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

D5.5 Design & development of the RESCUE MIMS, V2

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Executive Summary

The RESCUE-MIMS device delivered inside the SnR project can be used for the early detection of toxic environments for the first responders in terms of hazardous Volatile Organic Compounds (VOCs) or semi-Volatile Organic Compounds (semi-VOCs) identified in the disaster environment. It can also be mounted on fire-fighters vehicles (roving system) or tested as a payload on robotic platforms in order to serve as a screening tool for early warning. This configuration can protect first responders as well as canines from exposure to toxic environments. The RESCUE-MIMS prototype is foreseen to be tested on-board DFKI ground robot and demonstrated under UC4, in the framework of an Industrial Fire Scenario.

Moreover, the RESCUE-MIMS device, due to its low detection capabilities can also be used for measuring chemicals at low concentrations that have been correlated in literature with human presence, trying to mimic rescue dogs. It is foreseen to test the device under UC5 (Victims trapped under rubbles) for monitoring on-line indicative "human chemical signs". Though, it should be highlighted that such ambitious "artificial sniffer" should be seen as a complementary SAR technology to the existing ones, without trying to exclude the rescue dogs. It is foreseen to be used complementarily with the other conventional SAR methods, such as geophones, cameras etc., so that to endorse the first responders' spectrum of operational tools.

Deliverable D5.5 (M18) is a follow up of D5.1 (M10). Its main purpose is to focus on the design-configuration of the RESCUE-MIMS prototype for serving the specific needs of the two pilot scenarios that the RESCUE-MIMS will be used inside the SnR project, (a) for measuring on-line components relevant to human presence to possibly support the search and rescue operation of entrapped people in the rubbles (under the UC5 - see Chapter 4 of this document) and (b) for measuring on-line chemical hazards on-board robotic platforms for the safety of the first responders (under the UC4 - see Chapter 5 of this document).

In the above context, a summary of the KPIs assessed so far is provided, concerning the:

1. portability
2. robustness
3. ruins penetration capability
4. easy operation
5. friendliness to the user and
6. simple deployment

Moreover, the KPIs concerning the analytical performance of the RESCUE-MIMS, namely:

1. sensitivity
2. reliability
3. low Limit of Detection (LOD)
4. fast results (short response times)
5. detection capability of a wide range of concentrations (linearity)
6. monitoring in SIM mode (target analysis)

have been assessed through lab-scale experiments and the results are provided in Chapter 2 of this document.

In Chapter 3, a manual of operation for getting started with the RESCUE-MIMS device is drafted; the main steps of operation are described, taking into consideration that this manual is addressed to

operational users who are possibly beginners in mass-spectrometry based technologies. Moreover, indicative examples of on-line monitored target compounds are given (user interface and data interpretation). At the conclusion section of this document there is a summary of the KPIs achieved in the current version of the RESCUE-MIMS prototype (TRL) 6; proposals for optimisation in a possible future version (TRL>7) are also provided.

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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
BTX	Benzene, Toluene, Xylene
CAS	Chemical Abstracts Service
Da	Dalton
KPIs	Key performance indicators
LOD	Limit of detection
LEL	Lower Explosive Limit
MIMS	Membrane inlet mass spectrometer
MS	Mass spectrometer
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
ODS	Obstacle Detection System
OSHA	Occupational Safety and Health Administration
PDMS	Polydimethylsiloxane
PEL	Permissible Exposure Limit
Ppb	Parts per billion
Ppt	Parts per trillion
PTFE	Polytetrafluoroethylene
REL	Recommended Exposure Limit
rpm	Rotation per minute
SaR	Search and Rescue
SDS	Safety data sheet
SIM	Single Ion Monitoring
SnR	Search and Rescue project
STEL	Short Term Exposure Limit
TRL	Technology Readiness Level
UC	Use Case
VOC	Volatile Organic Compound
WHO	World Health Organisation

1 Introduction

1.1 Purpose and Scope

Deliverable D5.5 (M18) is a follow up of D5.1 (M10). Its main purpose is to focus on the design-configuration of the RESCUE-MIMS prototype for serving the specific needs of the two pilot scenarios that the RESCUE-MIMS will be used inside the SnR project, (a) for measuring on-line components relevant to human presence to possibly support the search and rescue operation of entrapped people in the rubbles (under the UC5 - see Chapter 4 of this document) and (b) for measuring on-line chemical hazards on-board robotic platforms for the safety of the first responders (under the UC4 - see Chapter 5 of this document).

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In Chapter 3, there is a draft manual of operation for getting started with the RESCUE-MIMS device and indicative examples of on-line monitored target compounds are given (user interface and data interpretation). At the conclusion section of this document there is as summary of the KPIs achieved in the current version of the RESCUE-MIMS prototype (TRL) 6; proposals for optimisation in a possible future version (TRL>7) are also provided.

1.2 KPIs for the design and development of the RESCUE-MIMS prototype

As presented in D5.1, the RESCUE-MIMS device is a prototype of technology readiness level (TRL) 6 that has been designed and developed in the prospect of satisfying the majority of the end-users requirements which have been indicated in D1.2. To summarise, the RESCUE-MIMS is provided in a configuration of a robust peli-box luggage meeting the KPIs of:

1. Portability: The RESCUE-MIMS prototype offers all the benefits of Mass Spectrometry in terms of high sensitivity and accuracy of measurements and at the same time is portable and can be transferred to the field with the potential to be used either as a handheld or backpack device (for more details see *Chapter 4* of this document).
2. Robustness: A peli-box case of about 60x50x20 cm encloses the inner parts of the mass analyser, to be robust and withstand the harsh operational environment (details are provided in D5.1).
3. Ruins penetration capability: Different types of sampling inlets could be adjusted to the MIMS luggage depending on the field application; inlet with membrane sheet for faster analysis and advanced selectivity, or extended sampling probe for penetrating the ruins (for more details see Chapter 4 of this document, *paragraph 4.2*).
4. Easy operation and friendliness to the user: The RESCUE-MIMS comes in a configuration of a luggage that can be easily handled by the user. Moreover, the customised software provides easy-readable messages on-line (user interface); intensities of the monitored compounds. A draft manual of operation, as well as indicative examples of on-line monitored target compounds are provided in *Chapter 3* of this document.
5. Easy to deploy: The Rescue-MIMS can be easily deployed in the field, and it can also be easily used as a payload, on-board robotic platforms, e.g. the DFKI SeekurJr unmanned ground vehicle (UGV) or on other speed platforms e.g. vehicles for mapping types of compounds and/or concentrations in the field (roving systems).

Moreover, for serving the KPIs indicated by the end-users concerning the analytical performance of the RESCUE-MIMS, such as sensitivity, specificity, resolution, accuracy, repeatability-precision, reliability, target substance identification, several KPIs such as:

1. sensitivity
2. reliability
3. low limit of detection (LOD)
4. fast results (short response times)
5. detection capability of a wide range of concentrations (linearity)
6. monitoring in SIM mode (target analysis),

have been assessed through lab-scale experiments and the results are provided in *Chapter 2* of this document.

2 Assessing the analytical performance of the RESCUE-MIMS prototype based on the end-users requirements

2.1 Summary of the analytical results provided in D5.3

Based on the results that were thoroughly presented in D5.3, a number of chemical compounds have been selected aligned with the end-users' requirements for testing and validation of the prototype: (a) testing with chemical hazards for the safety of the first responders (b) testing with components relevant to human presence to possibly support the search and rescue operation of entrapped people. The results obtained in lab-scale and field scale experiments are summarised.

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

2.1.1.1 Chlorinated compounds

Based on D5.1 overview on chemical hazards, in case of fire industrial accidents the products that prevail and 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, various chlorinated compounds were selected for lab-scale testing and validation of its analytical performance; response times, limit of detection, linearity (detection capability of a wide range of concentrations), 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 Scientic. 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 a concentration of 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 ^{o}C.

The MIMS sampled in the gas phase of the analytes. The total base pressure of the system with the sample inlet valve fully closed was 1 x10^{-7} Torr. Operating pressure during mass analysis with the membrane sampling probe attached and the sample inlet valve fully open was between 2.1 x 10^{-6} Torr and 2.1 x10^{-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 (Da)	119.378	98.959	133.404	167.849
Vapour pressure (kPa) at 25^{o}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

Table 2-2 shows the response times that were recorded for all 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-R^2	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, R^2 values and limits of detection)

2.1.1.2 Benzene

Benzene is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly evolved in forest fires and/or industrial fires [1-3] 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 (see paragraph 5.1).

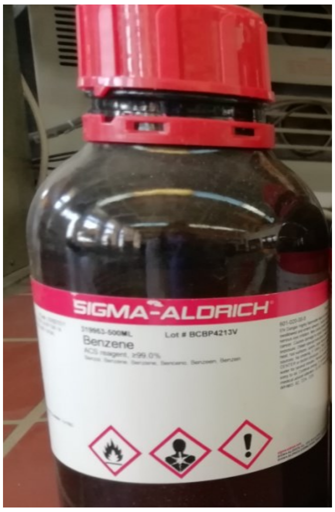
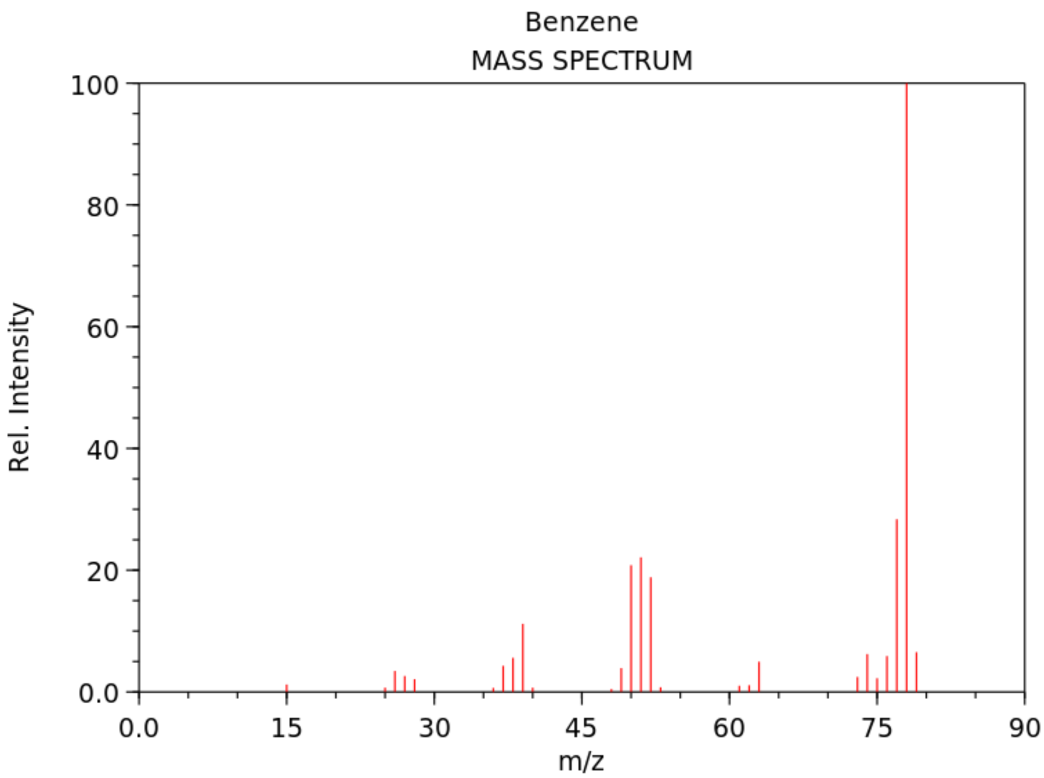


Figure 2-1: Standard solution of benzene with purity 99.8% for testing the RESCUE-MIMS

Based on the NIST chemistry webbook [4], the mass spectrum of Benzene is in the following (Figure 2-2), where the mass 78 is the more characteristic.



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

Figure 2-2: Mass spectrum of Benzene

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 2-1). 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 was selected by the operator at 0.03 Da. 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 2-3 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.

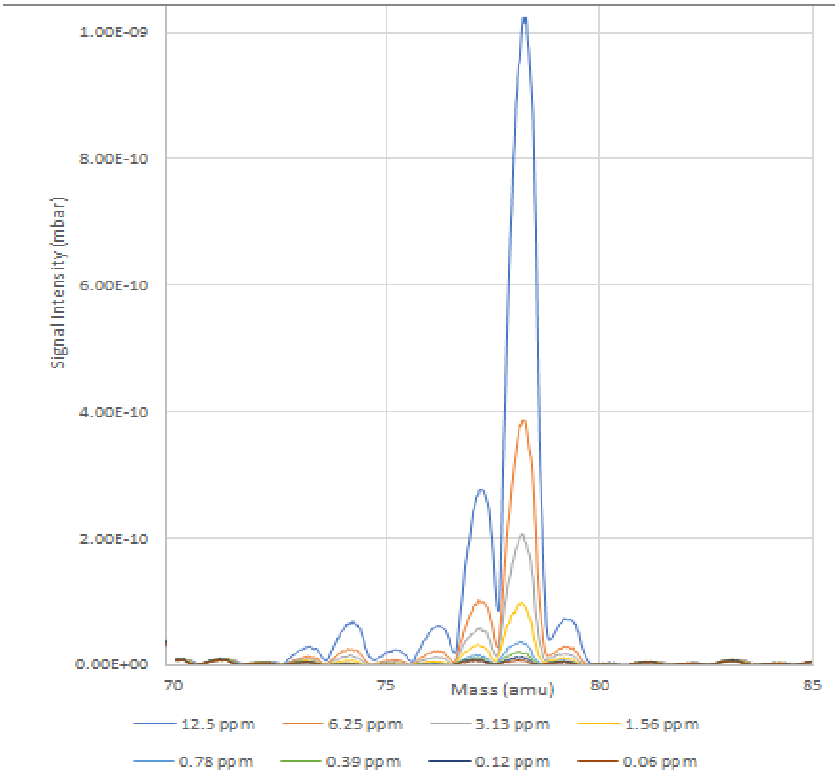


Figure 2-3: Mass spectra of Benzene recorded for different concentrations in the range of 70 to 85 amu; 12.5 ppm (in navy), 6.25 ppm (in red), 3.13 ppm (in grey), 1.56 (in orange), 0.78 ppm (in light-blue), 0.39 ppm (in green), 0.12 ppm (in dark-blue), 0.06 ppm (in purple)

2.1.2 Testing with components correlated with human presence

The RESCUE-MIMS will be used for detecting compounds relevant to human presence under UC5, which has to do with entrapped people under rubble (see paragraph 4.1). Hence, testing with Carbon Dioxide and acetone has taken place, because these compounds have been recorded in literature as characteristic components of the expired air. [5] However, it should be highlighted that in a real disaster scenario additional substances should be monitored (Table 2-4) in order to come to a conclusion that there is indeed a possibility of having an entrapped human under the rubbles; cross-checking with the rescue dogs is suggested.

