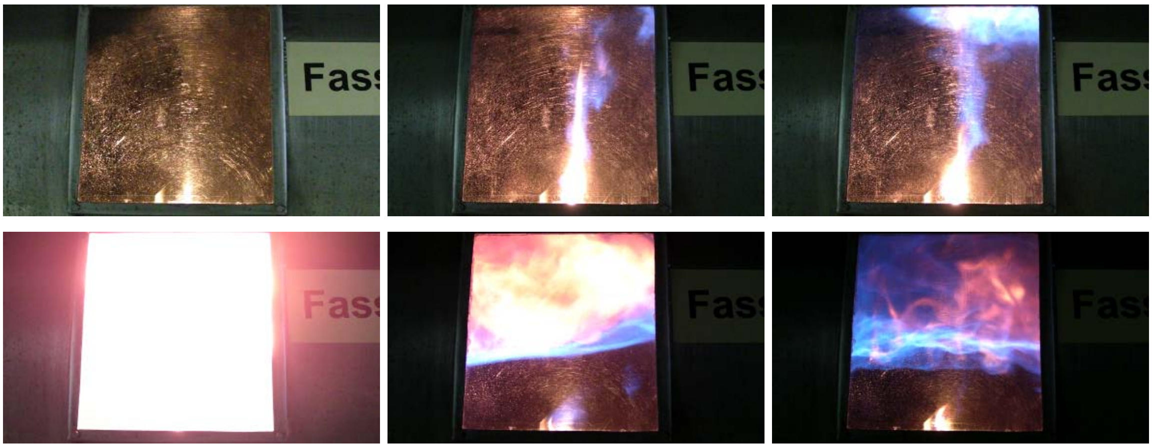


Fig. 15: Picture sequence from the video record of test no. ESI 09 (window view, release of HFO1234yf from the gas phase, no refrigerants flow limitation). Ignition was observed after 50 s.

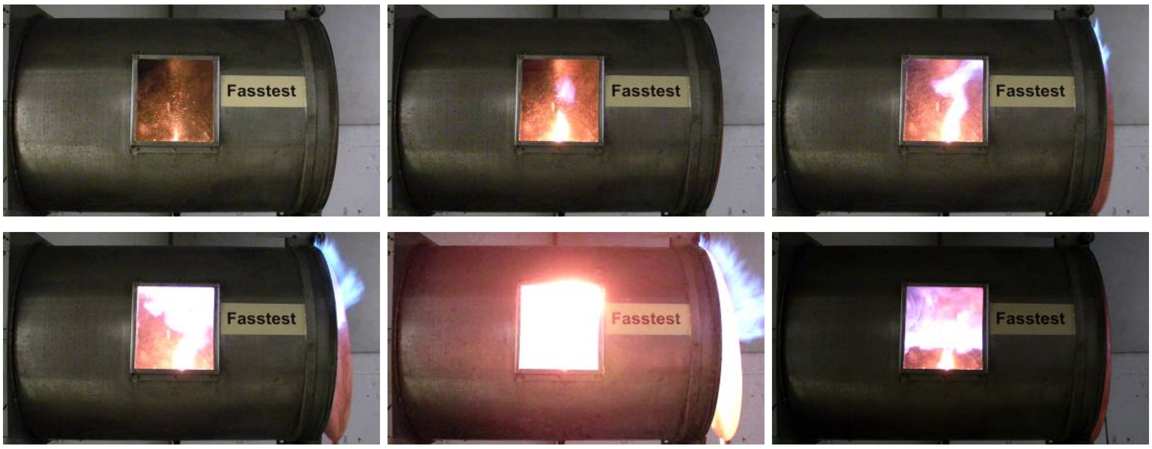


Fig. 16: Picture sequence from the video record of test no. ESI 10 (view of complete set-up, release of HFO1234yf from the gas phase, no refrigerants flow limitation). Ignition was observed after 50 s.

In test no. ESI 11 HFO1234yf was taken from the liquid phase of the gas cylinder. The liquid was latest vaporized when it entered the enclosed space. Release of the liquid HFO1234yf at these conditions led to highest HFO1234yf amounts in shortest times. Therefore the ignition delay was also the shortest ever detected in the test. Ignition was observed already after 15 s (Fig. 17).

