Technical Report
Investigations into the possible flammability of refrigerant R1234yf in motor vehicles

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942-7191376-00	07.10.2013	GP	Approved version
942-7191376-01	05.12.2013	GP	Correction of table 4

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0. General

This Technical Report contains observations, data and evaluations of the possible flammability of refrigerant R1234yf in motor vehicles.

We would point out that this report does not replace any official approval procedures prescribed by law. The report may, however, be useful for decision-making.

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This report is only transferable and valid for vehicles, components and structures which correspond to the tested samples in all respects.

1. Procedure

1.1. General information

1.1.1. Client

Kraftfahrt-Bundesamt

24932 Flensburg, Germany

1.1.2. Journal numbers

2013-942.2-0033	Subaru Impreza
2013-942.2-0034	Opel Mokka
2013-942.2-0035	Hyundai i30
2013-942.2-0036	Mercedes B180

1.1.3. QS Number

3 942 1 093

1.1.4. Testing period

27th of May 2013 to 11th of July 2013

1.2. Introduction

The Federal Motor Transport Authority (Kraftfahrt-Bundesamt — KBA) has been active, in its capacity as product safety authority in the motor vehicle sector, in conducting a risk assessment for the use of R1234yf in passenger car air conditioning systems.

TÜV Rheinland was commissioned by the KBA to assist the authority, in the context of this risk assessment, in developing test procedures and carrying out the necessary technical tests.

The definition of the test scenarios was discussed and developed in the project group, consisting of the KBA, the Umweltbundesamt [federal environmental authority] (UBA), the Federal Institute for Materials Research and Testing (BAM), the Federal Highway Research Institute (Bundesanstalt für Straßenwesen — BASt) and TÜV Rheinland. The final decision lay with the steering committee, consisting of the KBA, UBA, BAM, BASt and the Federal Ministry of Transport, Building and Urban Development (BMVBS). TÜV Rheinland acted exclusively as technical adviser to the steering committee.

The crash parameters were determined by means of evaluation by BASt of the GIDAS (German In-Depth Accident Study) database with regard to frequently occurring frontal collisions with damage to the air conditioning system. The crash tests were to reproduce an end-of-tailback collision with running, hot engine and running air-conditioning system. The KBA specified a ‘wet/warm’ crash, to be carried out with thermal preconditioning and with the engine running and the air-conditioning system activated.

As instructed, TÜV Rheinland obtained four vehicles as a blind purchase without specifying the intended use. The selection of the vehicles to be obtained was made by the KBA based on registration statistics.

The vehicles involved were a Subaru Impreza, an Opel Mokka, a Hyundai i30 and a Mercedes B180. An exact description of the test vehicles is provided in Annex T1.

It was decided to conduct the tests in two phases.

Phase 1:

Determination of maximum temperatures and warm/wet crash test. This means a crash with the engine at operating temperature and all automotive fluids.

Phase 2:

Defining the vents using the damage in the crash test and conducting the leakage tests with the vehicle conditioned to the target temperature.

As the first step, the maximum temperatures of components in the engine compartment under realistic driving conditions were determined. These temperatures would serve as target temperatures for the vehicle conditioning in the leakage tests to be carried out in the subsequent testing procedure.

After the crash tests, the vehicles were evaluated with regard to the damage to their air conditioning systems. From the damaged components of the air conditioning systems, vents for the subsequent leakage tests were generated, which were placed in the originally installed position after the crash. The vehicles were minimally repaired to make them drivable under their own power with an intact engine cooling system and an intact air conditioning system. As the subsequent tests took place on a closed-off test site, only drivability, but not traffic safety, was taken into account with the repairs.

For the leakage tests, the KBA specified three stages.

In Stage 1, only the air conditioning system components damaged in the crash were used as vents.

In Stage 2 there was minor extrapolation of the damage to the components. This means, for example, that in certain places in damaged but still airtight components, specific leaks were created such as, in the estimation of engineers, would be very likely to have been produced as a result of different arrangement of components in the crash situation.

Stage 3, which served to validate the results, took into account vents through components of the air conditioning system that might occur in the future, for example through ageing of the line material and/or higher impact speeds and/or higher temperatures around the engine.

Before all leakage tests, the vehicles were conditioned, by means of a towing dynamometer under load, to the engine compartment target temperatures determined in advance. Once constant target temperatures had been achieved, the vehicles were parked on the test site. The leakage tests were conducted in each case with the engine stopped and with the cooler fan electrically switched off. In addition to the vents for refrigerant, damage to the coolant radiator of each vehicle was also simulated by means of a vent. The hydrogen fluoride (HF) concentrations in the engine compartment were determined during the leaking of the refrigerant at points chosen in advance depending on the vehicle. For each test, the air conditioning systems of all the vehicles were filled with refrigerant to the respective manufacturer’s specified nominal filling level.

2. Testing procedure

2.1. Vehicle preparation and determination of target temperature

After the vehicles had been obtained, four temperature sensors were fitted in the engine compartment of each vehicle. By this means, the surface temperature of the exhaust manifold (or turbocharger if applicable), the catalytic converter and the manifold heat shield were determined, together with the temperature of the coolant in the engine cooling circuit. The exact positioning of the temperature sensors is shown in Annex T1.

The air conditioning systems of all of the vehicles were evacuated and filled with refrigerant R1234yf to the nominal filling level specified by the manufacturer. The compressor oil removed during the evacuation process was added again during the filling process. In order to render leaked refrigerant visible in the crash test, 5g of UV tracer fluid was added to the systems in each case.

The maximum temperatures at the measuring points on the components in the engine compartment needed to be determined under realistic driving conditions. Therefore, the vehicles were repeatedly driven at top speed over a long period until in each case a constant temperature was achieved at the measuring points. The maximum temperatures thus determined were used to specify the target temperatures for the leakage tests which followed later in the testing process. The target temperature for the leakage tests was set as follows: $T_{Test} = T_{max} - 50°C$. This was determined in the following way. The test is intended to simulate a crash event after fast driving on a motorway. It is assumed that braking occurs before impact. Such braking from high speed to impact speed (40 km/h) results in a cooling of the components in the engine compartment. In general tests it has been shown that a temperature drop of approximately 50°C occurs with such slowing down. This procedure for determining target temperatures is also used by the German Automobile Industry Association (VDA).

The temperatures were determined at ambient temperatures of 20 +/- 5°C. The air conditioning systems were set at the lowest temperature and the ventilation was set at the highest level. The vehicles were not additionally loaded and were occupied by two persons.

2.2. Crash tests

The crash tests took place on 10th and 11th of June 2013 at the crash facility of TÜV Rheinland TNO Automotive International B.V. in Helmond (the Netherlands). Representatives of the KBA and the BAM were present at the tests.

The crash parameters established from the BASt evaluation of the GIDAS database represented the following scenario:

The tests were conducted in conformity with ECE-R94. The only deviations from this related to the impact speed and the impact side. The crash speed for all the vehicles was 40 km/h. The vehicle crashed into a barrier with a normalised deformation element as also defined in ECE-R94. The offset amounted to 40 % of the vehicle width. The impact side was chosen, for each vehicle, as the side on which the air conditioning compressor and the lines feeding the refrigerant to the air conditioning condenser were integrated.

The crash tests were conducted with the engine running at operating temperature and the engine cooling fan electrically switched off. The engine fans were switched off before the crash tests in each case in order to prevent a drop in temperatures at the surfaces of the components in the engine compartment due to an in-flow of air upon acceleration of the vehicles to impact speed, and in order to ensure that the fan was not in operation in any of the vehicles after the impact.

For the tests, triple-axis acceleration sensors were mounted on each vehicle on the left and right sills at the height of the B-pillar and the data were registered during the crash. The temperatures at the four measuring points in the engine compartment were also measured and recorded during the tests. The measurement records of the acceleration and temperatures can be found in Annex T2. All of the tests were recorded from the exterior using high-speed cameras (right, left, above). In addition, two HD cameras were fitted in a crash-proof manner in each engine compartment.

The vehicles were run at high idling speed while stationary until a constant temperature at the exhaust manifold/turbocharger of greater than 300°C was reached, and the temperature in the engine cooling circuit, after switching off the cooling fan, exceeded 100°C, in order to ensure the conditions for a vaporous leakage of coolant in the engine compartment.

Directly after the impact test, the HF concentration was measured using a Dräger test tube in the region of the bulkhead of the engine compartment and in the region of the driver’s head in the cockpit.

After the crash tests had been conducted, an evaluation of obvious damage was carried out on the spot without dismantling any components.

2.3. Vehicle evaluation and preparation for the leakage tests

Afterwards, the vehicles were examined in detail. For this purpose, parts of the front of the vehicle were dismantled. All the relevant components of the air conditioning and cooling system were assessed in detail for damage. Traces of leakage of the refrigerant were detected in the engine compartment and on the components using UV light. The results of these examinations can be found as photo documentation in Annex T3.

After that, the cooling and air conditioning systems were repaired. In the process, vents for refrigerant and coolant were applied at the places where there had been damage after the crash tests. The vents were thus located more or less at the original position after the crash. In the vehicles in which the air conditioning circuit was intact after the crash tests, the vents for the second and third stages were placed where there were marks (points of contact/traces of pressure) on the air conditioning components due to reduction of installation space, or where the manufacturer had supplied empirical data about damage with high energy inputs.

The vents were created from the damaged air conditioning components and, depending on where in the air conditioning system they were sited, refrigerant had flown through them by means of solenoid valves on the high pressure or the low pressure side. In addition, a vent was integrated into the engine cooling circuit in each vehicle.

As a preventive measure, all of the vehicles were fitted with a CO2 fire extinguisher in the engine compartment.

2.4. Leakage tests

The leakage tests took place on 9th to 11th of July 2013 with the support of BAM at its testing site in Horstwalde (Baruth/Mark) in the presence of representatives of the KBA. Representatives of the UBA and the BASt were also present for part of the time.

Before each leakage test, the air conditioning system was filled with refrigerant to the nominal filling level specified by the manufacturer. In addition, before the first leakage test, 5g of UV tracer fluid was added to the systems. The vents were selected according to the Stages (1 to 3) by means of the solenoid valves. The vehicle was driven hot on the closed-off test site using a towing dynamometer until the specified target temperature at the components in the engine compartment was constant. The vehicle was parked on the testing site and the engine and ignition were switched off. The cooling fan was switched off electrically shortly before being driven onto the testing site. The HF concentration was measured during leakage in the engine compartment with the aid of a LaserGas III measuring device and also using two hand pumps fitted with Dräger test tubes. The HF concentration in the cockpit was recorded using an automatic Dräger pump, likewise fitted with a Dräger test tube, fitted to the sun visor in the region of the driver’s head.

The visual assessment of the leakage in the engine compartment was again done using two HD cameras in the same positions as in the crash tests. In addition, an HD camera was fitted to the probe of the LaserGas III measuring device

Details of the settings of the air conditioning system, the target temperatures, the temperatures at the start of leakage and the measured HF concentration can be found in Tables 3 and 4 and the diagrams and photos in Annexes T5 to T7.

3. Crash tests

3.1. Overview of the crash parameters

The following table gives an overview of the parameters of the crash tests conducted.

	Hyundai i30	Mercedes Class B	Opel Mokka	Subaru Impreza
Test No.	F13240103	F13240101	F13240102	F13240104
Test weight	1425 kg	1589 kg	1613 kg	1511 kg
Impact speed	39,7 km/h	39,8 km/h	39,7 km/h	39,7 km/h
Refrigerant fill quantity	500g	650g	570g	450g
Impact side	Right	Right	Right	Left
$T_{Coolant}$ (on impact)	112,3°C	102,5°C	115,2°C	103,2°C

Table 1: Crash parameter per vehicle

3.2. Overview of crash results

The following table gives an overview of the results of the crash tests.

	Hyundai i30	Mercedes Class B	Opel Mokka	Subaru Impreza
Test No.	F13240103	F13240101	F13240102	F13240104
Airbags deployed?	Yes (Driver's airbag and passenger's airbag)	Yes (Driver's airbag, passenger's airbag and knee airbag)	No	Yes (Driver's airbag, passenger's airbag and knee airbag)
Hazard warning lights on?	No	Yes	Yes	No
Does the engine run after the crash?	Yes, ignition switched off manually	No	No	approx. 5 sec
Does the interior fan run after the crash?	No	No	No	Yes
Cooling fan in running order?	Yes after dismantling	Yes after dismantling	Yes after dismantling	Left: No Right: Yes
Leakage of refrigerant?	Yes	No	No	Yes
Temperatures (on impact)	400,2°C exhaust manifold	373,1°C turbo charger	350,4°C turbo charger	340,4°C exhaust manifold

Table 2: Crash results per vehicle

3.3. System evaluation of the vehicles' air conditioning systems after crash test

The following section describes the damage to the vehicles after the crash tests, as ascertained after detailed examination of the vehicles. In addition, details are given of the repairs which were needed in order to restore the rudimentary driveability of the vehicle.

3.3.1. Hyundai

The impact on the Hyundai occurred with 40 % offset on the right side of the vehicle.

Without dismantling work, the front bumper, the bonnet, the right wing and the right headlamp could be identified as damaged parts.

After dismantling of these parts, damage to the front cross-member and to the radiator support was visible.

On the right longitudinal member, the crash box had been absorbed by the impact; the longitudinal member was buckled right up to behind the right wheel housing and was in contact with the side of the belt drive of the engine. The poly-V-belt had been pushed of the pulley.

The air conditioning condenser was deformed and presented leakage points. In addition, the air conditioning lines to the air conditioning condenser were deformed; the low-pressure return collector line of the air conditioning system was damaged in the region of the right longitudinal member in the flexible hose area, which resulted in heavy leakage of refrigerant. Traces of refrigerant were found on the condenser, on the water cooler, in the region of the right longitudinal member, on the right side of the engine, on the right wheel housing and also on the bulkhead to the passenger compartment.

The water cooler was deformed and presented breaches in the region of the tank and damage to the radiator core in the region of the impact.

As a result of the impact, the radiator assembly was displaced towards the engine, the radiator frame with fan was, in the area of the air conditioning compressor and the intake manifold, in contact to the engine.

Observation of the underside of the vehicle showed that the front underbody panelling was damaged.

Furthermore, when the underside of the engine was exposed, it was noticeable that the central screw of the crank shaft pulley had become loose and was projecting by approximately 30 mm at the side.

The photo documentation of the damage can be found in Annex T3.

In order to restore the driveability of the vehicle for the leakage tests, the water cooler, the cooling fan including the radiator frame, the air conditioning condenser, the air conditioning lines to the air conditioning condenser, the crankshaft pulley including the retaining screw, the poly-V-belt and the alternator regulator were replaced. The right longitudinal member was only straightened to the extent that there was no longer any contact with the engine and the engine could move within the engine mounts.

3.3.2. Mercedes

The impact on the Mercedes occurred with 40 % offset on the right side of the vehicle. Without dismantling work, the front bumper including the radiator grille, the bonnet, the right wing and the right headlamp could be identified as damaged parts.

After dismantling of these parts, damage to the front cross-member, the radiator support and the intercooler was visible.

On the right longitudinal member, the crash box had been absorbed by the impact; the longitudinal member itself showed slight deformation in the front region.

The poly-V-belt had been pushed of the pulley.

The air conditioning condenser was deformed and showed marks in the radiator core at the front. There was no point of leakage of refrigerant. The air conditioning lines were deformed by the impact, but showed only crash marks in the region of the air conditioning compressor and the right longitudinal member, but no leaks.

The water cooler was deformed and presented breaches in the region of the tank and damage to the radiator core in the region of the impact.