Compound	Type	Characteristic mass fragments (m/z)
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 2-4: 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 [5]

2.1.2.1 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 2-4, the characteristic mass fragments (m/z) of Carbon Dioxide, namely 12 and 44 are clearly recorded on-line by the system.

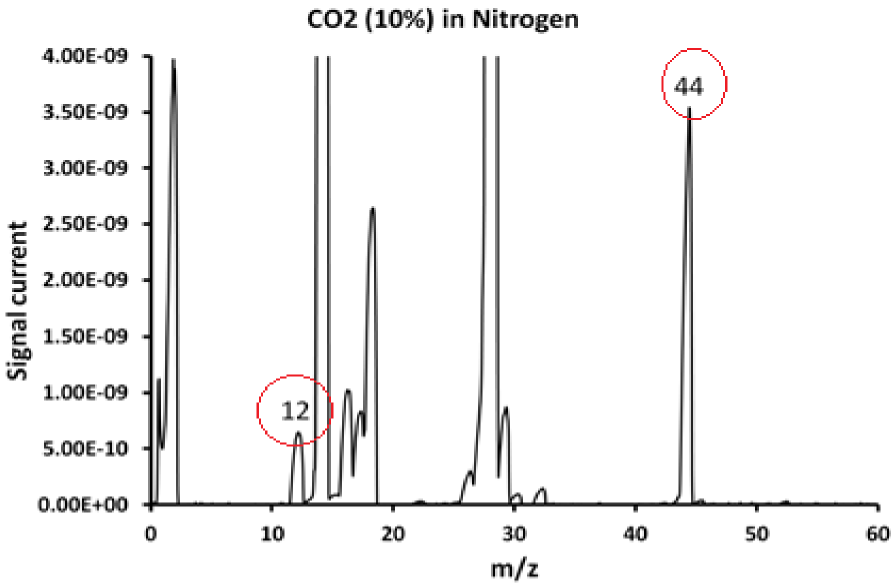


Figure 2-4: Mass spectrum received by 10% Carbon Dioxide in nitrogen with a direct leak. The key mass fragments (m/z) of 12 and 44 attributed to Carbon Dioxide (CO2) are obviously recorded by the RESCUE-MIMS

2.1.2.2 Acetone

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

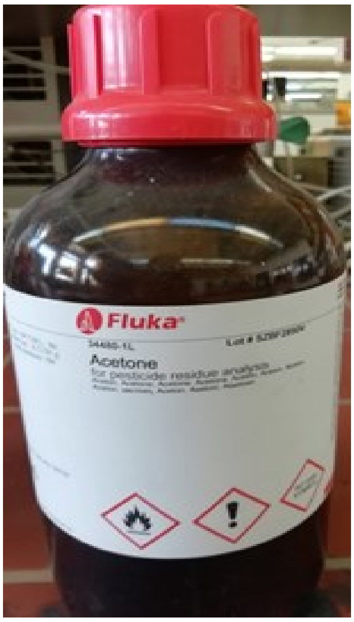


Figure 2-5: Standard solution of acetone with purity >99.5% for testing the RESCUE-MIMS

According to the NIST chemistry webBook, the mass spectrum of Acetone is provided in Figure 2-6; the masses 43 and 58 are considered the more characteristic for monitoring with mass spectrometry-based technologies.

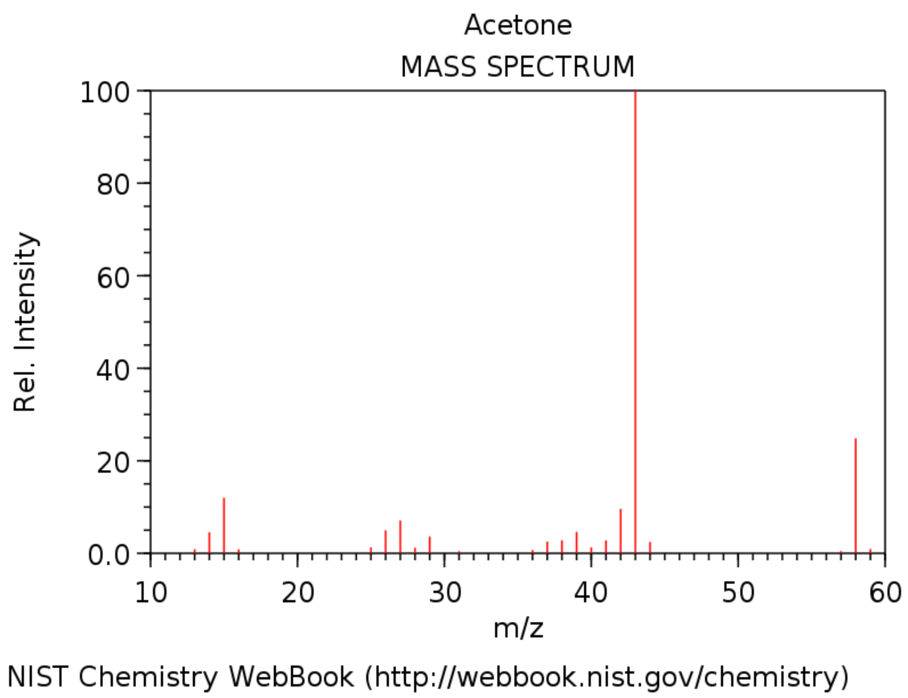


Figure 2-6: Mass spectrum of Acetone.

Figure 2-7 shows 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.

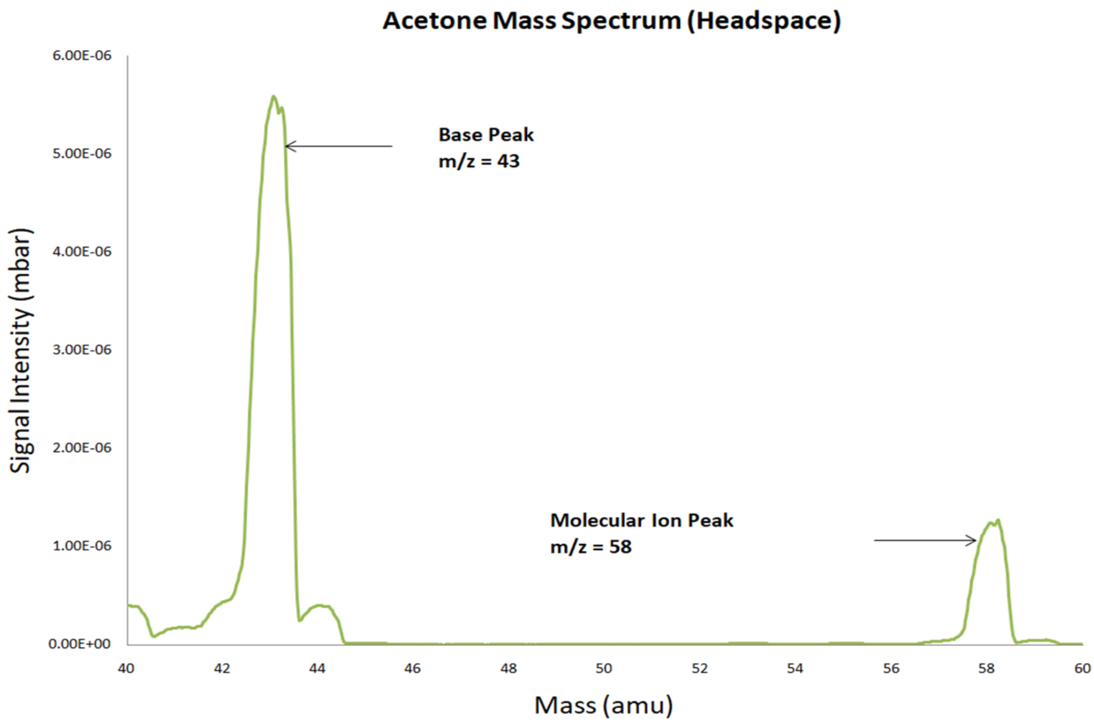


Figure 2-7: Signal intensity of masses 43 and 58 recorded by the RESCUE-MIMS in the headspace of an acetone sample; 25 mL neat acetone with purity > 99.5%.

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 spectrums for the different concentrations are shown in Figure 2-8.

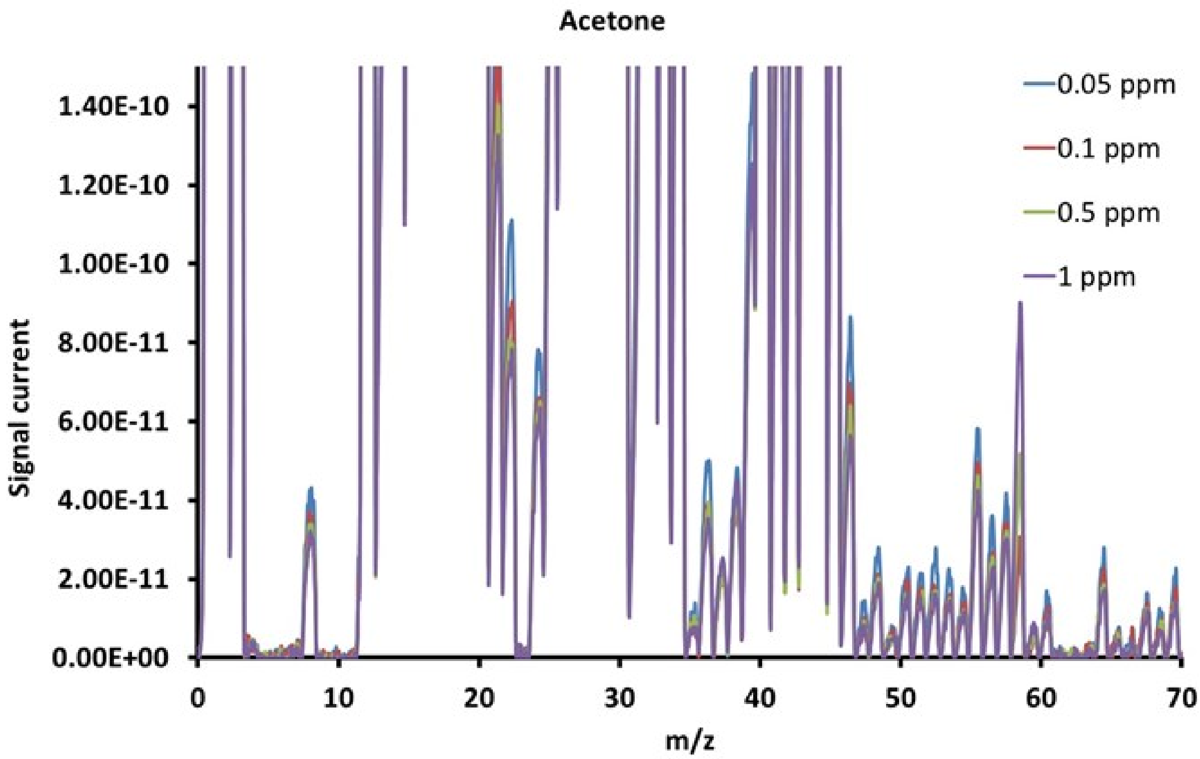


Figure 2-8: Mass spectrums obtained by different concentrations of Acetone: 0.05 ppm (in blue), 0.1 ppm (in red), 0.5 ppm (in green) and 1 ppm (in purple).

Based on the calibration curve prepared by the using the aforementioned concentrations of Acetone, namely 0.05, 0.1, 0.5 and 1 ppm, it proved that the system has an excellent performance in terms of linearity, since the linearity coefficient was found 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.

2.1.3 Summarising the analytical performance of the RESCUE-MIMS

The RESCUE-MIMS was tested and validated with chlorinated compounds because they are considered dominant in industrial fire accidents and because the RESCUE-MIMS will be demonstrated in such an industrial fire incident scenario under (UC4). For the same reason, Benzene was used for testing since it is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly produced 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 time in few seconds (real time measurements) (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 (see paragraph 5.1).

Due to the fact that the RESCUE-MIMS is also foreseen to be used for detecting compounds relevant to human presence, trying to mimic canine dogs (artificial sniffing), testing with Carbon Dioxide and Acetone has taken place; these two compounds have been recorded in literature as characteristic components of expired air. [7] 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, 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.

Furthermore, it has to be mentioned that with the prospect of selecting key components for measuring them on-line in UC5- Victims trapped under rubble pilot scenario, a field trial with canines that are trained to locate alive people under ruins has been conducted; details are provided in D5.3. The main scope was to identify representative "human chemical odours" based on the rescue dogs' responses to different chemical mixtures; interest or not to hidden "chemical human odours" at specific field sites. In that context, different combinations of chemicals have been prepared in the lab that resembled human breath, sweat and axilla, based on literature recordings. It was 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; background measurements will take place in the field to avoid any false positives.

2.2 Further experimentation with target compounds

Based on the results obtained in the framework of D5.3, Acetone was selected as target compound for more experimentation in the lab with the MIMS device in the prospect of preparing the monitoring method for the field analysis.

The physicochemical characteristics and the respective exposure limits for Acetone are summarised in the following:

Acetone (CAS number: 67-64-1)

- *Physicochemical characteristics*

Vapor Pressure: 231 mm Hg at 25 °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, Oxidising 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

The characteristic masses for monitoring Acetone with the MIMS are the masses **58 and 43,** as shown in Figure 2-6 (Mass spectrum of Acetone by the NIST library).

Pure Acetone by Honeywell (purity> 99%) was used for running the experiments; 2 mL were inserted to a vial of 25mL, as shown in Figure 2-9.

Then, the vial was transferred close to the sampling inlet, as shown in Figure 2-10 and the respective mass spectrums were recorded on-line. The sampling inlet was the probe with membrane sheet of polydimethylsiloxane (PDMS); it has a 0.12 mm thickness and 32 mm^2 area, mounted inside Swagelok vacuum fitting union (more details of the membrane probe are provided in D5.1).