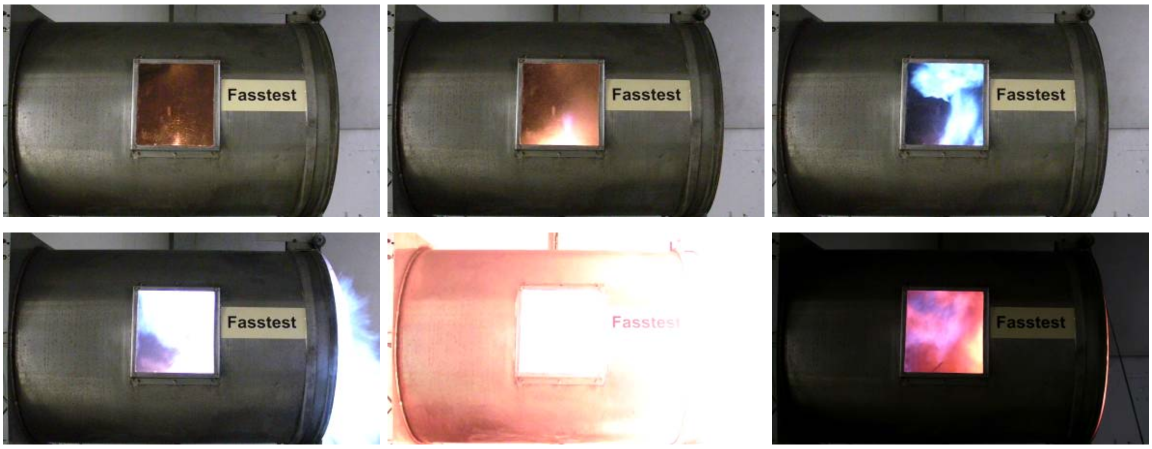


Fig. 17: Picture sequence from the video record of test no. ESI 11 (release of HFO1234yf from the liquid phase, no refrigerants flow limitation). Ignition was observed after 15 s.

8 Work package 6: Ignition tests in a passenger compartment of a car

8.1 Introduction

In chapters 3 to 7 described tests in which the explosion region of HFO1234yf (chapter 3) and the HF formation were determined in principle (chapter 4) or different release scenarios were re-enacted (chapters 5 to 7). Actually the use of HFO1234yf in MAC of cars is discussed. Therefore further tests were carried out in order to demonstrate the applicability of the main achievements of the already carried out model tests.

8.2 Test procedure

A commercially available car was prepared for the release of HFO1234yf through a ventilation slot. As location for the release or leakage into the passenger compartment the ventilation slot closest to the front passenger was chosen (Fig. 18). Close to this area very often the heat exchange device of the car ventilation and the MAC is placed. The leakage was simulated by the end of a ¼`` pipe with a reduction part to an inner diameter of 2 mm (the same as it was used for tests described in chapter 5).

Two different test series were carried out:

- Activation of different ignition sources directly in the leakage stream and
- Ignition of the gas phase in the passenger compartment after the complete amount of refrigerant was released into the compartment.

Fig. 18: Leakage pipe with a reduction part (inner diameter: 2 mm) installed in the ventilation slot of the front passenger

8.2.1 Ignition of the leaking stream

For the first test series a high voltage spark ignition was installed to the neck-rest of the front passenger (Fig. 19, left picture). Alos, two “exploding wire igniters” (after their activation burning arcs between two electrodes burn) were installed close to the place where usually the head of the front passenger is located (Fig. 19, left picture). In a further test the high voltage spark igniter was modified in order to ignite a match after its activation (Fig. 19, right picture).

Fig. 19: Location of ignition sources in order to ignite a leakage stream of HFO1234yf (left picture: high voltage spark and “exploding wire”; right picture: modified high voltage spark for the ignition of a match)

Finally an open flame (small torch lamp operated with propane) was installed on the front passenger seat with an upwards directed flame (Fig. 20). The burner was operated for approximately 120 s.

After each initiation of an ignition source the amount of HF in the passenger compartment was determined by use of detector tubes from the company Dräger (type Hydrogen fluoride 0.5/a, measuring range 0.5 to 15 ppm respectively 10 to 90 ppm).