As a result of the impact, the radiator assembly was displaced towards the engine; the radiator frame with fan was in contact to the air conditioning compressor, the right hose of the intercooler, the intake plenum of the turbocharger and the thermostat case.

Observation of the underside of the vehicle showed that the front underbody panelling was damaged.

The photo documentation of the damage can be found in Annex T3.

In order to restore the driveability of the vehicle for the leakage tests, the water cooler, the cooling fan including the radiator frame, the air conditioning condenser, the air conditioning lines to the air conditioning condenser, the poly-V-belt, the turbocharger, the intake plenum, the turbocharger lines, the right hose of the intercooler, the intercooler, and the water pump including the thermostat case were replaced.

3.3.3. Opel

The impact on the Opel occurred with 40 % offset on the right side of the vehicle. Without dismantling work, the front bumper including the radiator grille, the bonnet, the right wing and the right headlamp could be identified as damaged parts.

After dismantling of these parts, damage to the front cross-member, the radiator support and the intercooler was visible.

On the right longitudinal member, the crash box had suffered almost no deformation from the impact; however, the longitudinal member showed buckling in the region behind the front axle. The poly-V-belt had been damaged as a result of the contact with components.

The air conditioning condenser was deformed and showed crash marks in the radiator core at both the front and the back. There was no leakage of refrigerant. The air conditioning lines had been deformed by the impact, but, apart from crash marks in the right longitudinal member region and in the region of the air conditioning compressor, showed no leaks.

The water cooler was deformed and presented breaches in the region of the tank and damage to the radiator core in the region of the impact.

As a result of the impact, the radiator assembly was displaced towards the engine; the radiator frame with fan was in contact with the air conditioning compressor as well as the right hose of the intercooler and the thermostat case.

Observation of the underside of the vehicle showed that the front underbody panelling was damaged. Furthermore, when the underside of the engine was exposed, it was noticeable that the lower front axle beam had been displaced towards the back, and that the engine/gear unit had been slightly displaced to the side within the flexible mounting.

The photo documentation of the damage can be found in Annex T3.

In order to restore the driveability of the vehicle for the leakage tests, the water cooler, the cooling fan including the radiator frame, the air conditioning condenser, the air conditioning lines to the air conditioning condenser, the poly-V-belt, the right hose of the intercooler, the intercooler and the thermostat case were replaced.

3.3.4. Subaru

The impact on the Subaru occurred with 40 % offset on the left side of the vehicle.

Without dismantling work, the front bumper, including the radiator grille, the bonnet, the left and right wing and the left headlamp could be identified as damaged parts. After dismantling of these parts, damage to the front cross-member and to the radiator support was visible.

On the left longitudinal member, the crash box had been absorbed by the impact; the left longitudinal member was buckled right up to the middle of the wheel housing in the region of the impact and was in contact with the engine.

The air conditioning condenser was deformed and presented leakage points. In addition, the air conditioning lines to the air conditioning condenser were deformed.

Traces of refrigerant were found on the water cooler and on the front side of the engine. However, despite crash marks on the air conditioning lines, no leakage of refrigerant was found on these components.

The water cooler was deformed and presented breaches in the region of the tank on the impact side.

As a result of the impact, the radiator assembly was displaced towards the engine. The radiator frame including the left engine fan was in contact with the engine in the region of the impact; the poly-V-belt had been pushed of the pulley.

Observation of the underside of the vehicle showed that the front underbody panelling was damaged. The panelling under the engine showed heavy buckling as a result of the displacement of the front location points.

The photo documentation of the damage can be found in Annex T3.

In order to restore the driveability of the vehicle for the leakage tests, the water cooler, the left cooling fan including the radiator frame, the air conditioning condenser, the air conditioning lines to the air conditioning condenser and the poly-V-belt were replaced. The left longitudinal member was only straightened to the extent that there was no longer any contact with the engine and the engine could move within the engine mounts.

4. Leakage tests

4.1. Definition of the vents (type and location)

The vents were defined based on the damage to the air conditioning system which occurred during the crash tests.

The vents were operated by means of a solenoid valve in each case. The tapping in the air conditioning system was chosen such that the vents were loaded with the same refrigerant pressure as they are at the same points in the undamaged air conditioning system.

The cooling water vent was also operated by means of a solenoid valve; the tapping was done on the upper water cooler inlet. This type of leakage was chosen in order to approximate as closely as possible to the behaviour in a crash, while at the same time representing a worst-case scenario (escape of steam).

In all the tests, the cooling water vent was positioned near the lower connection of the water cooler.

On the vehicles, the following vents for the refrigerant were established:

4.1.1. Hyundai

For Stage 1, vents were established from the air conditioning condenser on the high pressure side, and from the damaged hose (split length approx. 10 cm) of the return line on the low pressure side. The damage corresponded exactly to the damage which had occurred during the crash test.

For Stage 2, the same vent locations were defined, with the difference that the opening in the hose was smaller in the damaged part of the return line. For this vent, an intact hose was slit for a length of approx. 2 cm using a blade.

For the tests in Stage 3, one time the hose from Stage 2 was used as the only vent. The hose was rotated by 90 degrees so that the slit in the hose was pointing in the direction of the engine. In a further test in Stage 3, in addition to the rotated hose already used, there was also a vent from the air conditioning condenser. Here, however, a baffle plate was also placed in front of the vent point, in order to create a different flow pattern of refrigerant into the engine compartment.

4.1.2. Mercedes

As the air conditioning system of the Mercedes showed no leakage after the crash test, no Stage 1 tests were conducted.

For Stage 2, the air conditioning condenser was perforated in the region of the crash marks, so that refrigerant could escape at these points.

For Stage 3, according to the manufacturer's advice, a hose injection of the high pressure line from the compressor to the condenser was indented so as to produce a concave oval opening (shaped like a fish mouth) towards the engine side. According to the manufacturer, this type of damage can be observed in impact tests with a higher energy input. In the tests in Stage 3, the leakage was through the condenser element and also through the damaged hose line. In further tests in Stage 3, the leakage was only through the damaged hose line.

4.1.3. Opel

As the air conditioning system of the Opel showed no leakage after the crash test, no Stage 1 tests were carried out.

For Stage 2, the air conditioning condenser was perforated in the region of the crash marks at the front and at the back, so that refrigerant could escape at these points.

For Stage 3, in addition, damage to the low-pressure side refrigerant line was simulated in the region of the right longitudinal member, as the line had been subject to heavy deformation in this region during the crash test. Stage 3 also comprised a leakage test with only this line vent, and a leakage test with this line vent rotated by 90 degrees with the leakage opening towards the engine. In a further test in Stage 3, in addition to the rotated line vent already used, there was also a vent from the air conditioning condenser. Here, however, a baffle plate was also placed in front of the vent point, in order to create a different flow pattern of refrigerant into the engine compartment.

4.1.4. Subaru

For Stage 1, a vent was established from the air conditioning condenser on the high pressure side. The damage corresponded exactly to the damage which had occurred during the crash test.

For Stage 2, an additional vent was created from a high-pressure refrigerant line. This line showed a crash mark after the crash test. This crash mark was manually deepened, so that a leakage point and thus a vent were produced.

4.2. Summary of leakage tests Stage 1 and Stage 2

In the leakage tests Stage 1 and 2, no ignition of the refrigerant was observed. The HF concentrations measured in the engine compartment in these tests were lower than 1 ppm. (see Annex T6, Figure 215)

4.3. Summary of leakage tests Stage 3

In the Stage 3 tests, there was ignition in the case of one vehicle. Here, only one vent had been used in the refrigerant line on the high pressure side. In order to investigate the reproducibility of this result, the test was repeated twice under the same boundary conditions (target temperatures): in the first repetition, there was no ignition and in the second repetition ignition occurred. In addition, a comparative test in this configuration was conducted with refrigerant R134a. No ignition was observed.

The flames were prevented from spreading to other parts of the engine compartment by deploying the CO2 fire extinguisher. The fire extinguisher was activated at least 10 seconds after detection of ignition.

In the tests where ignition of the refrigerant had occurred, HF concentrations of over 3 000 ppm were detected in the engine compartment for a short time. Upon detection of ignition, the measurement technicians were moved back from the vehicle for safety reasons. The measuring probe of the LaserGas III was removed from the engine compartment at the same time.

In other tests in Stage 3, an HF concentration greater than 95 ppm was also clearly detectable for a short period of time. The HF concentrations measured in the engine compartment are shown in the diagrams in Annex T6.

At the measuring points in the interior of the vehicle, no HF concentration was found in any of the tests.

The temperature progression during the leakage tests is shown in Annex T5 for each test individually.

Test No.	Target temperature	Air conditioning system setting	Vents used
V01	617°C	Fan max, temp min	Condenser, hose – large
V02	706°C	Fan max, temp min	Condenser
V03	617°C	Fan auto, temp 22°	Condenser, hose – large
V04	706°C	Fan auto, temp 22°	Condenser
V05	706°C	Fan auto, temp 22°	Condenser + line
V06	617°C	Fan auto, temp 22°	Condenser, hose – small
V07	617°C	Fan auto, temp 22°	Hose – small
V08	734°C	Fan max, temp min	Condenser
V09	734°C	Fan medium, temp 22°	Condenser
V10	734°C	Fan medium, temp 22°	Condenser + line
V11	734°C	Fan medium, temp 22°	Line
V12	660°C	Fan max, temp min	Condenser
V13	660°C	Fan medium, temp 22°	Condenser
V14	660°C	Fan medium, temp 22°	Condenser + line (“fish mouth”)
V15	660°C	Fan medium, temp 22°	Line (“fish mouth”)
V16	660°C	Fan medium, temp 22°	Condenser + line (“fish mouth”)
V17	660°C	Fan medium, temp 22°	Line (“fish mouth”)
V18	660°C	Fan medium, temp 22°	Line (“fish mouth”)
V19	734°C	Fan medium, temp 22°	Line, rotated
V20	734°C	Fan medium, temp 22°	Condenser + line with baffle plate
V21	660°C	Fan medium, temp 22°	Line (“fish mouth”) with 134a
V22	max	Fan medium, temp 22°	Condenser + hose – small, rotated + baffle plate

Table 3: Overview of leakage tests, test conditions

Test No.	Temperatures at start of leakage in °C				HF readings, LaserGas III maximum / in ppm
	Thermo 1	Thermo 2	Thermo 3	Thermo 4	
V01	635,3	474,4	132,8	109,7	0,10
V02	706,3	582,8	206,9	102,0	0,36
V03	617,7	441,1	107,9	92,4	0,12
V04	704,5	586,3	209,3	104,0	0,09
V05	706,8	584,4	227,8	104,8	0,08
V06	619,9	434,0	101,0	92,5	0,07
V07	615,0	387,5	104,0	91,6	0,18
V08	744,1	443,5	114,3	119,0	0,09
V09	749,5	374,4	132,9	104,4	0,41
V10	754,6	392,5	132,4	106,1	0,14
V11	751,8	385,6	127,3	101,6	0,35
V12	698,7	474,2	119,0	109,1	0,45
V13	690,8	496,6	107,5	104,6	0,23
V14	692,8	482,8	112,2	105,3	0,44
V15	694,1	479,6	112,8	103,9	5.364,98
V16	678,4	452,8	133,8	101,0	2,40
V17	696,4	473,9	119,8	104,5	3,57
V18	705,4	476,7	116,2	105,8	3.254,22
V19	764,0	426,9	124,8	104,0	17,97
V20	770,1	399,2	130,9	107,0	150,41
V21	698,2	443,8	121,4	102,4	3,12
V22	697,6	517,1	124,9	101,2	133,20

Table 4: Overview of leakage tests, readings

5. Summary

For the investigation of the possible flammability of refrigerant R1234yf in motor vehicles, as instructed, four vehicles specified by the client were obtained as a blind purchase from the market and extensive tests were carried out on these vehicles.

The tests were carried out in two phases. In the first phase, maximum-speed test drives were undertaken to determine the temperatures of components in the engine compartment. The temperatures thus measured, which would be needed in the subsequent tests, were recorded.

Cooperating with BASt and using the GIDAS database, a crash scenario appropriate to the test purposes was developed. An impact constellation based on ECE-R94 was considered, with an offset of 40 % relative to a deformable barrier, but with an impact speed of 40 km/h. For this, the vehicles were driven with the engine running at operating temperature and with the air conditioning turned on. The impact was on the side of the vehicle in which the main components of the air conditioning system are mounted.

In the tests, refrigerant was found to have escaped from the air conditioning system in two of the four vehicles. There were no ignitions.

In the second phase, based on the damage and crash marks on the air conditioning system components, vents were established for all four vehicles for the subsequent tests.

In some cases, the vents were created from the components damaged in the crash. In other cases, damage was caused deliberately in the places that had already sustained a degree of damage, yet without indications of any leaks.

The leakage tests were conducted in three stages. The first stage corresponded to the damage to the air conditioning components sustained in the crash test. In the second stage, the vents with deliberate damage were also used. The third stage tested various vent configurations that could be expected to occur under unfavourable conditions.

No ignition of the refrigerants was observed in first and second stage tests. Ignition was observed in one of the four vehicles during third stage testing. This ignition was confirmed in one of two repeating tests conducted under the same boundary conditions.

In a comparative test under these boundary conditions using the R134a refrigerant, no ignition was observed.

6. Overview of the annexes

Annex T1:
Vehicle description and vehicle test configuration

Annex T2:
Crash tests

Annex T3:
Detailed photos of damages after crash tests

Annex T4:
Photos of the vents

Annex T5:
Temperature charts – leakage tests

Annex T6:
HF concentrations – leakage tests

Annex T7:
Pictures of the leakage tests

Annex T8:
Measuring equipment used

Cologne, 07th of October 2013

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GIDAS Accident data analysis for ‘R1234yf Project’

‘Car accidents with frontal damage’

Date: 8 July 2013

Authors: Jan Dobberstein, BASt
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1. Introduction

The aim of analysing the GIDAS accident data was to identify relevant crash conditions for appropriate vehicle testing, based on the accident information available in GIDAS, in order to permit examination of the risks inherent in the new R1234yf refrigerant. The analysis focused on the nature and extent of the damage to the vehicles concerned and the associated collision reconstructions. In this way, GIDAS data is able to provide indications of the cases in which refrigerant lines might potentially be damaged at critical points of the front region of the vehicle.

The German In-Depth Accident Study (GIDAS) has been running since 1999 as a joint project between BASt and the Research Association of Automotive Technology (FAT) of the German Association of the Automotive Industry (VDA). For 2 000 accidents recorded per year, the database contains an average of 2 600 variables relating to the circumstances of the accident, the vehicle and the individuals involved, and correlates results from on-the-spot examination of traces of the accident with reconstruction results and the coding of injuries from hospital records, for example.

Evaluation of the available data suggests a multi-stage procedure:

- Descriptive preparation of collision configurations and accident features in potentially relevant accidents
- Identification of a test set-up, taking into account the aims of the project
- Examination of the relevance of the selected scenarios in relation to the whole population
- Estimation of probability of occurrence

2. Descriptive analysis of potentially relevant frontal collisions

The first step in the accident data analysis involved compiling information from real accidents in GIDAS in respect of collision configuration and accident features, for the purpose of developing a test scenario. It should be noted that, by definition, GIDAS is a representative sampling of accidents involving personal injury, whereas the risks to be examined relate at present only to damage to vehicles. Thus, the distribution of accidents in GIDAS does not correspond to the distribution of accidents involving damage to property, which could involve refrigerant damage while not necessarily entailing injuries.

The following selection criteria were established for the relevant vehicle population:

- Car with collision and main damage in the front area
- Year of manufacture more recent than 2003, in order to obtain a more or less homogenous and meaningful sample, in terms of mechanical/structural aspects, in respect of the vehicles to be tested.