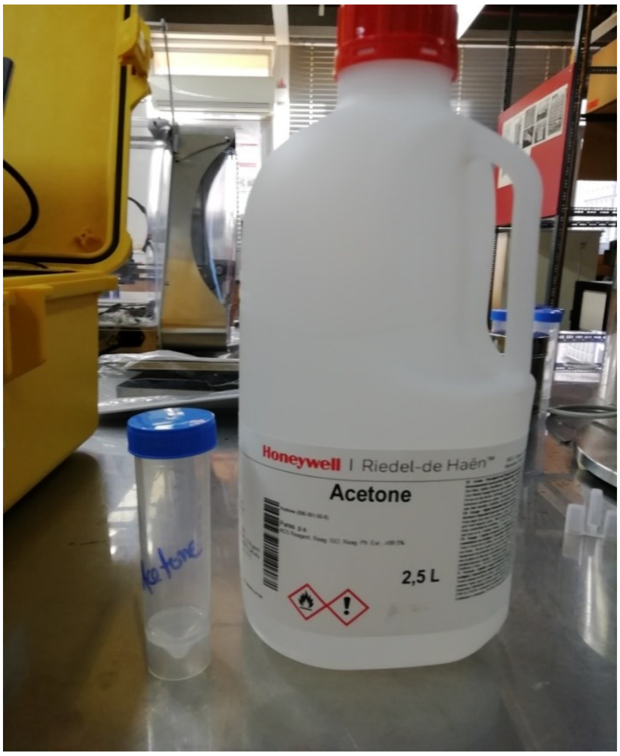


Figure 2-9: Pure Acetone by Honeywell (purity> 99%) was used for running the experiments; 2 mL were inserted to a vial of 25mL.

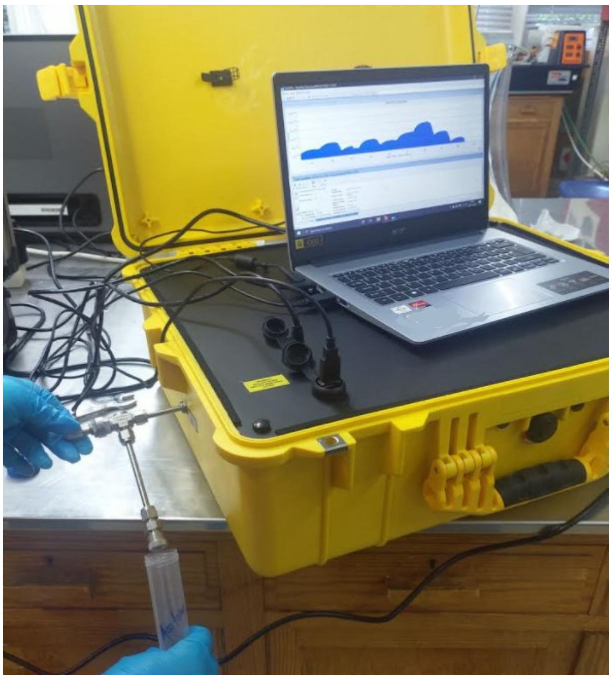


Figure 2-10: The vial including 2 mL of pure Acetone was transferred close to the sampling inlet and the respective mass spectrums were recorded on-line.

The area of masses to be scanned (mass range of scanning) was selected to be from 50 amu to 64 amu (see step 9 of the operational manual that will be provided in the next chapter). The idea was to monitor Acetone via mass 58.

In that context, the MIMS started measuring before the vial approached the sampling inlet (Figure 2-10); mass 58 is indicated (Figure 2-11). These results were considered as background measurements of the lab environment and were compared with the ones that obtained when the vial approached the sampling inlet, presented in Figure 2-12.

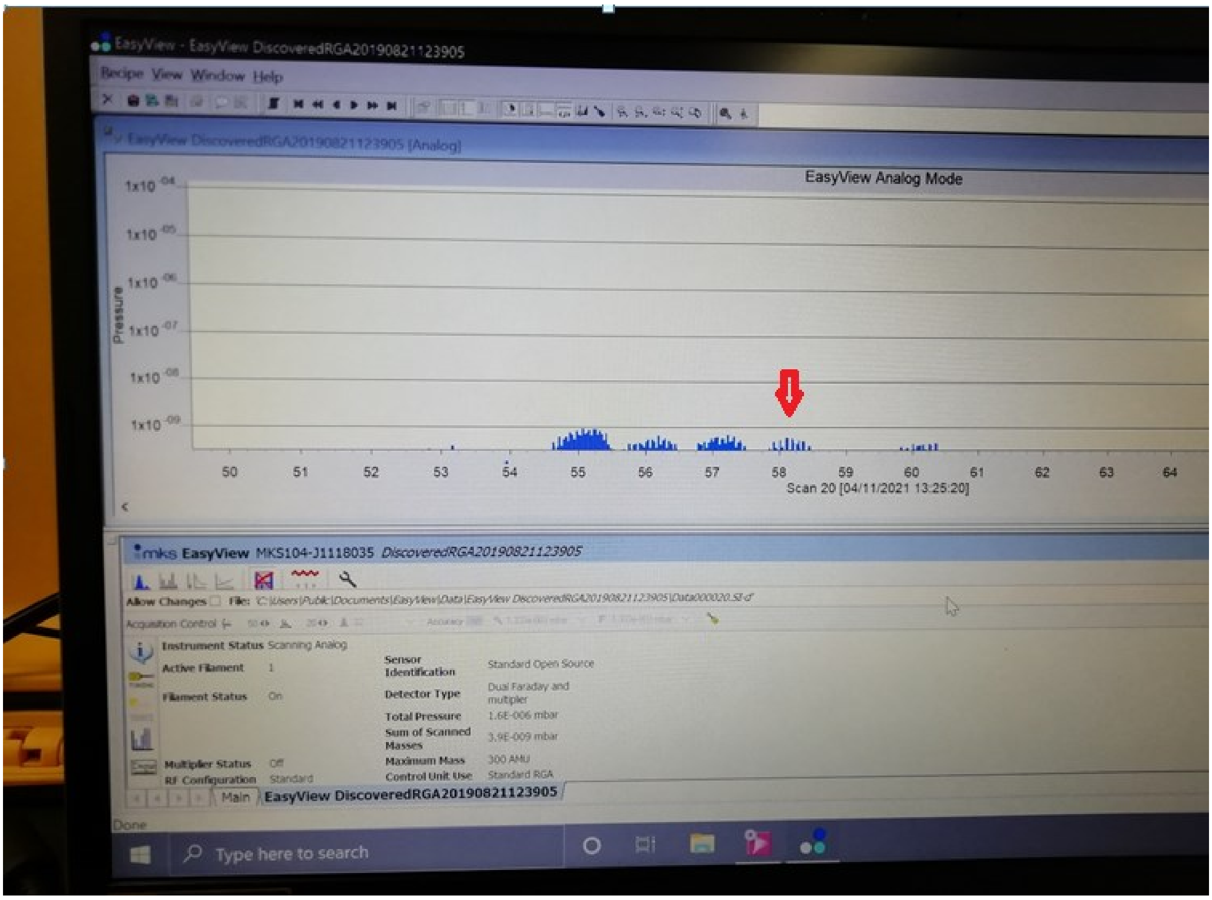


Figure 2-11: Background measurements of the lab environment were recorded by the MIMS; mass 58 that corresponds to Acetone is indicated.

Based on Figure 2-11, the background intensity of mass 58 was recorded in the area of $1x10^{-09}$, whereas the intensity recorded after approching the vial containing the pure Acetone in front of the sampling inlet reached the area of $1x10^{-8}$ (Figure 2-12). It is obvious that this increase is due to the Acetone molecules in the area of high ppm levels that were detected by the MIMS.

It was confirmed that mass 58 is suitable for measuring Acetone.

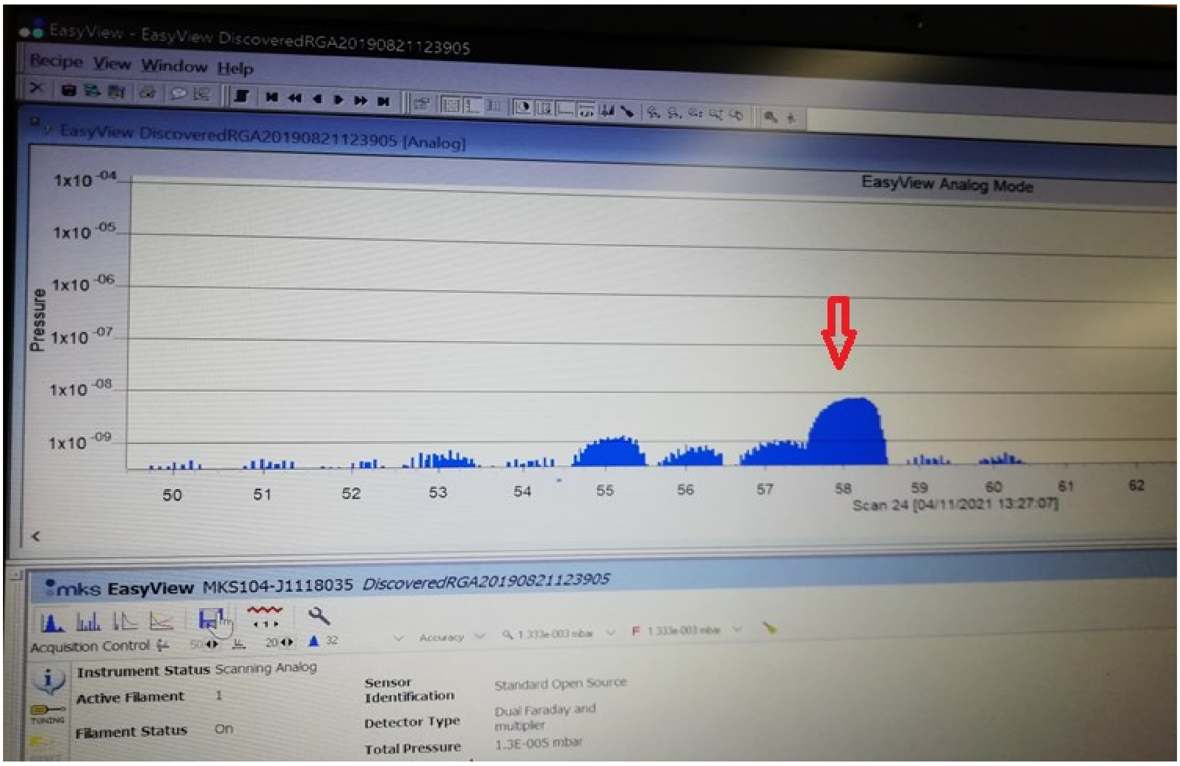


Figure 2-12: Increase of the intensity of mass 58 recorded by the MIMS was observed when the vial containing 2 mL of pure Acetone approached the sampling inlet; mass 58 that corresponds to Acetone is indicated.

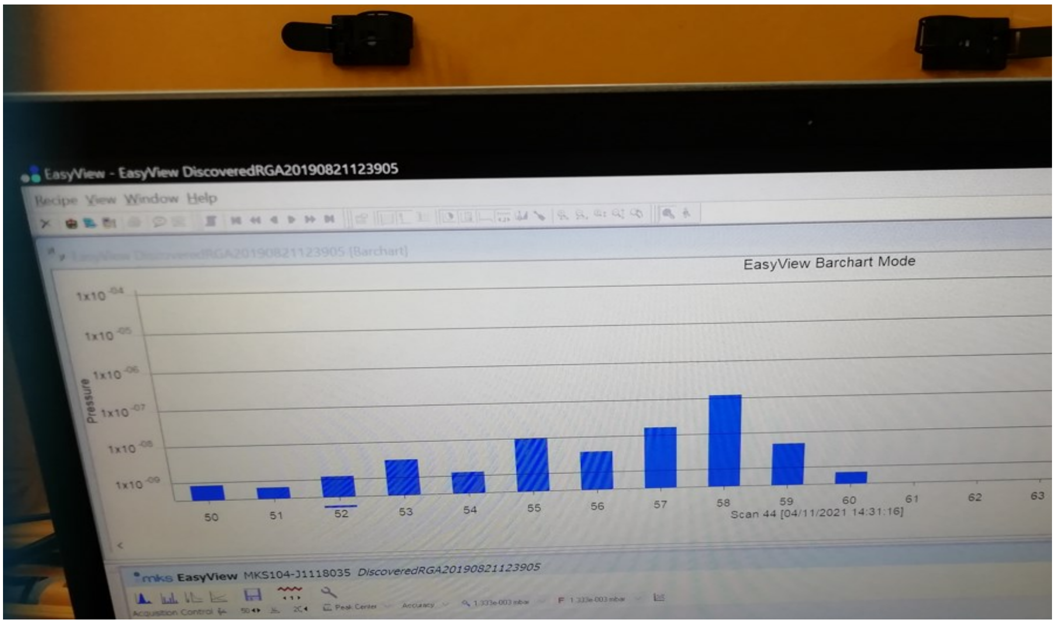


Figure 2-13: The mass spectrum of Acetone displayed as bar-graph by the MIMS.

In Figure 2-13, the measurements presented in Figure 2-12 for Acetone are displayed as bar-graphs; more details on this function of the mass spectrometer software are provided in paragraph 3.2 of this document. The spectrum recorded by MIMS for Acetone in Figure 2-13 is similar to the one provided by the NIST library (Figure 2-6).

3 Getting started with the RESCUE-MIMS prototype

3.1 Draft manual of operation

In this paragraph, an easy guidance for getting started with the MIMS device is provided; steps for operating the instrument accompanied with the relevant photos, taking into consideration that the manual is addressed to operational users who are possibly beginners in mass-spectrometry based technologies. In that context, the manual of operation is drafted in the following comprehensive steps:

1. Open the peli case and connect the two cables (Figure 3-1); one cable connects the PC with the pump unity (pressure monitoring software) and the other one connects the PC with the mass analyser.

Figure 3-1: The two cables for connecting the PC with the MIMS device are plugged in the inner part of the peli-box.

2. Open the PC and check that it is connected with the MIMS device (the pressure unity and the mass analyser) (Figure 3-2).

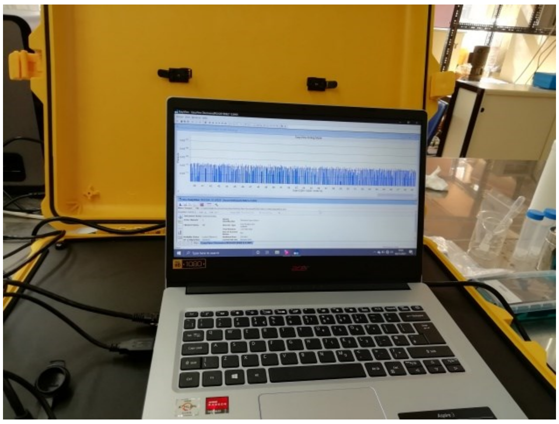


Figure 3-2: The PC is connected with the MIMS device.

