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Testing of Commercially Available Detectors  
Against Chemical Warfare Agents:  
Summary Report

Terri L. Longworth  
Juan C. Cajigas  
Jacob L. Barnhouse  
Kwok Y. Ong  
Suzanne A. Procell

February 1999

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Soldier and Biological Chemical Command, AMSSB-REN, Aberdeen Proving Ground, MD  
21010-5424

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| 13. ABSTRACT (Maximum 200 words)<br>Five commercial detector types including photoionization, flame ionization, and colorimetric detector tubes, were tested against HD, GB and GA vapor at various conditions. These detectors were also challenged with potential interferent vapors. This summary report characterizes the chemical warfare (CW) agent detection potential of these detectors. It is intended to provide the emergency responders concerned with CW agent detection an overview of these detectors' characteristics based on results of the evaluation. .   |   |  |  |  |
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## Preface

The work described herein was authorized under the Expert Assistance (Equipment Test) Program for the U. S. Army Soldier and Biological Chemical Command (SBCCOM) Program Director for Domestic Preparedness.

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## Testing of Commercially Available Detectors against Chemical Warfare Agents: Summary Report

### 1. INTRODUCTION

In 1996, responding to Public Law 104 - 201, the Department of Defense (DOD) formed the Domestic Preparedness Program. One of the objectives is to enhance federal, state and local capabilities to respond to NBC terrorism incidents. Emergency responders who encounter a contaminated or potentially contaminated area must survey the area for the presence of toxic or explosive vapors. The vapor detectors commonly used are not designed to detect and identify chemical warfare (CW) agents.

Little data are available concerning the ability of these most commonly used commercially available detection devices to detect CW agents. The U.S. Army Soldier and Biological Chemical Command (SBCCOM) established a program to address this need.

This report is an overview of the evaluation of the detectors listed in Table 1 using representative CW agents. It is primarily intended for emergency response organizations and managers concerned with detecting CW agents and other hazardous vapors. The report presents abbreviated descriptions of test procedures and results, and attempts to identify capabilities and weaknesses of the items. The Design Evaluation Laboratory (DEL) at Aberdeen Proving Ground, Edgewood, Maryland, performed all work. Detailed test reports will be issued separately.

Table 1 lists the different models of detectors and two types of colorimetric tubes described and selected for use in this test. This was based on a Battelle Memorial Institute (BMI) survey<sup>1</sup>, which identified the detectors likely to be used by the local responders in the event of a terrorist incident involving CW agent(s) in the Baltimore vicinity.

**Table 1. Chemical Detectors Tested**

| Detector Name                     | Manufacturer              | Detector Type                       | Short Name     |
|-----------------------------------|---------------------------|-------------------------------------|----------------|
| MiniRAE Plus                      | RAE Systems, Inc.         | Photoionization (10.6eV PID)        | RAE            |
| Passport II Organic Vapor Monitor | Mine Safety Appliance Co. | Photoionization (11.7eV PID)        | Passport       |
| Model PI-101 Trace Gas Analyzer   | HNU Systems, Inc.         | Photoionization (11.7eV PID)        | HNU            |
| TVA 1000B Toxic Vapor Analyzer    | Foxboro Company           | Photoionization (10.6eV PID)        | TV PID         |
| TVA 1000B Toxic Vapor Analyzer    | Foxboro Company           | Flame Ionization (FID)              | TV FID         |
| Phosphoric Acid Ester Tubes       | Draeger Corp.             | Colorimetric Tubes for nerve agents | Draeger Tube-P |
| Thioether Tubes                   | Draeger Corp.             | Colorimetric Tubes for HD detection | Draeger Tube-T |

The MiniRAE Plus was tested in place of the Mini-FID from Perkin Elmer that was identified in the BMI survey. Mini-FID was not included in this round of testing because of a delay in delivery, but will be tested in a follow-on program in FY99. Two units of each model were tested under each condition. Detectors with the highest available voltage PID lamps (10.6 and 11.7 eV) were chosen in an attempt to provide sufficient ionization energy needed for detecting the CW agents, if possible.