In addition, only cases that were complete in terms of the relevant variables were filtered, so that percentage statements would always be based on a total without any unknowns.

All cars in GIDAS:		n = 29 674
	- of which date of first registration > 2003	n = 6 079
	- of which exhibiting frontal damage	n = 3 362
	- of which fully coded	n = 2 602

Some 50 % of all the more recent cars in GIDAS thus exhibit main damage in the front area. For relevant accidents involving damage to property, this proportion is presumably higher, as other types and characteristics of accidents exhibit a higher probability of personal injury. Thus, for example, the probability of a single-vehicle accident or a side impact without at least minor personal injuries is less than with a rear-end collision.

GIDAS includes numerous variables relating to the nature and severity of vehicle damage. Appropriate aspects in the form of GIDAS variables include:

- **Vehicle fire:** Accident configurations involving a fire are considered so as to be able to examine potential fire events with accident data. However, GIDAS lists few vehicle fires resulting from accidents; therefore, this variable does not deliver sufficient findings. The few cases that resulted in a fire do, however, indicate causes and processes in the fire events that do not relate to the existing question.

- **Radiator damage:** The condenser is the most exposed part of the refrigerant system in a frontal impact because it is integrated into the radiator and because of its construction. GIDAS differentiates between deformation and separation of the radiator. This coding is not further differentiated according to type and severity. The accident investigator at the scene of the accident is not required to note damage to individual lines or the escape of refrigerant, so this is not recorded.

- **Intrusion depth/degree of deformation:** The conflict of aims in a worst-case accident from the point of view of the refrigerant system is that the level of damage has to be sufficient to damage lines and allow refrigerant to escape. However, as regards intrusion depth, the damage must not be too extensive, since either this could trigger other fire hazards, or else no residual volume would remain capable of giving rise to a flammable mixture. Because of the position of the high-pressure side components of the refrigerant system, a intrusion depth of between 3 and 4 at the most is relevant.

- **Energy Equivalent Speed:** The EES is a theoretical value serving to describe the degree of deformation energy of a vehicle in a collision. The EES is obtained from the energy balance and is expressed as km/h. The EES equates to the collision speed of the vehicle in question against a non-deformable rigid barrier in which, in the collision, all the energy is converted into strain energy to achieve the same damage pattern. Thus, the EES is an appropriate measurement for defining a test scenario based on GIDAS accident data, in which the EES of a vehicle is determined.

- **Offset:** The 'vehicle damage index' classifies, among other things, the degree of overlap of frontal damage in such a way that it is possible to differentiate between 'full overlap' (100 %) and 'offset' (e.g. 33–50 %), and also other horizontal damage situations. Where the degree of overlap is slight, even fairly low speeds are sufficient appreciably to deform the structure of the struck side of the vehicle. Thus, not only is the respective half of the condenser impacted: refrigerant lines in the interior of the engine compartment may also be impacted.

In addition to these relevant filtering criteria for describing and classifying the damage to the selected vehicles, other variables such as vehicle weight and vehicle segment are also necessary for the purposes of studying the vehicle population with a view to possible test processes.

The following figures summarise, first of all, an analysis with the **focus on radiator damage**. In other words, based on the grouping of vehicles that exhibit deformation (n = 998) and/or separation of the radiator (n = 219), the other parameters are distributed, and/or distribution and average values are shown.

- All cars in GIDAS: n = 29 674
  - of which date at first registration > 2003 n = 6 079
  - of which exhibiting frontal damage n = 3 362
  - of which with detailed deformation pattern n = 2 602
  - *with deformed/demolished radiator* *n = 1 255*
  - *fully coded (no NAs)* *n = 1 117*

• Collision opponent

	Demolished (n = 219)	**Deformation (n = 998)**
Object impact	18.9 %	28.0 %
Collision with another participant	81.1 %	72.0 %

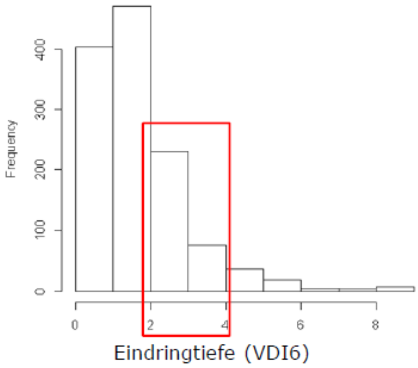
• Offset

	Demolished (n = 219)	**Deformation (n = 998)**
Full-width	53.9 %	40.5 %
Offset	26.5 %	35.2 %
Other (e.g. small overlap)	19.6 %	24.3 %

Both types of damage show similar distribution in terms of intrusion depth, whereby 24.4 % of cases in which the radiator was damaged indicate a intrusion depth deemed critical of VDI6 = 3,4. In the case of separation, the intrusion depth is somewhat greater.

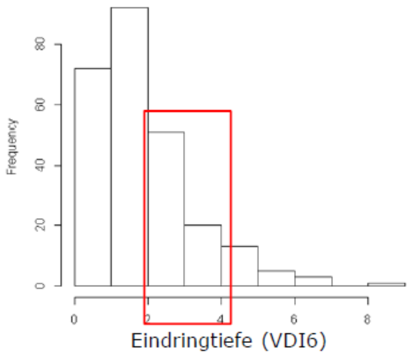
Cases of damage to the radiator: Cases of separation of the radiator:

24.4 % with VDI6 = 3,4 (n = 1 255)



Intrusion depth (VDI6)

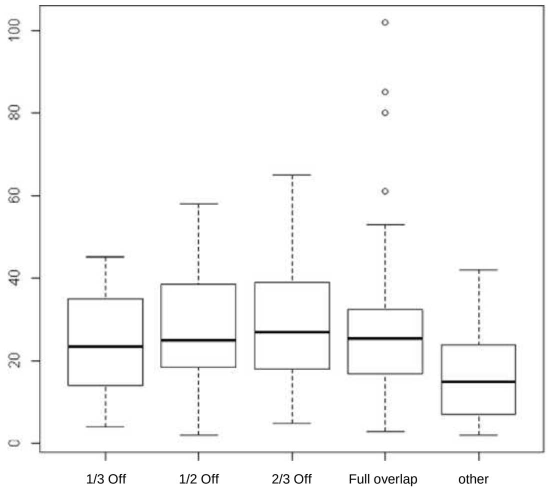
27.6 % with VDI6 = 3,4 (n = 257)



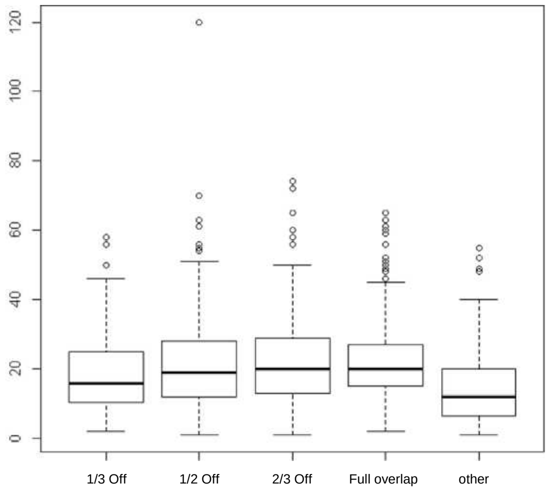
Intrusion depth (VDI6)

Analogous to the intrusion depth, the EES is on average also higher for vehicles in which the radiator was demolished. Across all cases, as the overlap increases, so does mean EES. Note: For a ‘100 % overlap (full overlap)’, the coding tends to be radiator damage – both deformation and separation; for this reason, the proportion of 100 % overlaps is greater and the associated box plot indicates a lower mean EES.

Mean EES (radiator demolished) = 26.2 km/h



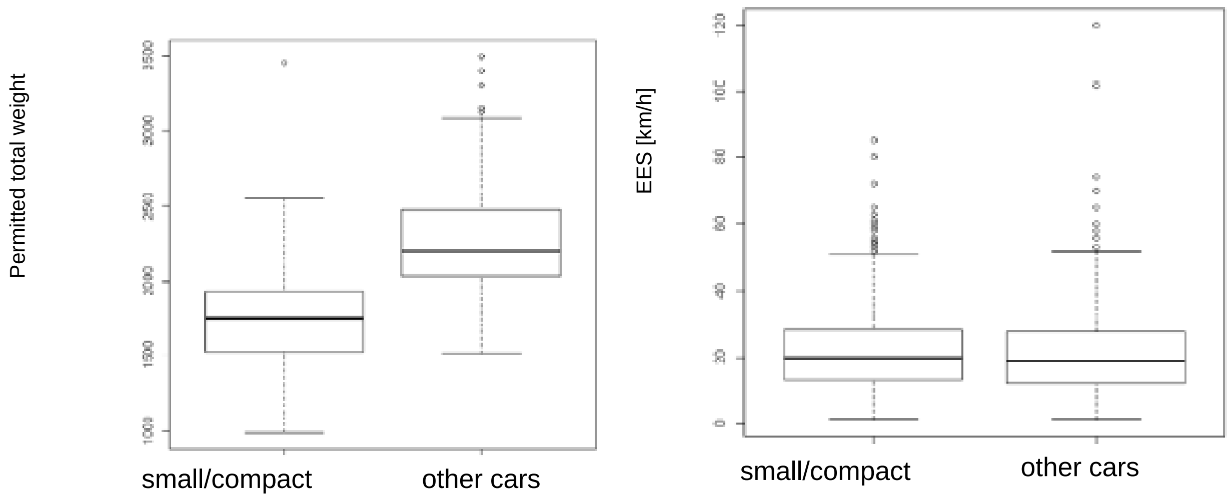
Mean EES (radiator deformation) = 21.0 km/h



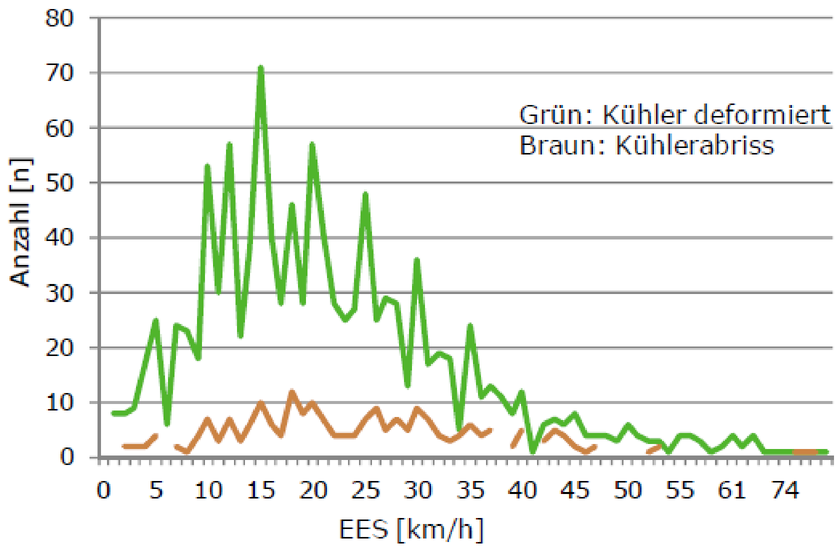
A breakdown of the vehicle population by permitted total weight shows the existence of distinct differences in mass between the segments. However, as EES is comparable to the collision speed in a crash test against the rigid wall, no differences dependent on mass are apparent.

Permitted total weight EES [km/h]

Illustration of vehicle population in relation to vehicle class Mini/Small/Compact/Medium (71.7 %) versus mid-range/executive, SUVs (28.3 %)



In addition, a chart plotting cases against EES shows that the proportion of demolished radiators associated with an essentially verifiable damage pattern increases concurrent with an increase in EES. From EES of approximately 40 km/h upwards, there is not a meaningful number available to judge.



Anzahl = number

Green: radiator deformation; Brown: radiator demolished

As the next step, the following illustrations summarise an analysis with the **focus on degree of deformation**. The breakdowns of the other variables are shown based on a categorisation of vehicles by type of deformation.

GIDAS analysis — focus on degree of deformation / intrusion depth

- All cars in GIDAS: n = 29 674
  - of which date at first registration > 2003 n = 6 079
  - of which exhibiting frontal damage n = 3 362
  - of which with detailed deformation pattern n = 2 602

Modified analysis approach:

- Vehicle with 'mean' intrusion depth VDI6 = 2,3,4 n = 870
- Vehicle with 'high' intrusion depth VDI6 = 3,4 n = 302

- Collision opponent

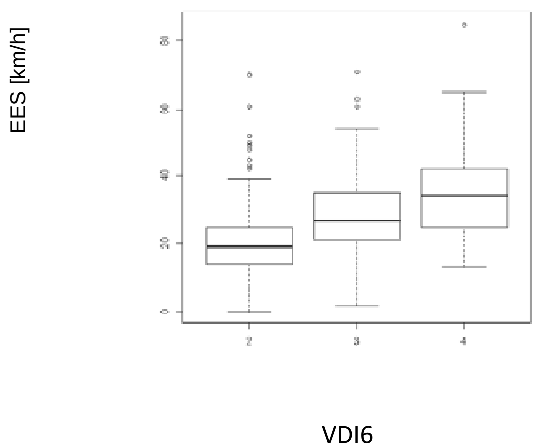
	High (n = 302)	Medium & High (n =870)
Object impact	21.1 %	17.6 %
Collision with another participant	78.9 %	82.4 %

- Offset

	High (n = 302)	Medium & High (n =870)
Full-width	39.4 %	38.0 %
Offset	34.6 %	32.6 %
Other (e.g. small overlap)	26.0 %	29.4 %

When compared to EES, the three degrees of deformation investigated show a consistent increase — the higher the degree of deformation, the higher the EES. The investigation distinguishes between a wider range of severity ('medium/high') with VDI6 = 2,3,4 and a high severity of deformation. In comparison to the selection according to radiator damage, the EES mean values are higher here, as radiator damage can also occur in significantly less severe collisions (and are coded accordingly).

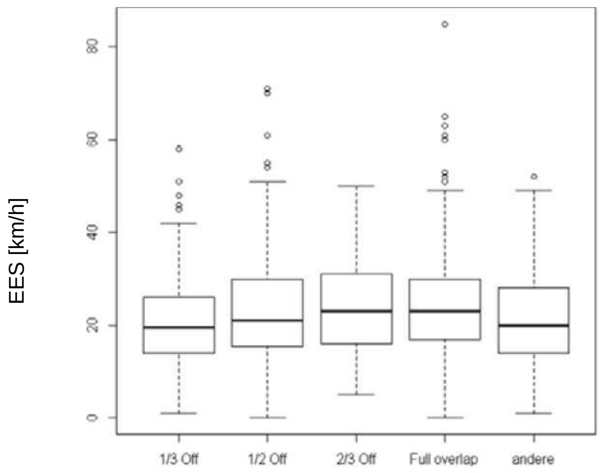
GIDAS analysis — focus on degree of deformation/intrusion depth EES according to degree of deformation



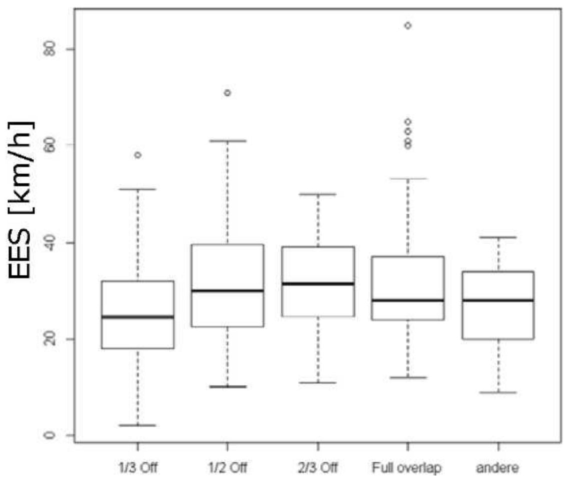
Mean EES 'deformation high'
VDI6 = 3,4):29.95 km/h
Mean EES 'deformation medium/high'
(VDI6 = 2,3,4):23.47 km/h

In the selection of vehicles by degree of deformation, too, an increase in EES is evident concurrent with the increasing degree of overlap required to deform the vehicle to the relevant degree. With high deformation only, there is a greater degree of scattering, so the correlation with 'full overlap' no longer applies.

