



Application Note  
CBRNE 1825475

## Detecting Chemical Warfare Agents using the $\mu$ RAID

### Abstract

The personal protection of military personnel against chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) is essential and can only be achieved using reliable, rapid and sensitive detection equipment. The micro Rapid Alarm and Identification Device ( $\mu$ RAID) is a personal detector that has been designed to detect low concentrations (ppb range) of CWAs and TICs rapidly. It provides direct identification of an agent and quantifies the concentration range.

### Introduction

CWAs are classed as weapons of mass destruction and use the toxic properties of the chemicals to disable, injure or kill personnel. The chemicals are classified by their effects on human health into discrete groups; nerve, blister, choking and blood agents. Typical examples and their toxicological characteristics are listed in Table 1.

A period of disarmament started by the end of the cold war; around 1990. The Chemical Weapons Convention (CWC) is the most recent arms control agreement. It outlaws the production, stockpiling and use of chemical weapons with the force of international law. The compliance of the CWC is supervised by the Organization for the Prohibition of Chemical Weapons (OPCW), who were a Nobel Peace Prize winner in 2013. 189 nations signed the convention, covering

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approximately 98 % of the global population [1]. Despite this convention there have still been proven cases of CWAs being used in recent years; for example, in the Iraq War in Abu Sayda in 2007 [2] and in the Syrian civil war around Damascus in 2013 [3]. These examples serve to prove the continued need for military and emergency response personnel to be protected against such threats.

Ion mobility spectrometry (IMS) is well suited for the gas phase detection and identification of hazardous chemicals. Due to the documented advantages of speed and sensitivity, the technique is highly appropriate in personal detection devices where a rapid response is essential. In this Application Note we describe the use of a novel instrument applicable for personal chemical detection in the field.

## Experimental

### Material

CWA standards were kindly provided by the VPO CZ s.p., division VTÚO Brno. The purity of the material was 89.2 to 99.3 % according to the provider.

### Laboratory test

For the determination of detection limits, response and recovery times, analyses were performed on the compact  $\mu$ RAID personal detector in laboratory tests. For this purpose two standard instruments were used in parallel and connected to the GCWA\_2011, a lab type gas device that produces constant and defined agent concentrations at adjustable humidity. The air inlet used bespoke gas tubes connected to the GCWA\_2011. The experimental setup is shown in Figure 1.

All of the tubing that was used for this experiment was made of Teflon as it is chemically inert and the risk of vapour adsorption on to the tube walls is extremely low.

The  $\mu$ RAID is equipped with its own integrated sampling pump that is rated at approximately 20 L·h<sup>-1</sup>. Analyses were carried out at ambient temperature (24 ... 25 °C; 33 °C for VX) and ambient pressure (994 ... 1007 mbar). The humidity in the gas flow was between 12 and 20 % for G agents, 22 and 80 % for HD, respectively.

### Quantitative references for CWAs

The quantitative reference for the agent concentration was taken by sampling the agent containing air from the generator to a Tenax sampling tube (see Figure 1) followed by an analysis by the Ellman enzymatic method [4] and/or gas chromatography pulsed flame photometric detector (GC-PFPD; for organophosphorus compounds), by thymolphthalein (T-135) method [5] and/or GC-PFPD (sulphur mustard) or by gas chromatography mass spectrometry (GC-MS, nitrogen mustard). Tenax tubes were extracted with 2-propanol.

### Software

The Bruker IMS software XIMS plus was used for detailed analyses of the experiments.

### Field test

To show the usability and robustness of the instrument under realistic conditions supplementary outdoor tests were performed in addition to the laboratory test. Field tests were done at the Nevada Test Site in the United States in an open air test region. Chlorine (Cl<sub>2</sub>) was used as CWA test agent and released at IDLH level (Immediately Dangerous to Life or Health, 10 ppm) from a storage cylinder. The purity was stated to be > 99 %. To simulate possible interferences a reference type smoke was released in addition to the test sample from a storage cylinder as well.

## Results

### Detectable agents

The detection capability of the  $\mu$ RAID includes a clear identification of an agent and not only an agent group (e.g. nerve, blister). Identification is achieved by the detection of corresponding agent peaks in the spectra measured in the positive and negative mode. An example IMS spectrum of Soman (GD), exhibiting a monomer dimer system recorded in the positive mode, is shown in

Figure 2. The ratio of the resulting peak areas changes dependent on the agent concentration. At a two peak system (monomer and dimer) the peak area of the monomer decreases and the peak area of the dimer increases with a rising agent input. In general, identification based on a dimer system leads to more reliable detection results.