3. Be sure that the needle valve of the sampling inlet is closed**!!** (Figure 3-3).

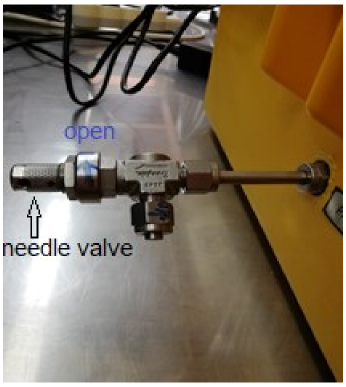


Figure 3-3: The needle valve needs to be completely closed before activating the MIMS (turn it to the opposite side of "open" presented here).

4. Switch on the device using the button at the right side of the peli-case (Figure 3-4).

Figure 3-4: The power switch of the MIMS is at the right side of the peli-case.

5. On the tablet PC, open the pressure monitoring software, and activate the turbo-molecular pump by clicking the button "connection wizard" (Figure 3-5).

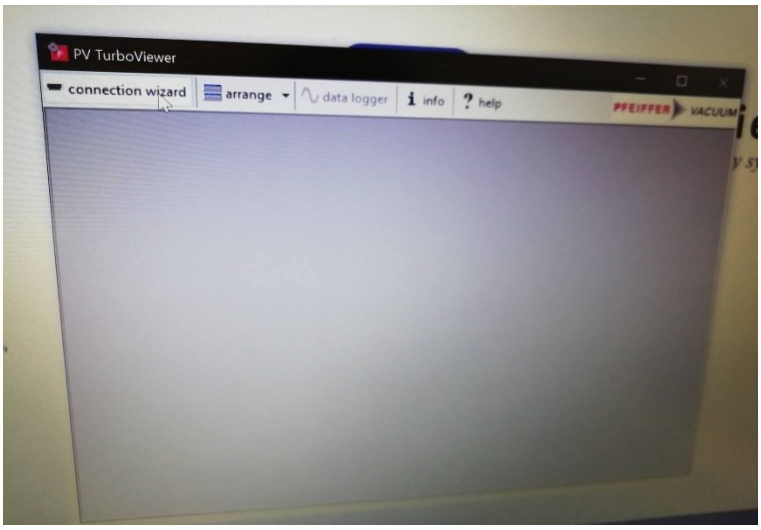


Figure 3-5: Activation of the turbo-molecular pump is done via the pressure monitoring software.

6. Wait until the turbo-molecular pump reaches about 90.000 (rpm) (Figure 3-6).

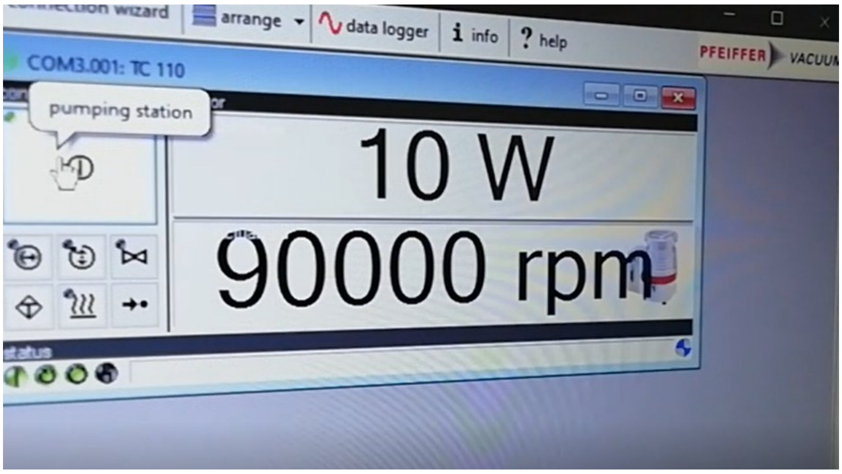


Figure 3-6: The rotation per minute of the MIMS turbo-molecular pump starts increasing until it reaches about 90.000 rpm.

7. Allow the pressure to stabilise at the base level (E-007 to E-006 mbar).

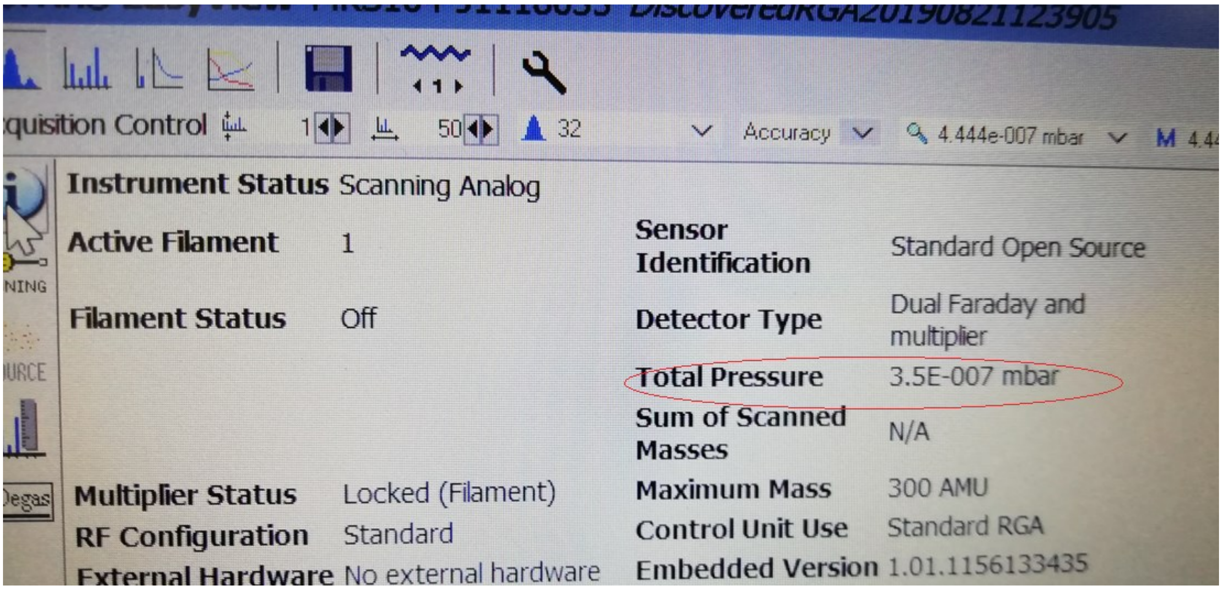


Figure 3-7: The total pressure of the system, having the needle valve closed, should reach a vacuum level of E-007 mbar.

8. Open **smoothly** the needle valve of the sampling inlet (following the blue arrow presented in Figure 3-3), in order to sack sample and allow pressure to reach operational level at about E-006 to E-005 mbar. NOTE: THE PRESSURE MUST NOT REACH the E-004 mbar. **IN SUCH CASE CLOSE IMMEDIATELY THE NEEDLE VALVE.**

9. Select the mass range of scanning (lower and upper mass unit), e.g. for monitoring the mass 44 which is the main mass of Carbon Dioxide, you can select lower mass 1 and upper mass 50 (Figure 3-8)

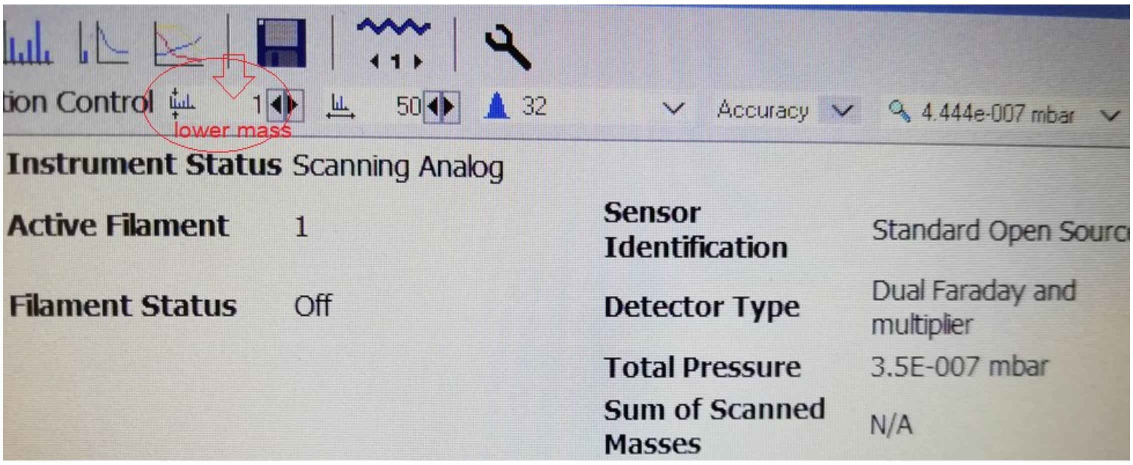


Figure 3-8: For monitoring the mass 44 which is the main mass of Carbon Dioxide, you can select lower mass 1 and upper mass 50 for scanning with the MIMS.

10. Select the accuracy which corresponds to resolution (choose accuracy 5, no less than that) (Figure 3-9)

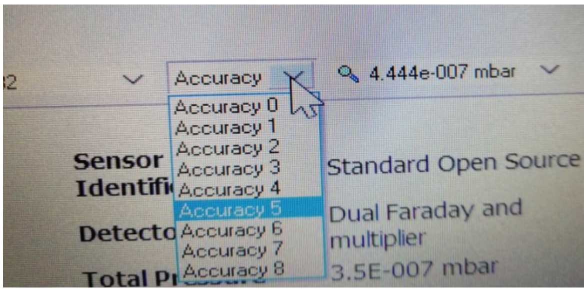


Figure 3-9: Selection of accuracy corresponds to resolution; accuracy 5 is suggested.

11. Select the detector which is correlated to the sensitivity: F (Faraday), M1 (Multiplier 1), M2 (Multiplier 2), M3 (Multiplier 3). The less sensitivity is achieved with the F and the maximum with the M3. The F is selected when measuring concentrations at higher levels e.g. high ppm to % level, whereas M3 is for low concentration, like ppm to low ppb levels.

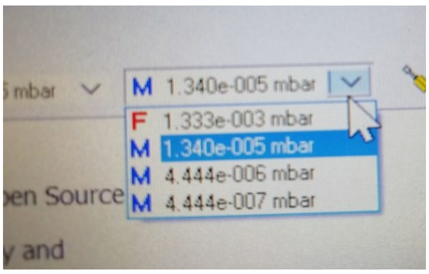


Figure 3-10: Selection of the detector corresponds to the sensitivity: F (Faraday), M1 (Multiplier 1), M2 (Multiplier 2), M3 (Multiplier 3); the less sensitivity is achieved with the F and the maximum with the M3.

12. Start measurement. When the system's pressure is stable and below 3-4 E-005 mbar having the valve open, **activate the filament** on the ion source by clicking on it via the mass spectrometer software (Figure 3-11); it will be turned from blue to red.

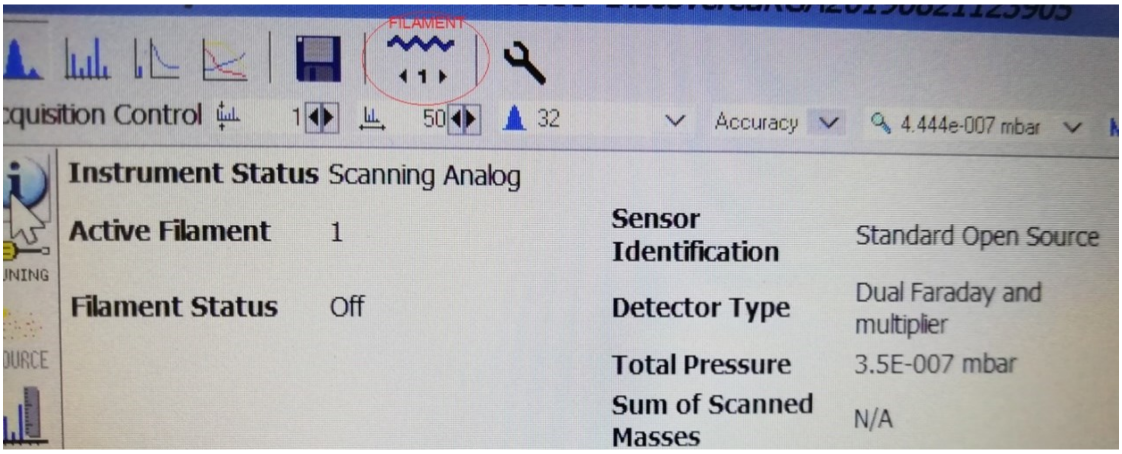


Figure 3-11: Activation of the filament on the ion source via the mass spectrometer software is achieved by clicking on it (from blue it turns to red) for starting the on-line measurements with the MIMS.

13. Data acquisition-Storage

Click on the storage button to save the data recorded as csv files (Figure 3-12)

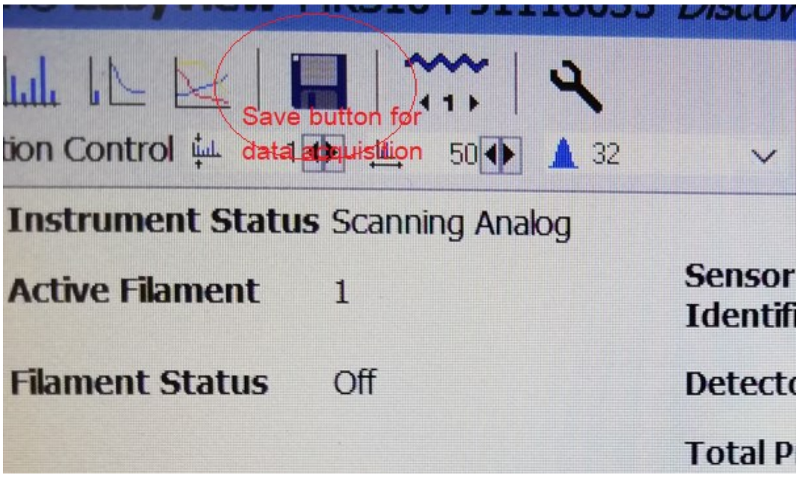


Figure 3-12: The save button is used to storage the data presented on-line.