EES according to the nature of offset (VDI6=2,3,4) 'medium/high deformation'



EES according to nature of offset (VDI6=3,4) 'high deformation'



andere = other

The following tables take into account the vehicle segments (in the columns), because in vehicle-vehicle collisions, in particular, small and compact vehicles can tend to sustain a higher degree of deformation.

GIDAS analysis — focus on degree of deformation / intrusion (depth / degree) Frequency — vehicle class / nature of offset

Deformation 'medium/high'	Vehicle class	
	Small/compact	Mid-range/executive
Full overlap	27.7 %	10.3 %
Offset	22.9 %	9.8 %
other	21.4 %	7.9 %

Deformation 'high'	Vehicle class	
	Small/compact	Mid-range/executive
Full overlap	28.2 %	11.2 %
Offset	25.9 %	8.6 %
other	17.9 %	8.2 %

In conclusion, testing is conducted to establish whether there is any distinct deviation in EES mean value in the sub-populations. Thus, the test process might have to take it into account if small vehicles sustain a high degree of deformation even under significantly lesser loads. A comparison of the left-hand column and the right-hand column in the table shows that this is not the case.

GIDAS analysis — focus on degree of deformation / intrusion (depth / degree) EES according to vehicle class / nature of offset and

- EES according to vehicle class and analysis of degree of deformation

EES [km/h]	Vehicle class	
	Small/compact	Mid-range/executive
	71.95 %	*28.05 %*
High (n = 302)	**23.45**	**23.48**
Medium & High (n =870)	**29.78**	**30.21**

- EES according to vehicle class and analysis of the offset (high deformation only)

EES [km/h]	Vehicle class	
(only VDI6 = 3,4)	Small/compact	Mid-range/executive
	71.95 %	*28.05 %*
Full overlap (38 %)	**31.07**	**30.61**
Offset (32.6)	**30.20**	**30.00**

In summary, the following findings emerge from the GIDAS data:

- The selection of potentially relevant vehicles both in terms of the nature of the damage and in terms of the degree of deformation results in a high proportion relative to all vehicles.

- The severity of radiator damage (separation rather than distortion) increases as EES and deformation increase.

- A similar intrusion (depth/degree) (degree of deformation) requires a higher collision speed/EES where the degree of overlap is greater.

- When the total number are grouped according to the individual vehicle class (compact versus executive), the breakdown by EES and offset changes, but collision opponent does not change.

3. Identification of a testing set-up and checking of the relevance of the chosen scenario in the total population

The requirements for the test scenario can be summarised as follows:

- The vehicle is damaged badly enough at the front for the refrigerant lines to be potentially damaged. In addition, a worst case is assumed not in relation to discharge from the condenser, but from the refrigerant line that leads away from the compressor under high pressure.

- The intention is to make the test realistic through high coverage of accident data.

- Where possible, the test should be selected based on an existing or recognised test procedure.

- The test should enable distribution of the refrigerant/air mix.

A test based on ECE R94 seems appropriate with 40 % offset and the speed reduced to 40 km/h.

- Accident data shows: Accidents with EES < 37 km/h and offset between 33 and 50 % account for approx. 30 % of the frontal collisions investigated. The accident data actually also show a large proportion of instances of ‘100 % overlap’ that have relevant frontal damage in GIDAS but are similar in all scenarios, thus also enabling investigation of the offset case.

- Discharge and mixing of the refrigerant is achieved in the offset test set-up, as engine compartment volume remains the same after the test.

- The test set-up is similar to recognised testing methods, so the test procedure and the equipment are familiar and the test setup and results are comparable to ECE R94.

4. Estimation of probability of occurrence

The objective of this investigation is to estimate the probability of occurrence of the damage depicted in the test procedure in an actual accident. The German Product Safety Law (Produktsicherheitsgesetz – ProdSG) transposes the EU General Product Safety Directive into national law. It defines risk as a combination of the probability of occurrence of a hazard and the magnitude of the potential damage. In this calculation, the risk per vehicle and year is shown.

The following should be noted in relation to this calculation:

- The purpose of the GIDAS database is to portray a representative sample of accidents involving personal injury, i.e. all accidents in which at least one participant is injured. Accordingly, the sample of vehicles drawn on and the accidents they were involved in do not necessarily correspond to all the relevant car accidents in this context.

- As regards incidences of general physical damage, Germany does not have any such data offering a sufficient depth of information to enable any correction here. Therefore, comparable, detailed investigation like that provided by GIDAS is not possible in terms of relevance of the test configuration.

- It is probable that a frontal impact, compared to other impacts and thus to other types of accidents, occurs fairly frequently without any resultant injuries. In other words, the relevant incidence of physical damage (purely damage to property) would tend to indicate a higher proportion of frontal collisions or frontal damage. Thus, an assumption based on a sampling of accidents involving personal injury is to be regarded as conservative and the risk estimation as probably too low.

Individual probabilities:

- Accident – yes/no: this is the general risk of a car being involved in an accident in a given year. All accidents in Germany attended by the police serve as a reference figure (1.8 million per year), approximately 70 % of which involve a car. Thus, the risk per car of being involved in an accident is 0.7*1.8 million/43.4 million cars = 0.029.

- Accident with frontal impact: GIDAS indicates a proportion of 55 % of newer vehicles with a date of first registration >2003 with frontal damage. For all cars (with no age limitation), this proportion is 52 %, while according to the Accident Research Department of the German Insurance Association (UDV), for all cars in its accident database, which also tends to include more serious accidents, i.e. those involving personal injury, the proportion is 60 %. The risk of having a frontal collision in an accident is thus p = 0.5.

- Collision parameters as per the test procedure: An EES of 35–45 km/h and an offset of 33–50 % are indicated in 2 % of the vehicles investigated.

This gives an estimated probability of occurrence for the scenario of 0.029 x 0.5 x 0.02 = $2.9*10^{-4}$ per vehicle per year.

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Registration figures for vehicle types approved with R1234yf in Q1 of 2013

Model	Approval number	Jan 13	Feb 13	Mar 13	Total 13	Total	
Mercedes-Benz A180, A180CDI, A200, A200CDI, A250	e1*2007/46*0928*00	5	4	4	13		
	e1*2007/46*0928*01	209	178	150	537		
	e1*2007/46*0928*02	1710	644	365	2719		
	Total	1924	826	519	3269	3.269	
Mercedes-Benz B180, B180CDI, B200, B200CDI	e1*2007/46*0751*00	1	0	0	1		
	e1*2007/46*0751*01	45	15	9	69		
	e1*2007/46*0751*02	326	178	169	673		
	Total	372	193	178	743	743	**4.012 ***
Cadillac ATS	e13*2007/46*1338*00	2	6	0	8		
	Total	2	6	0	8	8	
Chevrolet Trax/Tracker	e4*2007/46*0696*00	0	0	1	1		
	Total	0	0	1	1	1	
Fisker Karma	e13*2007/46*1239*00	0	0	1	1		
	Total	0	0	1	1	1	
GM Korea KL1G Buick V300 Chevrolet Malibu Pontiac Sunfire	e9*2007/46*0188*00	0	0	0	0		
	e9*2007/46*0188*01	0	0	0	0		
	e9*2007/46*0188*02	2	3	1	6		
	e9*2007/46*0188*03	2	2	4	8		
	e9*2007/46*0188*04	2	8	4	14		
	e9*2007/46*0188*05	6	11	11	28		
	e9*2007/46*0188*06	0	1	0	1		
	Total	12	25	20	57	57	
Hyundai Santa Fe	e11*2007/46*0633*00	184	178	109	471		
	e11*2007/46*0633*01	0	0	27	27		
	Total	184	178	136	498	498	
Hyundai i30	e11*2007/46*0337*00	40	38	28	107		
	e11*2007/46*0337*01	213	202	123	539		
	e11*2007/46*0337*02	714	946	524	2184		
	e11*2007/46*0337*03	692	1121	660	2473		
	e11*2007/46*0337*04	1	442	1568	2011		
	Total	1660	2749	2903	7314	7.314	
Kia Cee'd	e4*2007/46*0496*00	159	105	79	343		
	e4*2007/46*0496*01	95	45	56	196		
	e4*2007/46*0496*02	992	989	1244	3225		
	e4*2007/46*0496*03	0	38	636	674		
	Total	1246	1177	2015	4438	4.438	**11.752 ***
Kia Carens/Rombo	e4*2007/46*0633*01	0	44	0	44		
	Total	0	44	0	44	44	
Kia Optima	e4*KS07/46*0009*00	10	9	10	29		
	Total	10	9	10	29	29	
Kia Sorento	e11*2007/46*0634*00	0	0	0	0		
	e11*2007/46*0634*01	65	168	168	401		
	Total	65	168	168	401	401	
Land Rover	e11*2007/46*0649*00	188	145	72	405		
	e11*2007/46*0649*03	9	64	155	228		
	Total	197	209	227	633	633	

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Registration figures for vehicle types approved with R1234yf in Q1 of 2013

Model	Approval number	Jan 13	Feb 13	Mar 13	Total 13	**Total**	
Lexus GS 250	e6*2007/46*0034*00	3	9	5	17		
	Total	3	9	5	17	17	
Lexus GS 450 H	e6*2007/46*0035*00	10	13	19	42		
	Total	10	13	19	42	42	
Maserati Quattroporte	e3*2007/46*0224*00	1	0	8	9		
GTS	Total	1	0	8	9	9	
Mitsubishi	e1*2007/46*0951*00	0	0	1	1		
Mirage/Spacestar	e1*2007/46*0951*01	0	3	0	3		
	e1*2007/46*0951*02	0	0	419	419		
	Total	0	3	420	423	423	
Opel Mokka	e4*2007/46*0537*00	31	45	28	104		
	e4*2007/46*0537*01	613	218	186	1017		
	e4*2007/46*0537*02	394	1009	2088	3491		
	Total	1038	1272	2302	4612	4.612	**4.612**
Peugeot 301	e2*2007/46*0224*00	1	0	0	1		
	e2*2007/46*0224*01	1	0	0	1		
	Total	2	0	0	2	2	
Mercedes-Benz	e1*2007/46*0803*00	13	13	31	57		
SL350, SL500, SL63	e1*2007/46*0803*01	34	20	21	75		
AMG, SL65 AMG	e1*2007/46*0803*02	79	46	109	234		
	Total	126	79	161	366	366	
Subaru Forester	e13*2007/46*1305*00	20	54	263	337		
	Total	20	54	263	337	337	
Subaru Impreza	e1*2007/46*0597*01	62	63	137	262		
	e1*2007/46*0597*02	123	253	337	713		
	Total	185	316	474	975	975	**975**
Subaru Z	e13*2007/46*1281*00	5	5	18	28		
	Total	5	5	18	28	28	
Ford Tourneo	e11*2007/46*0676*00	183	187	307	677		
Custom, Transit	e11*2007/46*0676*01	0	0	32	32		
Custom	Total	183	187	339	709	709	
Toyota Prius plus	e11*2007/46*0157*00	52	43	31	126		
	e11*2007/46*0157*01	46	56	63	165		
	Total	98	99	94	291	291	
Toyota Z	e13*2007/46*1287*00	86	231	247	564		
	e13*2007/46*1287*01	0	0	3	3		
	Total	86	231	250	567	567	

* same platform in each case

Combustion of R1234yf and HF analytics in leak testing of car refrigerant R1234yf

Combustion of R1234yf

Stoichiometric reaction of R1234yf with atmospheric oxygen:

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

Carbonyl fluoride (COF2) can also be produced as a very short-lived intermediate, but this immediately reacts further with ambient humidity:

$$COF2 + H2O \rightarrow 2\ HF + CO2$$

The amount of HF formed depends on many boundary parameters such as surface temperature, refrigerant concentration, contact time, etc.

Previous measurements by the Federal Institute for Materials Research and Testing (BAM) showed, depending on the test set-up, HF concentrations up to

45,9 Mol-% (459.000 ppm) → 10 min; 350 °C autoclave
0,07 Mol-% (700 ppm) → refrigerent leakage at 500 °C metal block

AEGL values (Acute exposure guideline levels)

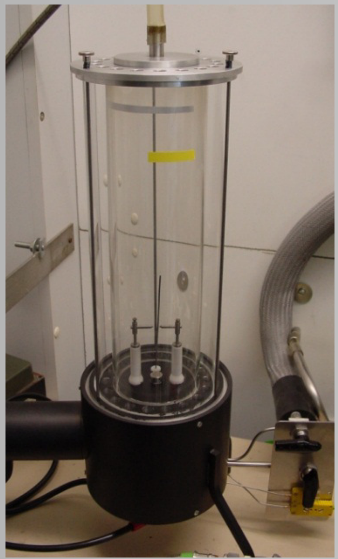
- toxicologically substantiated peak concentration values for various relevant exposure periods
- 3 different degrees of severity:
  - ➢AEGL 1: threshold of perceptible malaise;
  - ➢AEGL 2: threshold of severe, chronic or escape-hampering effects;
  - ➢AEGL 3: threshold of fatal effect.

AEGL-Werte für HF

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

http://www.umweltbundesamt.de/nachhaltige-produktion-anlagensicherheit/anlagen/AEGLWEB/Downloads/Results.PDF

Combustion of R1234yf
- Explosion limits -



Minimum disclosure in safety data sheet
(MSDS Honeywell, Version 1 from 11/10/2008):
- lower explosion limit LEL = 6.2 vol%
- upper explosion limit UEL = 12.3 vol%

BAM measurement
- lower explosion limit LEL = 6,0 Mol-%
- upper explosion limit UEL = 14,4 Mol-%

Test method
- Open glass tube
- ∅ 80 mm, lenght: 300 mm)
- Spark ignition
- „Flame detachment“

Ignition at 13.0 mole-% R1234yf

Pure R-1234yf can also burn with a bright yellow flame. The colour of the flame depends mainly on the concentration of the refrigerant.