<sup>1</sup> Battelle Memorial Institute, CBIAC Task 252, Effect of Emergency Responder Chemical Detection Equipment for the Detection of Chemical Warfare Agents Study, 17 July 1997.



The detection devices tested were new and evaluated in the "as received" condition. No attempt was made to optimize their chemical agent detection capability. This evaluation is limited to measurement of their CW agent detection performance using Tabun (GA), Sarin (GB), and Mustard (HD) as representative agents. No pre-test theoretical assessment was made on any of the items except to learn their operating procedures using the manuals provided with the detectors. Conclusions are based solely on the results of the detector responses to CW challenges during this test. No other aspects of the test items were investigated.

## **2. TEST PROCEDURES**

The objective of this testing is to screen the different detection devices currently being used by some first responder organizations for their ability to detect chemical warfare agent vapors. The approach was to seek the concentration level where a detection signal is indicated for the respective agent. It was impractical to cover every conceivable agent and condition. Conditions were selected to include the assessment of temperature, humidity, and concentration effects. Each observation was confirmed with repeated trials.

### **2.1 CALIBRATION:**

Each detector was started and stabilized, then calibrated before each use according to the instructions provided with the respective instrument. Calibration included adjusting the detector baseline using the "zero" air, then challenging the detector with the calibration gas, then adjusting the detection span so that the display reflected the concentration of the calibration gas used. Isobutylene and methane were used at 100 PPM concentration for calibrating the PID and FID detectors, respectively. The detectors drew samples from Mylar sample bags filled with the zero air or the appropriate calibration gas. The detector was allowed to sample until its reading stabilized. The detector response was adjusted to reflect the known concentration of the calibration gas. Once adjusted, the detector was considered calibrated and ready for testing.

### **2.2 AGENT SENSITIVITY:**

The detectors were each tested with the agents GA, GB and HD with different concentration levels at the 20°C ( $\pm 2^\circ$ ) and 0% relative humidity condition (measurement tolerance 2%) in an attempt to determine the minimum detectable level (MDL) and to establish a response curve. The detectors were also tested at different temperatures and relative humidities to observe the temperature and humidity effects. The Multipurpose Chemical Agent Vapor Generation System<sup>2</sup> (Vapor Generator) was used. Figure 1 is a flow schematic of the vapor generation system. The generator system permits preconditioning of the detector with humidity and temperature conditioned air prior to challenging it with similar air containing the CW agent. This corrects for any potential influence of a different background air condition. Occasionally, the detectors were rechecked with the 100 PPM calibration gas after the detector had cleared, after the agent challenges, to observe residual effects and/or calibration drift

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<sup>2</sup> Ong, Kwok Y., Multi-Purpose Chemical Agent Vapor Generation System, ERDEC-TR-424, Aberdeen Proving Ground, MD, July 1997.