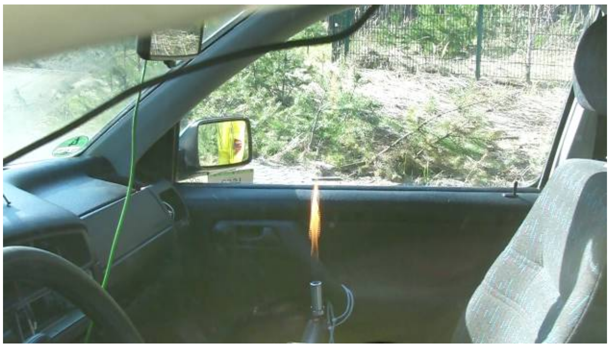


Fig. 20: Open flame of a small torch lamp operated with propane in order to ignite a leakage stream of HFO1234yf

8.2.2 Ignition of homogeneous HFO1234yf-air mixture in the compartment

For the second test series in the passenger compartment a more extensive data acquisition system was installed. Six small fans were used to homogenize the gas phase after leakage of 900 g of HFO1234yf. 900 g was the maximum allowed mass of the refrigerant according to the instruction manual of the car (850 g ± 50 g).

During the test one piezoresistive pressure transducer from the company Keller (type PAA-10, measuring range 0 bara up to 5 bara; limiting frequency f > 30 kHz; Fig. 21) as well as three thermocouples connected to digital thermometer from the company Greisinger (type GTH 1200 A) were installed at following locations:

- pressure transducer: between the seats of the driver and the front passenger
- thermocouple 1: back of front passenger
- thermocouple 2: head of driver
- thermocouple 3: head of back passenger (right side).

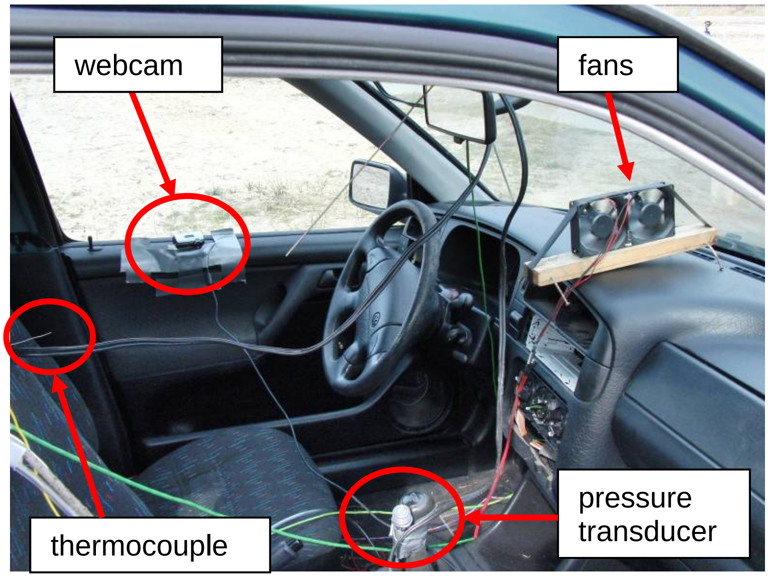


Fig. 21: View of the front passenger compartment with installed pressure transducer, fans, thermocouple and webcam

In order to get information about the gas mixture composition inside the compartment before and after the leakage of HFO1234yf a small flexible tube was installed close to the place where usually the back of the front passenger is located (Fig. 22, left picture). This tube was connected to an oxygen analyzer from the company Servomex (type 5200 Multipurpose, measuring range 0 to 100 vol-% O_2, resolution: 0.1 vol-%).

Three pyrotechnical igniters were used as ignition sources for this test series. They were modified in order to ignite matches. Each of them could be activated separately. First location was as well close to the place where the back of the front passenger is located (Fig. 22, left picture). The ignition was initiated this location at first, for here information about the gas phase composition was available due to the installed flexible tube. Two further igniters were installed at the seats of the front passenger and the right back passenger (Fig. 22).

The density of the refrigerant is bigger than the density of air. Therefore the HFO1234yf would be collected at the bottom of the compartment. However, the target of this test was to ignite a homogeneous mixture. In order to achieve this homogeneous mixture six fan bundles to a stack of two were installed at three locations: on the middle top of the dashboard, between the neck-rest and the seat-rest of the front passenger and below the roof of the driver (Fig. 23).