Combustion of R1234yf
- Auto Ignition Temperature -

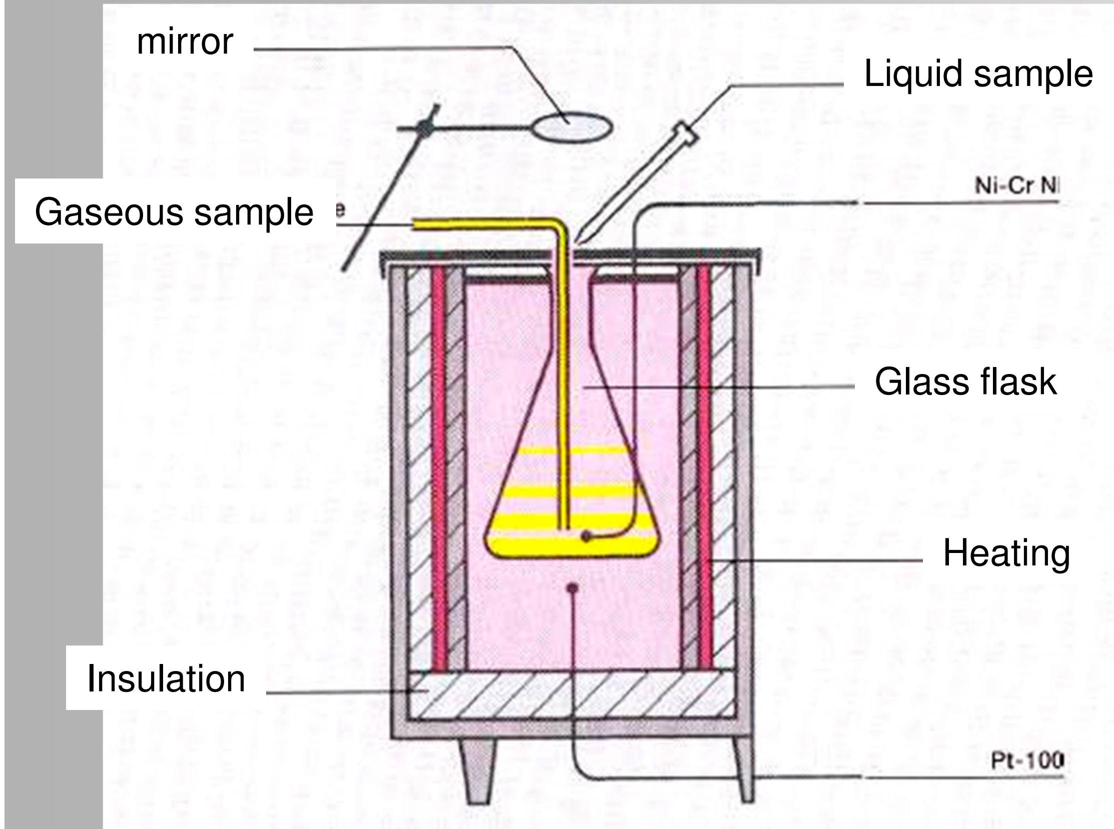
Minimum disclosure in safety data sheet
(MSDS Honeywell,
Version 1 from 11/10/2008):
- MIT (AIT) = 405 °C

BAM measurement
- MIT (AIT) = 390 °C

Actual test set-up

Erlenmeyer flask before and after testing

Combustion of R1234yf
- Auto Ignition Temperature -



Quelle: Merkblatt R 003, BG Chemie

Determination of ignition temperature in accordance with DIN EN 14522:2005

The minimum temperature of the glass-stoppered conical flask (Erlenmeyer flask) at which the sample still ignites in air is to be investigated.

For this, a sample is put into the flask and observed to see whether ignition occurs. For the investigation, the amount of sample and the temperature are varied incrementally.

Ignition delay time IDT (“contact time”)

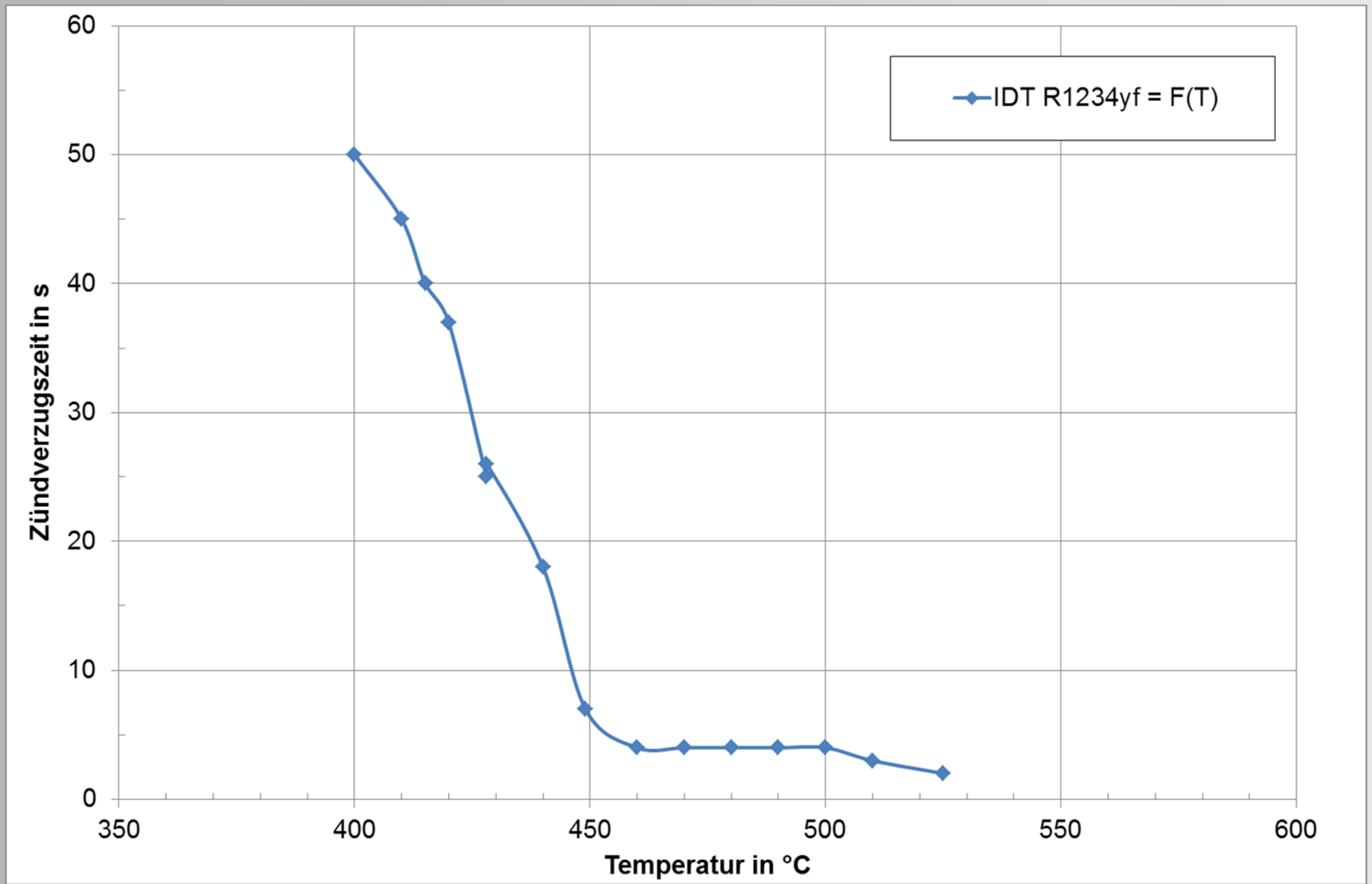
Determination of ignition delay time in spontaneous ignition of R1234yf

- Ignition delay time (IDT):
  the time that elapses between dosing of the test substance and ignition in the test vessel.

- Method:
  Deviating from the standard procedure for determining the ignition temperature of gases (EN 14522), ignition delay time is determined at temperatures above the minimum ignition temperature.

Ignition delay time IDT

- Results IDT = f(T) -

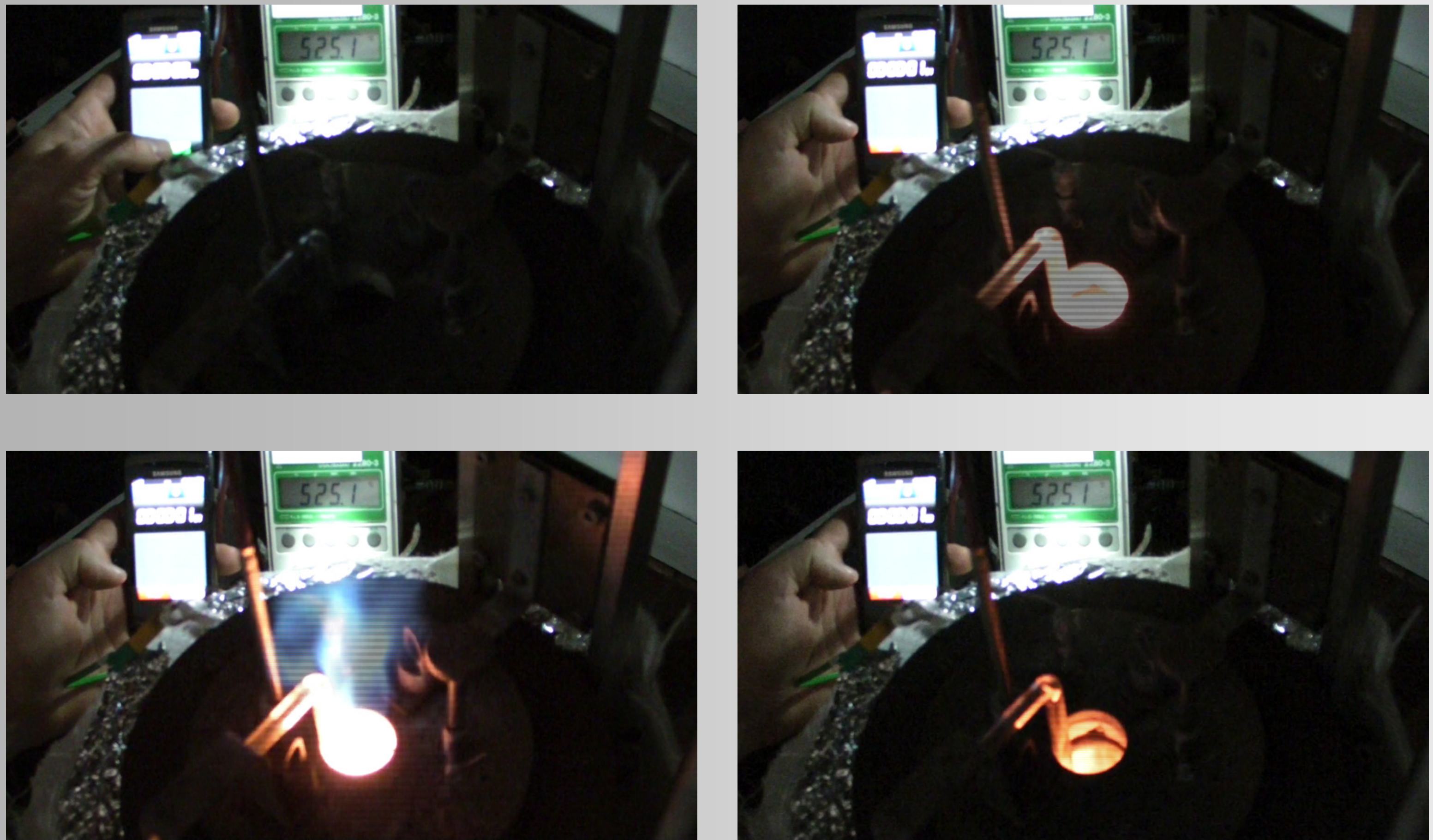


As surface temperature rises, the ignition delay time reduces. Taking account of the triggering time of 2s for 20ml of R-1234yf, at temperatures > 525 °C immediate ignition is to be expected.

Ignition delay time IDT

- Sequences of images -

Test at 525 °C (IDT = 2 s)

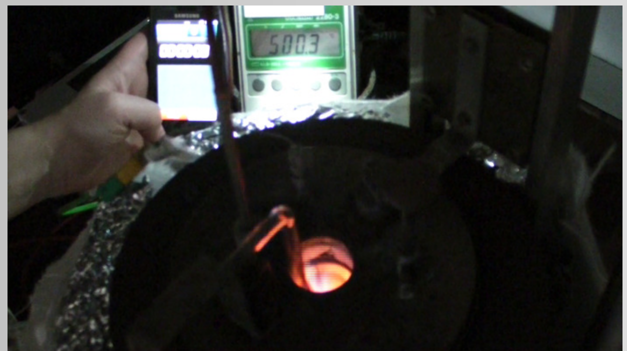
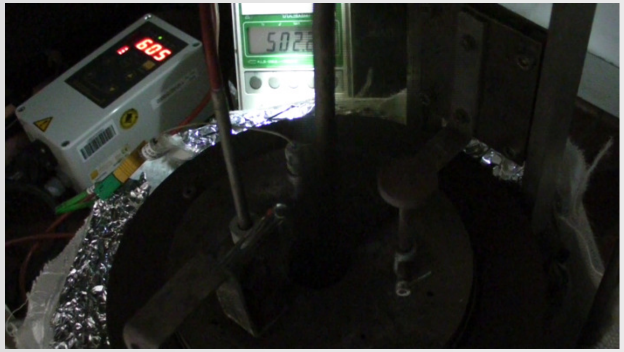


Ignition delay time IDT
- Sequences of images -

Test at 500 °C (IDT = 4 s)





Spülvorgang mit Druckluft (Ruß)

HF analytics

Requirements:

- Online analytics in order to avoid having to take samples for subsequent analysis, e.g. via ion chromatography
- ‘Chamber analytics’, i.e. monitoring of one or more large volumes (engine compartment, passenger space)
- Time-dependent concentration measurement
- Selective analysis method (no cross-sensitivities)
- High measuring accuracy and resolution

HF analytics

Possible methods:

- Spectroscopy: diode laser spectrometer from Bernt Messtechnik GmbH
- Absorption: Dräger short-term tube

Bernt Messtechnik GmbH:

LaserGas ^{TM} II

- integral absorption measurement between radiation source and detector (3–5 m)
- max. HF concentration: 200 ppm (higher concentration with uncertainty of more than than 50ppb)
- detection threshold: 3–5 ppb
- response time 1 second possible
- no cross-sensitivity to other gases
- no gas removal required
- compact field device, IP66, 24 VDC
- suitable for gases with high dust content
- maximum resolution (ppb and lower ppm region)

Bernt Messtechnik GmbH:

LaserGas TM III Portable

- gas sample extraction via Teflon hose with internal pump
- max. HF concentration: 100 ppm (higher concentration with uncertainty of more than than 50ppb)
- detection threshold: 50 ppb
- response time 1 second possible
- no cross-sensitivity to other gases
- no gas removal required
- compact field device, IP66, 24 VDC
- suitable for gases with high dust content
- maximum resolution (ppb and lower ppm region)

Dräger X-act® 5000
Automatic Dräger Tube pump

- Automated gas sampling (up to 30 m hose line available)
- max. HF concentration: 95 ppm
- Response time: 5 s – 15 min
- Cross-sensitivity to other gases possible

Dräger short-term detector tube with hand pump

- manual gas sampling
- major source of error in sampling
- max. HF concentration: 95 ppm
- response time: 5 s – 15 min
- cross-sensitivity to other gases possible

Dräger X-am® 5100 single-gas detector

- manual gas sampling
- max. HF concentration: 30 ppm
- 0.1 ppm resolution
- response time: 60 s
- cross-sensitivity to other gases possible
- Calibration?

HF analytics “at a glance”

Gerät	Kosten	Verfügbarkeit	Vorteile	Nachteile
LaserGas ™ II		Devices are manufactured to order, Delivery currently possible by July; Possible to hire only a single device of each type!	Selectivity Resolution Response time Max. 200 ppm Low detection threshold	Cost HF cloud must pass through laser beam
LaserGas ™ III Portable			Selectivity Resolution Response time Max. 100 pm Low detection threshold	Cost Sampling through hoses (location fixed), additional gas flow control
Dräger X-act® 5000 (automatische Pumpe)		Delivery time reportedly 2–6 weeks!	Easy to use No high costs	Full protection during sampling Localised result Instantaneous gas measurement
Dräger Handpumpe				
Dräger X-am® 5100				

Summary report

Evidence of hydrogen fluoride in tests by the KBA project group 'Fire behaviour of R1234yf'

Various analysis methods are available to demonstrate the presence of hydrogen fluoride (HF), e.g. spectroscopy, gas chromatography, ion chromatography and classic wet chemistry methods. However, the number of procedures is greatly reduced if it is desired to use online analytics, i.e. time-resolved evidence of the occurrence of HF in exothermal reactions during the crash and leak tests undertaken within the project group's framework. The following requirements were set for the analysis method used:

- No samples were to be taken for subsequent analysis, as sampling, in particular, could be a potential source of error.
- The analytics had to permit time-resolved evidence of hydrogen fluoride.
- The analysis method had to selectively detect HF only. Cross-sensitivities to other reaction products had to be avoided.
- The analysis method had to offer high measuring accuracy and resolution.
- If possible, the evidence of HF also had to be resolved spatially in order to facilitate subsequent statements on the extent of the 'HF cloud', notably in the area of the engine compartment and passenger space.

