



**Emerging technologies for the
Early location of Entrapped victims under Collapsed Structures & Advanced
Wearables for risk assessment and First Responders Safety in SAR operations**

D5.3 Testing & Validation of the RESCUE MIMS

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Executive Summary

In the framework of D5.3 the testing and validation of the analytical performance of the Rescue-MIMS prototype of TRL6 has been successfully achieved by conducting a number of lab-scale experiments. Specifically, various chemical compounds have been selected with the prospect of studying RESCUE-MIMS performance upon: (a) chemical hazards for the safety of the first responders (b) components relevant to human presence recorded in literature (c) other relevant compounds.

The RESCUE-MIMS system was evaluated by addressing the following analytical criteria: (a) response times (b) linear dynamic range within the examined concentration area, (c) sensitivity (LODs), (d) repeatability. Specifically, RESCUE-MIMS was tested and validated with chlorinated compounds since they are considered potentially hazardous product in case of industrial accidents and because the RESCUE-MIMS will be demonstrated in such a fire industrial incident scenario under UC4. For the same reason, Benzene was also used for testing because it is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly evolved in forest fires and/or industrial fires. Since the RESCUE-MIMS will be also used for detecting compounds relevant to human presence, trying to mimic the rescue dogs' work by artificial sniffing, laboratory testing with carbon dioxide and acetone has taken place, because these two compounds have been recorded in the literature as characteristic components of expired air. The RESCUE-MIMS prototype has shown excellent linearity within the concentration range that was examined, high sensitivity (limit of detection < 10 ppb), good repeatability (relative standard deviation, RSD < 5%) and response times in real time in few seconds. Except for the lab-scale experiments, field-scale testing has also been conducted as a preliminary work for identifying key-components to be monitored in the field at the upcoming pilot scenario of UC5- Victims trapped under rubble. RESCUE-MIMS is a promising field technology, as described thoroughly in D5.1 that can be used as a complementary tool to the existing ones in order to help first responders in search and rescue operations; it can be used for on-line monitoring of chemicals that can be related to the safety of the first responders, as well as for possibly tracking "human signs" under rubble. However, trying to mimic the rescue dogs in the disaster scene is quite a complex issue, since hundreds of chemical compounds can be present with different origins. The main challenge is to select a core of components that can be possibly related to alive human under rubbles that can be monitored by the respective field chemical technology, such as the RESCUE-MIMS, in order to support the search and rescue operation while the rescue dogs need to get some rest, or for cross checking a positive response (barking) of a dog. Selecting a small group of compounds for monitoring may improve the analytical performance of a chemical instrument, such as the RESCUE-MIMS, in terms of reducing the response times, as well as increasing the resolution. Though, an important issue when monitoring on-line in the field is to consider the possible background interferences that may create false positives or negatives; for that reason background measurements will be taken by the RESCUE-MIMS in the respective pilots.

In the above context, a field trial has been organised and run by NTUA and HRT in Kalamata, Greece with rescue dogs trained to locate alive people under rubble. The main scope was to record canines' responses (interest or not) to different chemical mixtures that have been prepared in the laboratory, under the perspective of creating indicative "synthetic odours" of alive humans trapped under rubbles, for future testing of the RESCUE-MIMS. Human odour though, is quite a complex issue and can be affected by a numerous parameters, like gender, diet, habits etc.; hence, a limited number of characteristic substances have been selected beyond these particularities based on literature documentation for preliminary testing.

These innovative experiments have provided some quite promising initial results; the dogs show interest in odours created to emulate those emanating from living people. However, due to the limitations described in the conclusions paragraph, further testing is required for enhancing those results and for more comprehensive conclusions.

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List of Abbreviations

Abbreviation / acronym	Description
ACGIH	American Conference of Governmental Industrial Hygienists Chemical Abstracts Service (division of the American Chemical Society)
Amu	Atomic mass unit
Bf	Beaufort
Da	Dalton
IRC	International Agency for Research on Cancer
KPIs	Key performance indicators
LC50	Lethal concentration, 50 percent
LD50	Lethal dose, 50 percent
LOD	Limit of detection
MIMS	Membrane inlet mass spectrometer
NFPA	National Fire Protection Association (USA)
NIOSH	National Institute for Occupational Safety and Health
NW	Northwest
OSHA	Occupational Safety and Health Administration
PBT	Persistent, Bioaccumulative and Toxic
PEL	Permissible Exposure Limit
Ppb	Parts per billion
PPE	Personal Protective Equipment
Ppt	Parts per trillion
REL	Recommended Exposure Limit
RH%	Relative humidity
SaR	Search and Rescue
SDS	Safety data sheet
SIM	Single ion monitoring)
SnR	Search and Rescue project
TLV	Threshold Limit Value
Torr	Torrighelli (Unit of Pressure)
TRL	Technology readiness level
UC	Use case
VOCs	Volatile organic compounds
vPvB	very Persistent and very Bioaccumulative
WHO	World Health Organization

1 Introduction

1.1 Purpose and Scope

The main purpose of deliverable D5.3 (M10) was first of all the testing and validation of the analytical performance of the RESCUE-MIMS prototype of TRL6 in lab-scale, by conducting a number of experiments. For that reason, different types of components needed to be selected and tested, namely: (a) chemical hazards for the safety of the first responders (b) components relevant to human presence, based on literature recordings (c) other relevant compounds.

The scope of D5.3 was to provide information regarding the analytical performance of the RESCUE-MIMS in terms of: (a) response times (b) linear dynamic range within the examined concentration area, (c) sensitivity (LODs), (d) repeatability, so as to answer to the respective KPIs relevant to the end-users' requirements addressed in D1.2.

A further objective of D5.3 was also to provide preparatory inputs concerning the compounds that should be selected as key indicators to be monitored on-line in field-scale and specifically, during the pilots UC4- Forest fire expanded and threat to industrial zone (Attica Region, Greece) and UC5-Victims trapped under rubbles (France).

In the above context, pre-testing with canines in the field was also under D5.3 perspective; the scope was to record canines' responses (interest or not) to different chemical mixtures that have been prepared in the laboratory, in the prospect of creating possible indicative "synthetic odors" of alive humans entrapped under rubbles for future testing of the RESCUE-MIMS. Selecting a small group of compounds for monitoring may improve the analytical performance of a chemical instrument, such as the RESCUE-MIMS, in terms of reducing the response times, as well as increasing the resolution. Though, an important issue when monitoring on-line in the field is to consider the possible background interferences that may create false positives or negatives; for that reason background measurements will be taken by the RESCUE-MIMS in the respective pilots.

1.2 Human chemical signatures-General Overview

Human chemical signatures can be considered the total of chemical compounds, such as the Volatile Organic Compounds (VOCs) and the gases e.g. CO₂ that can be evolved by the human body, e.g. the compounds' evolution by the human skin (axilla and sweat), as well as those in human breath [1] [2]. According to literature, the human body emits different types of VOCs like alcohols, aldehydes, amines, aromatics, ketones, etc. [3] while the majority of VOCs in breath may have concentrations ranging from ppb to ppt levels [4] [5]. The activity of the human armpit microbiota may triggers the formation of body odour [6]; numerous studies have examined the human skin volatiles, presented elsewhere

In Table 1-1, some of the most representative VOCs and gases that have been correlated with human presence and can be used for field analysis are summarized according to the conducted literature review (see D5.1, M10) [7]; the characteristic mass fragments of those compounds are also provided for monitoring in SIM mode by using the RESCUE-MIMS prototype.

Though, it should be stated that in the disaster scene it may be difficult to distinguish chemicals emitted by entrapped humans, e.g. ammonia or carbon dioxide, than by other sources, e.g. smoke under rubbles. That is why concentration profiles of such compounds need to be continuously monitored and also operational experience is needed for better assessing the recorded data. Also, environmental parameters like RH%, temperature and air flow inside the debris, as well as particles due to the collapsed structures can affect the final measurements. [8]

Compound	Type	Characteristic mass
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fragments		
Water vapors of the exhaled air	Gas phase	17,18
Ammonia	Inorganic gas	16,17
Carbon Dioxide	Inorganic gas	44
Oxygene	Inorganic gas	28,12
Acetone	VOC	43,58
Isoprene	VOC	53,67,68
Hexane	VOC	57,86
Pentane	VOC	41,42,57,72
1-Pentene	VOC	55,70
Lactic acid	VOC	45,90
Ethanol	VOC	27,29,30,31,45,46
Acetaldehyde	VOC	29
Limonene	VOC	68,121

Table 1-1: Representative VOCs and gases that have been correlated with “human presence” in literature and their characteristic mass fragments for monitoring with mass spectrometry- based technologies [7]

According to the literature, the above compounds behave differently as they permeate the ruins of buildings, interacting with brick, concrete, wood, furnishings and other materials etc. [9]
Based on another research work, a body-plethysmography camera was properly adjusted to study the changes in human chemical patterns during entrapment, as shown in Figure 1-1. [10]



Figure 1-1: Body-plethysmography chamber for the simultaneous monitoring of breath and skin emanations [10]

According to another study, a controlled environmental chamber was designed and built enabling precise control of ventilation temperature and humidity. The developed chamber consisted of three main parts: the void simulator; the collapsed building simulator; and, the environmental chamber. Throughout the scientific experiment, three types of entrapment were proposed [11], according to victim status:

- A. people in great anxiety, hyper-alert in panic after the event, with or without minor injuries;
- B. persons in intense stress with multiple injuries; and,
- C. dead victims.

These categories were further subdivided:

- A1, B1 less than 24h of entrapment;
- A2, B2 more than 24h.

The prototype was tested under real conditions with human volunteers remaining enclosed for 6 h, whilst the nature and the levels of volatile metabolic markers released by entrapped individuals into collapsed structure voids were monitored and detected; the experiment was named "Trapped Human Experiment" (THE) and it was an on-going 24 h per day in a five day experiment.

In these lab-based studies, some factors such as smoke, the heat of the presence of other contaminants from the buildings and their contents that affect the human scent profile cannot be reproduced. Nonetheless, the data could be useful for choosing known markers of the human presence to be detected by portable, sensitive instrumentation at the scene of the disaster. Canines (K-9) are especially trained dogs for capturing human scent in the disaster area [12]. However, due to this special and time consuming training, the number of available rescue dogs is limited. Moreover, they need to get rest during the search and rescue operation, the so-called "idle times" that may cost human lives, since time is a crucial factor for locating alive entrapped people under debris; this is mostly the case of a massive disaster like an earthquake, where limited means including the well-trained rescue dogs are available.

As thoroughly described in D5.1, M10 the alternative of using a chemical technology for "mimicking" canines, complementarily to the convectional search and rescue-methods, seems crucial. RESCUE-MIMS prototype will be tested in UC5 pilot scenario for tracking "signs of life under rubble" in the

framework of the SnR project. For that reason, characteristic chemicals that simulate “human odour” will be selected inside D5.3 for testing and validation of the RESCUE-MIMS (see Sections 2 and 3).

1.3 Chemical hazards in S&R-General overview

A number of safety and security issues for the first responders and the canines exist while operating in the disaster scene. During SAR in collapsed structures there is a possibility of toxic or explosive gases release, e.g. due to destruction of pipelines or explosion of gas cylinders under pressure that might be under the ruins, or fire spots that can be generated due to short circuits.

The above conditions create the necessity of field technologies capable of monitoring such hazardous environments on-site and on-line of and at a safe distance from the source, in order to protect the fire-fighters and the first responders and their canines in general. However, chemical hazards’ release creates a strong chemical background under the ruins that may burden search and rescue operation of entrapped victims.

In that prospect, the RESCUE-MIMS field technology will be tested under the SnR project framework for remote sensing on-board robotic platforms under a simulated scenario; UC4- Forest fire expanded and threat to industrial zone. For that reason, chemical hazards for the safety of the first responders will be selected inside D5.3 for initial testing and validation of the RESCUE-MIMS prototype in lab-scale (see Section 2).

2 Lab-scale testing of the RESCUE-MIMS prototype

2.1 Testing the RESCUE-MIMS's prototype analytical performance

2.1.1 Testing with compounds considered as chemical hazards for the first responders

- *Chlorinated compounds*

Based on D5.1 overview on chemical hazards, a serious product in case of industrial accidents that should be monitored for the safety of the first responders are the chlorinated compounds. Since the RESCUE-MIMS will be demonstrated in a fire industrial incident under the pilot scenario of UC4, a number of chlorinated compounds were selected for lab-scale testing and validation of its analytical performance; response times, linearity, limit of detection etc.

In that scope, standard methanolic solutions of chlorinated compounds were prepared by using the respective pure reagents purchased by Sigma Aldrich Co. and Fisher Scientific. The methanolic solutions of the chlorinated compounds (Figure 2-1) prepared, were: (a) trichloromethane, (b) 1,2-dichloroethane, (c) 1,1,1-trichloroethane and (d) chlorobromomethane, with concentration 200 mg/mL each. The solutions were in the liquid phase inside a vial of about 12 mL and stored in the fridge at 4 °C.



Figure 2-1: Methanol reagent $\geq 99.9\%$ was used to prepare the different standard solutions of chlorinated hydrocarbons into vials of 12mL, with concentrations of 200 mg/mL



Figure 2-2: RESCUE-MIMS lab-testing with different chlorinated compounds

The MIMS sampled in the gas phase of the analytes (headspace phase of the vial of 12mL shown in Figure 2-1). The total base pressure of the system with the sample inlet valve fully closed was 1×10^{-7} Torr. Operating pressure during mass analysis with the membrane sampling probe attached and the sample inlet valve fully open was between 2.1×10^{-6} Torr and 2.1×10^{-5} Torr for the different compounds and their characteristics, as shown in Table 2-1.

Compound	Trichloromethane	1,2-Dichloroethane	1,1,1-Trichloroethane	1,1,1,2-Tetrachloroethane
CAS Number	67-66-3	107-06-2	71-55-6	630-20-6
Molecular weight	119.378	98.959	133.404	167.849
Vapour pressure (kPa) at 25°C	26.2645	10.5191	16.5319	1.5998
Odour threshold (ppm)	3.3	3	100	1.5

Table 2-1: Chlorinated compounds characteristics that were used for testing the RESCUE MIMS prototype's analytical performance in lab-scale

An indicative mass spectrum recorded for Trichloromethane is provided in Figure 2-3. The basic mass fragments (m/z) of Trichloromethane were: 47, 83, 85 and 87. Similar mass spectra were recorded for the rest of the chlorinated compounds; namely, for 1,2-Dichloroethane, 1,1,1-Trichloroethane and 1,1,1,2-Tetrachloroethane.

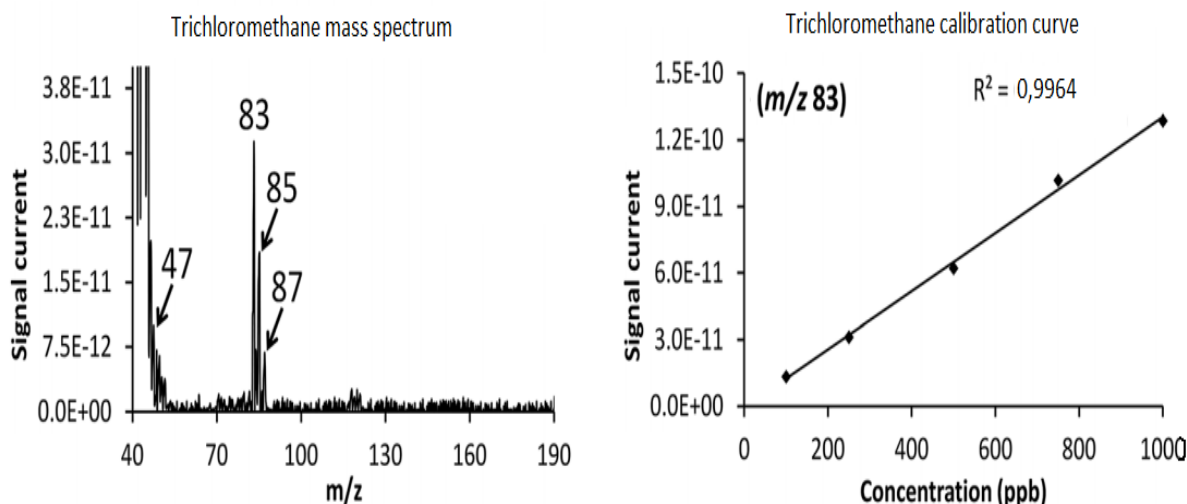


Figure 2-3: Mass spectrum and calibration curve of Trichloromethane by using the RESCUE-MIMS prototype

In Figure 2-3, the calibration curve prepared for trichloromethane is also provided. Concentrations from low ppb to low ppm levels, namely, 0, 200, 400, 600, 800 and 1000ppb (1ppm) were produced and the respective signal current was recorded by the RESCUE-MIMS; the mass fragment monitored for trichloromethane was m/z 83. Using linear regression in excel sheets, the R^2 that corresponds to linearity was calculated equal to 0,9964, which is very close to 1 and hence, the system has proved to have linear response. The LOD that is also calculated by the equation of the calibration curve was found equal to 2.18 ppb. The calibration curves for the rest of the 3 chlorinated compounds (1,2-Dichloroethane, 1,1,1-Trichloroethane and 1,1,1,2-Tetrachloroethane) were also produced by using the same concentration range (0-1000 ppm).

Table 2-2, summarizes the response times that were recorded for all of the above chlorinated compounds, as well as the linearity coefficient (R^2) and the limits of detection (LOD) as an outcome of the respective calibration curves' equations.