3.2 User interface

The RESCUE-MIMS interface provides the user with the on-line capability of displaying the mass scanning results either as curves (Figure 3-13) or as bar-graphs (Figure 3-14). Increase of the height either of the curve or of the bar-graph that corresponds to a specific mass e.g. 58 for Acetone, in fact is an on-line signal of the evolution of the monitored compound.

It has to be explained that the x-axis of the diagram corresponds to the masses that have been selected to be monitored (see step 9 of the manual) and y-axis corresponds to the intensity of each mass recorded by the detector (Faraday or Electron-multiplier-see step 11 of the manual). The intensity is directly correlated with the concentration of the component represented by the specific mass, e.g. intensity of mass 58 can be correlated with the concentration of Acetone. Correlation of concentrations with intensity can be achieved by preparing the relevant calibration curves for the compounds of interest e.g., Acetone, using the respective concentration standards; such a procedure was implemented in the lab-scale experiments presented thoroughly in D5.3 and summarised in paragraph 2.1 of this document.

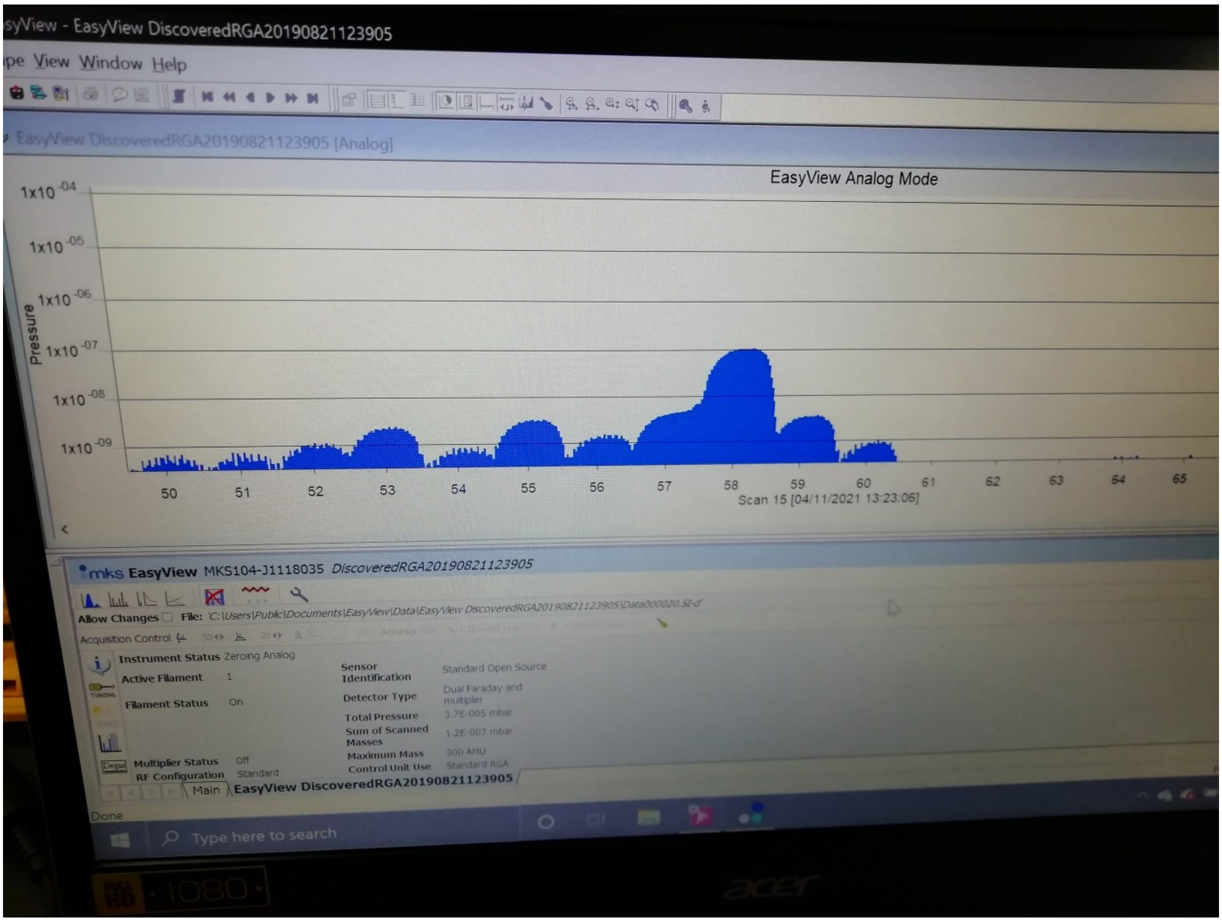


Figure 3-13: Mass scanning results displayed as curves by the MIMS for on-line monitoring.

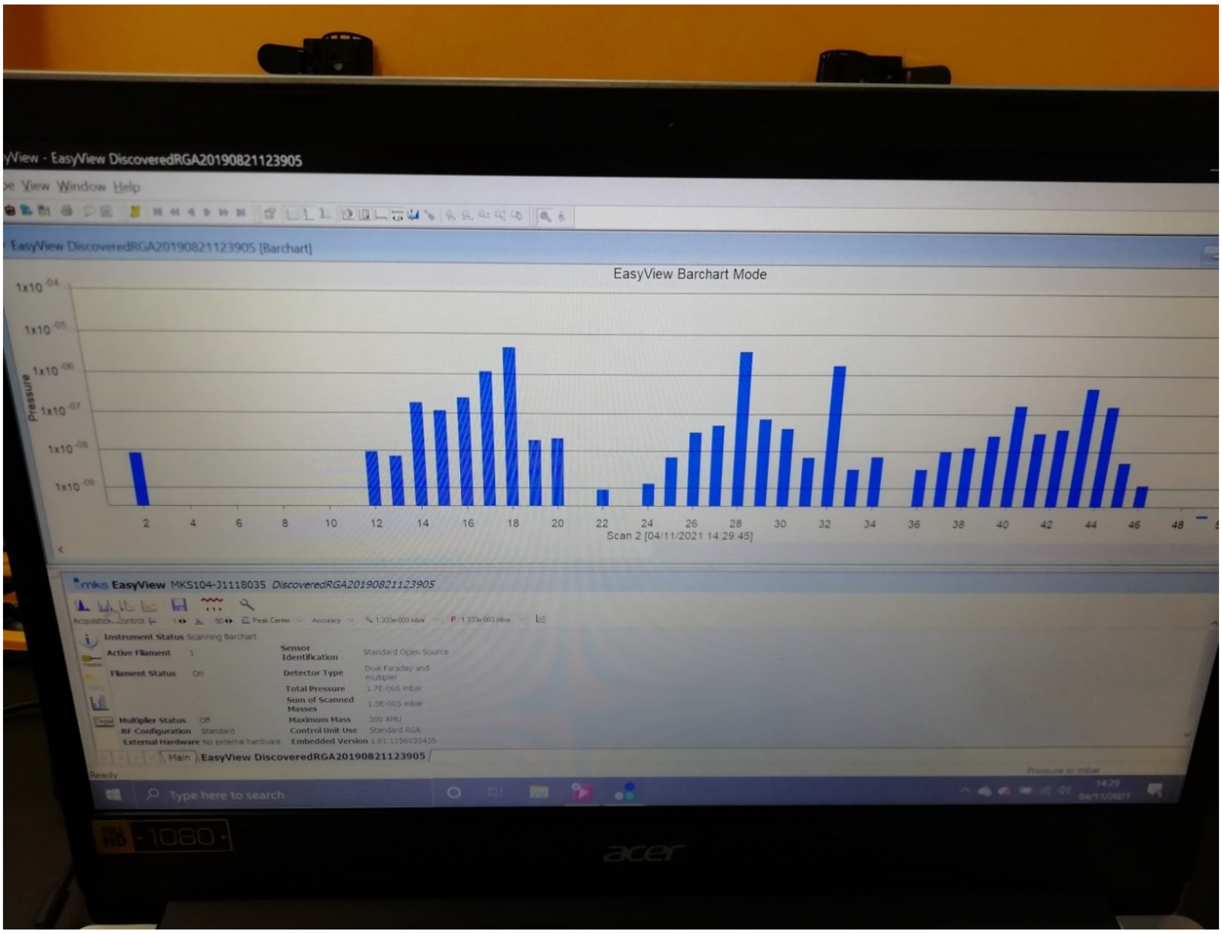


Figure 3-14: Mass scanning results displayed as bar-graphs by the MIMS for on-line monitoring.

The above two display capabilities are used for “full scan mode”, which means that the operator chooses to monitor on-line all the mass entailed in a specific mass scanning area. For example, if the operator selects to monitor the masses from 50 to 64 (step 9 of the manual), it means that the profiles of intensities of all the masses detected by MIMS in between 50 to 64 will be displayed on the PC screen.

However, when monitoring with mass spectrometry-based technologies it is important in some occasions to have targeted on-line monitoring of specific masses which are attributed to specific compounds of interest, e.g. monitoring only the evolution of Acetone (with mass 58), of Benzene (with mass 78), of Toluene (with mass 92) and of Xylene (with mass 106). In such case, instead of “full scan mode”, a “SIM mode” is selected (Single Ion Monitoring), as presented in Figure 3-15; the intensities of specific masses are displayed, colored in different shades e.g. mass 2 (black), mass 18 (blue), mass 28 (orange), mass 32 (purple), mass 40 (magenta), mass 84 (green), mass 129 (yellow).

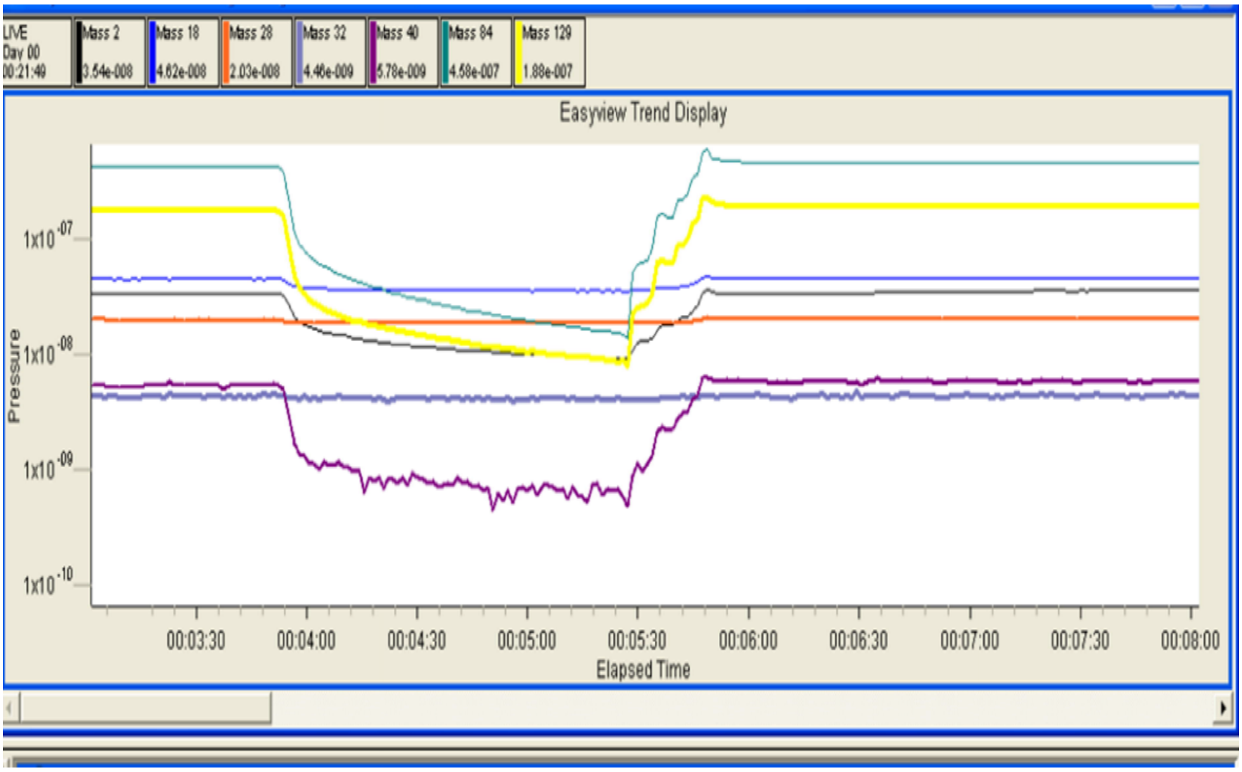


Figure 3-15: Single Ion Monitoring (SIM) mode can be selected for targeted on-line monitoring of compounds by the MIMS; the intensities of specific masses are displayed, colored differently: mass 2 (black), mass 18 (blue), mass 28 (orange), mass 32 (purple), mass 40 (magenta), mass 84 (green), mass 129 (yellow).

Selecting the SIM mode for mass scanning with the MIMS has a number of advantages, such as the reducing of the time needed for a mass scan and hence, having faster results (reduce of analysis time) and also, the increase of sensitivity which makes possible the detection of compounds at low concentrations (improve of LOD).

3.3 Data interpretation

Based on what has been presented in the previous paragraphs, the on-line monitoring data of target compounds, via their masses and their respective intensity profiles, can be easily interpreted by the user. An indicative example is given in Figure 3-16, were SIM mode of operation has been selected in order to monitor on-line the masses 43 and 58 for Acetone (black and orange, respectively), mass 78 for Benzene (pink colour), mass 18 for Water Vapours (blue), mass 40 for Argon (purple) and mass 44 for Carbon Dioxide (green).

These masses have been selected to be monitored in the prospect of running the field trials, e.g. Acetone and Carbon Dioxide for UC5 (see chapter 4), Benzene for UC4 (see chapter 5), while Water Vapours and Argon were chosen as reference compounds to measure the environmental background; as shown in Figure 3-17, the intensities recorded for mass 18 and 40 (Water and Argon) do not change with the elapsed time, they remain at about $1x10^{-6}$ (blue and magenta lines).