After establishing the requirements, it was decided, within the framework of the project group, to use a spectroscopy method (diode laser spectrometer from Bernt Messtechnik GmbH) and to use an absorption procedure (Dräger short-term detector tubes). The two methods used are described briefly below.

LaserGas™ III Portable from Bernt Messtechnik GmbH

The spectrometer works by the single line spectroscopy process, which excludes cross-sensitivities to associated gases. The absorption bands in the NIR spectrum are scanned with a diode laser; the spectrum of the gaseous analyte is then recorded in the receiver using a light detector. The gas concentration is then calculated from the frequency selective absorption. The measurement is independent of changing dust loads; changing process temperatures and pressures are compensated internally. The procedure offers an absolute zero and stable calibration. (Source: www.berntgmbh.de)

The LaserGas III spectrometer is a compact field device (IP66, 24VDC); it can be used for gas analysis in-situ, as the gas samples are extracted via a Teflon hose with an internal pump. Further specifications:

- HF concentrations up to 100 ppm: measurement uncertainty ± 50 ppb (measurement uncertainty increases with higher HF concentrations).
- linearity < 1 %
- detection threshold: 50 ppb
- response time 1–2 seconds
- no cross-sensitivity to other gases
- suitable for gases with high dust content
- maximum resolution (ppb and lower ppm region)

Dräger short-term detector tube

In earlier publications, HF concentrations were reported based on the Dräger short-term detector tube using the manual pump. This method is very simple and practical, but also requires the use of full personal protective gear (notably a chemical suit, gloves and gas mask or compressed-air breathing apparatus) for the operative. Sampling is then usually done by manually operating a pump with a volumetric displacement of 100 ml. Depending on the short-term detector tube or measuring range of the test tube, a defined sample volume is specified. If a 0.5/a HF test tube is used having a standard measuring range of 95 ppm HF, the specified volume is 200 ml and thus two cycles. These test tubes could also be used with a measuring range of up to 15 ppm HF; the sample volume would then be 10 cycles (1 000 ml). If 1.5/b HF test tubes are used (measuring range max. 15 ppm HF), a volume of 2 000 ml (20 cycles) would be specified. In all cases, there is uncertainty as to whether the correct number of cycles have been carried out or whether the cycles were complete, and hence it cannot be certain that the correct sample volume has been extracted. Thus, there is a latent danger that the analysis will be erroneous. For this reason, within the framework of the project group, automatic tube pumps were used in addition to the manual pumps.

Dräger X-act® 5000 automatic Dräger tube pump

The gas sampling is fully automated. The test tubes can be used directly in the device, or attached via hose lines up to 30 m in length. The test tubes are supplied with a factory barcode which can be read by the device. Thus, the basic settings, notably the specified sample volume to be extracted, are automatically in place. The maximum HF concentration is 95 ppm. Because this is an absorption process, the response times are up to 15 min.

Even when the largest source of error, 'sampling volume', is eliminated by using the automatic tube pump, cross-sensitivities with other gases cannot be excluded during the absorption process. Mineral acids in particular, e.g. hydrochloric acid, or high ambient humidity can affect the result or lead to failure to determine the actual HF concentrations.

Summary report

Refrigerant analytics in the leak tests of the KBA project group 'Fire behaviour of R1234yf'

After each leak test, the car air conditioning system was refilled using an automatic air conditioning service station specially for R1234yf. After several refills, the service station gas cylinder also had to be refilled in order to guarantee proper functioning of the station for refilling car air conditioning systems. A gas cylinder supplied by Air Products was used for this. In order to guarantee that the service station's newly refilled refrigerant was of the required purity, an FT-IR spectrum was taken and compared to a reference spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf).

Infrared spectroscopy is used to examine the excitation of energy states in molecules. Depending on the molecular structure, differing energies are absorbed; thus, FT-IR spectroscopy is extremely well suited for the qualitative analysis of known substances as well as for determination of any contamination.

Figure 1 shows the reference spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf), taken in a 10 % mix with argon in a 20 mm gas cell. The reduction in concentration is usually undertaken in order to avoid overloading various peaks (100 % absorption of radiation via a larger wave number range). The peaks typical of R1234yf occur at wave numbers 1 700 cm^{-1}, 1 390 cm^{-1}, 1 230–1 130 cm^{-1}, 950 cm^{-1} and 890 cm^{-1} as well as 615 cm^{-1} and 570 cm^{-1}.

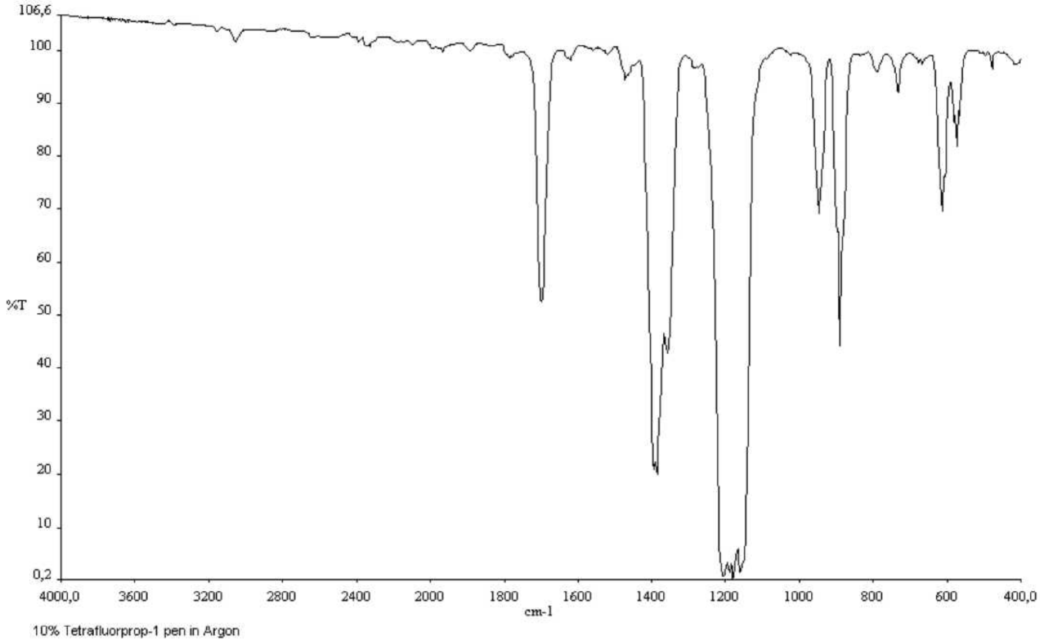


Figure 1: BAM-reference spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf); 10 % in argon, taken in a 20 mm gas cell

Figure 2 shows the FT-IR spectrum of R1234yf recorded, shortly before the automatic air conditioning service station gas cylinder was refilled, in a 20 mm gas cell using a Perkin Elmer Spectrum Two IR Spectrometer. It was not possible definitively to dilute the gas extracted from the gas cylinder, so the refrigerant was analysed pure. This resulted in overloading of the signals in various wave number ranges. Nevertheless, the characteristic peaks of R1234yf were clearly identifiable. The peaks on the baseline which were not very distinct in the reference spectrum were much more pronounced in the sample spectrum. There was no indication of peaks attributable to possible contamination.

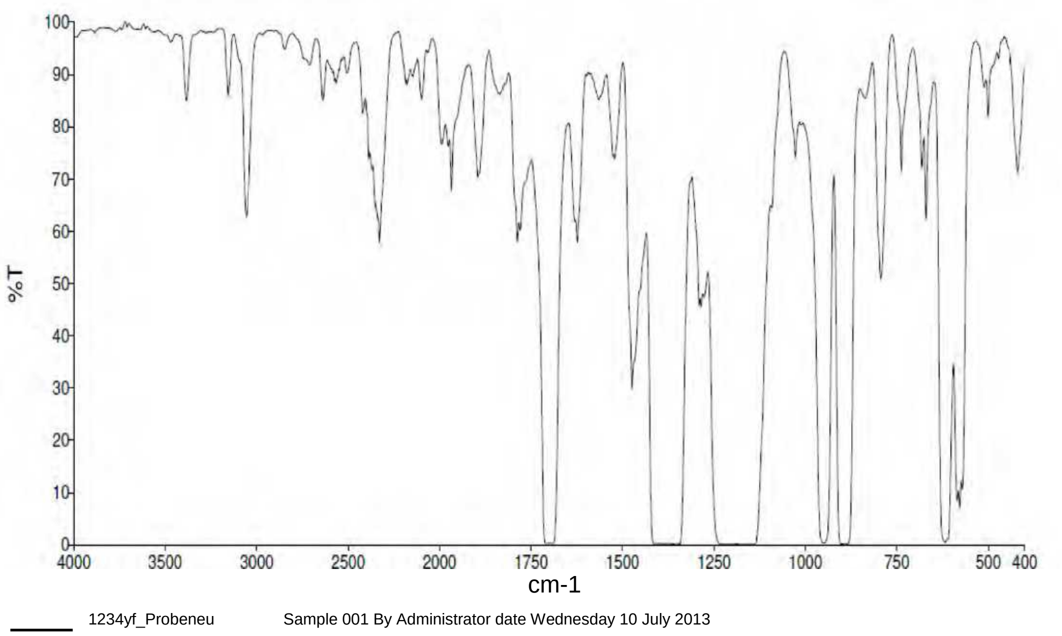


Figure 2: FT-IR spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf); gas sample from the gas cylinder for refilling the service station, taken in a 20 mm gas cell

Thus, it was guaranteed that all further refills of the car air conditioning systems from the refilled automatic air conditioning service station could continue to be filled with R1234yf as normal.

Figures 1 and 2 show the transmission spectra of the reference and refrigerant samples. In further illustrations, the absorption spectra will be represented in such a way as to reduce the overloading of signals in the recording of the FT-IR spectra of the pure, undiluted gas samples, simplifying comparison with various different spectra.

Retrospectively, it should be verified that in the previous leak tests, too, the car air conditioning systems were properly filled with R1234yf. To this end, for example, after testing the Hyundai i30 and the Opel Mokka, gas samples from the service interfaces of the air conditioning systems were fed into the gas cell and subsequently analysed. The absorption spectra are illustrated in Figures 3 and 4. In both cases, it is clear that the air conditioning systems were filled with the R1234yf refrigerant. Under these conditions, no oil fractions were included in the sampling.

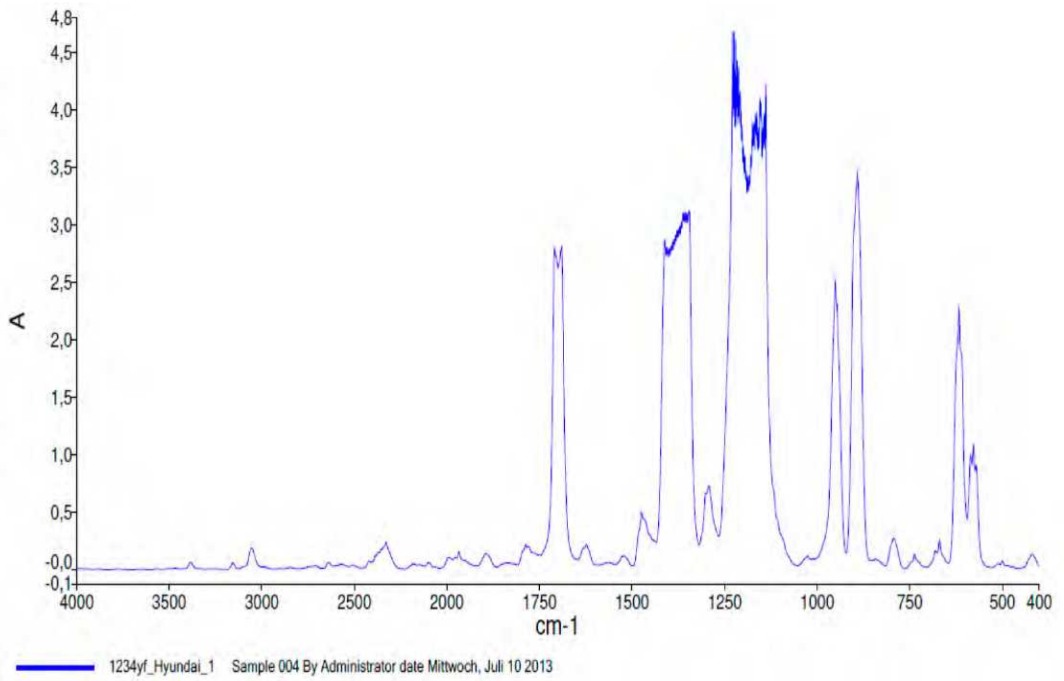


Figure 3: FT-IR spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf); gas sample from the service interface of the Hyundai i30's air conditioning system after a leak test, taken in a 20 mm gas cell.

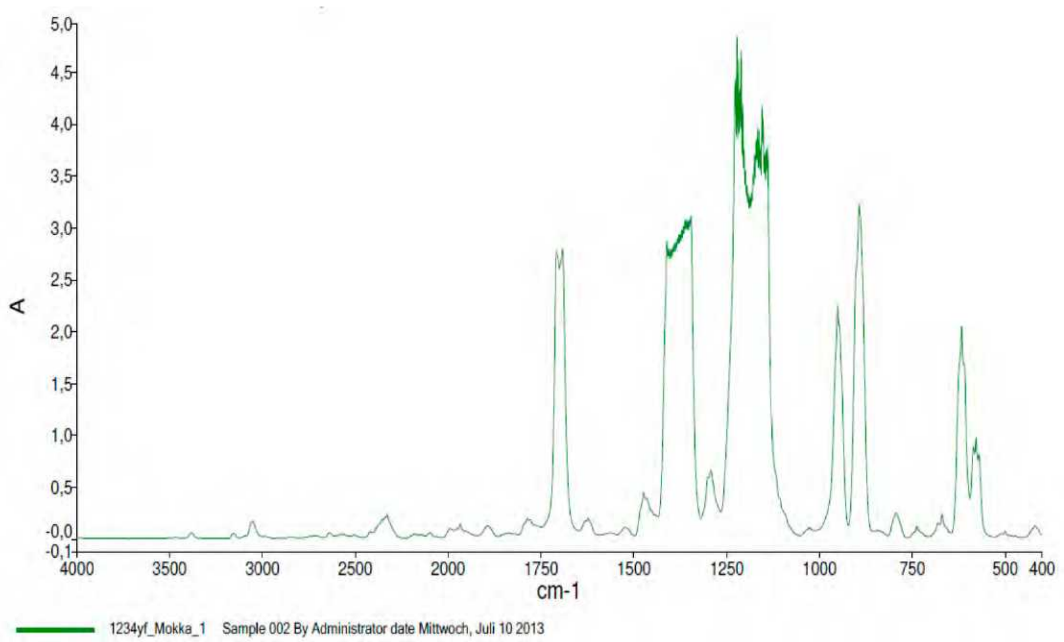


Figure 4: FT-IR spectrum of 2,3,3,3-tetrafluoroprop-1-ene (R1234yf); gas sample from the service interface of the Opel Mokka's air conditioning system after a leak test, taken in a 20 mm gas cell.