Compound	Trichloromethane (m/z 83)	1,2-Dichloroethane (m/z 62)	1,1,1-Trichloroethane (m/z 97)	1,1,1,2-Tetrachloroethane (m/z 131)
Characteristic mass fragments (m/z)	47, 83, 85, 87	62, 64, 98, 100	61, 97, 99, 117, 119	60, 61, 95, 97, 117, 119, 131, 133, 135

Response time (sec)	24	23	22	22
Linearity index-R²	0.9964	0.9992	0.9988	0.9996
Sensitivity- LOD (ppb)	2.18	2.05	2.74	3.57

Table 2-2: Analytical performance of the RESCUE-MIMS prototype for selected chlorinated compounds (response times, R2 values and limits of detection)

- *Benzene*

Benzene is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly evolved in forest fires and/or industrial fires [13] [14] [15] and hence, it is planned to be used as a key indicator for monitoring the hazardous environment in UC4 Industrial fire pilot scenario with the RESCUE-MIMS prototype.

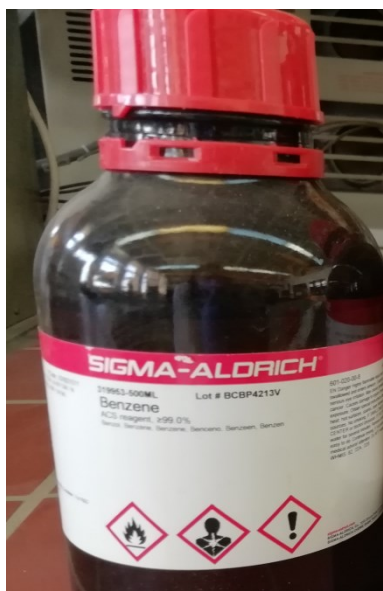
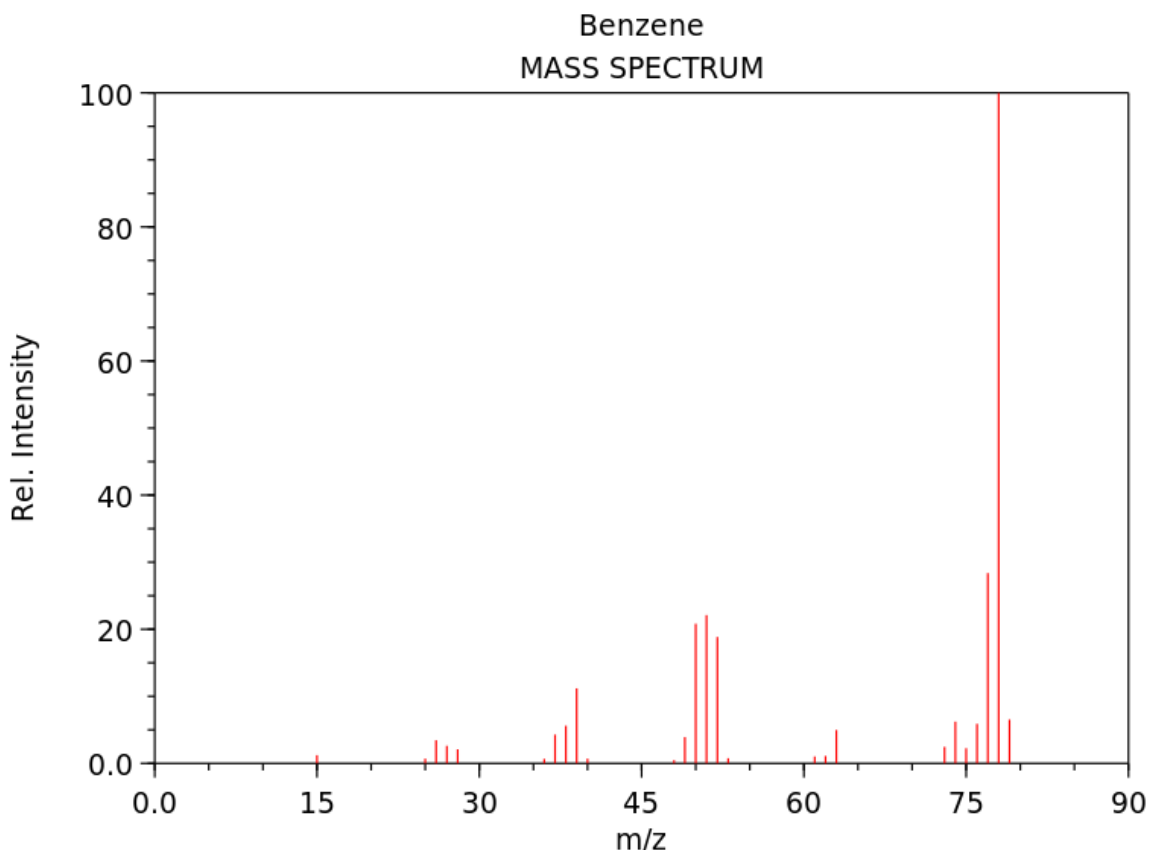


Figure 2-4: Standard solution of benzene with purity 99.8% for testing the RESCUE-MIMS

Based on the NIST chemistry webBook, the mass spectrum of Benzene is in the following (Figure 2-5), where the mass 78 is the more characteristic.



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 2-5: Mass spectrum of Benzene

In order to test the performance of the RESCUE-MIMS when measuring Benzene, different Benzene concentrations have been prepared from ppb to ppm levels, namely 0.06, 0.12, 0.39, 0.78, 1.56, 3.13, 6.25 and 12.5 ppm, by using a pure standard solution by Sigma Aldrich (Figure 2-4). Measurements proceeded from low concentrations to high concentrations (not the other way around) to eliminate any memory effect of the membrane inlet of the RESCUE-MIMS.

An indicative example of the intensities recorded by the RESCUE-MIMS corresponding to different mass fragments (m/z) between 77.97 and 78.31 Da that are attributed to Benzene, is shown in Table 2-3; the scan rate selected was 0.03 Da, though its value can be selected by the operator. A typical scan rate of the RESCUE-MIMS is 1 Da/sec. The relative standard deviation RSD was < 5% which shows very good repeatability of the system.

Masses scanned by the RESCUE-MIMS (m/z)	12.5 ppm	6.25 ppm	3.13 ppm	1.56 ppm	0.78 ppm	0.39 ppm	0.12 ppm	0.06 ppm
77.97	7.93E-10	3.01E-10	1.65E-10	8.21E-11	2.97E-11	1.76E-11	1.01E-11	5.44E-12

78.00	8.30E-10	3.20E-10	1.74E-10	8.09E-11	3.21E-11	1.75E-11	9.59E-12	5.51E-12
78.03	8.85E-10	3.34E-10	1.84E-10	8.66E-11	3.35E-11	1.89E-11	1.23E-11	6.50E-12
78.06	9.07E-10	3.48E-10	1.85E-10	9.09E-11	3.34E-11	1.82E-11	1.11E-11	6.56E-12
78.09	9.43E-10	3.62E-10	1.93E-10	9.59E-11	3.31E-11	2.04E-11	1.02E-11	6.93E-12
78.13	9.56E-10	3.79E-10	2.01E-10	9.41E-11	3.56E-11	1.87E-11	1.12E-11	6.36E-12
78.16	9.85E-10	3.77E-10	2.04E-10	9.64E-11	3.50E-11	1.90E-11	1.08E-11	6.44E-12
78.19	1.01E-09	3.85E-10	2.07E-10	9.70E-11	3.50E-11	1.70E-11	1.23E-11	6.46E-12
78.22	1.02E-09	3.86E-10	2.04E-10	9.48E-11	3.24E-11	1.73E-11	9.91E-12	5.46E-12
78.25	1.01E-09	3.86E-10	1.94E-10	9.17E-11	3.36E-11	1.73E-11	1.01E-11	6.83E-12
78.28	1.02E-09	3.76E-10	1.92E-10	8.82E-11	3.27E-11	1.78E-11	1.02E-11	5.14E-12
78.31	9.90E-10	3.62E-10	1.81E-10	8.28E-11	2.86E-11	1.69E-11	9.36E-12	4.55E-12

Table 2-3: Indicative example of the intensities recorded by the RESCUE-MIMS corresponding to different mass fragments (m/z) between 77.97 and 78.31 Da attributed to Benzene and for different concentration levels (0.06 to 12.5 ppm)

Figure 2-6 presents the mass spectrum of Benzene recorded by the RESCUE-MIMS prototype for different concentrations, scanning in the mass range of 70 to 85 amu; 12.5 ppm (in navy), 6.25 ppm (in red), 3.13 ppm (in grey), 1.56 (in orange), 0.78 ppm (in light-blue), 0.39 ppm (in green), 0.12 ppm (in dark-blue), 0.06 ppm (in purple). It's clear that mass 78 recorded is the most abundant.

A magnified screenshot of the mass spectra recorded for Benzene focusing on the masses 77, 78 and 79 is provided in Figure 2-7.

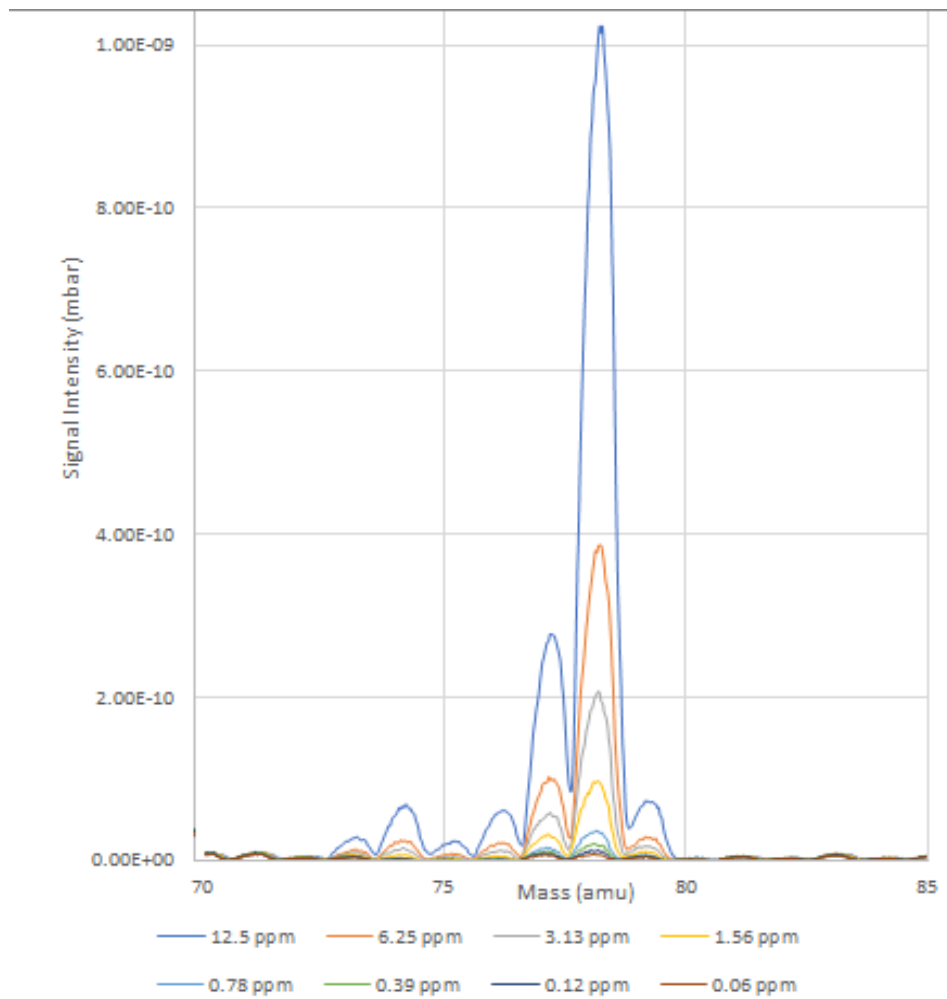


Figure 2-6: Mass spectra of Benzene recorded for different concentrations in the range of 70 to 85 amu; 12.5 ppm (in navy), 6.25 ppm (in red), 3.13 ppm (in grey), 1.56 (in orange), 0.78 ppm (in light-blue), 0.39 ppm (in green), 0.12 ppm (in dark-blue), 0.06 ppm (in purple)

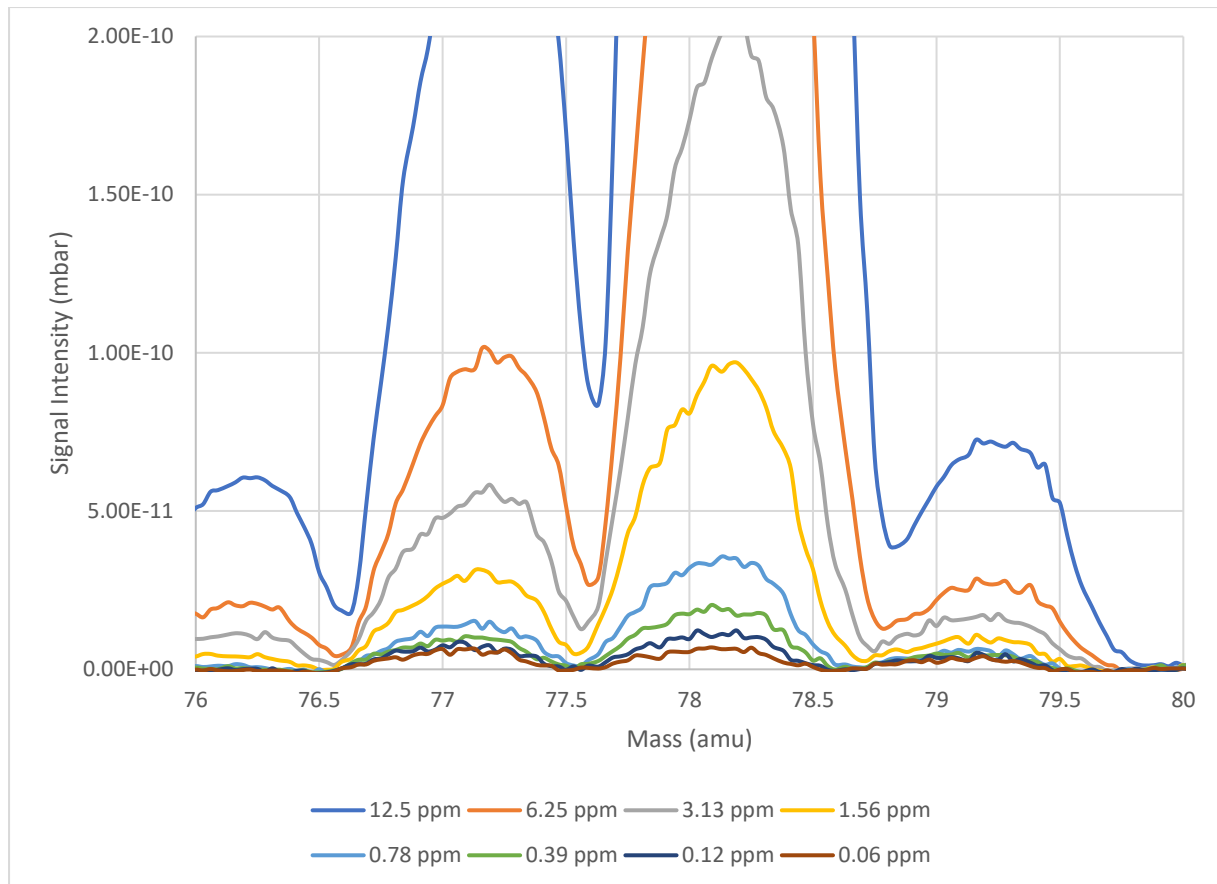


Figure 2-7: Magnified screenshot of the mass spectra recorded for Benzene by the RESCUE-MIMS, focusing on the masses 77, 78 and 79; 12.5 ppm (in navy), 6.25 ppm (in red), 3.13 ppm (in grey), 1.56 (in orange), 0.78 ppm (in light-blue), 0.39 ppm (in green), 0.12 ppm (in dark-blue), 0.06 ppm (in purple)

2.1.2 Testing with components relevant to human presence

Since the RESCUE-MIMS will be also used for detecting compounds relevant to human presence under UC5, testing with carbon dioxide and acetone has taken place; these two compounds have been recorded in literature as characteristic components of the expired air. [7]. However, it should be emphasized that in a real disaster event more than these two substances should be monitored (see table 1-1) in order to conclude that there is a possibility of having an entrapped human under the rubbles.

More information on the configuration of the RESCUE-MIMS prototype in terms of ruins penetration, protection inside the debris, environmental conditions etc. will be provided in D5.3 version 2, under UC5 preparation.

- *Carbon dioxide*

For this testing 10% carbon dioxide (CO₂) in Nitrogen gas has been directly emitted in front of the sampling probe of the RESCUE-MIMS. In Figure 2-8 the characteristic mass fragments (m/z) of carbon dioxide, namely 12 and 44 are clearly recorded on-line by the system.