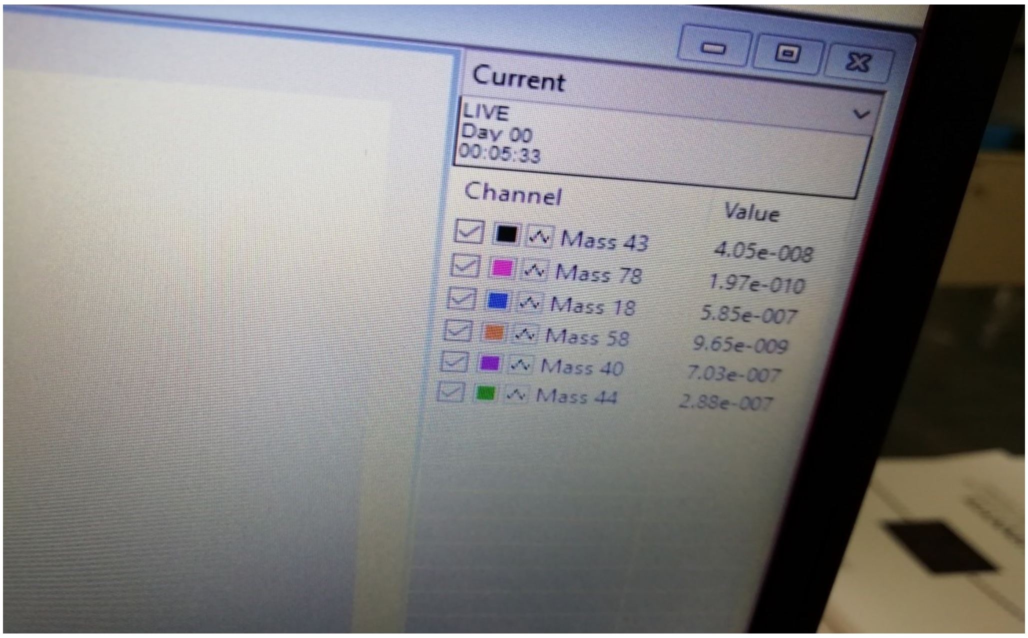


Figure 3-16: SIM mode of operation for monitoring on-line the masses 43 and 58 for Acetone (black and orange, respectively), mass 78 for Benzene (pink), mass 18 from Water Vapours (blue), mass 40 for Argon (purple) and mass 44 for Carbon Dioxide (Green).

Figure 3-17: Intensities' profiles of target compounds masses: 43 and 58 for Acetone (black and orange, respectively), mass 78 for Benzene (pink), mass 18 from Water Vapours (blue), mass 40 for Argon (purple) and mass 44 for Carbon Dioxide (Green), displayed on-line by the MIMS.

Also, in Figure 3-17, at the time 00.02.00 it can be seen the on-line increase of the intensities' profiles of masses 43 and 58 that are attributed to Acetone (black and orange profiles), because a vial with pure Acetone reached the sampling probe (see Figure 2-10); It has to be mentioned that the MIMS is capable of measuring also in the liquid phase via the membrane inlet, hence it is safe to transfer the vial with the liquid acetone close to the system. The vial was removed right after, resulting to black and orange lines drop.

At the time 00.04.00 an NTUA/LPAD member exhaled in front of the MIMS sampling probe; the green line (corresponding to Carbon Dioxide) was directly increased, compared to the intensity value before that time. Hence, recording the background values can provide with "alarms" of target compounds evolution, compared to an intensity increase might be observed on-line. As already mentioned, correlation of intensities with concentrations should be prior done through calibration curves in lab-scale (see paragraph 2.1).

4 Human signs monitoring with the RESCUE-MIMS prototype

4.1 Brief description of the U5 pilot scenario

The pilot scenario of UC5 deals with victims trapped under rubble and will be conducted on June 2022, in France. The Leader is the PUI team who has provided with the following possible work sites and the respective scenarios (Figure 4-1 to Figure 4-4):

WORK SITE N°1 – WS 1 – SITE DE TRAVAIL N°1

Figure 4-1: Field site N°1 in France to be possibly used for testing the MIMS device under the UC5 scenario of the SnR project: Victims Trapped under Rubble

2 victims buried under the slab, SIDE ACCESS ONLY,

Drilling an oblique facade,

Opening in a triangle shape,

Use of listening devices and cameras,

Status of the victim from the medical team,

Evacuation, transport to MEDICAL STATION

1/Vertebral lesions, quadriplegia
Aware, reacts to verbal stimulation
During the research: silent

2/ open fracture, right arm
Aware, reacts to verbal stimulation
During the research: silent

Timetable:

Duration: 3 hours

Number of entrapped victims: 2

WORK SITE N°2 – WS 2BIS – SITE DE TRAVAIL N°2 BIS

The Car Park – Le Parking

Figure 4-2: Field site N°2 in France to be possibly used for testing the MIMS device under the UC5 scenario of the SnR project: Victims Trapped under Rubble

Car park – Car Parking and buses

2 victims inside a burried car under the rubbles,

Single access through the nozzle, closed by a 10mm steel plate, and a 20mm vertical concrete plate

Use of listening devices and cameras,

Drilling the steel plate, drilling the concrete plate

Status of the victim from the medical team

Evacuation from the nozzle of entry, transport to PRV MEDICAL STATION

1/ (inside the car) Head trauma, right side, Unconscious, During the research: silent, 2/(inside the nozzle) Various wounds of small severity, face, arm, hands, conscient, able to walk, During the research: screaming, losing consciousness as soon as he/she comes out from the rubbles	Timetable: Duration: 3 hours Number of entrapped victims: 2

WORK SITE N°3 – WS 2BIS – SITE DE TRAVAIL N°2 BIS

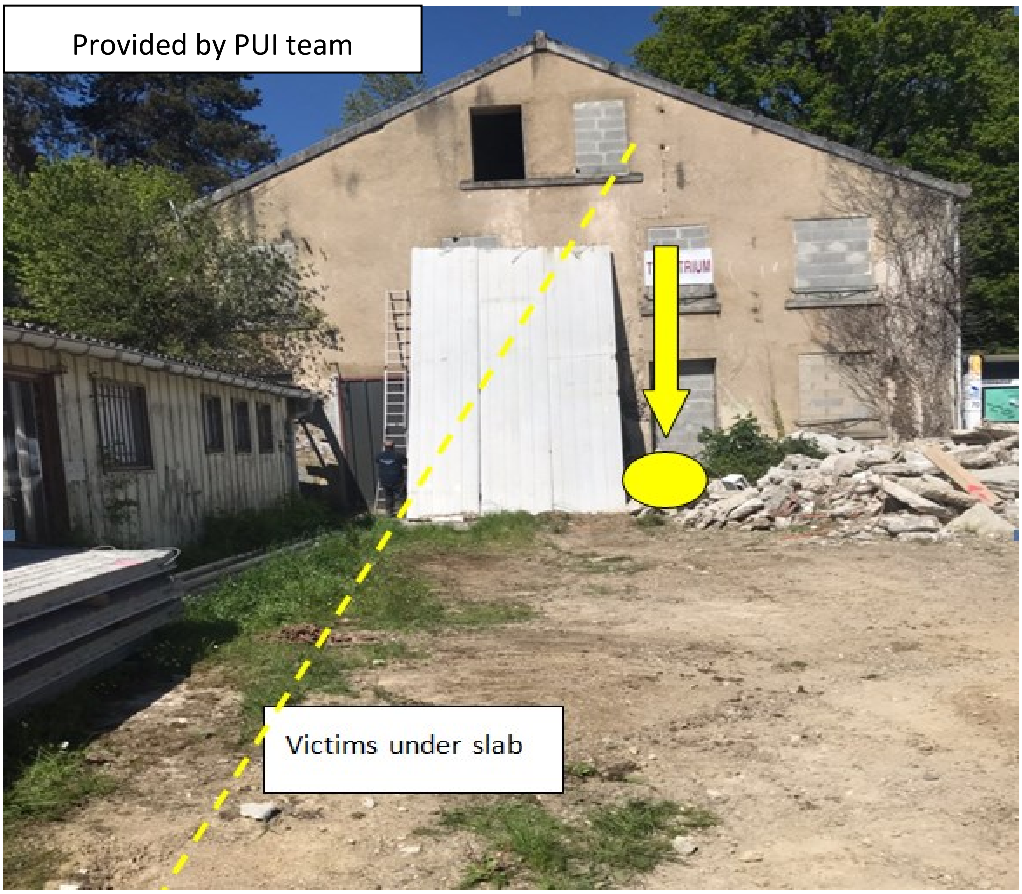


Figure 4-3: Field site N°3 in France to be possibly used for testing the MIMS device under the UC5 scenario of the SnR project: Victims Trapped under Rubble

Access by the Car Park nozzle, climb up to the first floor, installation of a device for the rescuers to come down to the slabs in inclined planes, **DO NOT CUT THE SLAB REINFOREMENTS = DANGER**

Drilling the slabs from the rope rescuers, use of drilling tools, do not cut the rebars,

Ascent of the victim to the top, evacuation by zip line

1/ Under slab:

Bilateral fracture of the legs, femur and tibia, Aware, wakes up to verbal stimulation,

During the research: silent

2/No apparent injury; conscious, losing consciousness from the beginning of the treatment,

During the research: silent

Timetable:

Duration: 3 hours

Number of victims: 2

WORK SITE N°4 – WS 7 – SITE DE TRAVAIL N°4

Victim in a survival place located under a bus,

Access to the victim through a nozzle,

Wedging,

Cutting of the steel IPN part to enter the nozzle,

Wedging

Timetable:

Duration: 1 hour

1/ victim in crush syndrome, apathic,

Compression in the left arm, elbow

During the research: apathic

Figure 4-4: Field site N°4 in France to be possibly used for testing the MIMS device under the UC5 scenario of the SnR project: Victims Trapped under Rubble

The exact work sites will be selected the coming period under the preparation of the specific scenario. The RESCUE MIMS device will be used as a handheld device by the rescuer to monitor key compounds of human presence, like Acetone and/or Carbon Dioxide, as presented in paragraph 2.1.2 of this document. The specific configuration of the RESCUE-MIMS for being able to penetrate the rubbles will be presented in the next paragraph.

The individuals role-laying the "victims" should be professionals and they have to stay inside the voids for about 30-40 minutes in order to achieve an accumulation of the emitted volatiles, either in the exhaled air or emanated by the human skin and body; this procedure will simulate the first hours of entrapment and search and rescue operation at that time.

4.2 Configuration of the RESCUE-MIMS device for the needs of UC5

The RESCUE-MIMS device is provided in a peli-box configuration that can be used in various applications. For that reason, different types of sampling inlets can be used, such as the inlet with membrane sheet or the penetration probe, as shown in Figure 4-5.

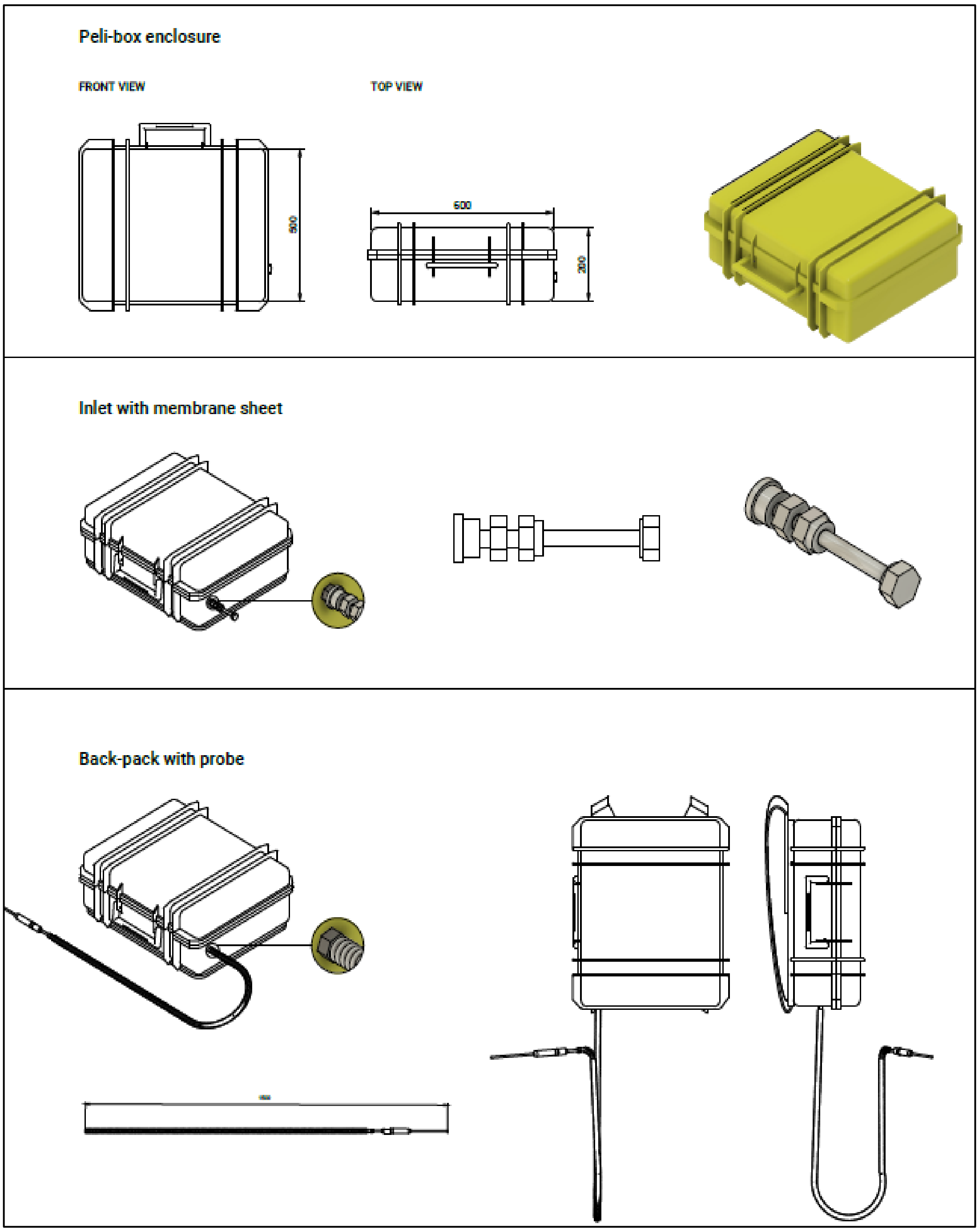


Figure 4-5: Different types of sampling inlets can be used with the RESCUE-MIMS peli-box device based on the application; inlet with membrane sheet or penetration probe for hand-held or backpack use of the device.

In Figure 4-6, the design of the RESCUE-MIMS configuration that is suggested for penetrating the rubbles to monitor the airborne phase inside the voids is provided; handheld or back-pack device with penetration capabilities.