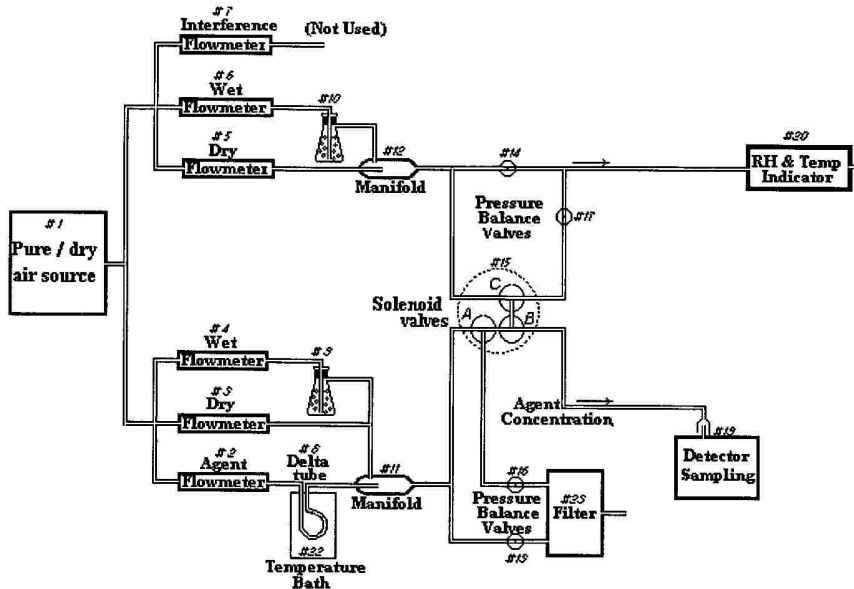


Fig. 1 Basic Agent Generator

Agent sensitivity testing began after the detector had been calibrated. The detectors were preconditioned at the specific temperature and humidity prior to challenging with agent. The agent challenge was generally 1 to 5 minutes, or more, to allow time for the maximum detector response at each condition. Agent challenge occurs when the solenoids are energized to switch the air streams from conditioning air only to similarly conditioned air containing the agent. The long exposure times were used to observe the different detection characteristics for the different detector types. Each detector was tested three times under each condition. The detectors clear down times were also measured after the agent challenge was stopped.

The colorimetric tubes (Draeger Tubes) were tested according to the directions provided with the respective tubes. The agent vapor was drawn directly from the vapor generator into the prepared tube using the bellow pump provided with the tubes. The tubes were activated as directed and color development was observed.

The phosphoric acid ester tube normally changes from yellow to pink when functioned after exposure to nerve agent. If it has been exposed to a detectable level of GA or GB, the pink color persists longer than 60 seconds. The pink color becomes more intense and persists longer with increased agent concentration. Blank tests were run as references by using the Draeger Tubes to sample the generator's conditioned air without agent at the different temperature and humidity conditions. The pink color faded within 60 seconds on blank tests. The threshold detection limit was determined by the observable color change to pink which persisted longer than 60 seconds.

The thioether tube will form an orange color band on the yellow portion of the tube when exposed to detectable levels of HD. The color intensity increases with increased concentration. The threshold detection limit was determined by the observable appearance of the orange color

band. Blank tests were also run using the generator's conditioned air output at the different temperature and humidity conditions as references. No color change was observed on blank tests.

### 2.3 RELATIVE HUMIDITY EFFECTS

The effects of relative humidity (RH) and air temperature on the sensitivity of the detectors were observed during tests using agent concentrations that were higher than the previously determined MDL listed in Table 2. The tests were conducted at air temperatures of 0°C, 20°C and 40°C with RH values of 0%, 50% and 90%, not to exceed the operating range of the detectors. Two units of each detector type were tested three times each at the different conditions. The detectors were placed in the environmental temperature chamber for temperature conditioning. Each detector was started and calibrated within the chamber using the calibration gas delivered from the sample bag. Conditioned air at the desired temperature and humidity from the vapor generator system was sampled to establish the "background reading" for air at that condition. Then the detector sampled the similar temperature and humidity controlled test air containing the prescribed concentration of chemical agent when the generator's solenoids were activated. The concentration measurement reported by the detector in PPM was recorded and converted into a Response Factor (RF) by dividing the actual agent concentration in the test air (in PPM) by the "net detector reading". The net detector reading is the detector reading minus the detector background reading.

Similarly, the Draeger tubes were placed in the chamber for temperature conditioning before they were tested. Both blanks and agent challenges took place in the temperature environment within the chamber for all cases except ambient temperatures. Draeger Tubes, which differ from the other detectors, were tested to seek their respective detection limits at the different conditions by observation of tube color changes.