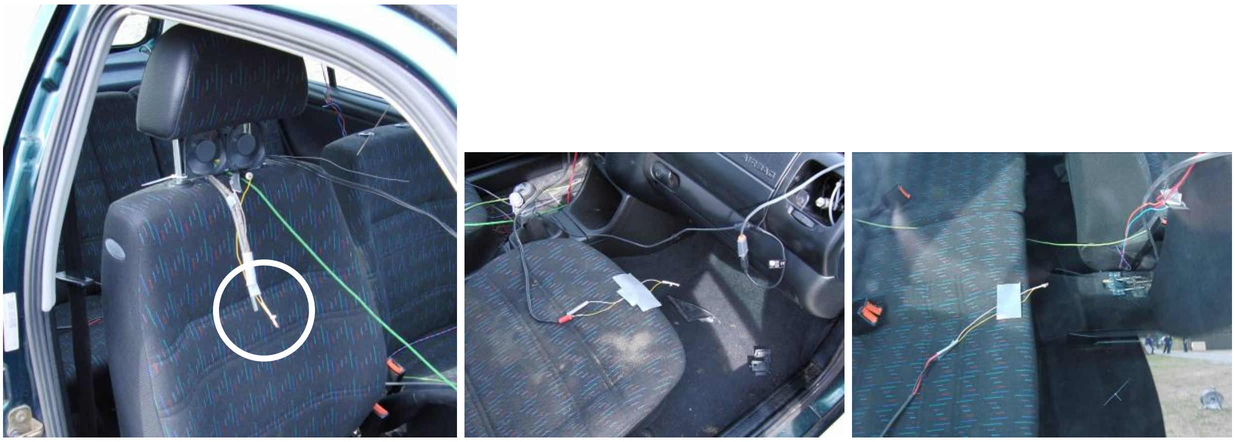


Fig. 22: Location of the modified pyrotechnical igniters for match ignition and location of the O_2-analysis tube

left picture: O_2-analysis tube and igniter
middle picture: igniter at the front passenger seat
right picture: igniter at the right back passenger seat

Fig. 23: Location of the fans for mixture homogenization

left picture: fans on the dashboard
middle picture: fans between the neck-rest and the seat-rest of front passenger seat
right picture: fan below the roof of the driver’s side

8.3 Results

8.3.1 Ignition of the leaking stream

In all together three tests the ignition of leaking streams of 260 g (first test), 160 g (second test) and 320 g HFO1234yf (third test) no flame propagation or any flame phenomena comparable to those described in the previous chapters, e. g, chapters 5, 6 and 7, were observed. In Fig. 24 a picture sequence is presented where the modified high voltage spark igniter was used in order to ignite a match. Due to the turbulences in the leaking stream the flame was extinguished soon after initiation.

Fig. 24: Picture sequence from the video record where a HFO1234yf stream was ignited by use of a modified high voltage spark igniter with a match

After each test the amount of HF possibly formed during the tests were detected. A person wearing protective clothing took three samples by opening the doors for approximately 30 s, at first behind the front passenger seat, then behind the driver's seat and finally at the driver's location. When the high voltage spark, the exploding wire igniter or the match were activated, no amounts of HF were detected. In case of the small propane torch lamp, where the open flame was much larger than the flame of the match, at all locations HF amounts over 90 ppm were detected.

8.3.2 Ignition of homogeneous HFO1234yf-air mixture in the compartment

For this test 900 g HFO1234yf were released to the passenger compartment of the car. During the filling process the six fans operated. The amount of oxygen in the compartment was analyzed during the test. As long as HFO1234yf was filled into the compartment the O_2-amount was lowered starting at 20.9 mol-%. The lowering of 0.1 mol-% O_2 resulted in approximately 0.5 mol-% HFO1234yf which were filled into the compartment. After the leakage of 900 g HFO1234yf into the compartment a O_2-amount of 19.9 mol-% were determined at the back-seat of the front passenger (location of the flexible tube for the O_2-analysis). Therefore the O_2-amount was reduced by 1 mol-%, so that finally approximately 5 mol-% HFO1234yf were filled into the compartment.

Before the first ignition was initiated the fans were switched off in order to avoid turbulences during the ignition which could influence a possible flame propagation. No "explosion" or flame propagation could be observed. The match burned and ignited the flexible tube located close to the ignition source. The test was recorded with two camcorder and the webcam. Picture sequences are presented in Fig. 25 and Fig. 27.

The seat of the front passenger started burning 25 s after ignition, at first the back-rest and afterwards the neck-rest. 50 s after ignition smoke development was observed. The smoke was collected below the roof. More important was the fact that at this time the windows got translucent from the inner side like milk glass. This was caused by the HF corrosion, which was first observed at the back window (Fig. 25, second row).