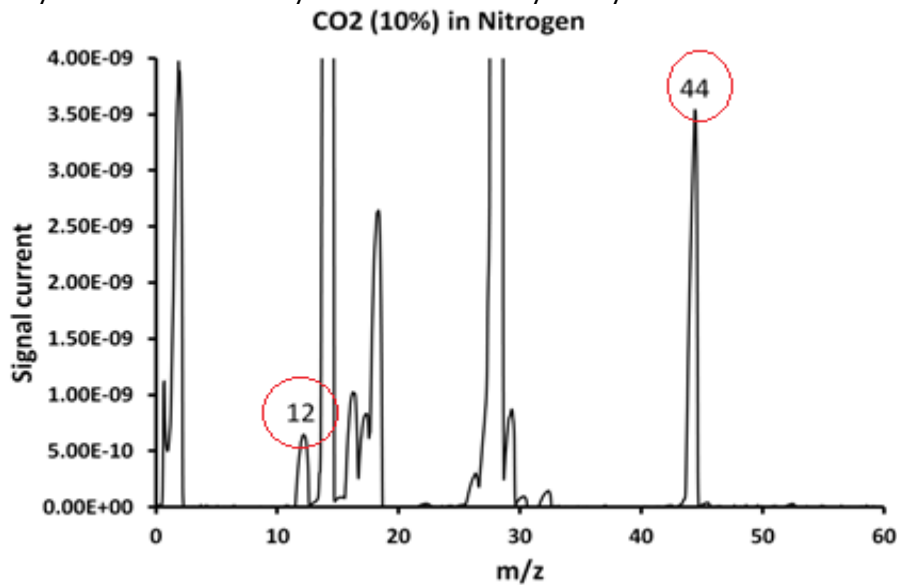


Figure 2-8: Mass spectrum received by 10% carbon dioxide in nitrogen with a direct leak. The Key mass fragments (m/z) of 12 and 44 are visibly recorded by the RESCUE-MIMS

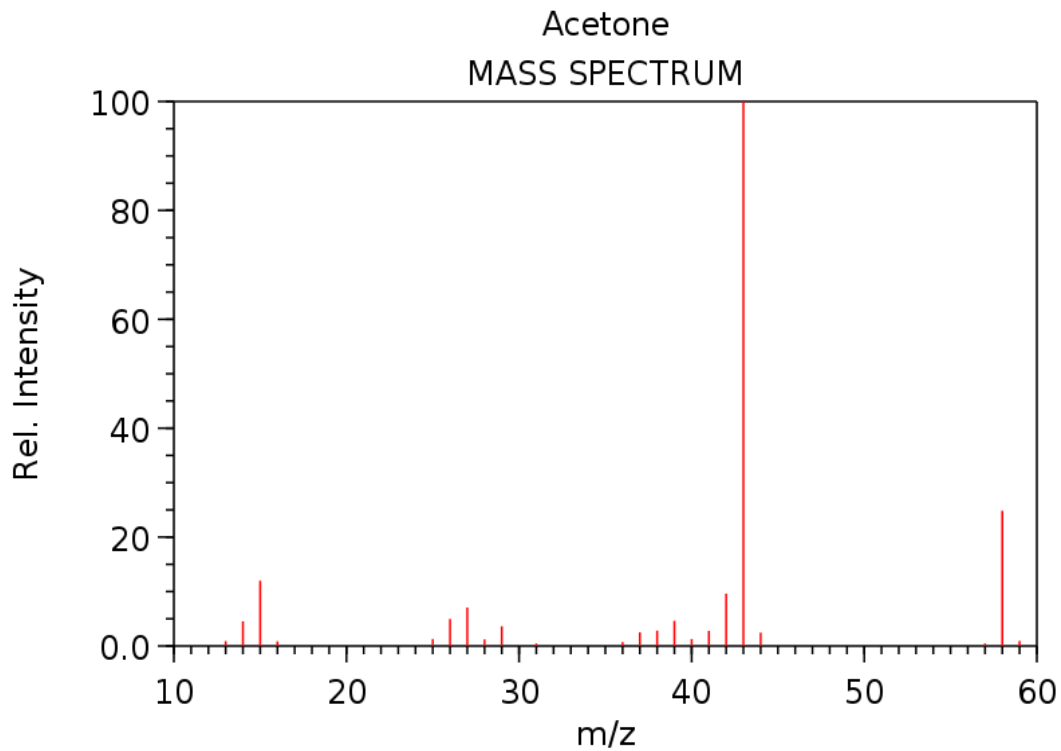
- *Acetone*

Acetone is considered one of the core substances of expired air. [5] [7] [16] A standard solution of acetone by FLUKA was used of > 99.5% purity (Figure 2-9).



Figure 2-9: Standard solution of acetone with purity >99.5% for testing the RESCUE-MIMS

Based on the NIST chemistry webBook, the mass spectrum of Acetone is shown in the following, where the masses 43 and 58 are the more characteristic (Figure 2-10).



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Figure 2-10: Mass spectrum of Acetone

Figure 2-11 demonstrates the signal intensity of masses 43 and 58 recorded by the RESCUE-MIMS; headspace analysis using a sample of 25 mL neat acetone inside a tube of 50 mL (Figure 2-12).

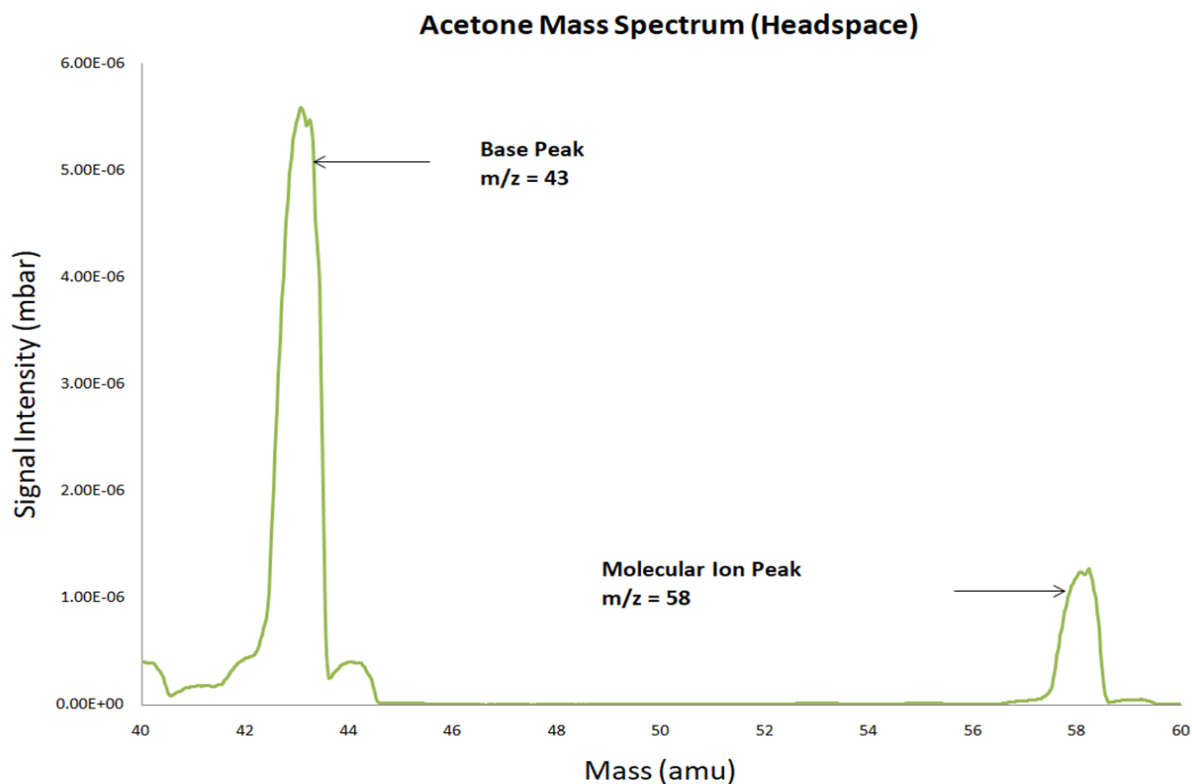


Figure 2-11: Signal intensity of masses 43 and 58 recorded by the RESCUE-MIMS in the headspace of an acetone sample; 25 mL neat acetone with purity > 99.5%



Figure 2-12: Test-tube of 50mL where the neat acetone sample of 25mL was inserted for running the headspace sampling tests with the RESCUE-MIMS

In order to test the RESCUE-MIMS's analytical performance in detecting Acetone, a number of different concentrations from 0.05 to 1 ppm have been prepared, monitoring in SIM mode the characteristic masses of Acetone, namely 43 and 58. The respective mass spectra are shown in Figure 2-7.

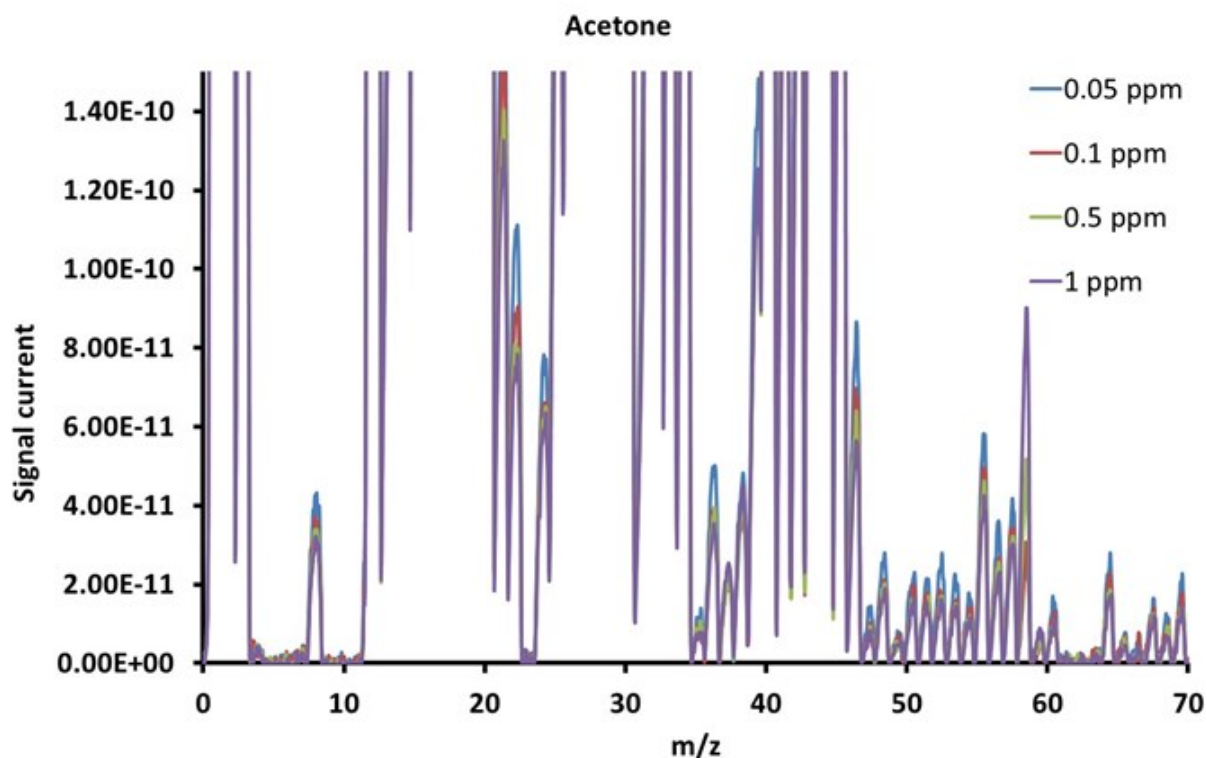


Figure 2-13: Mass spectra obtained by different concentrations of Acetone: 0.05 ppm (in blue), 0.1 ppm (in red), 0.5 ppm (in green) and 1 ppm (in purple)

For the above concentrations, namely 0.05, 0.1, 0.5 and 1 ppm, the calibration curve for Acetone has been also prepared and is shown in Figure 2-14. For generating the calibration curve, the signal current of mass 58 was recorded by the RESCUE-MIMS for the respective concentrations of Acetone prepared.

It seems that the system has an excellent performance in terms of linearity, since the linearity coefficient was found by the calibration curve equal to 0.9927, almost 1, which is the ideal value for a linear performance; the LOD for acetone after linear regression calculation in excel file was found equal to 14.7 ppb. The relative standard deviation RSD was < 5% which shows very good repeatability of the system.

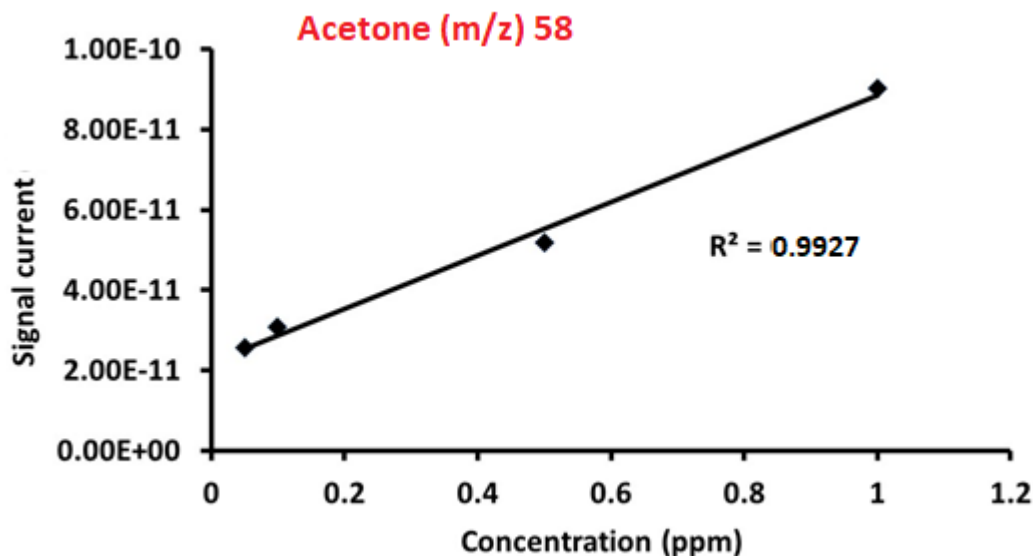


Figure 2-14: Calibration curve of Acetone for the concentrations of 0.05, 0.1, 0.5 and 1 ppm, measured by the RESCUE-MIMS

2.1.3 Testing with other compounds

Taking into consideration that the search and rescue environment is considered chemically complex by nature due to the different types of compounds that can be emitted, such as alcohols, aldehydes, ketones etc. e.g. in industrial fires, RESCUE-MIMS's analytical performance was also tested with a list of such compounds, additionally to the ones already presented in 2.1.1 and 2.2.2, in order to have a more broad assessment.

In that concept, standard solutions of ketones (Acetophenone: m/z 120, Cyclohexanone: m/z 98), alcohols (1-Pentanol: m/z 70, 1-Heptanol: m/z 70), aldehydes (Propanal: m/z 58), and esters (Ethyl acetate: m/z 88, Ethyl propionate: m/z 102) have been used and the respective calibration curves have been prepared in the range of low ppb to low ppm levels; 0.05, 0.1, 0.5 and 1 ppm as was done for Acetone (Figure 2-14). The linearity coefficient (R^2) and the LODs calculated for these type of compounds are summarised in Table 2-4.

Type	Ketones		Alcohols		Aldehydes	Esters	
Compound	Acetophenone (<i>m/z</i> 120)	Cyclohexanone (<i>m/z</i> 98)	1-Pentanol (<i>m/z</i> 70)	1-Heptanol (<i>m/z</i> 70)	Propanal (<i>m/z</i> 58)	Ethyl acetate (<i>m/z</i> 88)	Ethyl propionate (<i>m/z</i> 102)
CAS Number	98-86-2	108-94-1	71-41-0	111-70-6	123-38-6	141-78-6	105-37-3
Molecular weight	120.1485	98.143	88.1482	116.2013	58.0791	88.1051	102.1317
Characteristic mass fragments (<i>m/z</i>)	51, 77, 105, 120	55, 98	55, 70	55, 56, 57, 69, 70, 83, 98	57, 58	61, 70, 88	57, 73, 74, 75, 102
Linearity index- R ²	0.9945	0.9842	0.9833	0.9923	0.9904	0.9838	0.9957
Sensitivity- LOD (ppb)	27	10.5	13.8	14.5	6.7	17.4	37.4

Table 2-4: Summary of the analytical performance of the RESCUE-MIMS (R2 values and limits of detection) for different types of compounds (ketones, alcohols, aldehydes, esters)

2.2 Testing the RESCUE-MIMS's prototype functional performance

Lab-scale testing of the RESCUE-MIMS prototype includes experiments with selected chemicals in order to test the analytical performance of the RESCUE-MIMS prototype, as thoroughly presented in paragraph 2.1.

However, apart from the analytical performance evaluation, functional performance assessment of the RESCUE-MIMS prototype is quite important, since it is a device intended to be used by the first responders in the framework of the SnR project. This type of evaluation will be available after the pilot demonstrations of UC4 and UC5, considering the end-users' feedback, hence it will be provided in D5.3 version 2 (M30).

3 Field-scale testing of the RESCUE-MIMS prototype

3.1 Pre-testing with canine dogs in the field: Concept and Scope

RESCUE-MIMS is a promising field technology, as described thoroughly in D5.1 that can be used as a complementary tool to the existing ones in order to help first responders in search and rescue operations; it can be used for the on-line monitoring of chemicals that can be related to the safety of the first responders, as well as for possibly tracking “human signs” under rubble.

However, trying to mimic the rescue dogs in the disaster scene is quite a complex issue, since hundreds of chemical compounds can be present. The main challenge is to select a core of components that can be possibly related to alive people under rubbles, which can be monitored by the respective field chemical technology, such as the RESCUE-MIMS. Selecting a small group of compounds for monitoring may improve the analytical performance of a chemical instrument, such as the RESCUE-MIMS, in terms of reducing the response times, as well as increasing the resolution.

Overall, a core objective is to support the search and rescue operation in all cases where it is unsafe for the rescue dogs to approach. Moreover, chemical technologies could be used while the rescue dogs need to get some rest, or for cross-checking a positive response (barking) of a dog in the rubbles.

In that context and in order to select key compounds of human presence for monitoring them on-line in the field, a field trial with canines has been organized as a pre-testing and preparation of the pilot demonstration of UC5 (Victims trapped under rubble). The main scope was to record canines’ responses (interest or not) to different chemical mixtures that have been prepared in the laboratory, under the perspective of creating possible “synthetic odours” of alive humans entrapped in debris, for future testing of the RESCUE-MIMS.