### 2.4 FIELD INTERFERENCE

After the Agent Sensitivity tests, the units were qualitatively tested outdoors in the presence of common potential interferents such as gasoline, diesel fuel, jet propulsion fuel (JP8), kerosene, ethylene glycol anti-freeze, AFFF liquid (Aqueous Film Forming Foam used for fire fighting) and household chlorine bleach vapors. Vapor from a 10% HTH slurry (chlorinating CW agent decontaminant), engine exhausts, burning fuels and other burning materials were also tested. These were not laboratory tests but field experiments involving open containers, truck engines and fires producing smoke plumes which were sampled by the detectors placed at various distances downwind. Distances were chosen to obtain reasonable exposures for each detector. For example, 1-2 meters for fumes and 5-10 meters for smokes. Detectors were calibrated at the beginning of each testing day, not after every exposure. No attempt was made during the day to determine the degree of cleanliness of the detectors in the field. Testing continued using the next interferent when the detector display reading stabilized at approximately zero. The two units of each detector model and detector tubes were tested once with each interferent.

## 2.5 LABORATORY INTERFERENCE

This substest was used to show the CW agent detection capability of the detection devices in the presence of high concentrations of potential interferent vapors. Diesel and AFFF were chosen as representative interferents because of the likelihood of their presence during an emergency response by fire fighters.

The colorimetric tubes were also tested against a "1% concentration" of air saturated with the vapor of gasoline, JP8, household chlorine bleach, Windex, Spray 9 cleaner, floor wax, and 25 PPM ammonia (NH<sub>3</sub>) to observe potential interference with the detection reaction process.

To prepare the interferent test gas mixture, dry air at 20°C was saturated with interferent vapor by passing it through the interferent liquid in a bubbler or by passing it over the liquid in a tube. Thirty milliliters of this vapor saturated air was then mixed with 2.7 liters of either the conditioned air or the conditioned air containing agent from the agent generator to produce the "1% concentration" of interferent.

## 3. TEST RESULTS

### 3.1 AGENT SENSITIVITY

Agent sensitivity tests were conducted as described in section 2.2. The generated agent vapor was quantified by manual sample collection methodology using the Miniature Continuous Air Monitoring System (MINICAMS) equipped with a flame photometric detector (FPD). The system collects the air sample by adsorbing the CW agent onto the solid sorbent contained in a glass tube referred to as the pre-concentrator tube (PCT). The PCT is placed in the MINICAMS where the concentrated sample is heat desorbed into a gas chromatographic capillary column for subsequent separation, identification, and quantification. To eliminate potential loss of sample through sampling lines and the inlet assembly, the sampling method of the MINICAMS was modified to manual sample collection directly into the PCT.

The PCT is removed from the MINICAMS during its sample cycle and connected to a suction source to draw the vapor sample from the generator. The PCT is then re-inserted into the MINICAMS for analysis. The vapor concentration is derived based on the sample volume and the amount of agent found in the sample by comparing to a standard curve of calibrations using known concentrations. The calibration of the MINICAMS is completed daily for the appropriate agents.

Table 2 shows the minimum detectable level (MDL) of each agent determined for each detector type for vapor conditioned at the 20°C temperature and zero percent relative humidity (RH). The zero RH condition was used to establish the MDL because the detector calibration was done using zero gas. The concentrations are expressed in both mg/m<sup>3</sup> and parts per million (PPM) in parentheses, because the agent mixtures are analyzed in units of mg/m<sup>3</sup>, but the detectors display units of PPM. The values shown are the representative values recorded from both detectors of each type. The MDL expressed here represents a detector display of approximately 1 PPM. In the table, the concentration identified as 'No Response' means that the

detector was tested up to the given concentration with no response. Some detectors showed sub-PPM indications that could be construed as a “detection” but their responses remained less than 1 PPM even at the highest agent concentrations tested. Those results are identified in the table with footnote, "Minimal response to concentrations up to this level".