After 70 s an extreme smoke development was observed, attended with combustions especially in the back-room of the compartment. Smoke development stopped suddenly after 90 s. We supposed flame extinguishment at this moment. The O_2-analysis still operated. At this moment the amount of O_2 was only 10 to 11 mol-% and therefore too small to support a combustion. 230 s after the ignition was initiated the door was opened by use of a wire fixed to the handgrip of the front passenger door. No combustion was observed, only extensive yellow smoke got out of the compartment.

Fig. 25: Picture sequence from the video record of the ignition inside the passenger compartment.

Two pictures of the sequence presented in Fig. 25 were enhanced in order to show the corrosion of the window glasses in more detail. This corrosion was caused by the HF formed quickly after the combustion started in the compartment. The pictures were taken 50 s respectively 52 s after ignition.

Fig. 26: Enhancement of two pictures shown in Fig. 25 (first two pictures of the second row) in order to demonstrate the translucent glass as a matter of the HF corrosion 50 s resp. 52 s after the ignition started.

Another view of the test was given by the video record of the webcam (Fig. 27). Unfortunately the fixation became a bit loose, therefore ignition was only visible at the upper right side of the pictures. Nevertheless the start of the burning tube of the O_2-analysis could be seen as well as burning pieces from the roof fall down. The extreme smoke development after 70 s as well as the final flame after 90 s was recorded.

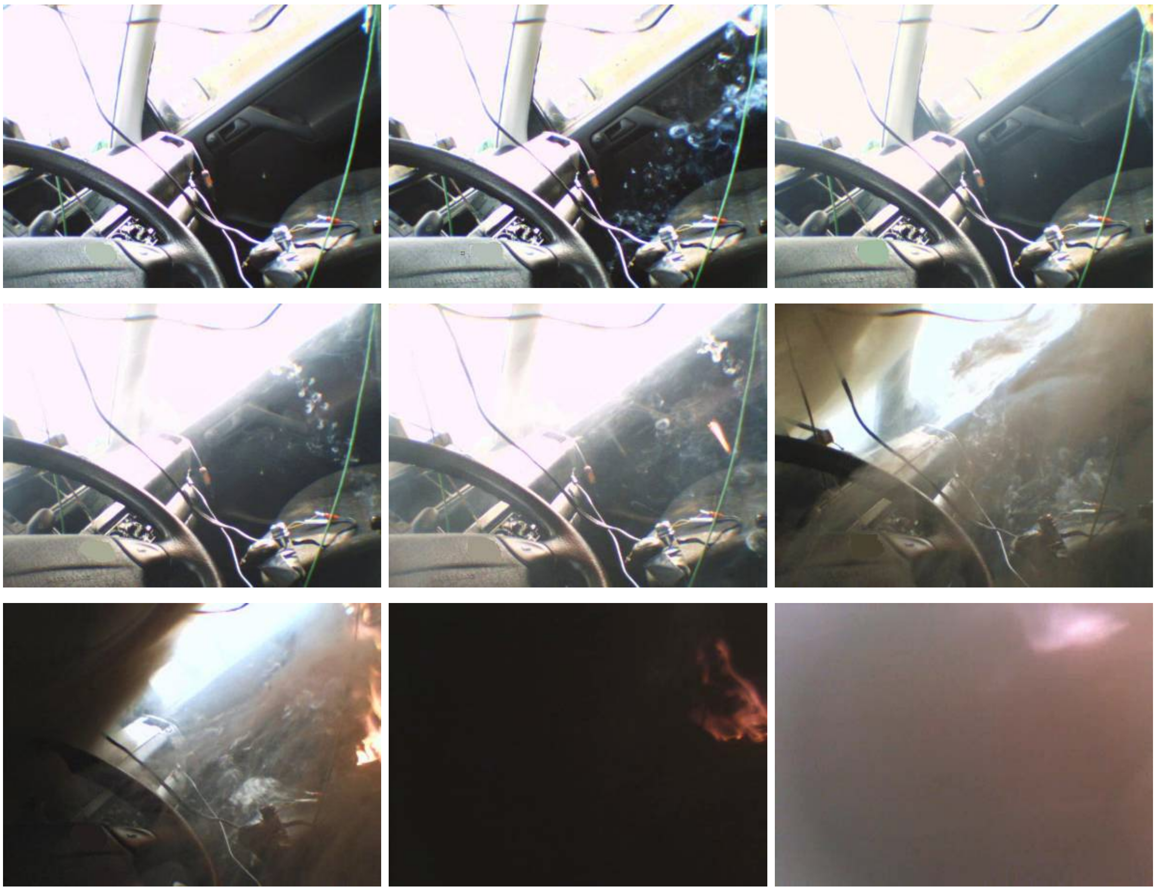


Fig. 27: Picture sequence from the webcam record inside the passenger compartment taken during the ignition.