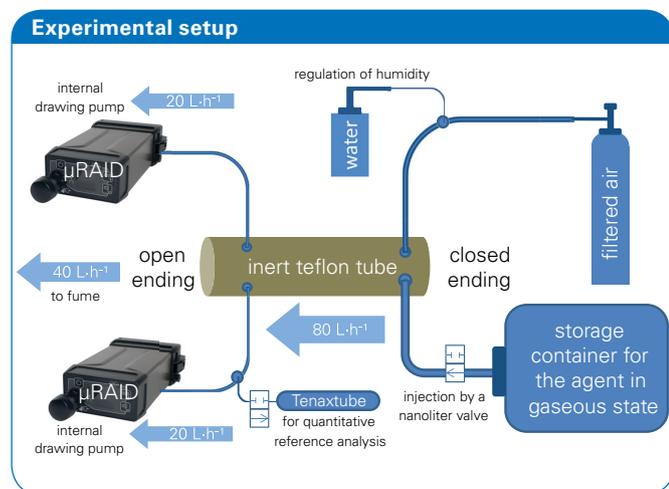


Figure 1: Schematic view of the setup of a gaseous agent supply at defined concentrations (GCWA\_2011 by VPO CZ) and detection by two devices in parallel.

Table 1: Detectable nerve, blister and blood agents and associated toxicological properties and determined alarm limits

Selected detectable agents						
Agent class	Abbr.	Agent name	LC <sub>t<sub>50</sub></sub> <sup>1</sup> [mg·min·m <sup>-3</sup> ] [6, 7, 8]	AEGL 3, <sup>2</sup> 10 min [ppb]	Alarm limit [mg·m <sup>-3</sup> ]	Alarm limit [ppb]
Nerve	GA	Tabun	135	110	≤ 0.05	≤ 7
	GB	Sarin	70	64	≤ 0.05	≤ 9
	GD	Soman	70	25	≤ 0.05	≤ 7
	GF	Cyclosarin	50	53	≤ 0.05	≤ 7
	VX	VX	30	3	≤ 0.05	≤ 5
	VXR	Russian VX	n.d. <sup>3</sup>	n. d.	≤ 0.05	≤ 5
Blister and Blood	HD	Sulphur Mustard	1,500	590	≤ 0.06	≤ 9
	HN	Nitrogen Mustard	1,500	311	≤ 0.03	≤ 4
	L	Lewisite	1,200	453	≤ 0.25	≤ 30
	AC	Hydrogen Cyanide	5,000	27,000	≤ 1	≤ 900

<sup>1</sup>LC<sub>t<sub>50</sub></sub> ... lethal concentration time (The concentration at which a gas kills 50 % of the exposed population)

<sup>2</sup>AEGL 3 ... Acute Exposure Guideline Levels (The airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death)

<sup>3</sup>n. d. ... no data

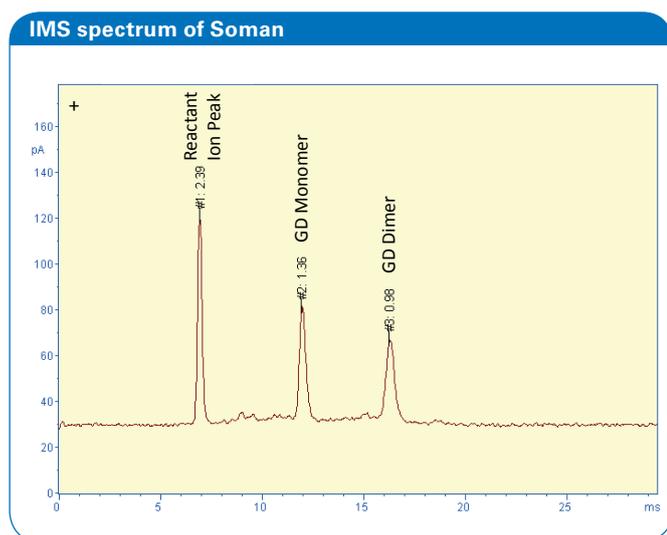


Figure 2: IMS spectrum of GD (80 µg·m<sup>-3</sup>) detected by the µRAID and depicted using the software XIMS plus. At K<sub>0</sub> = 2.39 cm<sup>2</sup>·Vs<sup>-1</sup> the reactant ion peak (RIP) is shown. The characteristic agent peaks are present at 1.36 cm<sup>2</sup>·Vs<sup>-1</sup> (monomer) and 0.99 cm<sup>2</sup>·Vs<sup>-1</sup> (dimer) in the positive mode.