Figure 3-1: The 6 rescue dogs of HRT trained for locating alive people that participated in Kalamata’s field trial

The field trial took place on the 16-17 of July 2021; on the 16th there was a preliminary survey of the fields and fixing of the final layouts of the testing, while on the 17th the trial was held. The place for running the experiments was Kalamata, Greece, where one of the training fields of HRT is located; HRT headquarters is in Thessaloniki with branches in various places in Greece (Figure 3-2). A total number of 6 dogs (Figure 3-1) participated, coming from HRT branches in Kalamata, Argos, Crete and Trikala (Figure 3-2); it is well-noted that the canines participated in the trial were trained only for alive people tracking. More details of the trial are described in following paragraphs.



Figure 3-2: A total number of 6 dogs from HRT participated in the field trial coming from Kalamata, Argos, Crete and Trikala, as indicated in the map of Greece

Following all the Health and Safety protocols, the chemicals that have been used were in line with the exposure limits provided by International Health and Safety Organizations, like NIOSH in order to not put the dogs at any risk; the Safety Data Sheets of the chemicals used, as well as the Personal Protective equipment used are indicated in Annex II "Safety Data Sheets of the Chemicals used and PPE for the lab-scale and field-scale experiments".

The tests fully complied with the UNESCO - Universal Declaration of Animal Rights 17-10-1978. The dogs' trainers were at the field during the whole trial and all the procedures were according to the Ethics provided in detail at Annex III "Ethical considerations in using canines at field trials input". More details of the trial are described in paragraphs 3.2 and 3.3.

3.2 Design of the field trial

3.2.1 Materials and Equipment

Several vials with volume of 16mL containing different chemicals were used for the preparation of the different chemical mixtures of “synthetic human odour” and then incubated into a specific metallic cup, as shown in Figure 3.3.



Vial of 16mL, Diameter x Height: 20.6 x 71 mm Metallic cup: DiameterxHeight: 7x9.5 cm

Figure 3-3: Several vials with volume 16mL was used for inserting the different chemicals, enclosed to a metallic cup

The metallic cups were then settled to the field at marked sites for running the experiments with the canines, which are trained for tracking alive entrapped people. The responses of the deployed dogs to the different chemical mixtures were recorded (more details on the experimental protocol of the field trial is presented in the next paragraph).

3.2.2 Chemicals for the preparation of indicative “synthetic human odours”

Based on the respective literature that was presented in paragraph 1.2, the following chemicals that were selected to be used for the preparation of indicative synthetic human odors are listed, together with their physicochemical characteristics, their respective exposure limits and the characteristic masses (m/z) [17] [18] [19] [20] [21] [22] [23] [24], for monitoring them on-line with the RESCUE-MIMS prototype.

It should be emphasized though that human odor is quite a complex issue and can be affected by a numerous parameters, like gender, diet, habits etc. (see D5.1, M10); hence, a number of characteristic substances have been selected beyond these particularities, based on literature recordings:

Acetone (CAS number: 67-64-1)

- *Physicochemical characteristics*

Vapor Pressure: 231 mm Hg at 25 deg C

Autoignition Temperature: 465 °C

Boiling Point: 56.08 °C

Odor Threshold: Odor low: 47.5 mg/cu m; Odor high: 1613.9 mg/cu m

LEL: 2.5% (10% LEL, 2,500 ppm)

Incompatible materials: Bases, Oxidizing agents, Reducing agents, Acetone reacts violently with phosphorous oxychloride.

Water Solubility: miscible

- *Exposure Limits:*

ACGHI

TLV-TWA: 500ppm, STEL: 750 ppm

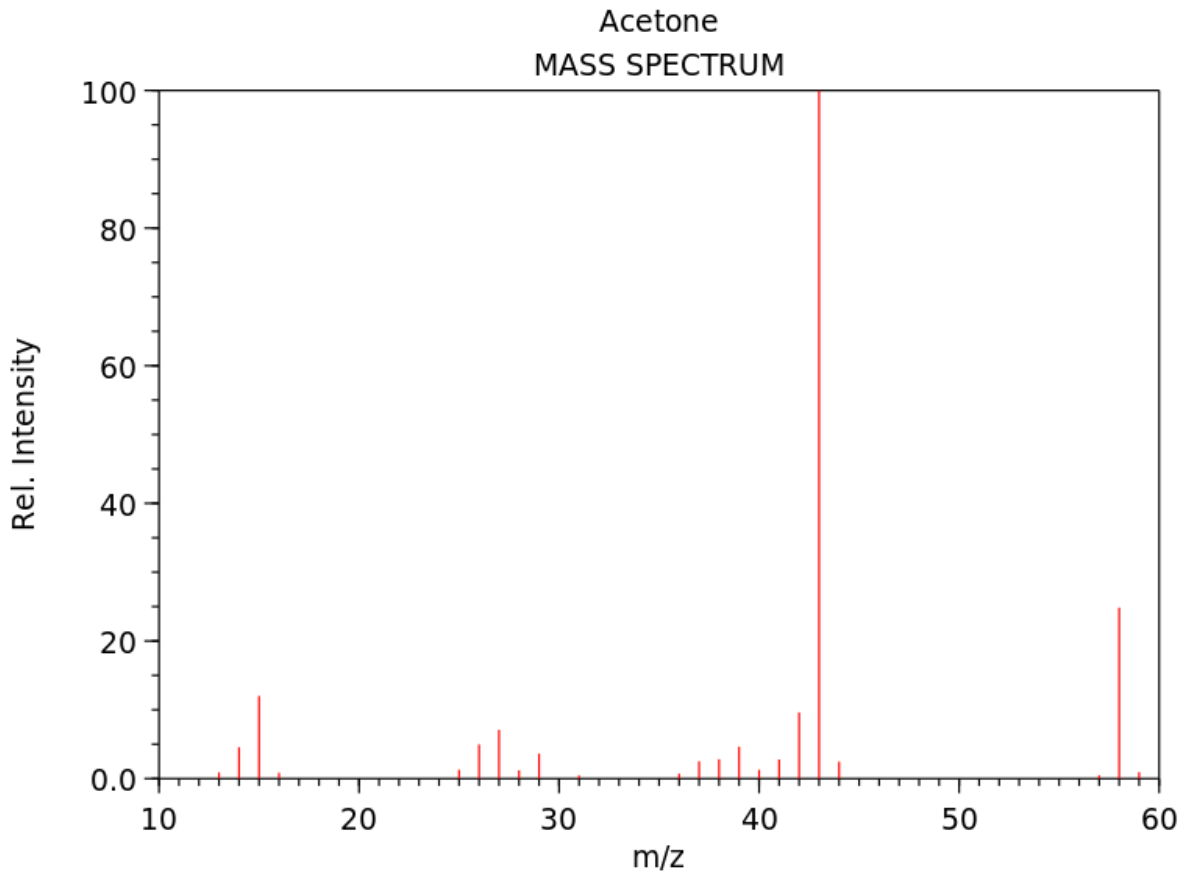
OSHA

PEL: 1000 ppm, STEL: -

NIOSH

REL: 250 ppm, STEL: -

IDLH: 20,000 ppm



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-4: Mass spectrum of Acetone

- *Acetone masses for monitoring: 58, 43*

Lactic acid (CAS number: 50-21-5)

- *Physicochemical characteristics*

Vapour Pressure: 0.62 (vs air)

Boiling Point: 122 °C at 15 mmHg

Ignition temperature: No data available

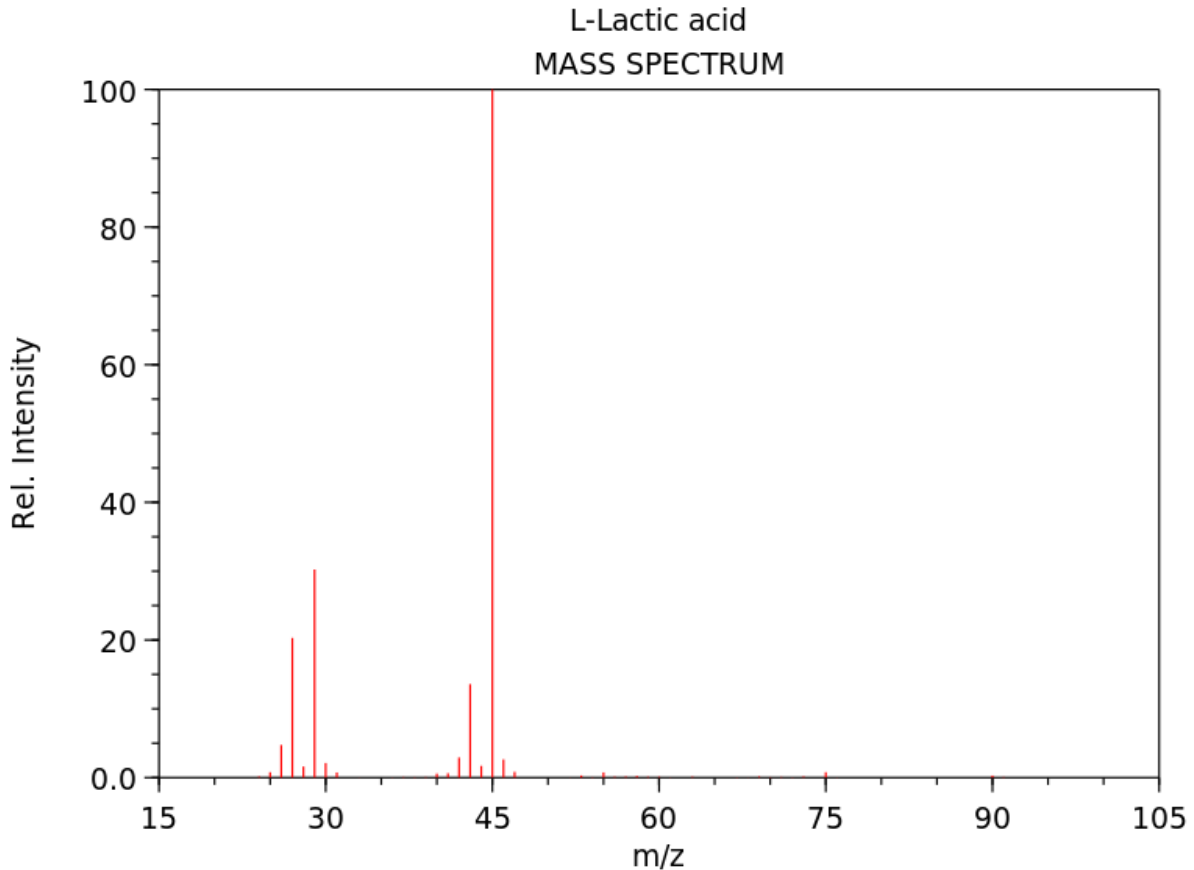
Odor Threshold: Lactic acid is odorless. It consists of a mixture of lactic acid (C₃H₆O₃) and lactic acid lactate (C₆H₁₀O₅).

Incompatible materials: Strong oxidizing agents

Miscible with water and with ethanol (96 per cent).

- *Exposure Limits*

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-5: Mass spectrum of Lactic acid

- *Lactic acid masses for monitoring: 45, 90*

Propanoic acid (CAS number: 79-09-4)

Vapour Pressure: 2.4 mm Hg (20 °C)

Boiling Point: 141°C

Explosive limit: 2.1-12%(V)

Odor Threshold: 0.0057ppm

Incompatible materials: Incompatible with strong oxidizing agents. Flammable.

Water Solubility: 37 g/100 mL

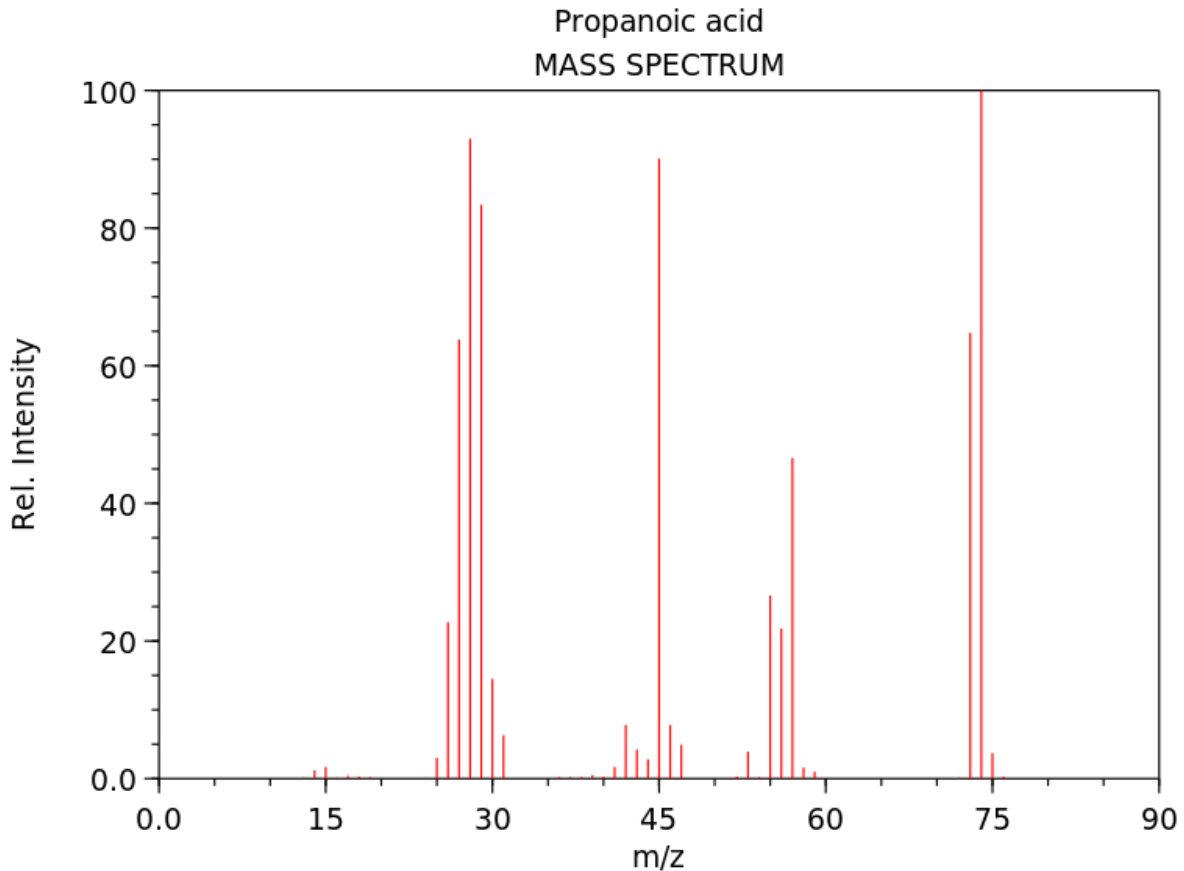
Soluble in water and alcohol; Dilution with water causes release of heat.

- *Exposure Limits*

ACGHI

TLV-TWA:10 ppm

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-6: Mass spectrum of Propanoic acid

- *Propanoic acid masses for monitoring: 73, 74*

Acetic acid (CAS number: 64-19-7)

Vapour Pressure: 11,4 mm Hg (20 °C)

Boiling Point: 117-118 °C

Explosive limit: 4- 19.9% (V)

Odor Threshold: 0.006ppm

Water Solubility: miscible

Incompatible materials: Acetic acid reacts with alkaline substances.

- *Exposure Limits*

ACGIH

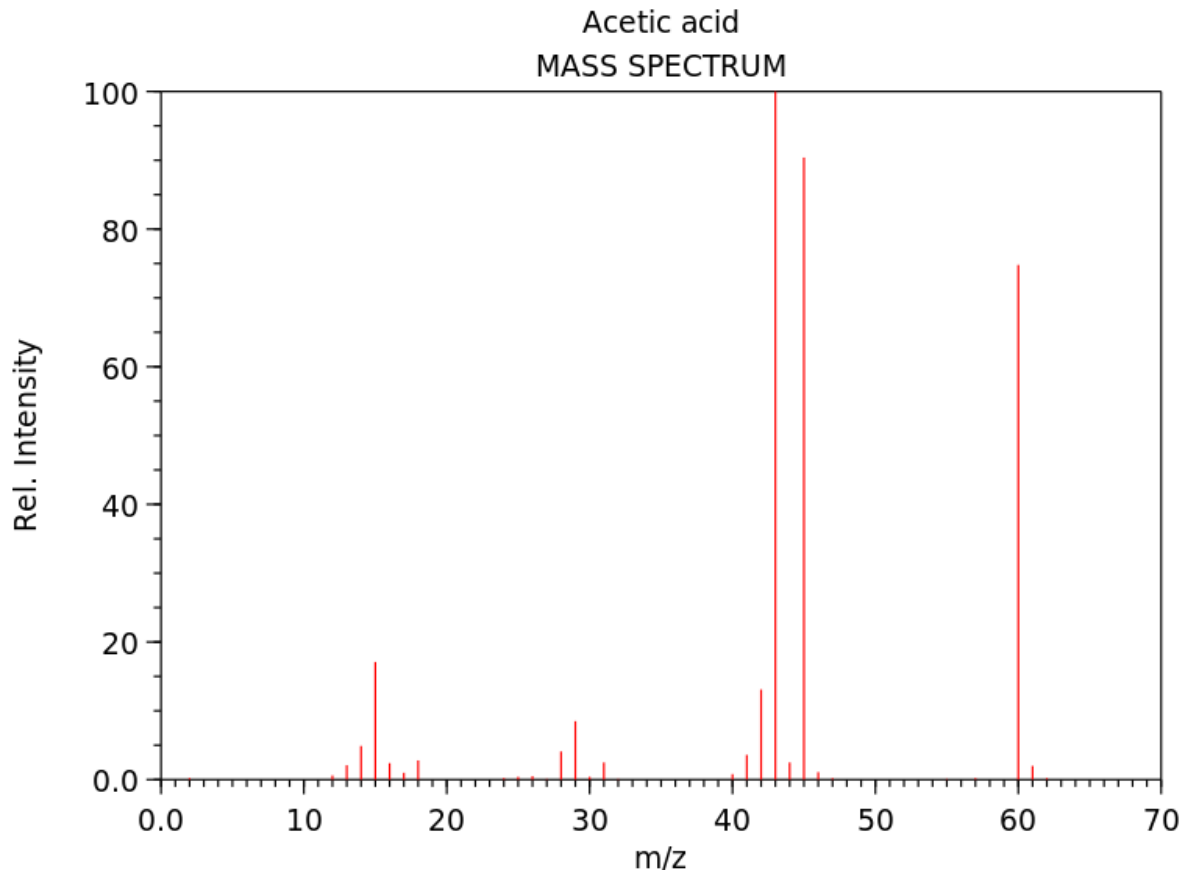
TLV-TWA: 10ppm, STEL: 15 ppm

OSHA

PEL: 10 ppm, STEL: -

NIOSH

REL: 10ppm, STEL: 15 ppm



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-7: Mass spectrum of Acetic acid

- *Acetic acid masses for monitoring: 60, 43*

n-Hexane (CAS number: 110-54-3)

Vapour Pressure: 40 mm Hg (20 °C)

Boiling Point: 68.95 °C

Explosive limit: 1.0-8.1% (V)

Odor Threshold: 1.5ppm

Water Solubility: Insoluble

Incompatible materials: Stable. Incompatible with oxidizing agents, chlorine, fluorine, magnesium perchlorate. Highly flammable. Readily forms explosive mixtures with air.