In the case of ignition of the R1234yf in one of the leak tests performed, an additional test with R134a was to be carried out under the same conditions. In order to guarantee, where applicable, that the air conditioning system previously filled with R1234yf and subsequently filled with R134a contained only pure R134a, a prior spectrum was taken of the R134a (sample taken from the automatic air conditioning service station specific to R134a) and compared to that of the R1234yf (absorption spectrum of the transmission spectrum shown in Figure 2). A comparison of the two spectra is shown in Figure 5.

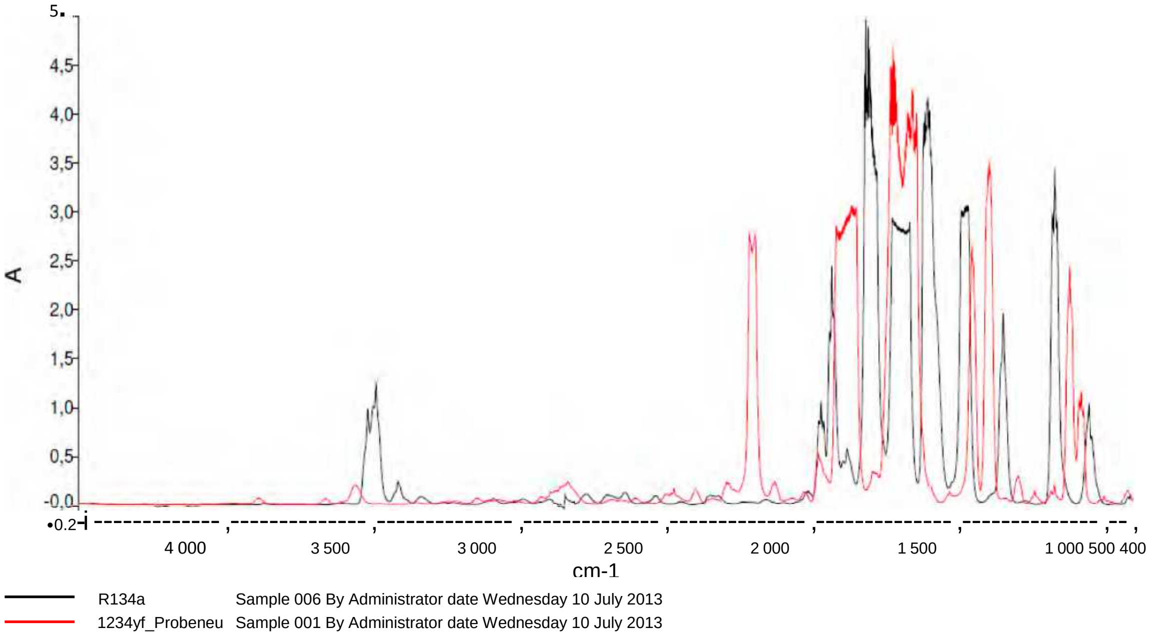


Figure 5: FT-IR spectrum of 2,3,3,3-tetrafluoroprop-1-ene and 1,1,1,2-tetrafluorethane (R134a) respectively, each taken in a 20 mm gas cell

Distinct differences emerge between the two spectra. The biggest differences are the individual peak for R134a at a wave number of 3 000 cm^{-1} and the isolated peak for R1234yf at a wave number of 1 700 cm^{-1}.

Ignition of R1234yf was observed in a leak test with a car, so the air conditioning system was filled with R134a for a final test. After the leak test, once again a gas sample was taken via the car's air conditioning service interface and compared to the absorption spectrum of pure R134a. The result is illustrated in Figure 6. No deviations were visible, so it is assumed that the car's air conditioning system was filled cleanly with R134a without any residue of R1234yf. In this case, again, under these conditions, no oil fractions were included in the sampling.

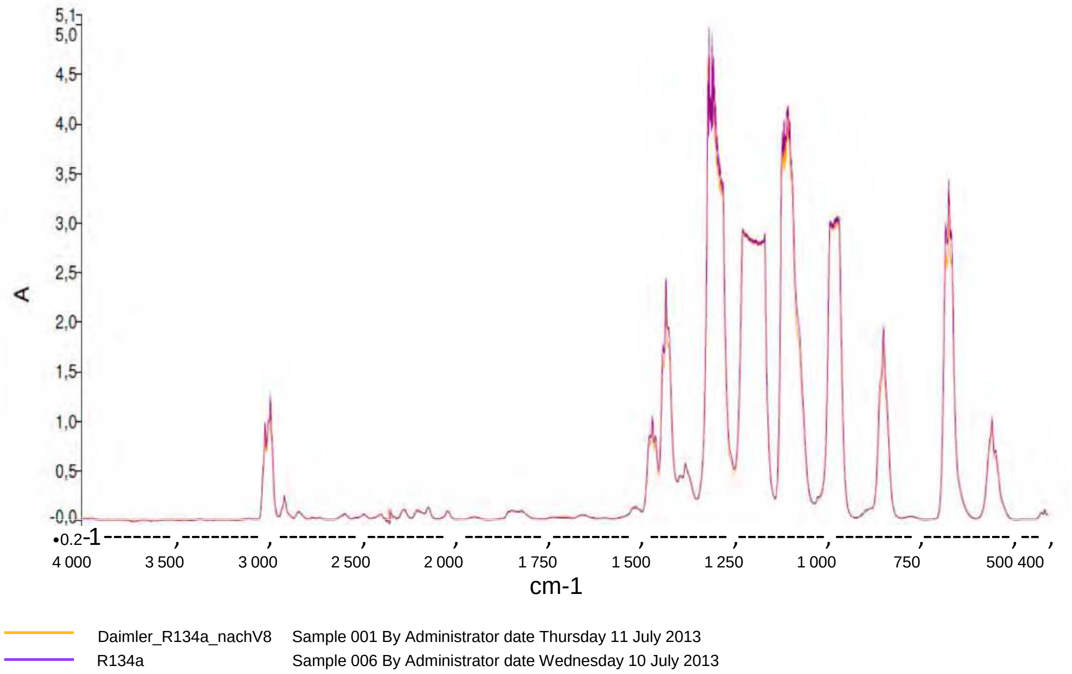


Figure 6: FT-IR spectrum of 1,1,1,2-tetrafluorethane (R134a)); gas sample from the service interface of the Daimler B-Class air conditioning system after a leak test using R134a and from the automatic air conditioning service station, each taken in a 20 mm gas cell

Annex

Opinion of the German Federal Institute for Risk Assessment (BfR) dated 12 September 2013 in the revised version of 7 October 2013 concerning the enquiry from KBA concerning R1234yf dated 10 September 2013

1 Scope of the opinion

In an e-mail dated 10 September 2013, the Federal Motor Transport Authority (Kraftfahrt-Bundesamt — KBA) requested an opinion on the results of tests that it had asked TÜV Rheinland to conduct in the matter of safety testing of refrigerant R1234yf (KBA 2013).

Specifically, KBA asks for an assessment of the health risks that could arise from the hydrogen fluoride (HF) concentrations measured in these tests in relation to persons in the immediate vicinity of a corresponding incident.

The measurement data was initially provided in the form of a measurement sheet showing a number of HF measurement graphs (see Figure 1 in the Annex).

On 11 September 2013, BfR, after consulting the Federal Office for Chemicals (BfC), telephoned its contact at KBA in order to clarify some unresolved questions. Following on from this conversation, KBA sent another two measurement graphs (Figures 2 and 3 in the Annex), and a table showing the peak concentrations determined (Table 2 in the Annex) directly to BfR.

2 Result

The information provided by KBA do not allow for a conclusion on whether damage to health from HF could be expected in the event of a real accident. For this, first of all, KBA's exact test conditions would need to be known (e.g. the measuring process and the position of the measuring points); secondly, an estimate would have to be made of exposure, particularly in the vehicle interior, taking account of the conditions in a real accident situation; BfR is currently not able to undertake this with the existing information.[1]

As discussed on the telephone with KBA, BfR is therefore only in a position to make a generalised statement in the matter of whether, and if so what, damage to health is to be expected from inhalation

[1] On 2 October 2013, BfR received a draft version of the report on KBA's findings (without annexes). From this, it emerges that the HF concentrations were measured in the engine compartment of the vehicles. (BfR does not have any measurement results from the vehicle interior.) The hydrogen fluoride released will be diluted to an unknown extent as it spreads from the engine compartment. Accordingly, the HF concentration that persons in the vicinity of the engine compartment might inhale will be lower, to an unknown extent, than the measured values.

of certain HF concentrations for a given exposure period. The following picture emerges for the concentrations communicated by KBA:

■ Concentrations < 0.5 ppm HF, as measured in Tests 1–14, do not raise any expectation of damage to health.

■ In Tests 16, 17, 19 and 21, HF concentrations in the range of 2.4 to 18 ppm were obtained, for which the occurrence of slight, reversible irritation of the respiratory passages, skin and eyes — i.e. not associated with any permanent damage to tissue — is probable.

■ In Tests 20 and 22, HF concentrations were obtained from which severe, irreversible damage [severe irritation or chemical burns to the respiratory tract with possible tissue destruction (formation of necroses) and restriction of lung function, chemical burns to skin and eyes] is probable.

■ At concentrations as found in Tests 15 and 18, the observed range of mortality in tests on animals is 50–100 %. In this respect, acute danger to life is to be assumed for persons suffering this level of exposure.

BfR also points out that, according to the literature, carbonyl difluoride (COF_2) is another toxic degradation product that can occur in the combustion of R1234yf. In contact with water, this converts rapidly into HF (2 moles of HF per mole of COF_2). There are indications from animal testing that COF_2 itself has stronger acute toxic effects than the equivalent amount of HF.

Based on the available documentation, it is not evident whether the analysis procedure used in the testing by KBA covered COF_2 directly or indirectly (as HF). If this was not the case, it would appear that, for all the tests, a distinctly greater release of toxic gases was possible than is evident from the HF concentrations examined here.

The evaluation results are explained further in the following section. This section also includes an analysis of the uncertainties associated with this evaluation.

3 Explanation

3.1 Basis of the evaluation

The basis of the evaluation, besides the measurement results sent by KBA (see Annex), consists of HF reference values derived by BfR; if these are complied with, damage to health can in all probability be ruled out. The Acute Exposure Guideline Levels (AEGLs) of the US Environmental Protection Agency (EPA) are used for comparison.

3.2 Method

3.2.1 Reference values

For slight, reversible irritation of the respiratory passages or of the skin and eyes, BfR identified a reference value of 1 ppm for up to 10 minutes of exposure. As reference value for the occurrence of severe harm, in the case of exposure lasting up to two minutes, a value of 64 ppm was obtained; in the case of exposure lasting up to ten minutes, a value of 38 ppm was derived. In the event of exposure to 70 ppm or more for a period ≥ 10 minutes, life-threatening harm or fatalities are possible.

These values rest on the same test data (Dalbey et al., 1998) used to derive the Acute Exposure Guideline Level-2 (AEGL-2), which was essentially the basis of the risk assessment that the Society of American Engineers (SAE) commissioned on the use of R1234yf in car air conditioning systems (Gradient, 2009).

The AEGL-2 for severe harm after ten minutes of exposure was established as 95 ppm. The lower BfR value of 38 ppm is because, in the view of BfR and in accordance with the guidelines for risk assessment of chemicals under the EU Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), a 2.5-fold higher safety factor (25 instead of 10) has to be applied when extrapolating the results from animal testing to humans.

As explained in Section 3.3 (see below), this difference is not significant in terms of the result of the present assessment.

The US EPA derived an additional reference value, AEGL-3, of 170 ppm for life-threatening or lethal harm after ten minutes of exposure.

3.2.2 Level of exposure

Use of the correct dose metric must be observed when stating the level of exposure. The choice is between maximum concentration obtained, mean level of exposure, or total dose received. The nature of the toxicological effects under consideration is crucial for making the correct choice: for the irritant or corrosive effect in question in the case at hand, the maximum concentration should be used as the relevant dose metric because this is what determines the pH value in the target tissue, and hence the degree of corrosive effect of HF (cf. also Section 3.4).

3.2.3 RCRs

Potential health risks can be expressed as so-called 'Risk Characterisation Ratios' (RCRs). An RCR is the ratio between exposure and the relevant reference value. Where RCR > 1, this means that the level of exposure exceeds the relevant reference value and there is a potential health risk, thus further risk management measures should be considered.

3.3 The results in detail

In Table 1, the peak concentrations provided by KBA are compared with the relevant reference values in the form of RCRs. Tests showing RCRs > 1 for slight irritation are shaded grey, those showing RCRs > 1 for severe tissue damage are shaded yellow, and tests showing acute life-threatening peak concentrations are shaded red. In addition, the results based on the BfR reference values are compared with those based on AEGL-2.

A written summary of the results has already been provided in Section 2.

Table 1: Peak concentrations communicated by KBA, absolute and relative to the BfR reference value and to AEGL-2 and AEGL-3

Test	C_{max} (ppm)	RCR: C_{max}/BfR reference value		C_{max}/AEGL-2	C_{max}/AEGL-3
		Slight irritation	Severe harm	Severe harm	Life-threatening harm or death
V01	0.10360	0.10	0.0	0.0	0.0
V02	0.36170	0.4	0.01	0.0	0.0
V03	0.12080	0.12	0.0	0.0	0.0
V04	0.09220	0.09	0.0	0.0	0.0
V05	0.08180	0.08	0.0	0.0	0.0
V06	0.06900	0.07	0.0	0.0	0.0
V07	0.17540	0.18	0.0	0.0	0.0
V08	0.08680	0.09	0.0	0.0	0.0
V09	0.40760	0.4	0.01	0.0	0.0
V10	0.13650	0.14	0.0	0.0	0.0
V11	0.34550	0.4	0.01	0.0	0.0
V12	0.44560	0.5	0.01	0.0	0.0
V13	0.23290	0.2	0.0	0.0	0.0
V14	0.44340	0.4	0.01	0.0	0.0
V15	5 364.98340	5 365.0	83.8	56.5	31.6
V16	2.40240	2.4	0.04	0.03	0.01
V17	3.57030	3.6	0.06	0.04	0.02
V18	3 254.22120	3 254.2	50.9	34.3	19.1
V19	17.97360	18.0	0.3	0.19	0.1
V20	150.40690	150.4	2.4	1.6	0.9
V21	3.12280	3.12	0.05	0.03	0.02
V22	133.20400	133.2	2.1	1.4	0.8

* (RCRs were rounded to the last significant figure after the decimal)

3.4 Qualitative uncertainty considerations

3.4.1 Level of exposure

As already referred to at the beginning of Section 2, this opinion does not relate to an actual exposure situation in the event of an accident involving a vehicle, but to the concentrations communicated by KBA. The uncertainty as to whether the concentrations measured by KBA realistically reflect such a scenario, or the extent to which, for example, by taking samples in the engine compartment the concentrations in the vicinity of the vehicle and in the vehicle interior could be overestimated, will therefore not be discussed in the present assessment. This also applies, for example, to measurement uncertainties (e.g. precision, accuracy and reproducibility of the analytical method).

The problem area with regard to COF_2 already addressed in Section 2 potentially leads — in the event of non-recording of this analyte due to the measuring process used — to underestimation of the health risks which cannot, however, be quantified, as there is no comparable data available regarding the proportions of HF to COF_2 normally occurring in the combustion of R1234yf (or regarding transferability to the test design selected by KBA).