A selection of the CWAs that the µRAID can detect is shown in Table 1. This list is not exhaustive; further substances can be programmed into the integral libraries. In general, detection results are displayed by means of symbols and bar graphs (see Figure 3, left). Up to two detected agents can be displayed simultaneously by bars related to a specific agent concentration range. Additionally, the abbreviated names of the detected agents are given. In the right hand part of the result field a GHS hazard pictogram (Globally Harmonized System of Classification and Labelling of Chemicals) for toxic agents is displayed. Depending on the substance class the concentration bars are colour coded (red = nerve agent, yellow = blister agent, cyan = TICs, magenta = pulmonary and blood agents).

If the response signal does not correspond to any substance in the library so-called "pollution level indicators" display a substance unspecific contamination level. If the pollution level or the increase rate of the pollution level indicator exceeds a predefined threshold level, a pollution alarm is given (cf. Figure 3). Additionally, a warning symbol appears. The purpose of this pollution indicator is to warn the operator that other substances are present that are not contained in the detection library. If a chemical agent is detected the alarm for this agent will be displayed as a priority; despite the presence of a pollution alarm.

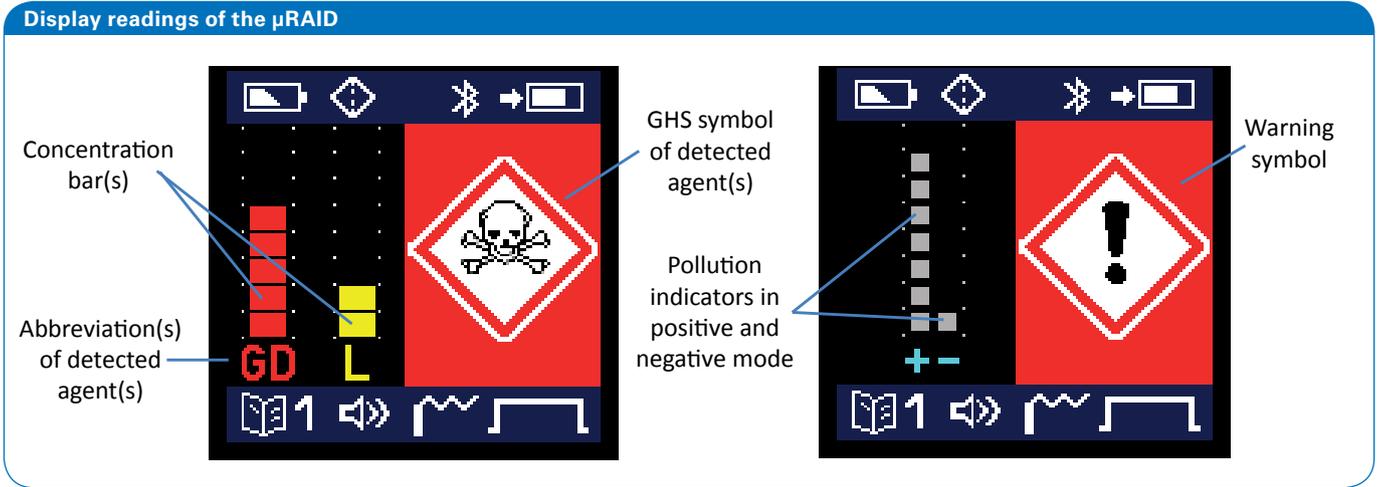


Figure 3: Left: display reading at an alarm of the agents GD and L; right: display reading at a pollution alarm.

### Response and recovery times

Response and recovery times are important parameters that show the true capability of the detection device. Response time is defined as the time elapsed between presence of the substance to be analyzed and the response of the detection system. Recovery time is the amount of time the device needs to get back to a clean status after the sample input has ceased. Low values for both response times and recovery times are essential for effective detection in the field. The aim of a personal detector is to provide an immediate alert and then be ready for the next detection as rapidly as possible.

In Figure 4 examples of the response ( $t_a$ ) and the recovery

time ( $t_b$ ) for GD are depicted. In Table 2 response times for several agents are summarized. For all agents the response time is within seconds. The response to the monomer is faster than to the dimer. Exemplarily a monomer of GD at  $80 \mu\text{g}\cdot\text{m}^{-3}$  can be detected at 23 seconds, the dimer will be detected at 39 seconds. Recovery times are in the range of seconds to a few minutes, depending on the agent and concentration applied; this is substance dependent because different chemical agents exhibit different physical properties.