- *Exposure Limits*

ACGHI

TLV-TWA: 50ppm

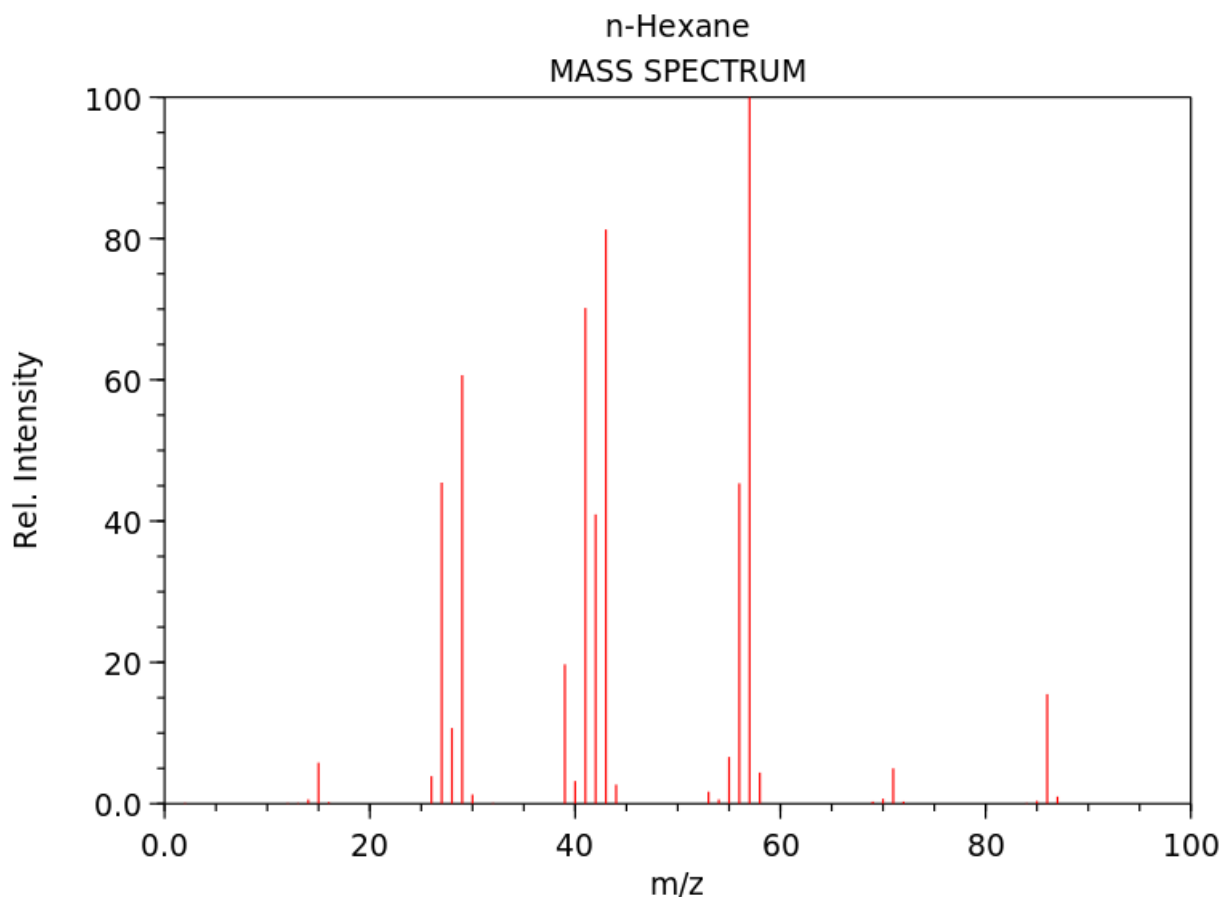
OSHA

PEL: 500 ppm

NIOSH

REL: 50pm

IDLH: 1100 ppm



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-8: Mass spectrum of n-Hexane

- *n-Hexane masses for monitoring: 86, 57*

Butyric acid (CAS number: 107-92-6)

- *Physicochemical characteristics*

Vapour Pressure: 0.43 mm Hg (20 °C)

Boiling Point: 162 °C (lit.)

Explosive limit: 2-12.3%(V)

Autoignition temperature: 440 °C

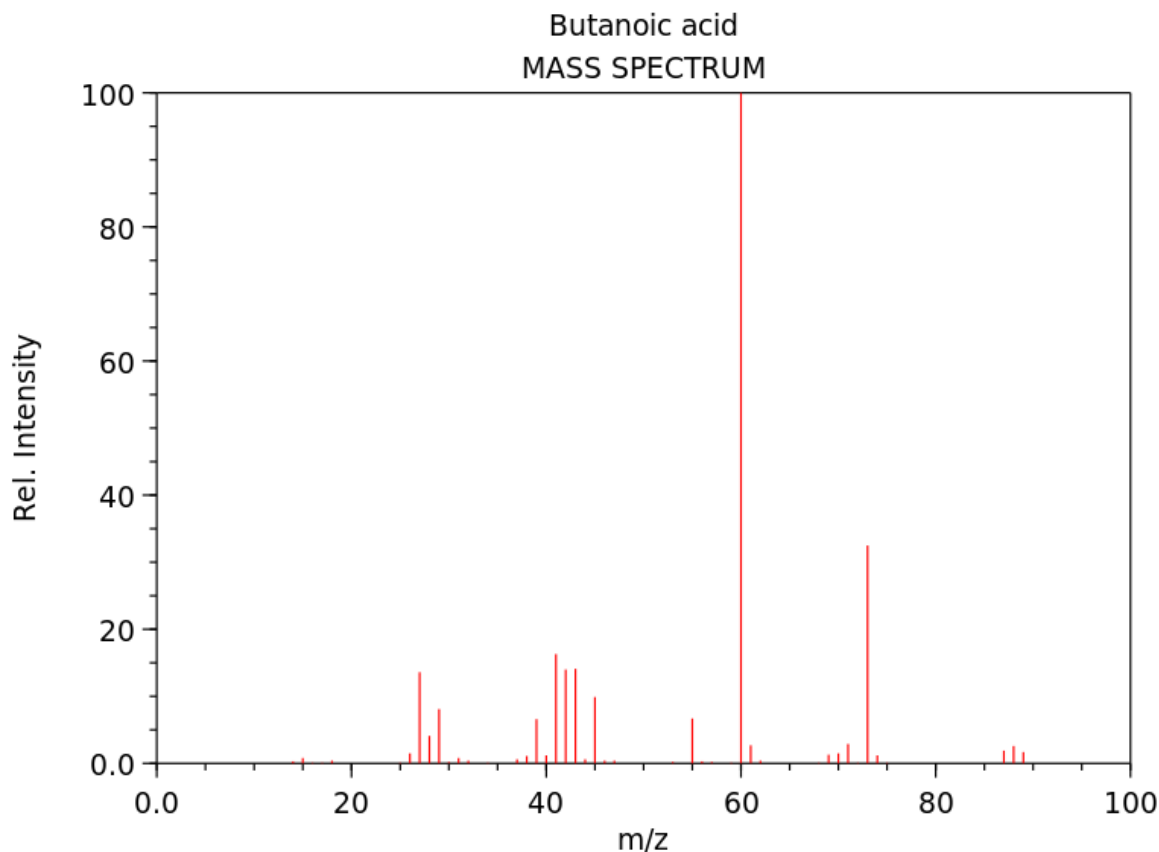
Odor Threshold: 0.00019ppm

Incompatible materials: Flammable. Incompatible with strong oxidizing agents, aluminium and most other common metals, alkalies, reducing agents.

Water solubility: Miscible

- *Exposure Limits*

No applicable occupational exposure limits



NIST Chemistry WebBook (<https://webbook.nist.gov/chemistry>)

Figure 3-9: Mass spectrum of Butyric acid (Butanoic acid)

- *Butyric acid masses for monitoring: 60, 73*

3.2.3 Experimental protocol

- *Selecting chemicals for the mixtures*

In the scope of preparing odours that resemble an alive person under the rubbles, 6 different combinations of chemicals were tested. Each different combination of chemicals was enclosed into a specific metallic cup (marked with a number from 1-6). The idea was that each metallic cup simulated a victim under the rubbles that the canines needed to search and locate, hence a total of 6 victims. It has to be noted that since there were two field sites, one opened and one closed as referred, the same combinations of mixtures were prepared for the both sites, hence in total 12 metallic cups were used.

The criteria for selecting the chemicals in order to prepare each mixture were the following:

- (a) The chemicals have been recorded in the literature as compounds evolved by alive people identified in exhaled air, skin, sweat and axilla.
- (b) The chemicals selected for preparing the different mixtures in each metallic cup needed to be compatible for safety reasons.

- (c) The chemicals should be used at the minimum concentrations according to the exposure limits presented in the previous paragraph, for ensuring no risk for the health and safety of the canines and the humans that were to be involved in the trial.
- (d) The number of the different mixtures should be limited in order to avoid any frustration or fatigue of the canine dogs, because they can operate for specific time duration in the field.

According to the above criteria, Table 3-1 demonstrates the different combinations of chemicals that have been finally selected for the trial (1-6 for the open-field and 1'-6' for the closed field).

Compound/ Origin	Acetone/ BREATH, SWEAT	Propanoic acid/ SWEAT	Lactic acid/ SWEAT	Hexane/ BREATH	Acetic acid/ AXILLA	Butyric acid/ AXILLA
No of metallic cup						
1 and 1'	X	X	X		X	X
2 and 2'	X	X	X	X	X	X
3 and 3'	X			X		
4 and 4'		X	X			X
5 and 5'	Empty (blank)					
6 and 6'	Cloth with human sweat					

Table 3-1: Metallic cups numbering and the respective combinations of chemicals that possibly simulate synthetic human odours, for testing them with the canines in the field trial

To provide a reference for assessing the canines' responses upon the different mixtures in the field, one of the six metallic cups was selected to be empty in order to act as a blank and one was filled with a piece of cloth damped with real human sweat. As already noted, the same process was followed for the both fields; the open-one and the closed-one.

- Preparation of the chemical mixtures*

Based on the limited number of "hidden persons" that can be searched without any rest time by the rescue dogs (five to six), the following chemical mixtures have been selected to be enclosed in six metallic cups for each field (No 1-6 for the open-field and No 1'-6' for the closed-field):

1. Metallic cups No 1 and 1': A mixture including compounds identified in breath, sweat and axilla, with high dilution ratio in water (1:100).
2. Metallic cups No 2 and 2': The same mixture with No1 but with medium dilution ratio in water (1:10).
3. Metallic cups No 3 and 3': A mixture with pure solutions (no dilution), including chemicals identified mainly in breath.

4. Metallic cups No 4 and 4': A mixture with pure solutions (no dilution), including chemicals identified mainly in axilla and sweat.
5. Metallic cups No 5 and 5': Blank. They were intentionally left empty.
6. Metallic cups No 6 and 6': Cloth soaked with human sweat- They were filled with a dumped cloth with human sweat when arrived at Kalamata field.

No of metallic cup	Compound/ Origin	Acetone/ Breath, sweat	Propanoic acid/Sweat	Lactic acid/ Sweat	Hexane /Breath	Acetic acid/ Axilla	Butyric acid/ Axilla
	Molecular weight	58	74	90	86	60	88
1 and 1'	Preparation procedure in brief	2.5 mL of pure solution diluted into 250mL with water (Dilution 1:100) Then, 4 mL of the diluted solution was put into a vial of 16 mL	>>	>>	no	>>	>>
2 and 2'	Preparation procedure in brief	1mL of pure solution diluted into 10mL with water (Dilution 1:10). Then, 4 mL of the diluted solution was put into a vial of 16 mL	>>	>>	no	>>	>>
3 and 3'	Preparation procedure in brief	2 mL of pure reagent inserted to a 16 mL vial	no	no	>>	no	no
4 and 4'	Preparation procedure in brief	no	2 mL of pure reagent inserted to a 16mL vial	>>	no	no	>>
5 and 5'	Preparation procedure	Empty (blank)					
6 and 6'	Preparation procedure	Cloth soaked with human sweat					

Table 3-2: Summary of the preparation procedure of the chemical mixtures (metallic cups 1-6 and 1'-6') selected for the field trial with the canines

Table 3-2 summarises the preparation procedure of the chemical mixtures selected for the field trial with the canines. A certain number of vials with volume 16 mL were used, as the one presented in Figure 3.3 and marked with numbers 1-6; numbers 1-6 were attributed to the metallic cups used in the open field and number 1'-6' to the ones used in the closed field. It was selected to prepare the same mixtures for the both fields, open and closed, in order to have a reference of comparison.

According to Table 3-2, the mixtures that were enclosed in metallic cups No1 and No1' included solutions of 4mL of Acetone, Propanoic acid, Lactic acid, Acetic acid and Butyric acid with water (dilution rate 1:100) (Figure 3-10).



Figure 3-10: Metallic cup No1 included 4mL of dilute Acetone, Propanoic acid, Lactic acid, Acetic acid and Butyric acid- water solutions, with ratio 1:100

The mixtures were enclosed to metallic cups No 2 and No2', included exactly the same chemicals with No1, but with less dilution ratio (1:10). Figure 3-11 shows how a dilute acetone-water solution with ratio 1:10 was prepared, by using a pure acetone reagent.

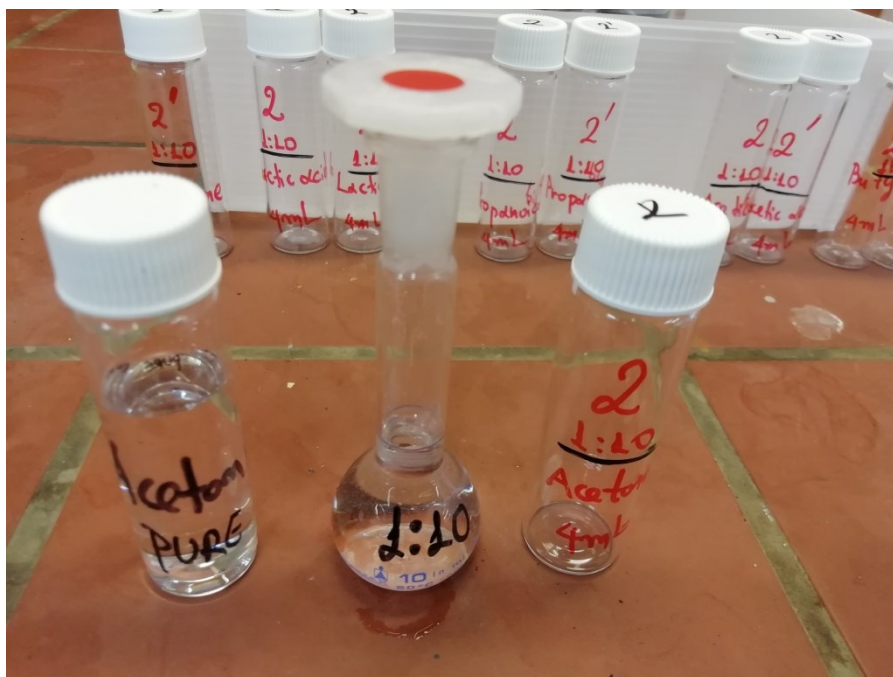


Figure 3-11: Dilute acetone-water solution with ratio 1:10 was prepared by using a pure acetone reagent (Metallic cup No 2)

The mixtures were enclosed to metallic cups No 3 and No 3', included 2 mL of pure acetone and 2 mL of pure hexane reagents (Figure 3-12).



Figure 3-12: Volume of 2 mL of pure acetone and 2 mL of pure hexane reagents were inserted to the metallic cups No 3 (for the open field) and No 3' (for the closed field)

All the chemical mixtures were prepared at NTUA premises one day before the trip to Kalamata. They were stored at about 4°C within a thermal insulator container filled with ice cubes and also during

transportation, for safety reasons and for avoiding any losses (Figure 3-13); a parafilm tape was also wrapped around each vial's cap to avoid any vapours' losses or leakages of the chemicals (Figure 3-14).