Figure 4-6: Design of the RESCUE-MIMS that can be used as a handheld or back-pack device with penetration capabilities.

In order to preliminary test the device in the lab for preparing the UC5 field demonstration, a Teflon tube that is considered an inert material so that to avoid secondary chemical reactions has been set-up as a penetration sampling probe. In front of the tube with length about 1 m, a filter has been adjusted in order to protect the instrument from the dust, taking into account that it will be used inside the voids of the collapsed structures; a parafilm tape was used to seal the connections (Figure 4-7).

Figure 4-7: Preliminary set-up of the penetration sampling probe; in front of the teflon tube a filter has been adjusted in order to protect the instrument from the dust; a parafilm tape was used to seal the connections.

The filter used for protection from particles is shown in Figure 4-8; PTFE has been selected because it is a hydrophobic material and inert and hence suitable for our application, since it does not absorb polar compounds like Acetone, which is a compound of interest in human presence monitoring; avoid any sample loss.

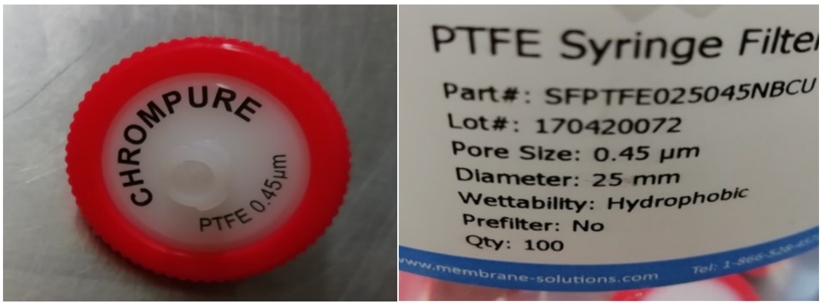


Figure 4-8: A PTFE filter has been selected because it is hydrophobic, hence does not absorb polar compounds like Acetone which is a compound of interest in human presence monitoring.

Any updates or optimisation of the above configuration will be investigated the coming period in the prospect of preparing the field trial to be held in June 2022.

4.3 Compounds to be measured with the RESCUE-MIMS in the field-Alarms

Based on the lab-scale results conducted so far, the compounds to be selected for monitoring human presence in the field will be Acetone and/or Carbon Dioxide. These two compounds are considered core emissions of exhaled air [5-7].

Taking into account the experiments presented in paragraph 2.2, the masses to be monitored on-line with the MIMS in the field will be 58 for Acetone and possibly 44 for the Carbon Dioxide, if it will be finally decided to be also monitored.

The MIMS will start measuring on-line inside the voids of simulated debris for getting the background intensity values of mass 58. After the individual, who is role-playing the victim, enters the voids and stays there for about 30 minutes the MIMS will measure again via the sampling probe with penetration capabilities. Any difference recorded in the intensity of mass 58 will be attributed to the Acetone contained in the exhaled air of the victim and hence, this will be an alarm for the rescuer and to the DSS platform that an alive person is under the debris.

4.4 Communication with the SnR platform

The RESCUE-MIMS produces csv files, as presented in Table 4.1. Such a file includes the monitored masses that correspond to specific compounds, recorded by using a specific scan rate, e.g., 0,1 amu, as shown in Table 4.1.

Time& Date	**$Flags$**	**mass 40.0**	**mass 40.1**	**mass 40.2**	**mass 40.3**	**mass 40.4**	**mass 40.5**	**mass 40.6**	**mass 40.7**	**mass 40.8**	**mass 40.9**	**mass 41.0**
36:23.4		2.00E-08	2.24E-08	2.40E-08	2.47E-08	2.54E-08	2.43E-08	1.97E-08	1.12E-08	6.43E-10	6.55E-10	8.07E-10
37:33.3		1.88E-08	2.14E-08	2.30E-08	2.39E-08	2.43E-08	2.33E-08	1.90E-08	1.17E-08	7.66E-10	7.25E-10	9.17E-10
38:43.4		1.86E-08	2.13E-08	2.29E-08	2.38E-08	2.44E-08	2.35E-08	1.90E-08	1.18E-08	8.16E-10	7.46E-10	9.72E-10
39:53.6		1.84E-08	2.11E-08	2.29E-08	2.37E-08	2.42E-08	2.33E-08	1.90E-08	1.19E-08	8.54E-10	7.62E-10	9.91E-10
41:04.2		1.84E-08	2.12E-08	2.29E-08	2.37E-08	2.43E-08	2.34E-08	1.91E-08	1.19E-08	8.68E-10	7.87E-10	9.96E-10

Table 4-1: Example of a csv file produced by MIMS (raw data).

The connection of RESCUE-MIMS with the DSS system will be achieved as follows (derived from D5.1):

- The RESCUE-MIMS will communicate with a connector (e.g., router installed inside ambulances) using agreed protocols (e.g., Bluetooth, Restful APIs) in order to transfer data through an Enterprise Service Bus (ESB) to the data lake of SnR for data aggregation. Those data will be filtered using a canonical model created in T6.2 "S&R Data Communication Interoperability framework". In particular, the canonical model will facilitate the process of filtering out the non-relevant data, as well as the transformation of the data to the required format.

- Then the data will be preprocessed, clustered, and empowered with machine learning algorithms that can facilitate decision making (e.g., detection algorithms). Upon their processing and transformation, the data will be retrieved as homogeneous data by both the Concorde Platform and the DSS, in order to help first responders with decision making.

5 Chemical hazards monitoring with the RESCUE-MIMS prototype

5.1 Brief description of the UC4 pilot scenario

UC4 includes a Forest Fire expansion and threat of Industrial Zone scenario where different technologies provided in the SnR project will be used for the incident management. A number of those technologies will be integrated and tested in UC4; the robotic platform provided by DFKI with its sensors (Cameras and LIDAR), the chemical device (RESCUE MIMS) provided by the NTUA, the Obstacle Detection System (ODS) provided by THALIT, together with the drone provided by UHasselt (more details are provide in D5.4)

The pilot will take place on November 2022, in Greece. The leader is EPAYPS. The field selected for running the trial is the shooting training field of Korinthos (Figure 5-1). According to the scenario, there will be a prescribed burning (Figure 5-2) to produce smoke components that will be measured by the MIMS device mounted on the DFKI robot.

Figure 5-1: The field selected for running the UC4 trial is the shooting training field of Korinthos, Greece (Photo credits: EPAYPS).

Figure 5-2: Prescribed burning will take place under the UC4 pilot scenario (Photo Credits: EPAYPS).

EPAYPS has recently arranged a visit to the field where UC4 will be conducted. Prescribed burning of typical Mediterranean forest fuel took place at specific sites of the field terrain in order to better prepare the scenario (Figure 5-2).

Figure 5-3: The MIMS device mounted on the DFKI's robot will measure in UC4 the chemical hazards of the smoke produced for the safety of the first responders (Photo Credits: EPAYPS).

The main target for the MIMS device is to measure the chemical hazards of the smoke produced for the safety of the first responders (Figure 5-3).

5.2 Configuration of the RESCUE-MIMS device for the needs of UC4

The RESCUE-MIMS device is provided in a configuration of a peli-box case that encloses the inner parts of the mass analyzer (Figure 5-4); a PC laptop is connected to display the measurements recorded on-line. It has to be noted that the peli-box need to be robust enough to sufficiently protect the "heart of the RESCUE-MIMS" which is the analyzer, the embedded ion-source and the detector, because it is fragile (more details are available in D5.1)

Figure 5-4: The RESCUE-MIMS peli-box with a PC laptop to display the data recorded on-line.

The RESCUE-MIMS will be tested together with the DFKI's ground robot SeekurJr (Figure 5-5), the obstacle detection system by THALIT and the UHASSELT drone, DJI Phantom 4 Pro v2, under the UC4.

Figure 5-5: The SeekurJr robotic platform by DFKI (D5.1-Provided by DFKI).

As presented in D5.1, the SeekurJr platform should be operated mostly on flat terrain with small obstacles due to low ground clearance; that is why the training field in Korinthos has been selected. During operation, the batteries can be hot-swapped without restarting the robot. For hot-swapping the batteries, the white cover on top of the base of the platform needs to remain accessible (Figure 5-4). Hence, the RESCUE MIMS will have to be mounted towards the front or back of the platform using brackets, which fit the whole pattern on the robot and the used Peli-Case for the RESCUE MIMS. More details will be provided in the next paragraph.

5.3 Mounting the RESCUE-MIMS device on-board DFKI's ground robot

Figure 5-6, presents the Physical Connections Block Diagram among all the different technologies that will be integrated under D5.4 (Testing of Rescue MIMS on-board robotic platforms and drones).

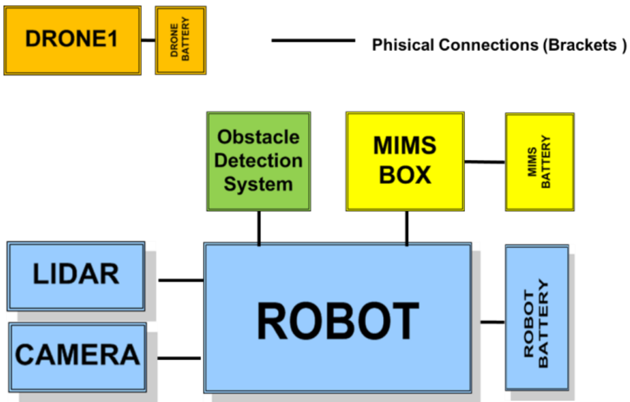


Figure 5-6: Physical Connections Block Diagram (D5.4- Provided by THALIT).

The Robot shall provide a hardware interface (like metal brackets or straps) to mount all the additional components. Figure 5-7, shows a preliminary testing by DFKI on how to mount a payload on the SeekurJr robotic platform in the prospect of selecting the best alternative for mounting the RESCUE-MIMS peli-box under UC4; the red straps can be used to stabilise the payload, as presented; moreover, a special metallic frame has been constructed to attach all the payloads, so that the white cover on top of the base of the platform to remain accessible, in order to change the batteries directly in the field, if needed.

Figure 5-7: Preliminary testing on how to mount payloads on the SeekurJr robotic platform by DFKI (Provided by DFKI).

Moreover, the robot shall provide the proper power to the components that requires it, like the Obstacle Detection System (ODS). The RESCUE-MIMS shall be powered by its own battery pack, like the one presented is Figure 5-8; power autonomy of about 2-3 hours is required for running the field trial. In any case, the RESCUE-MIMS prototype may have the alternative to be powered by the Robot in case the battery will not work for any reason; this will be considered in the coming period for preparing the contingency plan of the UC4 pilot.

Figure 5-8: Battery back that can be used for providing power autonomy to the MIMS prototype of about 2-3 hours in the field.

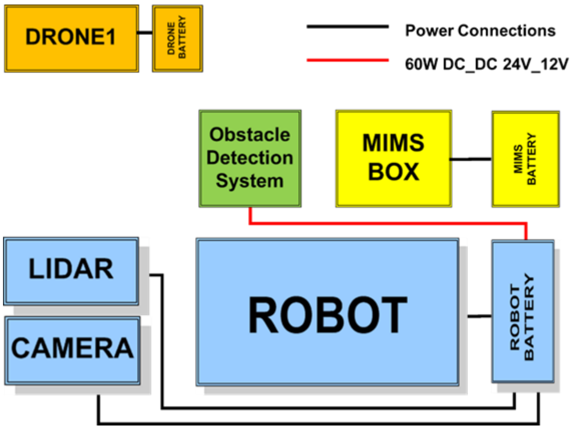


Figure 5-9: Power Connection Block Diagram (D5.4-Provided by THALIT).

In Figure 5-9, the Power Connection Block Diagram for all the different technologies that will be integrated under D5.4 (testing of Rescue MIMS on-board robotic platforms and drones) is presented.

5.4 Compounds to be measured with the RESCUE-MIMS in the field-Alarms

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

Benzene compound has a number of characteristic masses that can be used for monitoring it, such as 64, 74, 78, 79, with the most abundant to be the mass 78. As described in chapter 3, the users can decide which masses to monitor, by selecting the full scan or SIM mode of operation.

In table 5-1, the intensities recorded by the MIMS for the above masses, using different concentrations of benzene (standards), ranging from 0.06 to 12.5 ppm, are provided as an example.

Mass	**Intensities recorded by the MIMS**							
64	9.87E-12	7.97E-12	8.71E-12	9.46E-12	6.55E-12	8.26E-12	7.61E-12	7.66E-12
74	6.79E-11	2.27E-11	1.23E-11	6.41E-12	2.02E-12	1.06E-12	4.19E-13	1.00E-12
77	2.28E-10	8.35E-11	4.78E-11	2.70E-11	1.35E-11	9.08E-12	7.58E-12	6.39E-12
78	**9.43E-10**	**3.62E-10**	**1.93E-10**	**9.59E-11**	**3.31E-11**	**2.04E-11**	**1.02E-11**	**6.93E-12**
79	6.45E-11	2.57E-11	1.55E-11	9.78E-12	5.27E-12	4.66E-12	3.87E-12	3.56E-12
Concentration	**12.5 ppm**	**6.25 ppm**	**3.13 ppm**	**1.56 ppm**	**0.78 ppm**	**0.39 ppm**	**0.12 ppm**	**0.06 ppm**

Table 5-1: The intensities recorded by the MIMS for masses 64, 74, 78, 79 attributed to Benzene, using different concentration standards from 0.06 to 12.5 ppm.

As also referred in UC5 (chapter 4), background measurements with the MIMS are necessary in order to have them as a reference, before the fire ignition. Since in urban areas there is a strong evolution of BTX by different sources of pollution it is expected to have background measurements at about E-11 or E-12 level.
According to the UC4 scenario prescribed burning will take place, so BTX will be produced. Since MIMS will monitor on-line and continuously the intensity of mass 78, it will record an increase of its intensity that will correspond to benzene exposure.
According to OSHA, for Benzene the current OSHA PEL is 1 ppm TWA, and the STEL is 5 ppm. So, benzene should not exceed 5ppm for more than 15 minutes. Based on Table 5-1, an alarm of benzene exposure could be triggered if the intensity of 78 recorded is over 2E-10; more experimentation with benzene standards will be conducted the coming period under the UC4 needs.