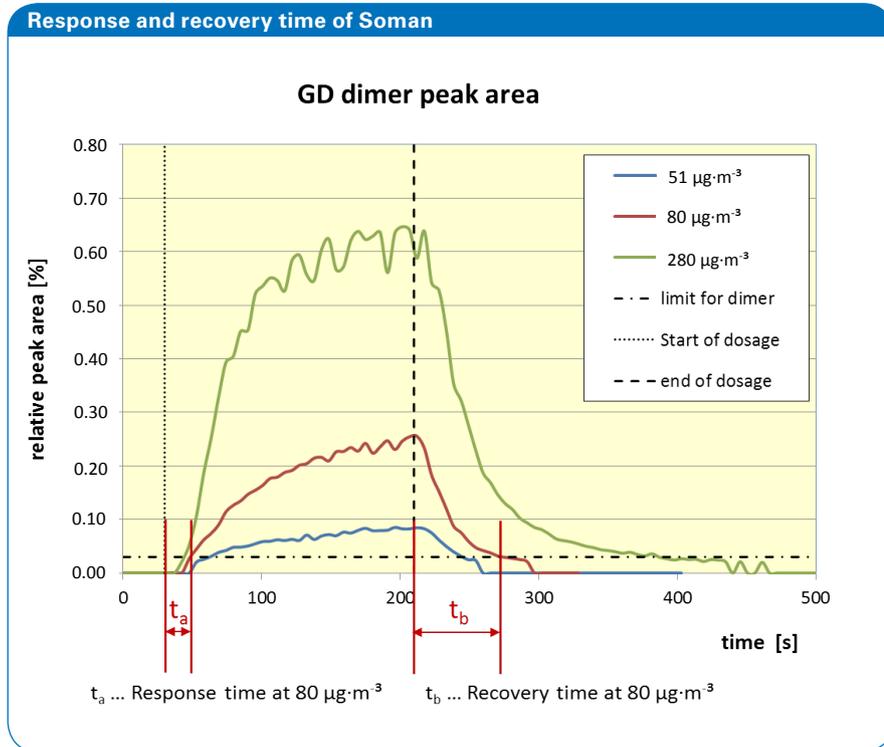


Figure 4: Relative dimer peak area of GD ( $K_0 = 0.99 \text{ cm}^2\cdot\text{Vs}^{-1}$ ) during the agent challenge at three selected concentrations. Response time ( $t_a$ ) and recovery time ( $t_b$ ) are shown for an agent concentration of  $80 \mu\text{g}\cdot\text{m}^{-3}$ .

Table 2: Determined response times for CWAs using the  $\mu$ RAID.

Response times		
Agent	Test concentration [ $\mu\text{g}\cdot\text{m}^{-3}$ ]	Response time [s]
GA	57	26
GB	97	21
GD	80	39
GF	64	50
VX	84	8
HD	104	5
HN	29	23
L	380	39

### Alarm limits

Table 1 details the alarm limits determined for the CWAs based on a dimer system obtained with the experimental setup described in Figure 1. All alarm limits were in the ppb range and are significantly below the AEGL 3, 10 min values (see also Table 1) except for VX. Due to the very low response time of only 8 seconds for VX the detection of this agent in the relevant range can be ensured nevertheless.

Due to the fact that the determination of the alarm limits relies on the detectability of a monomer and a dimer, the real detection limits of the  $\mu$ RAID, based on only monomer identification, are significantly below the alarm limits depicted in Table 1. When very low agent concentrations are expected, a special library based on a monomer identification can be used, albeit that the reliability of the identification result is lowered. Considering the  $\text{LCt}_{50}$  and AEGL 3 values (Table 1) the alarm limits and response times determined demonstrate the extreme suitability of the  $\mu$ RAID as an early warning tool for CWAs in the field.