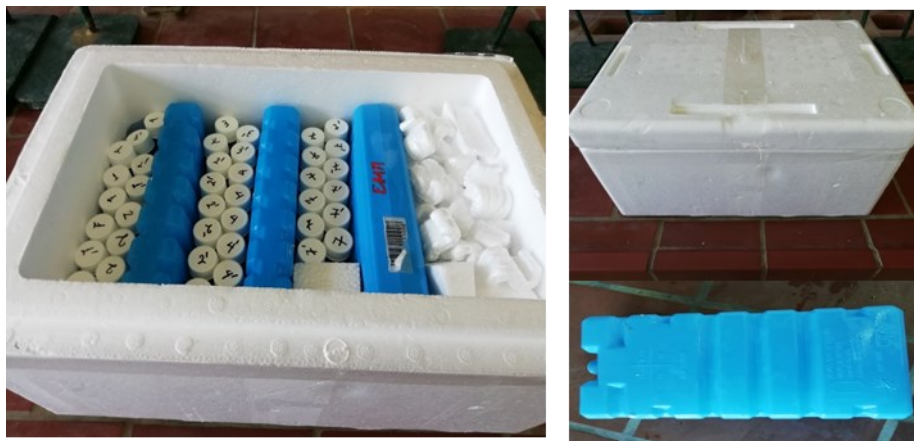


Figure 3-13: All the vials with the chemicals were stored at about 40C within a thermal insulator container filled with ice cubes



Figure 3-14: A parafilm tape was wrapped around each vial's cap to avoid any vapours' losses or leakages of the chemicals

Using the respective vials containing the chemicals of Table 3.2, the different metallic cups (from 1 to 4 and from 1' to 4') were filled (Figure 3-15); 5 and 5' were intentionally left blank; 6 and 6' contained a piece of cloth soaked with human sweat.



Figure 3-15: Metallic cups filled with vials of 16mL that contained different chemicals for simulating indicative “synthetic human odours”

The total number of the vials needed to fill one metallic cup in order to stay steady and avoid any chemicals’ spill, was seven. Hence, a certain number of empty vials were added to the ones with the mixtures, for covering any voids inside the metallic cups; the empty vials used had no numbering on their cap to be distinguished from the ones filled with chemicals.

3.3 Set-up in the field

As already mentioned, the place for running the experiments was Kalamata, Greece, where one of the training fields of HRT is situated. HRT and NTUA team were in close cooperation for about one month before the trial for the preparation of the experimental protocol and for arranging the field terrain characteristics in Kalamata in order to better simulate the collapsed structures.

For the needs of the trial, two different field sites were selected for comparing the results; an open-one and a closed-one (Figures 3-16 and Figure 3-17 in respect). As mentioned, 6 metallic cups were used for each field containing exactly the same mixtures from 1 to 6, or 1’-6’, as they are indicated in Table 3.2.



Figure 3-16: Open-field for testing the synthetic human odours with canines: Metallic cup No1, hidden under a specific wooden structure, is indicated



Figure 3-17: Closed-field for testing the synthetic human odours with canines: Metallic cup No1', hidden under a specific wooden structure, is indicated

One day before the trial, on the 16th of July 2021 there was a preparatory meeting in the two fields in order to mark the sites where the metallic cups would be settled and also for the rehearsal of the experimental protocol. Specific wooden structures were used for hiding the metallic cups, as shown in Figure 3-16 and Figure 3-17. At the closed-field it was decided to settle some of the mixtures under simulated debris, as shown in Figure 3-18.



Figure 3-18: Simulated debris at the closed-field: Metallic cup No 4' position is indicated as an example

On the 17th of July, which was the day of the trial, the following procedure was followed:

1. 7:00-8:00 a.m. All the HRT crew with the canines and the involved personnel from NTUA arrived at the field in the morning in order to avoid exposure to high temperatures for everyone. The operational centre was deployed in the field, as shown in Figure 3-19; the bag containing all the chemicals' equipment is shown in Figure 3-20.



Figure 3-19: Deployment of the HRT operational centre at the field



Figure 3-20: Bag containing all the chemicals' equipment for transferring it to the field

2. 8:00 a.m. The meteorological conditions forecast was recorded; Temperature: 27-33°C; RH%: 52-38%; Wind speed and direction: 3-4Bf NW.
3. 8:30 a.m. Two persons from HRT and NTUA settled the metallic cups carefully at the different marked sites from 1 to 6, at the open-field, hiding them under specific wooden structures (see

Figure 3-16). The NTUA member uncapped all the vials that contained the chemicals inside the metallic cups by using protective gloves (see Annex II). In order to not confuse the dogs with human masking odour, the two persons wore a full-protection uniform (see Annex II) so as to avoid emission of body smell at the field sites (Figure 3-21).



Figure 3-21: Two persons from HRT and NTUA settled carefully the metallic cups at the different marked sites from 1 to 6 at the open-field, wearing a full-protection uniform so that to avoid emission of body smell at the field sites

4. 9:00 a.m. All the metallic cups were settled at the marked site with uncapped vials. This was considered the $t=0$ min for the trial. To avoid any "human background" at the field, all the metallic cups were left at the sites for about 30 min before starting the operation with the canines
5. 9.30 a.m. Starting of the operation at the open-field. The first dog was released for searching "entrapped people", under the guidance of its dog handler (Figure 3-22).



Figure 3-22: The first dog started the operation at the open field at 9:30 a.m., under the guidance of its dog handler

6. 9:30 a.m.-10:25 a.m. The total number of the dogs that operated was 6; 4 of them were mature well-trained dogs and the other two were new comers. The 4 mature dogs operated first. For all the dogs it took about 5 min for searching the 6 different sites. The trainers communicated with the operation centre through wireless devices; for each site/metallic cup the responses of the dogs were recorded (interest or not of the dog).
7. 10:30 a.m. End of the open-field trial
8. 10:30 a.m. -11:45 a.m. Break for the canines to get rest. The two persons from HRT and NTUA settled the metallic cups carefully at the different marked sites from 1 to 6, at the closed-field (Figure 3-23), following the same procedure and protective equipment as described in the open-field testing before.



Figure 3-23: The metallic cups 1'-6' were settled at the specific marked sites at the closed-field

9. 11:45 a.m. Starting of the operation at the closed-field. The first dog was released for searching "entrapped people" under the guidance of its trainer (Figure 3-24).



Figure 3-24: The first dog started the operation at the closed-field at 11:45 a.m., under the guidance of its dog handler

10. 11:45a.m. – 12.40 p.m. As for the open-field, the 6 dogs searched the closed-field for “entrapped people” and their responses were recorded, informing the operational centre accordingly through wireless communication.
11. 12:45 p.m. End of the closed-field trial
12. 13:00 p.m. End of the whole trial.
13. 13:00- 13:30 p.m. Briefing of the trial and wrap-up.
14. 13:30-14:00 p.m. Interview with local journalists for dissemination purposes.

3.4 Results

In the Tables 3-3 and 3-4 the responses of the dogs to the different synthetic odours, categorised as no interest, slight interest and interest recorded during the trial, are summarized for the open-field and the closed field, in respect:

Canines’ response to different chemicals at the open-field

Metallic cup number	Dog 1	Dog 2	Dog 3	Dog 4	Dog 5	Dog 6
1	No interest	No interest	No interest	No interest	No interest	No interest
2	No interest	No interest	No interest	No interest	No interest	No interest
3	Interest	Interest	Slight Interest	Interest	No interest	Interest
4	Slight interest	No interest	No interest	Interest	Strong interest	Slight Interest
5	No interest	No interest	No interest	No interest	No interest	No interest
6	No interest	No interest	No interest	No interest	No interest	No interest

Table 3-3: Canines’ response to different chemicals during the open-field testing

‘Slight interest’ was recorded in the cases that the dog approached the site of interest for some seconds and left, while ‘Interest’ was recorded when the dog remained at the site for a while. The dog-handlers were the ones who reported their dogs’ responses.

It seems that none of the dogs have shown interest to the metallic cups No 1 and 2 that contained the diluted chemicals with dilution ratio 1:100 and 1:10, in respect (see Table 3-2); on the contrary they showed interest in the metallic cups No 3 and 4, where the pure solutions were contained. This is quite expected since evaporation of the liquid chemicals is more probable to happen in the open air and under sun radiation; hence, denser solutions as the pure ones will create vapours with higher concentration that can be detected by the sniffer dogs.

Moreover, the majority of the canines have shown interest to mixture No 3, which contained 2mL of pure acetone and pure hexane; these two chemical compounds have been identified mostly in human breath [5, 7, 16]. This is quite an encouraging result, since the HRT canines which are trained to

locate alive people, responded to a mixture that simulates the human expired air, which is definitely a sign of life.

It is also important that some of the canines have shown interest to compounds that have been correlated in the literature with human sweat and axilla, like Propanoic acid, Lactic acid and Butyric acid [1, 2, 3, 6, 7] that was mixture No 4.

All the canines confirmed a negative response to metallic cup No5 which was empty. Concerning the metallic cup No 6 that contained a cloth soaked with real human sweat, although a positive response by the dogs was potentially expected it was not observed during the trial. However, this could be explained due to the cloth being inside the metallic cup and hence, the off-gassing of volatiles relevant to human sweat by the cloth might not have been at enough concentrations to be detected by the dogs in the open space, where the dilution factor prevails due to the wind.

Canines' response to different chemicals at the closed-field

The responses of the dogs to the chemical mixtures that have been used in the open-field testing were also recorded for the closed-field testing, as shown in the following table:

Metallic cup number	Dog 1	Dog 2	Dog 3	Dog 4	Dog 5	Dog 6
1'	No interest	No interest	No interest	No interest	No interest	No interest
2'	No interest	No interest	No interest	No interest	No interest	No interest
3'	No interest	No interest	No interest	No interest	No interest	No interest
4'	No interest	No interest	No interest	No interest	No interest	No interest
5'	Slight interest	Slight interest	No interest	Slight interest	Slight interest	No interest
6'	No interest	No interest	No interest	No interest	No interest	No interest

Table 3-4: Canines' response to different chemicals during the closed-field testing

Based on the first observations of the open-field testing, it was finally decided to replace the metallic cup No5' which was the empty one (blank) with a mixture of breath, sweat and axilla of higher density than No1 and No2. Namely, the mixture contained 2 mL of each of the following pure reagents: Acetone, Lactic acid, Propanoic acid, Butyric acid, Acetic acid, and Hexane. This was because the dogs had already confirmed a negative response to an empty metallic cup in the open-field, presenting a good opportunity to test one more mixture.

It seems that none of the dogs have shown interest in the metallic cups No 1 and 2 that contained the dilute solutions with dilution ratio 1:100 and 1:10, in respect (see Table 3-2), as also happened in the open-field.

However, contrary to the open-field testing observations, there was no interest either for No 3' or for No 4' metallic cups that contained the pure reagents of simulated "exhaled air" and "axilla/sweat", in respect. Though, a slight interest was captured for mixture No 5' that contained 2mL of pure reagents,

as No3' and 4'. The difference is that No5' included all the components together; those attributed to exhaled air (Acetone, Hexane) and those to axilla/sweat (Lactic acid, Propanoic acid, Butyric acid, Acetic acid). This can be possibly explained due to the fact that the closed-field testing took place almost midday, hence the temperature was raised, affecting the evaporation rate of the chemicals; low detection capability due to vapours dispersion. Moreover, the dogs were a little bit tired after the morning testing at the open-field, which is quite an important parameter to consider. In fact, chemical technologies like the RESCUE-MIMS, strive to cover this type of idle times that dogs need to get some rest during the search and rescue operation and also for cross checking the "signs of life" indicated by canines in the disaster scene. This is mostly the case of a massive disaster like an earthquake, where limited number of rescue dogs are available for the SAR operations.

Concerning the metallic cup No 6' that contained a cloth soaked with real human sweat, dogs have shown no interest, as happened also in the open-field testing.

4 Conclusions and Proposals

4.1 Lab-scale experiments

One of the objectives of D5.3 was to test and validate the analytical performance of the Rescue-MIMS prototype, which has been successfully achieved by conducting a number of lab-scale experiments. Specifically, a various chemical compounds have been selected for testing and validation of the prototype with the prospect of having: (a) chemical hazards for the safety of the first responders (paragraph 2.1.1) (b) components relevant to human presence (paragraph 2.1.2) (c) other relevant compounds (paragraph 2.1.3).

- (a) Specifically, RESCUE-MIMS was tested and validated with chlorinated compounds since they are considered a serious product in case of industrial accidents and because the RESCUE-MIMS will be demonstrated in such a fire industrial incident scenario under (UC4). For the same reason, Benzene was also used for testing because it is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly evolved in forest fires and/or industrial fires. The RESCUE-MIMS prototype has shown excellent linearity within the concentration range examined (0, 200, 400, 600, 800 and 1000ppb), high sensitivity (limit of detection < 10 ppb), good repeatability (relative standard deviation, RSD < 5%) and response times in real time in few seconds (see Table 2-2).

Benzene will be possibly used as key compound to be monitored on-line with the RESCUE-MIMS in UC4- Forest fire expanded and threat to industrial zone, forthcoming pilot scenario.

- (b) Since the RESCUE-MIMS will also be used to detect compounds relevant to human presence, trying to mimic canine dogs (artificial sniffing), testing with carbon dioxide and acetone has taken place, since these two compounds have been recorded within the literature as characteristic components of expired air. In that context, a number of different concentrations from 0.05 to 1 ppm of acetone have been prepared, monitoring in SIM mode the characteristic masses of acetone, namely 43 and 58. It seems that the system has an excellent performance in terms of linearity, since the linearity coefficient was calculated through the calibration curve equal to 0.9927, hence almost equal to 1 which is the ideal value for a linear performance; the LOD for acetone after linear regression calculation in excel file was calculated equal to 14.7 ppb.
- (c) Taking into consideration that the search and rescue environment is considered as chemically complex by nature because a number of different types of compounds may be evolved e.g. in industrial fires, the RESCUE-MIMS's prototype analytical performance was also tested by using such compounds, like ketones (acetophenone-m/z 120, cyclohexanone- m/z 98,), alcohols (1-pentanol-m/z 70, 1-heptanol-m/z 70), aldehydes (propanal-m/z 58), and esters (ethyl acetate-m/z 88, ethyl propionate-m/z 102) in order to have a more broad assessment of its performance. The respective calibration curves have been prepared in the range for the above chemicals using concentrations from low ppb to low ppm levels; 0.05, 0.1, 0.5 and 1 ppm as was done for acetone. The linearity coefficient (R^2) and the LODs calculated for these compounds are summarised in Table 2-4.

4.2 Field-scale experiments

The tests that have been conducted in the Kalamata field trial with the canines are considered preliminary. The main scope was to identify representative "human chemical odours" based on the rescue dogs responses' (interest or not) for future testing of the RESCUE-MIMS and also for monitoring on-line these compounds during the upcoming UC5- Victims trapped under rubble, pilot scenario. In that context, different combinations of chemicals have been prepared in the lab that resembles human breath, sweat and axilla, based on literature recordings. Although human breath consists of hundreds of volatile organic compounds, only Acetone and Hexane were selected in our case as representative ones of exhaled air due to the limited number of metallic cups that can be searched by the dogs one by one without any rest. Under the same perspective, a limited number of chemicals have been selected as representative of the human sweat and axilla.

It should be noted that compatibility of the chemicals is a substantial parameter to be considered when preparing chemical mixtures and limits the type of compounds that can be enclosed in a metallic

tube for safety reasons; physicochemical characteristics must be taken into account, like explosivity, flammability etc. (see paragraph 3.2.2).

Another limitation is that the compounds to be selected need to be the least hazardous for the canines. For example, ammonia, although it is considered a marker of human presence according to the literature, it is categorized as irritant and can harm the detection capability of canines; if decided to be used it should be at very low concentrations in order not to put the canines at risk.

Additionally, it should be considered that different dogs may react differently to specific chemical components. That is why we have tried to include as many dogs as possible (six in total) in Kalamata's trial. The dogs participated in the trial were trained for tracking alive people; though there are more variables than chemical processes for human odour and dogs can take different references out of this chemical procedures. For conducting further experiments with dogs it should be taken into consideration if they are trained as rescue dogs or for detecting chemical substances.

It should also be emphasized that human odour is quite a complex issue and can be affected by a numerous parameters, like gender, diet, habits etc. (see D5.1, M10).

As a conclusion, more mixtures can be tested in the future considering the limitations previously referred, in order to cross-check the current results and also for research purposes. However, for the needs of the SnR project and the D5.3 objective of selecting key compounds for on-line monitoring with the RESCUE-MIMS in the future field-scale demonstration, the tests can be characterised as successful and the results as quite encouraging. It has been proven that Acetone could be used as a key compound for monitoring on-line "human signs" with the RESCUE-MIMS under UC5-Victims trapped under rubble, while lab-scale testing has also confirmed the good analytical performance of the RESCUE-MIMS for Acetone (see paragraph 5.1 of current document). Background measurements will take place in the field to avoid any false positives.

5 Future work

The next steps for D5.3 includes further testing of the RESCUE-MIMS in lab-scale by using the chemicals that have been identified as markers for “human presence” by the rescue dogs in the field trial of Kalamata; e.g. additionally to Acetone that has already been tested, Lactic acid, Propanoic acid, Butyric acid, Acetic acid etc. could be tested.

Moreover, scale-up testing and validation of the RESCUE-MIMS in the framework of SnR pilots, namely UC4-Forest fire expanded and threat to industrial zone (Attica Region, Greece) and UC5-Victims trapped under rubbles (France) will take place; follow up on canines’ training for detection of humans under rubble will take place with the contribution of WP5 expert partners. In that context, the reliability and efficiency of operation of the RESCUE-MIMS prototype in the field will be tested and evaluated by the respective end-users.