**Table 2. Minimum Detectable Levels (20°C and 0% RH)**

| Agent | Detector Type and MDL, mg/m <sup>3</sup> (PPM) |                        |            |                        |                        |                          |               |
|-------|--|------------------------|------------|------------------------|------------------------|--------------------------|---------------|
|       | MiniRAE Plus                                   | Passport II            | HNU PI-101 | TVA 1000B<br>PID       | TVA 1000B<br>FID       | Draeger Tubes            |               |
|       |  |                        |            |                        |                        | Phosphoric Acid<br>Ester | Thioether     |
| HD    | 1.7 (0.26)                                     | 12.8 (1.94)            | 2 (0.3)    | 1.9 (0.29)             | 28 (4.27) <sup>a</sup> | No Capability            | 4.0 (0.6)     |
| GA    | 3.4 (0.50)                                     | 22 (3.23) <sup>b</sup> | 4.5 (0.67) | 4.1 (0.61)             | 4.1 (0.61)             | 0.01 (0.002)             | No Capability |
| GB    | 65 (11.2) <sup>b</sup>                         | 65 (11.2) <sup>a</sup> | 5 (0.86)   | 26 (4.46) <sup>b</sup> | 3.5 (0.60)             | 0.02 (0.003)             | No Capability |

<sup>a</sup> No response to concentrations up to this level

<sup>b</sup> Minimal response to concentrations up to this level

### 3.2 RELATIVE HUMIDITY EFFECTS:

Table 3 presents the range of response factor (RF) values calculated at each temperature and humidity condition for the detectors using the formula shown below. RF is an indication of the relative sensitivity of the detector to concentrations of the compound vapor at each condition as compared to the calibration gases used. It is used to enable the instrument to display the correct agent concentration reading when entered into its memory. Or, it could be used in determining the actual concentration of the “compound of interest” detected from the detector’s display.

$$\text{Response Factor} = \frac{(\text{Actual Challenge Concentration})}{(\text{Detector Reading}) - (\text{Background Reading})}$$

The RF values listed in Table 3 represent the results of multiple challenges of both test units of each model of detector at different agent concentrations and conditions. Ideally, the RF values for a given detector model should be similar and the lower the RF, the more sensitive the detector. In general it is acceptable to use a detector when RF values are less than 10. However, these detectors responded to CW agents differently than to the calibration gas, and exhibited wide ranges of RF values. Results consolidated in Table 3 reflect the wide ranges of RFs observed at different concentrations for the detectors tested. It presents the highest and the lowest RF calculated for each test. Negative values occurred when the background reading was greater than the reading observed during agent challenge. The NR (No Response) reading in the high RF column means the detector failed to respond at tested concentrations. Essentially, this gives a value of zero for the denominator of the RF equation causing the RF to go to infinity.