### Field Test

A field test was conducted to show the capabilities of the  $\mu$ RAID in real conditions. Four instruments were used in parallel arranged to cover almost all areas in a test field. Because of the high toxicity of the aforementioned CWAs the less toxic but quite dangerous TIC Chlorine was released at a level of 10 ppm (AEGL 3, 10 min ... 50 ppm). A picture of the test site is shown in Figure 5. Figure 6 illustrates the test setup and the obtained results. In interference tests (smoke) three out of four instruments

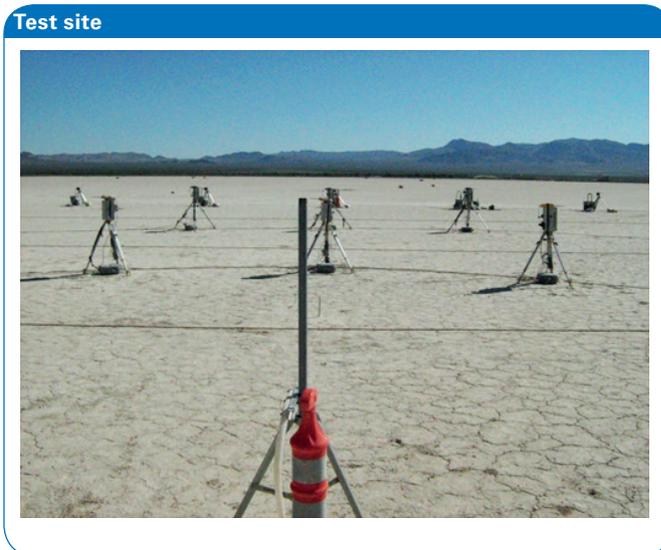


Figure 5: Outdoor testing at the Nevada National Security Site, United States.

gave very good detection results (75 to 100 %). Nevertheless, instrument #3803 gave lower detection alarms than the other instruments (67 and 38 %) and it was concluded that this was due to the position of the detector in the test area. Instrument #3803 was placed somewhat off to the side of the generated cloud. It was concluded that for instrument #3803 not all gas clouds reached its inlet.

### Conclusion

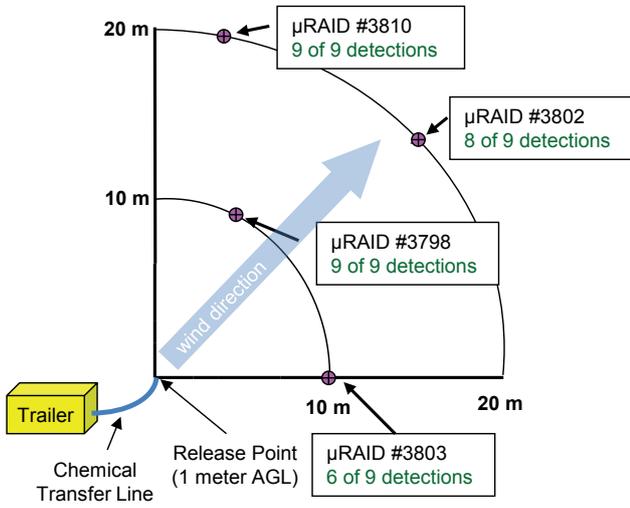
The  $\mu$ RAID is an extremely effective personal chemical detector and can provide essential threat detection in the field. Detection limits are in the ppb level and response times are in the region of a few seconds. Ease of use coupled with a low maintenance requirement make the  $\mu$ RAID highly suitable for all users in combating the threat from CWAs and TICs.

### Acknowledgements

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## Field test setup and obtained results

### Release and detection of Cl<sub>2</sub> without interferences



### Release and detection of Cl<sub>2</sub> with smoke interferences

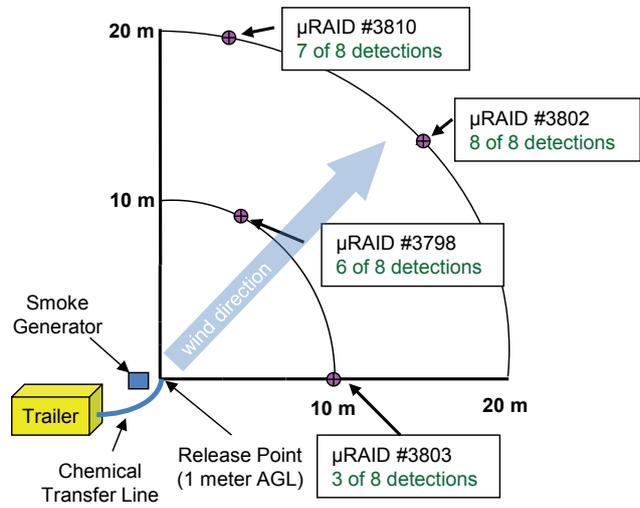


Figure 6: Field test using four instruments, Cl<sub>2</sub> release, left: intake without interferences, right: intake with smoke interferences (AGL ... above ground level).

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