Under the above pilots’ framework and in collaboration with the respective work packages, like WP6 and WP8, testing of the RESCUE-MIMS connection with the DSS system will take place. Additionally, assessment of the RESCUE-MIMS’s prototype functional performance and usability, either as a Search and Rescue tool (UC5), or as an early warning system for the safety of the first responders’ on-board robotic platforms (UC4), will be conducted. Ethical Evaluation of the RESCUE-MIMS technology according to the Ethic Evaluation Standard for Security Research (EESSR) will also be made available by the respective contributors, after the pilots.

ANNEX I: References

- [1] M. Callagher, C. J. Wysocki, J. J. Leyden, A. I. Spielman, X. Sun, G. Preti, "Analyses of volatile organic compounds from human skin," *British Journal of Dermatology*, pp. 780-791, 2008.
- [2] A. M. Curran, S. I. Rabin, K. G. Furton, "Analysis of the Uniqueness and Persistence of Human Scent," *Forensic Science Commun.* 7, 2005.
- [3] Norman Ratcliffe, "A mechanistic study and review of volatile products from peroxidation of unsaturated fatty acids: an aid to understanding the origins of volatile organic compounds from the human body," *Journal of Breath Research*, 2020.
- [4] Wang, C., Sahay, P., "Breath Analysis Using Laser Spectroscopic Techniques: Breath Biomarkers, Spectral Fingerprints, and Detection Limits," *Sensors*, p. 8230–8262, 2009.
- [5] Statheropoulos, M.; Sianos, E.; Agapiou, A.; Georgiadou, A.; Pappa, A.; Tzamtzis, N.; Giotaki, H.; Papageorgiou, C.; Kolostoumbis, D., "Preliminary Investigation of using Volatile Organic Compounds from Human Expired Air, Blood and Urine for Locating Entrapped People in Earthquakes," *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, p. 112–117, 2005.
- [6] Markus Egert, "rRNA-based profiling of bacteria in the axilla of healthy males suggests right-left asymmetry in bacterial activity," *FEMS Microbiology Ecology*, Volume 77, pp. 146-153, 2011.
- [7] Stamatis Giannoukos, Portable mass spectrometry for artificial sniffing, Thesis submitted in accordance with the requirements of the University of Liverpool for the degree of Doctor in Philosophy, Department of Electrical Engineering and Electronics, The University of Liverpool, 2015.
- [8] Statheropoulos, M., Agapiou, A., Pallis, G.C., "Factors that affect rescue time in urban search and rescue (USAR) operations," *Nat Hazards*, vol. 75, p. 57–69, 2015. doi: <https://doi.org/10.1007/s11069-014-1304-3>.
- [9] Steve Down, "Buried biomarkers: Rubble affects urinary volatiles in earthquake wreckage," 04 06 2012. [Online]. Available: <https://analyticalscience.wiley.com/do/10.1002/sepspec.137bddb94f8/full/>. [Accessed 24 08 2021].
- [10] Agapios Agapiou, Anton Amann, Pawel Mochalski, Milt Statheropoulos, and C.L.P. Thomas, "Trace detection of endogenous human volatile organic compounds for search, rescue and emergency applications," *Trends in Analytical Chemistry*, vol. 66, pp. 158-175, 2015.
- [11] A. Agapiou, "Physiology and biochemistry of human subjects during entrapment," *Journal of Breath Research*, vol. 7, 2013.
- [12] Habib, M. K., "Controlled Biological and Biomimetic Systems for Landmine Detection," *Biosensors and Bioelectronics*, vol. 23, pp. 1-18, 2007.
- [13] S. Karma, "Tools for Analyzing Risks from Human Exposure to Chemical Environments: The case of exposure to Smoke Components during Forest or Other Field Fires," in *Novel Approaches in Risk, Crisis and Disaster Management*, Nova Science Publishers, 2018, p. Chapter 9.
- [14] S. Karma, "Large-Scale Fire Incidents in Recycling Plants: Lessons Learned from two Indicative Case Studies and Future Needs," in *Novel Approaches in Risk, Crisis and Disaster Management*, Nova Science Publishers, 2018, p. Chapter 5.
- [15] S. Karma, "Challenges and Lessons Learned from past major Environmental. Disasters due to Technological or Wildland Urban Interface Fire Incidents," *Contributing Paper to Global Assessment Report on Disaster Risk Reduction (GAR) Available at: (https://www.preventionweb.net/publications/view/66718)*, 2019.
- [16] M. Statheropoulos, K. Mikedi, A. Agapiou, A. Georgiadou, S. Karma, "Discriminant Analysis of Volatile Organic Compounds data related to a new location method of entrapped people in collapsed buildings of an earthquake," *Analytica Chimica Acta*, vol. 566, no. 2, pp. 207-216, 2006. doi: <https://doi.org/10.1016/j.aca.2006.03.023>.
- [17] "WebWISER - Substance List," National Library of Medicine, [Online]. Available:

- <https://webwiser.nlm.nih.gov/knownSubstanceSearch>. [Accessed 24 08 2021].
- [18] "CDC - Immediately Dangerous to Life or Health Concentrations (IDLH): Acetone - NIOSH Publications and Products," The National Institute for Occupational Safety and Health (NIOSH), [Online]. Available: <https://www.cdc.gov/niosh/idlh/67641.html>. [Accessed 24 08 2021].
- [19] "Propionic acid CAS#: 79-09-4," [Online]. Available: https://www.chemicalbook.com/ProductChemicalPropertiesCB4138567_EN.htm. [Accessed 24 08 2021].
- [20] "Lactic acid CAS#: 50-21-5," [Online]. Available: https://www.chemicalbook.com/ProductChemicalPropertiesCB8193447_EN.htm. [Accessed 24 08 2021].
- [21] "Hexane CAS#: 110-54-3," [Online]. Available: https://www.chemicalbook.com/ProductChemicalPropertiesCB1852811_EN.htm. [Accessed 24 08 2021].
- [22] "Acetic acid CAS#: 64-19-7," [Online]. Available: https://www.chemicalbook.com/ProductChemicalPropertiesCB7854064_EN.htm. [Accessed 24 08 2021].
- [23] "Butyric Acid CAS#: 107-92-6," [Online]. Available: https://www.chemicalbook.com/ProductChemicalPropertiesCB3459186_EN.htm. [Accessed 24 08 2021].
- [24] "NIST Chemistry WebBook," [Online]. Available: <https://webbook.nist.gov/chemistry/>. [Accessed 24 08 2021].

ANNEX II. Safety Data Sheets of the Chemicals used and PPE for the lab-scale and field-scale experiments

A. Safety Data Sheets of the Chemicals used

(a) Acetone



LabChem
performance through chemistry

Acetone
Safety Data Sheet

according to Federal Register / Vol. 77, No. 58 / Monday, March 26, 2012 / Rules and Regulations
Date of issue: 11/12/1998 Revision date: 04/24/2018 Supersedes: 04/24/2018 Version: 1.3

SECTION 1: Identification

1.1. Identification

Product form	: Substance
Substance name	: Acetone
Chemical name	: 2-Propanone
CAS-No.	: 67-64-1
Product code	: LC10420, LC10425
Formula	: C ₃ H ₆ O
Synonyms	: 2-propanone / beta-ketopropane / dimethyl formaldehyde / dimethyl ketone / dimethylketal / DMK (=dimethyl ketone) / keto propane / methyl ketone / pyroacetic acid / pyroacetic ether / pyroacetic spirit

1.2. Recommended use and restrictions on use

Use of the substance/mixture	: Solvent Cleaning product Chemical raw material
Recommended use	: Laboratory chemicals
Restrictions on use	: Not for food, drug or household use

1.3. Supplier

LabChem, Inc.
Jackson's Pointe Commerce Park Building 1000, 1010 Jackson's Pointe Court
Zellienople, PA 16063 - USA
T 412-826-5230 - F 724-473-0647

1.4. Emergency telephone number

Emergency number : CHEMTREC: 1-800-424-9300 or +1-703-741-5970

SECTION 2: Hazard(s) identification

2.1. Classification of the substance or mixture



GHS-US classification		
Flammable liquids	H225	Highly flammable liquid and vapour
Category 2		
Serious eye damage/eye irritation Category 2A	H319	Causes serious eye irritation
Specific target organ toxicity (single exposure) Category 3	H336	May cause drowsiness or dizziness

Full text of H statements : see section 16

2.2. GHS Label elements, including precautionary statements

GHS US labelling

Hazard pictograms (GHS US) :

GHS02 GHS07

Signal word (GHS US) : Danger

Hazard statements (GHS US) :

H225 - Highly flammable liquid and vapour
H319 - Causes serious eye irritation
H336 - May cause drowsiness or dizziness

Precautionary statements (GHS US) :

P210 - Keep away from heat, hot surfaces, open flames, sparks. - No smoking.
P233 - Keep container tightly closed.
P240 - Ground/bond container and receiving equipment.
P241 - Use explosion-proof electrical, lighting, ventilating equipment.
P242 - Use only non-sparking tools.
P243 - Take precautionary measures against static discharge.
P261 - Avoid breathing mist, spray, vapors.

04/23/2019
EN (English US)
Page 1

Acetone

Safety Data Sheet

according to Federal Register / Vol. 77, No. 58 / Monday, March 26, 2012 / Rules and Regulations

6.4. Reference to other sections

See Heading 8. Exposure controls and personal protection.

SECTION 7: Handling and storage

7.1. Precautions for safe handling

- Precautions for safe handling : Use spark-/explosionproof appliances and lighting system. Take precautions against electrostatic charges. Keep away from naked flames/heat. Keep away from ignition sources/sparks. Measure the concentration in the air regularly. Work under local exhaust/ventilation. Comply with the legal requirements. Remove contaminated clothing immediately. Clean contaminated clothing. Handle undischarged empty containers as full ones. Thoroughly clean/dry the installation before use. Do not discharge the waste into the drain. Do not use compressed air for pumping over. Keep container tightly closed.
- Hygiene measures : Do not eat, drink or smoke when using this product. Wash contaminated clothing before reuse. Wash hands and other exposed areas with mild soap and water before eating, drinking or smoking and when leaving work.

7.2. Conditions for safe storage, including any incompatibilities

- Storage conditions : Keep only in the original container in a cool, well ventilated place away from : Heat sources, Direct sunlight, incompatible materials. Keep container closed when not in use.
- Incompatible products : Strong bases. Strong acids.
- Incompatible materials : Sources of ignition. Direct sunlight.
- Storage temperature : 15 - 20 °C
- Heat-ignition : KEEP SUBSTANCE AWAY FROM: heat sources, ignition sources.
- Prohibitions on mixed storage : KEEP SUBSTANCE AWAY FROM: oxidizing agents, reducing agents, strong acids, (strong) bases, halogens, amines.
- Storage area : Store in a cool area. Keep out of direct sunlight. Store in a dry area. Store in a dark area. Ventilation at floor level. Fireproof storeroom. Provide for an automatic sprinkler system. Provide for a tub to collect spills. Provide the tank with earthing. Meet the legal requirements.
- Special rules on packaging : SPECIAL REQUIREMENTS: closing, with pressure relief valve, clean, opaque, correctly labelled, meet the legal requirements. Secure fragile packagings in solid containers.
- Packaging materials : SUITABLE MATERIAL: steel, stainless steel, carbon steel, aluminium, iron, copper, nickel, bronze, glass. MATERIAL TO AVOID: synthetic material.

SECTION 8: Exposure controls/personal protection

8.1. Control parameters

Acetone (67-64-1)		
ACGIH	ACGIH TWA (ppm)	250 ppm
ACGIH	ACGIH STEL (ppm)	500 ppm
NIOSH	NIOSH REL (TWA) (mg/m³)	590 mg/m³*
NIOSH	NIOSH REL (TWA) (ppm)	250 ppm

8.2. Appropriate engineering controls

- Appropriate engineering controls : Emergency eye wash fountains should be available in the immediate vicinity of any potential exposure.

8.3. Individual protection measures/Personal protective equipment

Personal protective equipment:

Safety glasses. Gloves. Protective clothing. Face shield. High gas/vapor concentration: gas mask with filter type A.




Materials for protective clothing:

GIVE GOOD RESISTANCE: butyl rubber, tetrafluoroethylene. GIVE LESS RESISTANCE: chlorosulfonated polyethylene, natural rubber, neoprene, polyurethane, PVA, styrene-butadiene rubber. GIVE POOR RESISTANCE: nitrile rubber, polyethylene, PVC, viton, nitrile rubber/PVC

(b) Propanoic acid

www.sigmaldrich.com



Version 7.0
Revision Date 18.12.2020
Print Date 24.06.2021
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name : Propionic acid

Product Number : 402907
Brand : Sigma-Aldrich
Index-No. : 607-089-00-0
REACH No. : 01-2119486971-24-XXXX
CAS-No. : 79-09-4

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie GmbH
Eschenstrasse 5
D-82024 TAUFKIRCHEN

Telephone : +49 (0)89 6513-1130
Fax : +49 (0)89 6513-1161
E-mail address : technischerservice@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0800 181 7059 (CHEMTREC Deutschland)
+49 (0)696 43508409 (CHEMTREC weltweit)


SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Flammable liquids (Category 3), H226
Skin corrosion (Sub-category 1B), H314
Serious eye damage (Category 1), H318
Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335
For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 Label elements


Labelling according Regulation (EC) No 1272/2008
Pictogram



Sigma-Aldrich- 402907

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Signal word	Danger
Hazard statement(s)	Flammable liquid and vapor. Causes severe skin burns and eye damage. May cause respiratory irritation.
H226	
H314	
H335	
Precautionary statement(s)	
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P233	Keep container tightly closed.
P240	Ground and bond container and receiving equipment.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection/ hearing protection.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Supplemental Hazard Statements	none

Reduced Labeling (<= 125 ml)

Pictogram



Signal word	Danger
Hazard statement(s)	Causes severe skin burns and eye damage.
H314	
Precautionary statement(s)	
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection/ hearing protection.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Supplemental Hazard Statements	none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.
Rapidly absorbed through skin.

SECTION 3: Composition/information on ingredients**3.1 Substances**

Synonyms : Propanoic acid
Propanyl acid
Acid C3

Sigma-Aldrich® 402907

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Formula : $C_3H_6O_2$
 Molecular weight : 74,08 g/mol
 CAS-No. : 79-09-4
 EC-No. : 201-176-3
 Index-No. : 607-089-00-0

Component	Classification	Concentration
propionic acid	Flam. Liq. 3; Skin Corr. 1B; Eye Dam. 1; STOT SE 3; H226, H314, H318, H335 Concentration limits: >= 25 %: Skin Corr. 1B, H314; 10 - < 25 %: Skin Irrit. 2, H315; 10 - < 25 %: Eye Irrit. 2, H319; >= 10 %: STOT SE 3, H335;	<= 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first-aid measures

General advice

First aider needs to protect himself. Show this material safety data sheet to the doctor in attendance.

If inhaled

After inhalation: fresh air. Call in physician.

In case of skin contact

In case of skin contact: Take off immediately all contaminated clothing. Rinse skin with water/ shower. Call a physician immediately.

In case of eye contact

After eye contact: rinse out with plenty of water. Immediately call in ophthalmologist. Remove contact lenses.

If swallowed

After swallowing: make victim drink water (two glasses at most), avoid vomiting (risk of perforation). Call a physician immediately. Do not attempt to neutralise.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

SECTION 5: Firefighting measures

5.1 Extinguishing media

Suitable extinguishing media

Water Foam Carbon dioxide (CO₂) Dry powder


Sigma-Aldrich- 402907

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(c) Lactic acid



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SAFETY DATA SHEET
according to Regulation (EC) No. 1907/2006

Version 6.3
Revision Date 27.09.2019
Print Date 24.06.2021
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name : Lactic acid solution

Product Number : 252476

Brand : Sigma-Aldrich

REACH No. : A registration number is not available for this substance as the substance or its uses are exempted from registration, the annual tonnage does not require a registration or the registration is envisaged for a later registration deadline.

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie GmbH
Eschenstrasse 5
D-82024 TAUFKIRCHEN

Telephone : +49 (0)89 6513-1130

Fax : +49 (0)89 6513-1161

E-mail address : technischerservice@merckgroup.com

1.4 Emergency telephone number

Emergency Phone # : 0800 181 7059 (CHEMTREC Deutschland)
+49 (0)696 43508409 (CHEMTREC weltweit)

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008


Skin irritation (Category 2), H315

Serious eye damage (Category 1), H318

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008


Pictogram 

Signal word : Danger

Sigma-Aldrich- 252476

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Hazard statement(s)	
H315	Causes skin irritation.
H318	Causes serious eye damage.
Precautionary statement(s)	
P264	Wash skin thoroughly after handling.
P280	Wear eye protection/ face protection.
P280	Wear protective gloves.
P305 + P351 + P338 + P310	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a POISON CENTER/doctor.
P332 + P313	If skin irritation occurs: Get medical advice/ attention.
P362 + P364	Take off contaminated clothing and wash it before reuse.
Supplemental Hazard Statements	none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.2 Mixtures

Formula : $C_3H_6O_3$
Molecular weight : 90,08 g/mol

Component	Classification	Concentration
Lactic acid		
CAS-No. 50-21-5 EC-No. 200-018-0 Registration number 01-2119548400-48-XXXX	Skin Irrit. 2; Eye Dam. 1; H315, H318 Concentration limits: >= 10 %: Skin Irrit. 2, H315; >= 3 %: Eye Dam. 1, H318; 1 - < 3 %: Eye Irrit. 2, H319;	>= 90 - <= 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first aid measures

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.