During ignition further data were recorded in order to get as much information as possible during the test. Due to the fact that no explosion was observed no pressure peak was determined inside the compartment. Therefore the most important data were the temperature-time-histories recorded at different locations inside the compartment. The histories are presented in Fig. 28. The time scale differs from the above mentioned scaling, because the data acquisition started during the time period where the HFO1234yf was introduced to the compartment. Ignition was initiated after approximately 100 s after the start of the introduction of HFO1234yf to the compartment.

Due to the combustion development inside the passenger compartment the temperatures increased to a max. of 585 °C (location: head of front passenger) respectively 555 °C (location: head of driver) and 358 °C (location: head of back passenger). The max. temperature values at the different locations were reached after different times and validate the supposed combustion development inside the compartment.

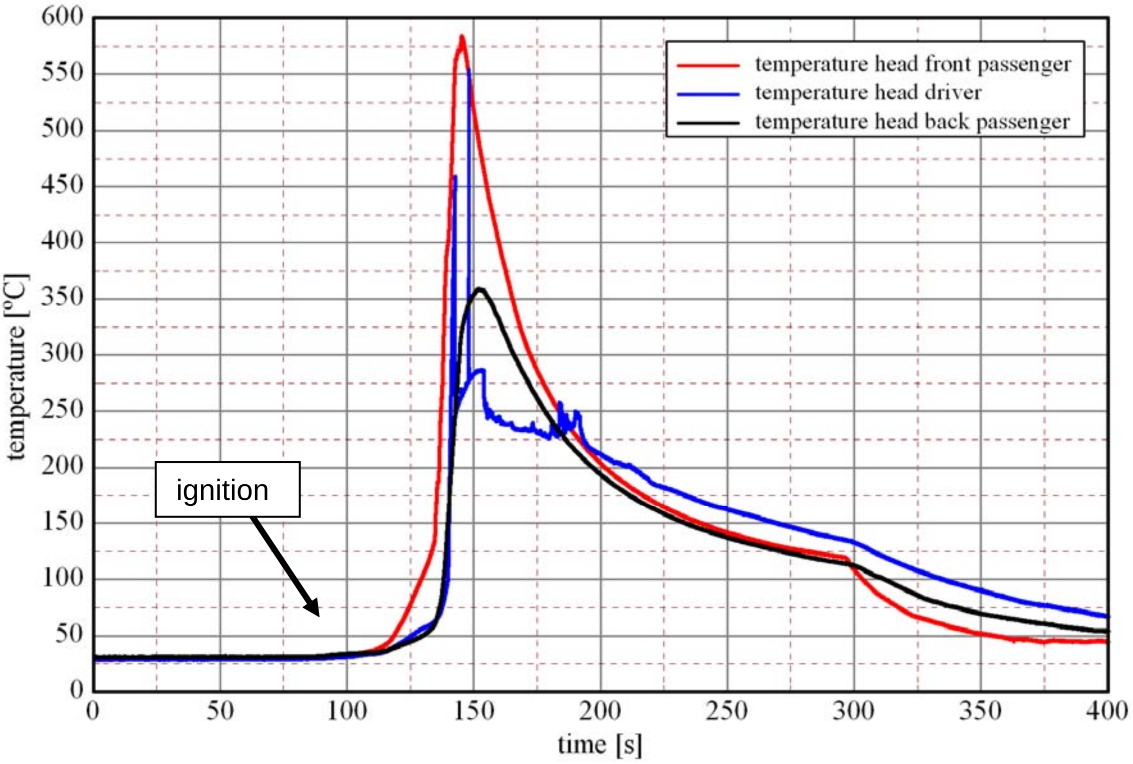


Fig. 28: Temperature-time-histories of the three thermocouple installed to the passenger compartment.

Fig. 29 presents pictures after the test. Beside the typical view of a combustion inside the passenger compartment of a car the translucent glasses caused by HF corrosion were most impressive. Such corrosion effects were initiated at high HF amounts which were supposed to be much higher than 90 ppm and already occurred 50 s after the combustion started. The HF amount was not validated by measurements.