3.4.2 Reference value derivation

The differences, already discussed in Section 3.2.1, between the BfR reference values and AEGL in terms of the selection of safety factors for extrapolation from animal testing to humans do not affect the result of the assessment.

3.4.3 Dose metric

The relevant dose metric to be applied in the case of irritant/corrosive effects is the peak concentration obtained (see Section 3.1.2). In animal testing, however, the concentration is kept more or less constant throughout the entire exposure period. Thus, theoretically, the effect of only very briefly exceeding the reference value in actual circumstances of exposure (a road traffic accident) could be overestimated. However, the evaluation of the definitive animal study in the present case (Dalbey et al., 1998) does not allow for a temporal resolution of less than two minutes; conversely, therefore, it cannot be ruled out that corresponding effects on the animals could have occurred after just one minute or 30 seconds. In view of the fact that (in the KBA tests in question) the HF reference values are always clearly exceeded, and also in view of the concentration profiles shown on the measurement graphs, this uncertainty does not appear significant overall.

3.4.4 Placement of the RCRs

Due to the safety factors used, very slightly exceeding the critical RCR of 1 will not necessarily result in damage to health. In Tests 15, 18, 20, and 22, however, exceedance is found in the range of 210 % to 8 380 % of the derived reference value for severe harm, and accordingly this theoretical uncertainty can be regarded as irrelevant here.

3.4.5 Result

Overall, the uncertainties considered do not qualify the statements in the present assessment. One relevant uncertainty factor is the failure to take account of COF_2, which, due to the stronger acute toxic effect of COF_2, could result in underestimation of the risk.

Quoted sources:

Dalbey et al. (1998): Short-term exposures of rats to airborne hydrogen fluoride, J Toxicol Environ Health, Part A 55, 241-275

Environmental Protection Agency (EPA): Acute Exposure Guideline Levels (AEGLs). Hydrogen fluoride results. http://www.epa.gov/oppt/aegl/pubs/results53.htm — last accessed on 4 October 2013

Gradient (2009): Risk Assessment for Alternative Refrigerants HFO-1234yf and R-744 (CO_2). Phase III. Prepared for SAE International, Cooperative Research Program 1234, 17.12.2009. http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OAR-2004-0488-0051 — last accessed on 4 October 2013

KBA (2013): Preliminary report on tests with vehicles relating to flammability and HF exposure with vehicle air conditioning systems using R1234yf. Flensburg, 07.08.2013 http://www.kba.de/cln_031/nn_124384/DE/Presse/Pressemitteilungen/2013/Allgemein/pm_25_13_risikobewertung_kaeltemittel_vorabbericht,templateId=raw,property=publicationFile.pdf/pm_25_13_risikobewertung_kaeltemittel_vorabbericht.pdf – last accessed on 4 October 2013

Annex: Measurement data provided by KBA

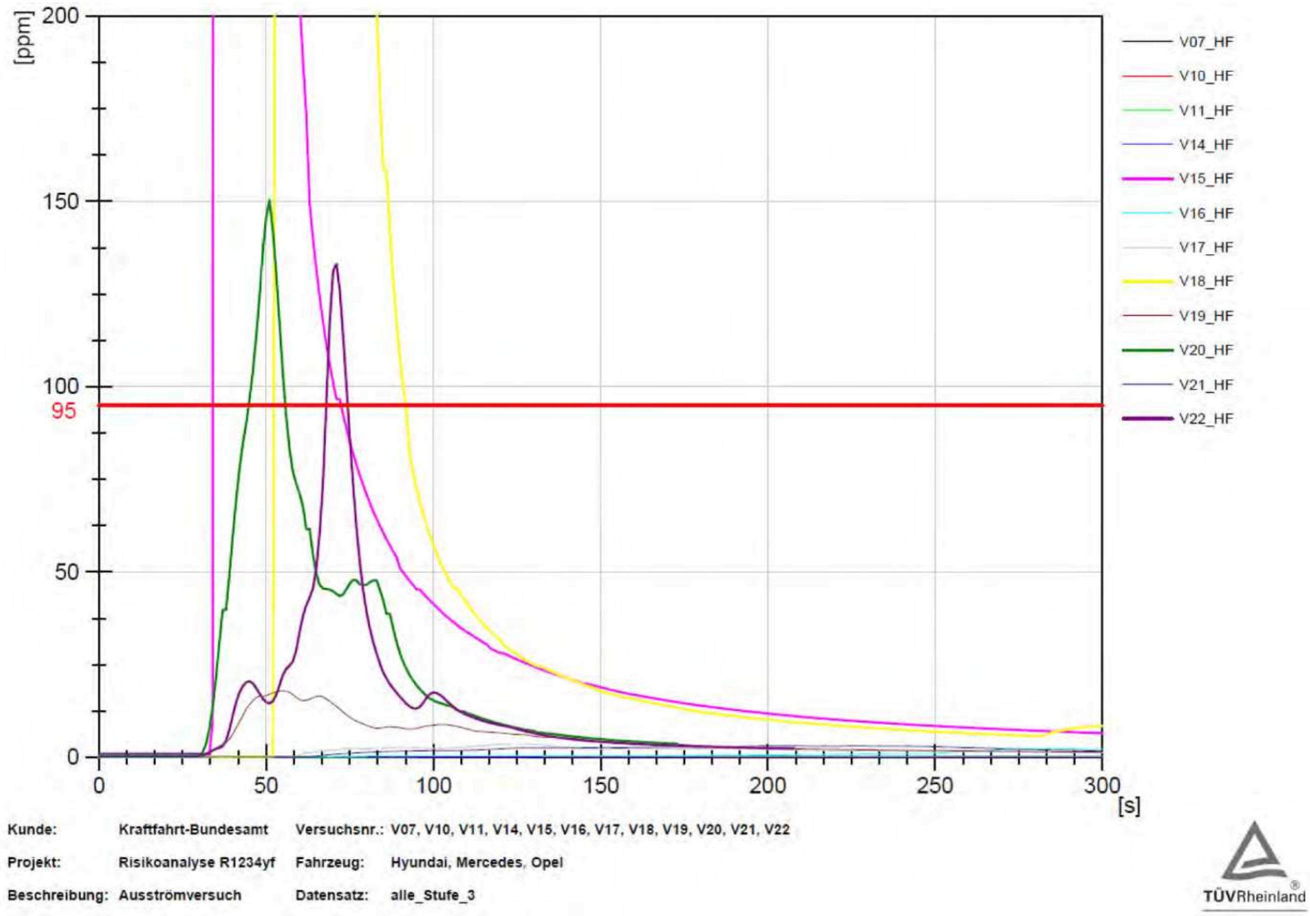


Figure 1: First measurement sheet provided by KBA

Client:	KBA	Test nos.:	V07, V10, V11, V14, V15, V16, V17, V18, V19, V20, V21, V22
Project:	Risk analysis R1234yf	Vehicle:	Hyundai, Mercedes, Opel
Description:	Discharge test	Data set:	all_stage_3

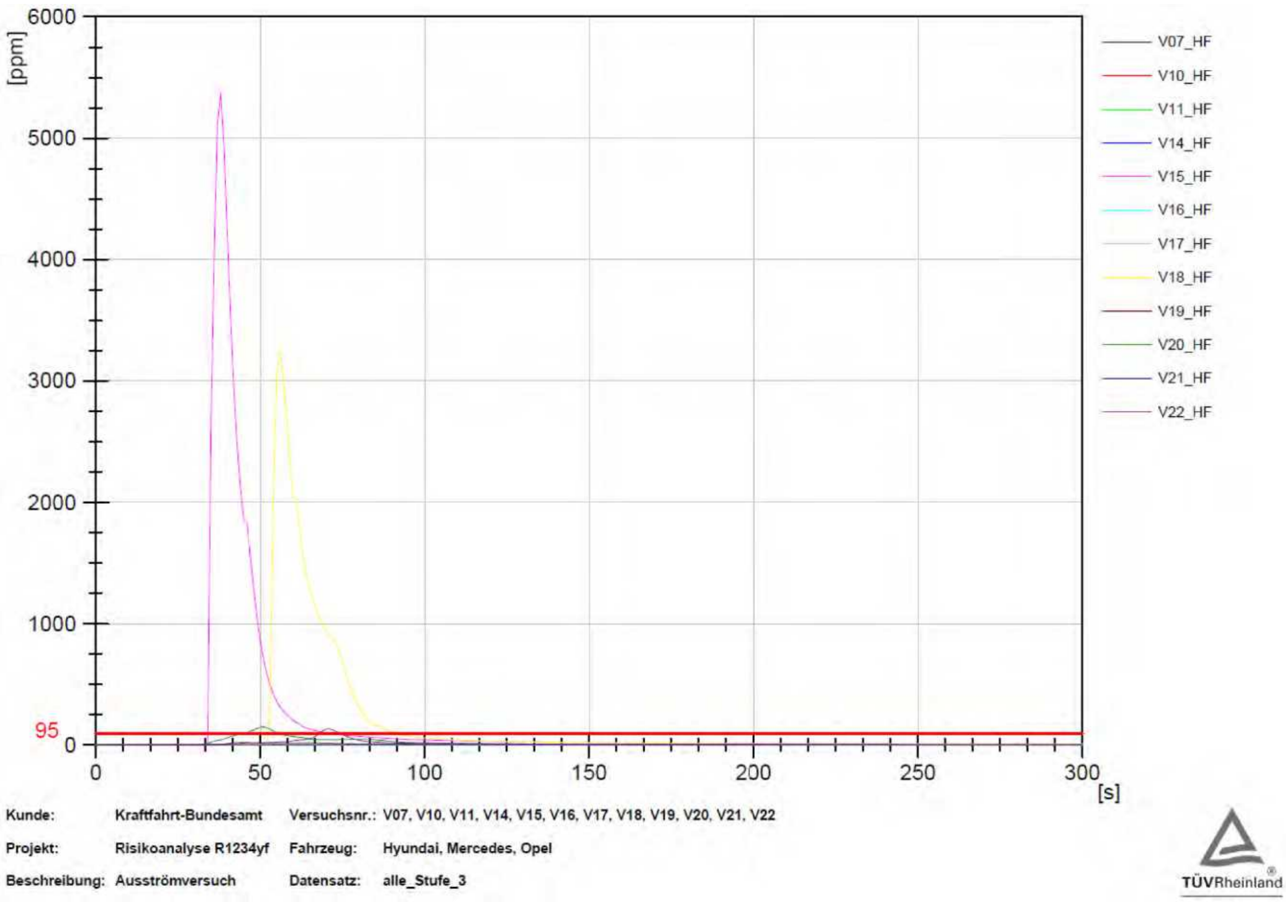


Figure 2: Second measurement sheet provided by KBA

Client:	KBA	Test nos.:	V07, V10, V11, V14, V15, V16, V17, V18, V19, V20, V21, V22
Project:	Risk analysis R1234yf	Vehicle:	Hyundai, Mercedes, Opel
Description:	Discharge test	Data set:	all_stage_3

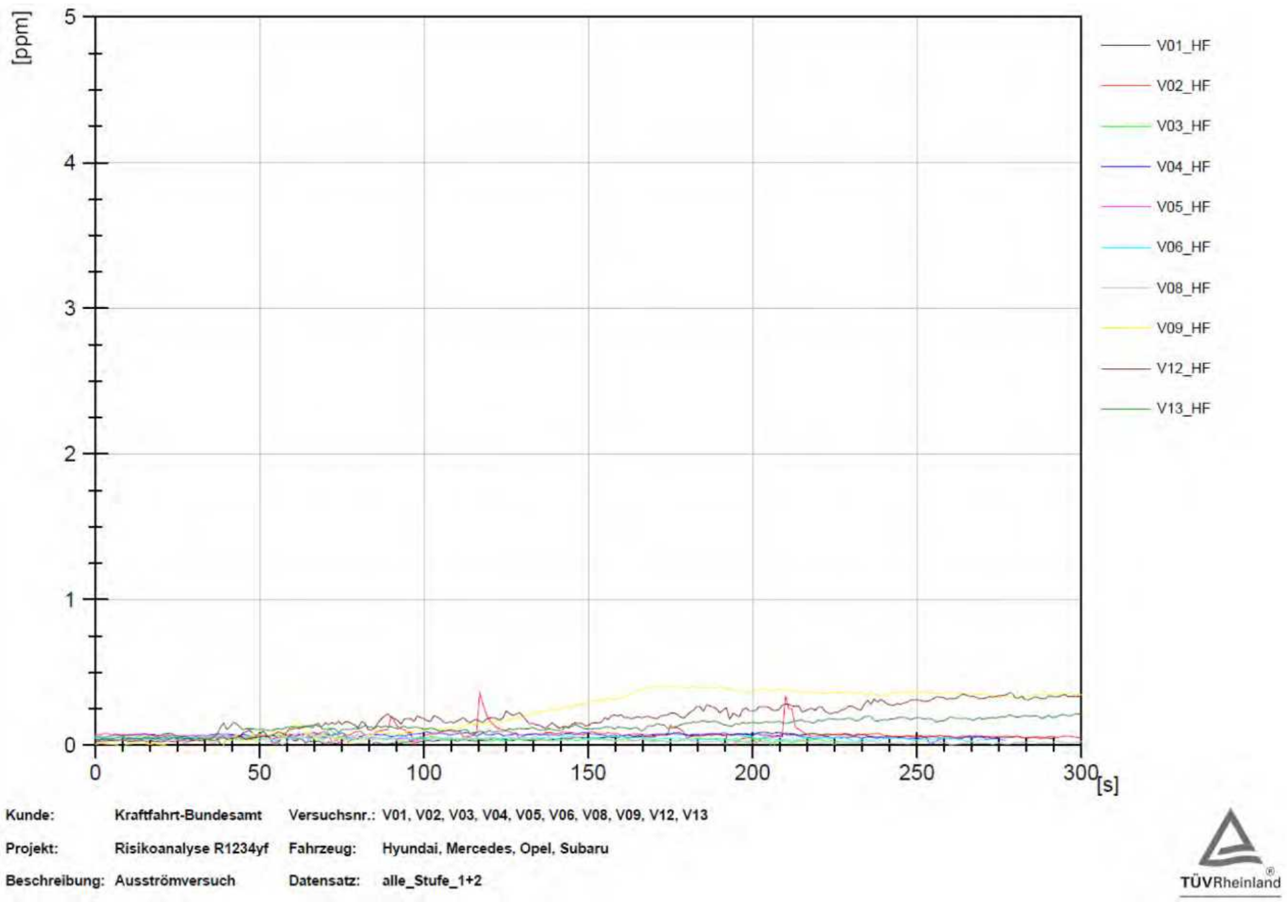


Figure 3: Third measurement sheet provided by KBA

Client:	KBA	Test nos.:	V07, V10, V11, V14, V15, V16, V17, V18, V19, V20, V21, V22
Project:	Risk analysis R1234yf	Vehicle:	Hyundai, Mercedes, Opel
Description:	Discharge test	Data set:	all_stage_2+1

Table 2: **Peak concentrations communicated by KBA in the individual test series**

No	HF measurement value LaserGas III maximum/in ppm
V01	0.10360
V02	0.36170
V03	0.12080
V04	0.09220
V05	0.08180
V06	0.06900
V07	0.17540
V08	0.08680
V09	0.40760
V10	0.13650
V11	0.34550
V12	0.44560
V13	0.23290
V14	0.44340
V15	5 364.98340
V16	2.40240
V17	3.57030
V18	3 254.22120
V19	17.97360
V20	150.40690
V21	3.12280
V22	133.20400

Stage 1	
Stage 2	
Stage 3	