5.5 Communication with the SnR platform

In the following there is a description on the communication channels provided in D5.4:

- The Robot shall provide a dedicated internal network where all networking components are linked via Ethernet
- The Robot shall navigate with a driver or in semi-autonomous mode with a 3D-Exploration Algorithm
- The Robot shall integrate the Obstacle Detection System to elaborate the output of the Detection SW and to decelerate/stop the Root movement, in particular the OBS will provide information to the onboard Robot System by outputting fused obstacles position and speed data in the robot reference system. Moreover the OBS output will be available on a ROS topic whose content describes objects position and Speed.

Figure 5-10, shows all Telecom connections foreseen in the Robot & Drone platform (based on version 1 of D5.4 that had been submitted; updates might be considered under D5.4, version 2):

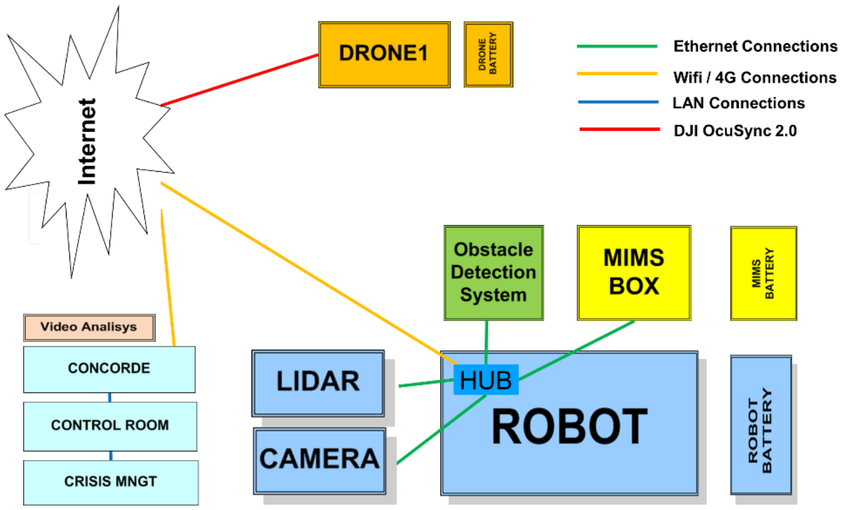


Figure 5-10: Telecom preliminary Block Diagram (D5.4-Provided by THALIT)

Specifically, the MIMS box together with all sensors (LiDAR sensor and Cameras) and ODS will be connected together with a HUB provided by DFKI which will be connected to the Control Room via WiFi or 4G connection; the Drone will be connected to Control Room with a specific telecom connection. Figure 5-11 provides the Robot Platform System Architecture.

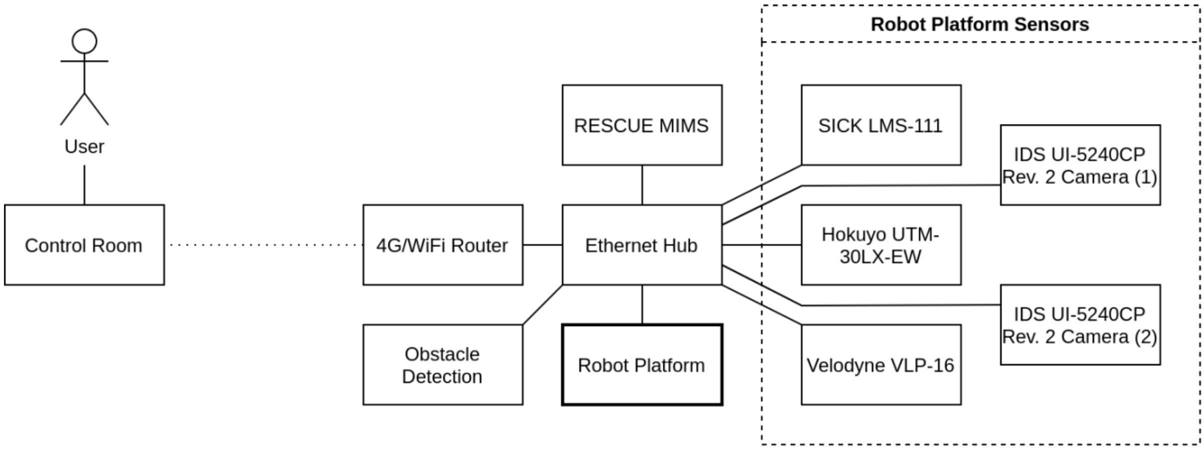


Figure 5-11: Robot Platform System architecture

More details concerning the connection of RESCUE-MIMS with the DSS platform is provided in D.5.4 (Testing of Rescue MIMS on-board robotic platforms and drones).

6 Conclusions and Proposals

The RESCUE-MIMS prototype of TRL 6 appears to satisfy the majority of the end-users requirements in terms of specific KPIS:

1. Portability: the RESCUE-MIMS prototype offers all the benefits of Mass Spectrometry in terms of high sensitivity and accuracy of measurements and at the same time is portable and can be transferred to the field with the potential to be used either as a handheld or backpack device (for more details see Chapter 4 of this document).
2. Robustness: a peli-box case of about 60x50x20 cm encloses the inner parts of the mass analyser, to be robust and withstand the harsh operational environment (details are provided in D5.1).
3. Ruins penetration capability: different types of sampling inlets could be adjusted to the MIMS luggage depending on the field application; inlet with membrane sheet for faster analysis and advanced selectivity, or extended sampling probe for penetrating the ruins (for more details see Chapter 4 of this document, paragraph 4.2).
4. Easy operation and friendly to the user: the RESCUE-MIMS comes in a configuration of a luggage that can be easily handled by the user. Moreover, the customised software provides with easy-readable messages on-line (user interface); intensities of the monitored compounds. A draft manual of operation, as well as indicative examples of on-line monitored target compounds are provided in Chapter 3 of this document.
5. Easy to deploy: the Rescue-MIMS can be easily deployed in the field, and it can also be easily used as a payload, on-board robotic platforms, e.g., the DFKI SeekurJr unmanned ground vehicle (UGV) or on other speed platforms, e.g., vehicles for mapping types of compounds and/or concentrations in the field (roving systems).

Concerning the analytical performance of the RESCUE-MIMS assessed via the KPIs of:

1. sensitivity
2. reliability
3. low limit of detection (LOD)
4. fast results (short response times)
5. detection capability of a wide range of concentrations (linearity)
6. monitoring in SIM mode (target analysis of compounds),

the results are summarised as follows:

The RESCUE-MIMS was tested and validated with chlorinated compounds because they are considered dominant in industrial fire accidents and since the RESCUE-MIMS will be demonstrated in such a fire industrial incident scenario under (UC4). For the same reason, Benzene was used for testing since it is one of the core compounds of BTX (Benzene, Toluene, Xylene) that is mainly produce 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 an industrial zone, forthcoming pilot scenario (see paragraph 5.1).

Due to the fact that the RESCUE-MIMS is also foreseen to be used for detecting compounds relevant to human presence, UC5 - Victims trapped under rubble pilot scenario trying to mimic canine dogs (artificial sniffing), testing with Carbon Dioxide and Acetone has taken place; these two compounds have been recorded in 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, 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.
As happened with the chlorinated compounds (Table 2-2), the system shown also excellent linear performance for Acetone, expressed through the linearity index (R^2). This is quite important because the system proven its capability of detecting wide range of concentrations. Specifically, based on the calibration curve prepared for different concentrations of Acetone, namely 0.05, 0.1, 0.5 and 1 ppm, the linearity coefficient was found equal to 0.9927, almost 1, which is the ideal value for a linear performance. When monitoring on-line in the field it is important to be capable of measuring at lower or higher levels of concentrations because dynamic phenomena and turbulences usually prevail.

According to the above, the RESCUE-MIMS prototype seems a promising field technology that can be sufficiently used in the operational environment. Though, improvements based on the specific field application might be needed to make it even more operational for the first responders.

Inside D5.1 (M10), several proposals for optimising the capabilities of the RESCUE-MIMS as an operational tool have been presented. In that prospect and aligned with the end-user requirements, it is additionally proposed in D5.5. (M18) to choose particle filters in front of the sampling inlet for protecting the instrument; the operational environment is very harsh in terms of particles generation (smoke in case of a fire or dust due to collapsed structures). In that case, proper material should be selected for the filter in order not to lose compounds of interest e.g., Acetone for monitoring entrapped victims; PTFE or quartz can be used because they are hydrophobic.

Especially for the search and rescue operations and for penetrating the rubbles, a telescopic probe can be investigated that should be flexible and at the same time has abrasion resistance. Moreover, the sampling probe can entail a heated capillary column; heating is encouraged for avoiding any condensation of compounds at the inner part of the sampling tube, while the capillary column may contribute to an initial resolution of the sampled chemical mixtures, increasing the accuracy of the measurements.

Library customisation, in terms of uploading mass spectrums databases, can be explored for the possible identification of unknown compounds; chemometrics can be used for voluminous data deconvolution of unknown chemical mixtures.

Concerning the display of the measurements, a software development for the on-line conversion of the intensities of compounds to concentration values can be investigated.

ANNEX I: References

[1] 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.

[2] 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.

[3] 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.

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[5] Stamatios 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.

[6] 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.

[7] 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.

ANNEX II. Personal Protective Equipment and Safety Data Sheets of the chemicals used for the experiments

A. PPE for running the 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 the experiments

B. Safety Data Sheets of the Chemicals

(a) Acetone

Sigma-Aldrich.

www.sigmaaldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 6.6
Revision Date 10.08.2021
Print Date 16.12.2021
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	:	Acetone
Product Number	:	179124
Brand	:	SIGALD
Index-No.	:	606-001-00-8
REACH No.	:	01-2119471330-49-XXXX
CAS-No.	:	67-64-1

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

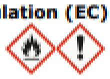
2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008
Flammable liquids (Category 2), H225
Eye irritation (Category 2), H319
Specific target organ toxicity - single exposure (Category 3), Central nervous system, H336

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

Hazard statement(s)

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

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.
P241	Use explosion-proof electrical/ ventilating/ lighting/ equipment.
P242	Use non-sparking tools.
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 information (EU)

EUH066 — Repeated exposure may cause skin dryness or cracking.

Reduced Labeling (<= 125 ml)

Pictogram

Signal word — Danger

Hazard statement(s) — none

Precautionary statement(s) — none

Supplemental Hazard information (EU)

EUH066 — Repeated exposure may cause skin dryness or cracking.

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

Formula : C_3H_6O
Molecular weight : 58,08 g/mol
CAS-No. : 67-64-1
EC-No. : 200-662-2
Index-No. : 606-001-00-8

Component		Classification	Concentration
acetone			
CAS-No. EC-No. Index-No.	67-64-1 200-662-2 606-001-00-8	Flam. Liq. 2; Eye Irrit. 2; STOT SE 3; H225, H319, H336 Concentration limits: >= 20 %: STOT SE 3, H336;	<= 100 %

Personal protective equipment

Eye/face protection
Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Safety glasses

Skin protection
This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN374 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).
Full contact
Material: butyl-rubber
Minimum layer thickness: 0,7 mm
Break through time: 480 min
Material tested:Butoject® (KCL 898)

This recommendation applies only to the product stated in the safety data sheet, supplied by us and for the designated use. When dissolving in or mixing with other substances and under conditions deviating from those stated in EN374 please contact the supplier of CE-approved gloves (e.g. KCL GmbH, D-36124 Eichenzell, Internet: www.kcl.de).
Splash contact
Material: Latex gloves
Minimum layer thickness: 0,6 mm
Break through time: 10 min
Material tested:Lapren® (KCL 706 / Aldrich Z677558, Size M)

Body Protection
Flame retardant antistatic protective clothing.

Respiratory protection
required when vapours/aerosols are generated.
Our recommendations on filtering respiratory protection are based on the following standards: DIN EN 143, DIN 14387 and other accompanying standards relating to the used respiratory protection system.
Recommended Filter type: Filter type AX

The entrepeneur has to ensure that maintenance, cleaning and testing of respiratory protective devices are carried out according to the instructions of the producer. These measures have to be properly documented.

Control of environmental exposure
Do not let product enter drains. Risk of explosion.

SECTION 9: Physical and chemical properties

9.1 Information on basic physical and chemical properties

a) Appearance — Form: clear, liquid

b) Benzene

Sigma-Aldrich.

www.sigmaaldrich.com

SAFETY DATA SHEET

according to Regulation (EC) No. 1907/2006

Version 6.9
Revision Date 25.11.2021
Print Date 16.12.2021
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	:	Benzene
Product Number	:	401765
Brand	:	Sigma-Aldrich
Index-No.	:	601-020-00-8
REACH No.	:	01-2119447106-44-XXXX
CAS-No.	:	71-43-2

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 2), H225
Skin irritation (Category 2), H315
Eye irritation (Category 2), H319
Germ cell mutagenicity (Category 1B), H340
Carcinogenicity (Category 1A), H350
Specific target organ toxicity - repeated exposure (Category 1), Blood, H372
Aspiration hazard (Category 1), H304
Long-term (chronic) aquatic hazard (Category 3), H412

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
Hazard statement(s)	
H225	Highly flammable liquid and vapor.
H304	May be fatal if swallowed and enters airways.
H315	Causes skin irritation.
H319	Causes serious eye irritation.
H340	May cause genetic defects.
H350	May cause cancer.
H372	Causes damage to organs (Blood) through prolonged or repeated exposure.
H412	Harmful to aquatic life with long lasting effects.
Precautionary statement(s)	
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.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P331	Do NOT induce vomiting.
Supplemental Hazard Statements	none

Restricted to professional users.

Reduced Labeling (<= 125 ml)

Pictogram	
Signal word	Danger
Hazard statement(s)	
H340	May cause genetic defects.
H350	May cause cancer.
H372	Causes damage to organs through prolonged or repeated exposure.
H304	May be fatal if swallowed and enters airways.
H412	Harmful to aquatic life with long lasting effects.
Precautionary statement(s)	
P301 + P310	IF SWALLOWED: Immediately call a POISON CENTER/ doctor.
P331	Do NOT induce vomiting.
Supplemental Hazard Statements	none

Personal protective equipment

Eye/face protection
Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU). Safety glasses

Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of Regulation (EU) 2016/425 and the standard EN 374 derived from it.

Full contact
Material: Fluorinated rubber
Minimum layer thickness: 0,7 mm
Break through time: 480 min
Material tested:Vitoject® (KCL 890 / Aldrich Z677698, Size M)

Splash contact
Material: Fluorinated rubber
Minimum layer thickness: 0,7 mm
Break through time: 480 min
Material tested:Vitoject® (KCL 890 / Aldrich Z677698, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the EC approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist

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The life science business of Merck operates as MilliporeSigma in the US and Canada