Fig. 29: Pictures taken after the combustion in the passenger compartment. Beside the typical view of such an event the translucent glasses caused by HF corrosion are impressive.

9 Safety evaluation

BAM was commissioned by the German Federal Environment Agency (UBA) to examine the reaction behaviour of 2,3,3,3-Tetrafluoroprop-1-ene (HFO-1234yf) when exposed to ignition sources like spark ignition or hot surfaces. It was published by different authors that this substance will be used as new refrigerant in MAC of cars as it has a much lower global warming potential than the actual refrigerant R134a. But the new refrigerant is a flammable gas. According to the Globally Harmonized System (GHS) HFO1234yf is classified as “extremely flammable” as it has a lower flammability below 13 mol-% [5]. Consequently, different institutes worldwide started examinations in order to determine potential hazards using HFO1234yf in MAC. The assessment of the hazards presented by a substance in normal use in technical equipment cannot take place based on only a single individual test series. Various systematic scenarios ("incidents") must be analysed and a holistic hazard analysis performed. Only then it is possible to comment reliably on the dangers posed by the use of such a substance in technical devices.

Therefore several studies were carried out and presented in this test report in order to examine some incidents and to determine possible hazards resulting from the exchange of the actual refrigerant R134a. The focus of all examinations was not only the determination of the flammability in different realistic scenarios. Also the formation of HF was of great interest due to hazards caused by the toxicity of HF. In this tests for UBA, lab scale tests as well as tests with a car have been carried out.

The main conclusions of all examinations presented in chapters 3 to 8 can be summarized as follows:

- The refrigerant HFO1234yf is not that easy to ignite as substances like propane or petrol vapours. Furthermore the LEL is higher compared to those substances.
- Ignition behaviour - when HFO1234yf is exposed to ignition sources like spark ignition etc. - is to describe as unpredictable and is strongly dependent on the circumstances at which the refrigerant is released and on the flammable mixtures with air occuring.
- Below the LEL concentration of about 6 mol-% HFO 1234yf no self sustaining flame propagations could be observed, but extreme stretches of typical blue flames.
- Once a flame stretch was observed parts of the flame were detached. These flames can lead to fires dependent on the surrounding of the flame detachments.
- The minimum ignition temperature of HFO1234yf is 405 °C. This is defined as the lowest temperature at which an ignition can occur when the most ignitable mixture is present. In release scenarios higher surface temperatures are needed for an ignition. This temperature can be decreased if other flammable substances are present, e. g. petrol in cars.
- Regarding fire and explosion hazards it can be pointed out that in a car, in addition to the air conditioning system refrigerant, many other substances like fuels and materials are used, which – depending upon the scenario – can also lead to hazards to humans and the environment. The additional hazard regarding fire and explosion caused by the HFO1234yf is comparable low compared to all other fuels and materials.
- Critical is the formation of hazardous amounts of HF when HFO1234yf is exposed to ignition sources like open flames and hot surfaces. In nearly all tests where the refrigerant was released at specified test conditions the detected HF amounts exceeded critical amounts for humans health. According to the “Acute Exposure Guideline Levels (AEGL) these amounts are that high that after 10 min exposure irreversible damages to somebody’s health can occur. In Tab. 6 the AEGL values for HF published by the US-National research council and the National Academy of Sciences are presented [9].
- The tests were carried out in comparison to R134a, the actual refrigerant in MAC. This refrigerant is non-flammable at atmospheric conditions. Nevertheless at elevated conditions of temperature and/or pressure or the presence of other fuels it can ignite.
- R134a is a fluorinated hydrocarbon which can also form HF when exposed to ignition sources. Nevertheless it is not that reactive as HFO1234yf so that the hazards regarding HF formation is evaluated to be lower for 134a than for the HFO1234yf.

Tab. 6: AEGL values for Hydrogen fluoride (ppm) [9]

time of exposure	10 min	30 min	60 min	4 h	8 h
AEGL 1 [ppm]	1.0	1.0	1.0	1.0	1.0
AEGL 2 (irreversible damages to humans health) [ppm]	95.0	34.0	24.0	12.0	12.0
AEGL 3 (life-threatening or lethal) [ppm]	170.0	62.0	44.0	22.0	22.0

Finally it can be summarized that in case of HFO1234yf usage a careful holistic hazard analysis has to be performed. Many precautions will have to be defined to assure that the hazards are ethical and justifiable according to the actual state of technology.

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