Sigma-Aldrich- 252476

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(d) Hexane


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Version 6.6
 Revision Date 28.05.2021
 Print Date 09.07.2021
 GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name : Hexane

Product Number : 296090
 Brand : Sigma-Aldrich
 Index-No. : 601-037-00-0
 REACH No. : 01-2119480412-44-XXXX
 CAS-No. : 110-54-3

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie GmbH
 Eschenstrasse 5
 D-82024 TAUFKIRCHEN

Telephone : +49 (0)89 6513-1130
 Fax : +49 (0)89 6513-1161
 E-mail address : technischer.service@merckgroup.com

1.4 Emergency telephone

Emergency Phone # : 0800 181 7059 (CHEMTREC Deutschland)
 +49 (0)696 43508409 (CHEMTREC weltweit)

SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008


Flammable liquids (Category 2), H225
 Skin irritation (Category 2), H315
 Reproductive toxicity (Category 2), H361f
 Specific target organ toxicity - single exposure (Category 3), Central nervous system, H336
 Specific target organ toxicity - repeated exposure, Inhalation (Category 2), Nervous system, H373
 Aspiration hazard (Category 1), H304
 Long-term (chronic) aquatic hazard (Category 2), H411

For the full text of the H-Statements mentioned in this Section, see Section 16.

Sigma-Aldrich- 296090

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2.2 Label elements

Labelling according Regulation (EC) No 1272/2008

Pictogram



Signal word

Danger

Hazard statement(s)

H225

Highly flammable liquid and vapor.

H304

May be fatal if swallowed and enters airways.

H315

Causes skin irritation.

H336

May cause drowsiness or dizziness.

H361f

Suspected of damaging fertility.

H373

May cause damage to organs (Nervous system) through prolonged or repeated exposure if inhaled.

H411

Toxic to aquatic life with long lasting effects.

Precautionary statement(s)

P201

Obtain special instructions before use.

P210

Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P273

Avoid release to the environment.

P301 + P310

IF SWALLOWED: Immediately call a POISON CENTER/ doctor.

P303 + P361 + P353

IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.

P331

Do NOT induce vomiting.

Supplemental Hazard Statements

none

Reduced Labeling (<= 125 ml)

Pictogram



Signal word

Danger

Hazard statement(s)

H304

May be fatal if swallowed and enters airways.

H361f

Suspected of damaging fertility.

Precautionary statement(s)

P201

Obtain special instructions before use.

P301 + P310

IF SWALLOWED: Immediately call a POISON CENTER/ doctor.

P331

Do NOT induce vomiting.

Supplemental Hazard Statements

none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.

SECTION 3: Composition/information on ingredients

3.1 Substances

Synonyms : n-Hexane

Sigma-Aldrich- 296090


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(e) Acetic acid

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Version 7.0
 Revision Date 27.03.2020
 Print Date 12.07.2021
 GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name : Acetic acid

Product Number : A6283
 Brand : SIGALD
 Index-No. : 607-002-00-6
 REACH No. : 01-2119475328-30-XXXX
 CAS-No. : 64-19-7

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie GmbH
 Eschenstrasse 5
 D-82024 TAUFKIRCHEN

Telephone : +49 (0)89 6513-1130
 Fax : +49 (0)89 6513-1161
 E-mail address : technischer.service@merckgroup.com

1.4 Emergency telephone number

Emergency Phone # : 0800 181 7059 (CHEMTREC Deutschland)
 +49 (0)696 43508409 (CHEMTREC weltweit)

SECTION 2: Hazards identification


2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
 Flammable liquids (Category 3), H226
 Skin corrosion (Sub-category 1A), H314
 Serious eye damage (Category 1), H318

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008


Pictogram 

Signal word : Danger

SIGALD - A6283

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Hazard statement(s)	
H226	Flammable liquid and vapour.
H314	Causes severe skin burns and eye damage.
Precautionary statement(s)	
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P301 + P330 + P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P305 + P351 + P338 + P310	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a POISON CENTER/doctor.
Supplemental Hazard Statements	none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.
Lachrymator.

SECTION 3: Composition/information on ingredients

3.1 Substances

Synonyms	: Glacial acetic acid
Formula	: $C_2H_4O_2$
Molecular weight	: 60,05 g/mol
CAS-No.	: 64-19-7
EC-No.	: 200-580-7
Index-No.	: 607-002-00-6

Component	Classification	Concentration
acetic acid		
	Flam. Liq. 3; Skin Corr. 1A; Eye Dam. 1; H226, H314, H318 Concentration limits: >= 90 %: Skin Corr. 1A, H314; 25 - < 90 %: Skin Corr. 1B, H314; 10 - < 25 %: Skin Irrit. 2, H315; 10 - < 25 %: Eye Irrit. 2, H319; 10 - < 25 %: Eye Irrit. 2, H319; 10 - < 25 %: Skin Irrit. 2, H315; 25 - < 90 %: Skin Corr. 1B, H314; >= 90 %: Skin Corr. 1A, H314; >= 90 %: Flam. Liq. 3, H226;	<= 100 %

SIGALD- A6283


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(f) **Butyric acid**

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SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 6.2
Revision Date 06.11.2019
Print Date 16.02.2021
GENERIC EU MSDS - NO COUNTRY SPECIFIC DATA - NO OEL DATA

SECTION 1: Identification of the substance/mixture and of the company/undertaking

1.1 Product identifiers

Product name : Butyric acid

Product Number : W222119
Brand : Aldrich
Index-No. : 607-135-00-X
REACH No. : 01-2119488986-11-XXXX
CAS-No. : 107-92-6

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich Chemie GmbH
Eschenstrasse 5
D-82024 TAUFKIRCHEN

Telephone : +49 (0)89 6513-1130
Fax : +49 (0)89 6513-1161
E-mail address : technischerservice@merckgroup.com

1.4 Emergency telephone number

Emergency Phone # : 0800 181 7059 (CHEMTREC Deutschland)
+49 (0)696 43508409 (CHEMTREC weltweit)


SECTION 2: Hazards identification

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Acute toxicity, Oral (Category 4), H302
Skin corrosion (Sub-category 1B), H314
For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008


Pictogram 

Signal word : Danger

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Aldrich - W222119

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Hazard statement(s)	
H302	Harmful if swallowed.
H314	Causes severe skin burns and eye damage.
Precautionary statement(s)	
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P301 + P312 + P330	IF SWALLOWED: Call a POISON CENTER/doctor if you feel unwell. Rinse mouth.
P301 + P330 + P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
Supplemental Hazard Statements	none

2.3 Other hazards

This substance/mixture contains no components considered to be either persistent, bioaccumulative and toxic (PBT), or very persistent and very bioaccumulative (vPvB) at levels of 0.1% or higher.
Stench.

SECTION 3: Composition/information on ingredients

3.1 Substances

Formula	: C ₄ H ₈ O ₂
Molecular weight	: 88,11 g/mol
CAS-No.	: 107-92-6
EC-No.	: 203-532-3
Index-No.	: 607-135-00-X

Component	Classification	Concentration
Butyric acid	Acute Tox. 4; Skin Corr. 1B; H302, H314	<= 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

SECTION 4: First aid measures

4.1 Description of first aid measures

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Consult a physician.

Aldrich- W222119

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B. PPE for the lab-scale and field-scale experiments

(a) Protective gloves



Nitrile gloves were used for protection from all the chemical hazards during the preparation and handling of the chemical solutions

(b) Goggles



3M goggles were used for the eye-protection during the preparation of the chemical solutions

(c) Uniforms



A special protective uniform was used for conducting all the lab-scale experiments



A special 3M coverall uniform was used in the field for settling the metallic cups with the chemical mixtures at specific marked sites in the field (see Figure 3-2)

(d) Masks



FFP2 masks were used for protection against particles and COVID-19 infection; all the people in the field were using such protective masks or surgical ones.

ANNEX III. Ethical considerations in using canines at field trials

(a) General overview

The intensive collaboration between a search dog and its handler creates specific roles and responsibilities. For the dog the handler forms the center point in its life. For both parts of the team forming a fundamental trust relationship is also deciding for working together. A challenging task can contribute to a dog's wellbeing, however, it may also result in the dog being exposed to particular risks in the respective field of use. In such high stake environments, such as search and rescue missions, the dog and its handler, forming a team, need to rely and trust each other. The dog follows orders, and therefore is dependent on the judgement of its handler (Rosell, 2014; Schiavone, 2019). This underlines the responsibilities of the dog handler and draws the focus to the ethical considerations that need to be made, in the context of SAR missions and related exercises.

Animal ethics generally focusses on the treatment of animals and the appropriateness of the use of animals in various contexts. It further investigates the moral responsibility as well as quality and quantity of care (Reiser, 2013). As living beings or 'sentient beings'¹ special consideration of the needs and wellbeing of canines has to be taken into consideration working with dogs in trials and exercises¹.

Animal welfare, as biological concept, different from animal rights, also refers to feelings and health of a living animal (Broom, 2017). The concept forms part of ethical considerations viewing animals as moral entities with intrinsic value (Broom 2003, Aaltola and Wahlberg 2015 in Broom, 2017).

Research, as well as existing regulations does not seem to go in depth regarding the pursuit of a concrete ethical approach towards the use of dogs in search and rescue activities (missions and trainings). Guiding for EU rules and regulations² on animal welfare are the so-called 'five freedoms', namely (1) freedom from hunger and thirst, (2) freedom from discomfort, (3) freedom from pain, injury and disease, (4) freedom to express normal behavior, (5) freedom from fear and distress (Broom, 2017; European Parliament, 2020). Taking into account these "five freedoms"³ the ESDP develops an Ethical Code⁴ aimed at volunteers and professionals working in the organization.

Regarding the (1) freedom and thirst the following considerations should be followed:

- Both the dog handler and the other members of the team are responsible for providing the rescue dogs with adequate food (quantity and composition) for the work they do, their species and their size, thus ensuring their health and performance.

¹ As described in the Treaty of Lisbon (Broom, 2017)

² It should be noted that focus primarily lies on farm animals – specific EU regulations concerning dogs (or more widely pets) focus mostly on trade and movement.

³ OIE (Organización Mundial de Salud Animal) - Código Sanitario para los Animales Terrestres – Bienestar animal, Cap. 7, 2019

⁴ Aldea Reyes, A; Funcia Izquierdo, S. Código Ético dirigido a profesionales y voluntarios de la ESDP. (2021) in https://escuelasalvamento.org/wp-content/uploads/2021/04/Codigo-Etico_vf.pdf

- They must have access to clean, drinkable water whenever they need it.
- When, due to the needs of the mission to which we are assigned, the dog must remain in a transport cage for a prolonged period of time, it shall be ensured that they have access to water and, if necessary, sufficient food for the entire journey.
- Avoid fear and distress.

Regarding (2) freedom from discomfort the following consideration should be followed:

- The facilities in which the dog is kept must be clean, protected from inclement weather and have dimensions in accordance with the size and periods of confinement of the dog.
- The transport cages must comply with safety regulations in terms of dimensions, ventilation, materials and structure to guarantee adequate protection for the animal.
- On long journeys, it shall be ensured that the animal is given sufficient time to walk and relieve itself before, during and after the journey.
- It is advisable to have a veterinarian on hand, especially in the case of real missions, where there may be situations of risk for the animal.
- It is an added value the training of its dog handlers in basic veterinary knowledge of dog care, so they can act in case of emergencies and accidents. Likewise, it will have revised and updated sanitary material for use both in regular training and during missions.
- In the context of research projects it should be taken into account:
 - Whenever a technology designed for working dogs is tested, the potential risks to the animal, direct or indirect, will be analysed beforehand.
 - The dog shall not be exposed to any unnecessary risk, which could seriously endanger its physical integrity or well-being.
 - If, for research purposes, a dog has to be trained to develop a specific function within the project, the organization will guarantee that the dog will be brought back to useful life and/or a home will be found for it at the end of the research project.
- It is essential to respect the working/rest times of the animal, not only to guarantee the good performance of its work, but also to respond to its physiological and psychological needs.

In relation to (3) freedom from pain, injury and disease the following consideration should be followed:

- The dog's international vaccination record must be kept up to date, as well as any other necessary legal documentation. This is a prerequisite for the dog to be considered as an operational member of the group.
- Before, during and after each work, the dog shall be examined to ensure that it is in perfect health. If the dog suffers any injury or wound that significantly alters its state of well-being, it shall be declared as "non-operational", either temporarily or absolutely, according to the decision of the vet.

- The sick animal shall be monitored (treatment, administration of medication, visits to the vet and any necessary treatment) until it recovers.
- Any dog that has suffered injuries that cause pain or suffering in the performance of its duties, shall be temporarily or permanently removed from the service, according to the medical diagnosis.

Regarding (4) freedom to express normal behavior, the following considerations should be followed:

- Dogs are considered to be cognitive animals, capable of basic conscious responses, and emotionally empathetic.
- Working dogs, undergoing training and employed in useful work, should not be deprived of the opportunity to express those behaviours that are unique to them as a species.
- One of our priorities is to ensure that training techniques and programmes include aspects of animal welfare related to the time dedicated to recreation and social interaction, in order to maintain and emotional balance.

Finally, regarding the (5) freedom from fear and distress the following consideration must be followed:

- The nature of rescue dogs' work can subject them to highly stressful situations related to transport and working scenarios. It will be a fundamental part of the work of dog handlers to prepare their dogs, through experience, to become accustomed to and normalise those situations in order to minimise the distress.
- Dog handlers should avoid subjecting dogs to unnecessary risk during training and intervention, always choosing alternative manoeuvres that are less physically and/or emotionally damaging to the dog.
- Training techniques used will always be aimed at avoiding physical and/or emotional violence to the dogs, limiting the pressure they receive during training.

The INSARAG Guidelines, which are important reference for internationally active SAR units, point to relevant aspects of consideration when working with search dogs in SAR operations. Responsibilities of a canine handler include ensuring the mission readiness (e.g. by looking after general health, food and water intake, rest and stress control) and continuous monitoring throughout an operation to observe the canine's state such as fatigue etc. and act upon as deemed necessary. Furthermore, the dog handler needs to guarantee a safe and secure place for the search dog at all times. Also, proper caging and hygiene needs to be provided. Where applicable emergency veterinary care should be made available (INSARAG, 2012).

While as a minimum requirement ethical considerations applied to K9 operations should also be taken into account for field trials, the latter offer a controlled environment which have the potential to allow further opportunities to minimize risks for all participants (human and canines) alike. In an exercise or trial setting, most circumstances are known and planned. With this organizers have the opportunity to check the training grounds or trial settings prior to the execution and therefore to analyze as well as to

minimize potential risks in order to save dogs from any unnecessary harm. As preparation for emergencies, trials have to be taken as serious as a mission in the sense of training the dog.

The International Search and Rescue Dog Organisation (IRO), a recognized international network of SAR dog organizations, aims for high quality of training and SAR dog work. In its member guidelines the importance to adhere to national animal welfare regulations is emphasized. This should be the basis for any work with dogs that is executed. Furthermore, a dog's health and wellbeing has to be respected as well as protected. Applying any form of force should be prohibited (IRO, 2020).

In relations to the division of competences and also the decision-making structures in the setting of a training or a trial, important decisions regarding the dog and its assignment should lie with the dog handler. He or she knows the dog and its behaviors well, which therefore allows an interpretation of the dog's condition. Moreover participation in an exercise ought to further be made dependent on the level of training and health (readiness). Role of the dog handler should be to understand the health status of their respective dog and take decisions respectively, in favor of the dog and its health. Other members of the team should adhere to the decisions of the dog handler with regards to the readiness and operational capability of their dog.

References:

Aldea Reyes, A; Funcia Izquierdo, S. Código Ético dirigido a profesionales y voluntarios de la ESDP.

(2021) in https://escuelasalvamento.org/wp-content/uploads/2021/04/Codigo-Etico_vf.pdf

Broom, P. D. M. (2017). Animal Welfare in the European Union. 78.

European Parliament. (2020, June 7). Animal welfare and protection: EU laws explained (videos) | News | European Parliament.

<https://www.europarl.europa.eu/news/en/headlines/society/20200624STO81911/animal-welfare-and-protection-eu-laws-explained-videos>

INSARAG. (2012). INSARAG Guidelines-2012. 217.

IRO. (2020). Manual for IRO NROs. IRO.

OIE (Organización Mundial de Salud Animal) - Código Sanitario para los Animales Terrestres –

Bienestar animal, Cap. 7, 2019

Reiser, D. (2013). Animal Ethics. In S. O. Idowu, N. Capaldi, L. Zu, & A. D. Gupta (Eds.), *Encyclopedia of Corporate Social Responsibility* (pp. 106–110). Springer Berlin Heidelberg.

https://doi.org/10.1007/978-3-642-28036-8_691

Rosell, F. (2014). Die Welt der Gerüche. Spezial-Spürhunde im Einsatz.

Schiavone, A. L. (2019). K-9 Catch-22: The Impossible Dilemma Of Using Police Dogs In Apprehension Of Suspects. *University of Pittsburgh Law Review*, 80(3). <https://doi.org/10.5195/lawreview.2019.630>

(b) Ethics declaration by HRT for the canine dogs experiments



HELLENIC RESCUE TEAM (HRT)

Ethics Declaration

With this document it is declared that HRT volunteers work together with specially-trained dogs in cases of search and rescue missions after destructive earthquakes or avalanches or in cases of locating missing people in open areas. HRT has been cooperating with the United Nations' [INSARAG \(International Search and Rescue Advisory Group\)](#) since 2005 and follows the organization's protocols for big scale emergencies.

The Hellenic Rescue Team K-9 dogs are trained mainly based on the American Rescue Dogs Association (ARDA) Standards and Certification Procedures (<https://www.ardainc.org/>).

In the above context, HRT as a partner of the SnR project certifies that HRT K-9 dogs' employment to the SnR project needs, and more specifically under the task T5.3 Testing and Validation of the Rescue-MIMS device, will fully comply with health and safety standards and will be aligned with the UNESCO - Universal Declaration of Animal Rights 17-10-1978. The simulants that will be used for mimicking human scent (e.g. acetone) will be at minimum concentrations and in accordance with NIOSH exposure limits so that dogs not to be put at any risk.

Respectfully