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 (µRAID) 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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- Instrumentation and Software
- Chemical Warfare Agents
- µRAID
- Personal detection
- XIMS plus
- Ion Mobility Spectrometry
The µRAID is equipped with its own integrated sampling pump that is rated at approximately 20 L·h⁻¹. 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 (Cl₂) 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 µRAID 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.
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.

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

<table>
<thead>
<tr>
<th>Agent class</th>
<th>Abbr.</th>
<th>Agent name</th>
<th>(L_{C50}) (^1 ) [mg·min·m(^{-3})] ([6, 7, 8])</th>
<th>AEGL 3 (^2) [10 min [ppb]]</th>
<th>Alarm limit [mg·m(^{-3})]</th>
<th>Alarm limit [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nerve</td>
<td>GA</td>
<td>Tabun</td>
<td>135</td>
<td>64</td>
<td>(\leq 0.05)</td>
<td>(\leq 7)</td>
</tr>
<tr>
<td></td>
<td>GB</td>
<td>Sarin</td>
<td>70</td>
<td>25</td>
<td>(\leq 0.05)</td>
<td>(\leq 7)</td>
</tr>
<tr>
<td></td>
<td>GD</td>
<td>Soman</td>
<td>70</td>
<td>25</td>
<td>(\leq 0.05)</td>
<td>(\leq 7)</td>
</tr>
<tr>
<td></td>
<td>GF</td>
<td>Cyclosarin</td>
<td>50</td>
<td>53</td>
<td>(\leq 0.05)</td>
<td>(\leq 7)</td>
</tr>
<tr>
<td></td>
<td>VX</td>
<td>VX</td>
<td>30</td>
<td>3</td>
<td>(\leq 0.05)</td>
<td>(\leq 5)</td>
</tr>
<tr>
<td>VXR</td>
<td></td>
<td>Russian VX</td>
<td>n. d.(^3)</td>
<td>n. d.</td>
<td>(\leq 0.05)</td>
<td>(\leq 5)</td>
</tr>
<tr>
<td>Blister and Blood</td>
<td>HD</td>
<td>Sulphur Mustard</td>
<td>1,500</td>
<td>590</td>
<td>(\leq 0.06)</td>
<td>(\leq 9)</td>
</tr>
<tr>
<td></td>
<td>HN</td>
<td>Nitrogen Mustard</td>
<td>1,500</td>
<td>311</td>
<td>(\leq 0.03)</td>
<td>(\leq 4)</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>Lewisite</td>
<td>1,200</td>
<td>453</td>
<td>(\leq 0.25)</td>
<td>(\leq 30)</td>
</tr>
<tr>
<td></td>
<td>AC</td>
<td>Hydrogen Cyanide</td>
<td>5,000</td>
<td>27,000</td>
<td>(\leq 1)</td>
<td>(\leq 900)</td>
</tr>
</tbody>
</table>

\(^1\)LC\(_{50}\) … lethal concentration time (The concentration at which a gas kills 50 % of the exposed population)

\(^2\)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)

\(^3\)n. d. … no data

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.

![IMS spectrum of Soman](image-url)
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 µg·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.
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 µRAID, 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 LC_{50} and AEGL 3 values (Table 1) the alarm limits and response times determined demonstrate the extreme suitability of the µRAID as an early warning tool for CWAs in the field.

Field Test

A field test was conducted to show the capabilities of the µRAID 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 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 µRAID 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 µRAID highly suitable for all users in combating the threat from CWAs and TICs.

Acknowledgements

Measurements of CWAs were done with the kind support of VPO CZ, division VTÚO Brno. Measurements of TICs in field tests at the Nevada National Security Site were done with the kind support of the U.S. Department of Homeland Security, Science and Technology Directorate, Chemical and Biological Defense Devision.

Table 2: Determined response times for CWAs using the µRAID.

<table>
<thead>
<tr>
<th>Agent</th>
<th>Test concentration [µg∙m^{-3}]</th>
<th>Response time [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA</td>
<td>57</td>
<td>26</td>
</tr>
<tr>
<td>GB</td>
<td>97</td>
<td>21</td>
</tr>
<tr>
<td>GD</td>
<td>80</td>
<td>39</td>
</tr>
<tr>
<td>GF</td>
<td>64</td>
<td>50</td>
</tr>
<tr>
<td>VX</td>
<td>84</td>
<td>8</td>
</tr>
<tr>
<td>HD</td>
<td>104</td>
<td>5</td>
</tr>
<tr>
<td>HN</td>
<td>29</td>
<td>23</td>
</tr>
<tr>
<td>L</td>
<td>380</td>
<td>39</td>
</tr>
</tbody>
</table>
Field test setup and obtained results

Figure 6: Field test using four instruments, Cl₂ release, left: intake without interferences, right: intake with smoke interferences (AGL … above ground level).

References


[5] F. M. Issa, H. Z. Youssef & R. M. Issa (1975); Spectrometric determination of bis(2-chloroethyl) sulfide (sulph mustard HD) and tris(chloroethyl) amine (nitrogen mustard HN) using thymolphthalein; Egypt J Chem. 18 (2): 257-64


[8] www.armystudyguide.com