**Table 3. Range of Response Factors (RF) at Various Conditions**

| Agent | Temp., °C | Relative Humidity, % | MiniRAE Plus |            | Passport II |            | HNU PI-101 |            | TVA 1000B (PID) |            | TVA 1000B (FID) |            |
|-------|-----------|----------------------|--------------|------------|-------------|------------|------------|------------|-----------------|------------|-----------------|------------|
|       |           |                      | Lowest RF    | Highest RF | Lowest RF   | Highest RF | Lowest RF  | Highest RF | Lowest RF       | Highest RF | Lowest RF       | Highest RF |
| HD    | 20        | 0                    | 0.35         | 0.86       | .92         | NR         | -1.51      | 0.38       | 0.28            | 0.64       | 17.99           | NR         |
| HD    | 20        | 50                   | 0.55         | 1.21       | 1.10        | NR         | 0.42       | 0.71       | 0.57            | 1.24       | 0.59            | 1.46       |
| HD    | 20        | 90                   | 0.48         | 1.29       | -5.54       | 2.22       | -0.15      | 0.38       | -1.06           | 1.10       | 0.51            | 1.02       |
| HD    | 0         | 0                    | 0.76         | 0.93       | 1.65        | NR         | 0.24       | 0.35       | -0.09           | 0.58       | 1.37            | 1.92       |
| HD    | 40        | 0                    | 0.43         | 0.48       | 0.75        | 1.13       | Failed cal | Failed cal | 0.39            | 0.48       | 0.76            | 0.91       |
| GA    | 20        | 0                    | .74          | NR         | 32.94       | NR         | 0.49       | 1.11       | 0.37            | 1.45       | 0.41            | 1.52       |
| GA    | 20        | 50                   | .83          | NR         | NR          | NR         | .52        | NR         | 0.96            | 1.42       | 0.55            | 0.71       |
| GA    | 20        | 90                   | 0.76         | 0.84       | NR          | NR         | NR         | NR         | -2.33           | 1.63       | 0.41            | 0.65       |
| GA    | 0         | 0                    | 0.55         | 0.70       | NR          | NR         | 0.5        | 0.77       | 1.01            | 1.01       | 1.26            | 2.02       |
| GA    | 40        | 0                    | 0.84         | 1.02       | 5.42        | 13.55      | Failed cal | Failed cal | 0.91            | 1.12       | 0.62            | 0.81       |
| GB    | 20        | 0                    | 2.23         | NR         | 27.90       | NR         | .99        | NR         | 2.61            | 15.02      | 0.27            | 0.65       |
| GB    | 20        | 50                   | 3.32         | 3.32       | NR          | NR         | 0.51       | 2.53       | 11.25           | 50.64      | 0.46            | 0.57       |
| GB    | 20        | 90                   | NR           | NR         | 1.91        | 2.61       | 0.07       | 0.27       | -254.1          | -1.28      | 0.33            | 0.48       |
| GB    | 0         | 0                    | 2.31         | 5.8        | NR          | NR         | 1.07       | 2.14       | -2.18           | 11.20      | 0.56            | 0.75       |
| GB    | 40        | 0                    | 9.75         | 18.71      | 9.35        | NR         | 1.89       | 3.15       | 17.05           | NR         | 0.59            | 0.75       |

NR = No response = division by zero = infinity  
 Failed cal = Detector would not calibrate correctly

The Draeger Tube results are shown in Table 4 which lists the threshold CW agent detection level observed for each CW agent at the different temperature and RH conditions listed. These colorimetric tubes performed consistently well under all conditions.

**Table 4. Temperature and Humidity Effects on Detection Limits of Draeger Tubes**

| Agent | Temperature Condition °C | Relative Humidity % | Thioether, mg/m <sup>3</sup> (PPM) | Phosphoric Acid Ester, mg/m <sup>3</sup> (PPM) |
|-------|--------------------------|---------------------|------------------------------------|--|
| HD    | 20                       | 0                   | 4.0 (0.6)                          | No Capability                                  |
| HD    | 20                       | 90                  | 3.3 (0.5)                          |  |
| HD    | 0                        | 0                   | 4.0 (0.6)                          |  |
| HD    | 40                       | 0                   | 4.7 (0.7)                          |  |
| GA    | 20                       | 0                   | No Capability                      | 0.01 (0.002)                                   |
| GA    | 20                       | 90                  |                                    | 0.02 (0.003)                                   |
| GA    | 0                        | 0                   |                                    | 0.01 (0.002)                                   |
| GA    | 40                       | 0                   |                                    | 0.02 (0.003)                                   |
| GB    | 20                       | 0                   | No Capability                      | 0.02 (0.003)                                   |
| GB    | 20                       | 90                  |                                    | 0.03 (0.005)                                   |
| GB    | 0                        | 0                   |                                    | 0.01 (0.002)                                   |
| GB    | 40                       | 0                   |                                    | 0.02 (0.003)                                   |

### 3.3 FIELD INTERFERENCE

Upon completion of the agent sensitivity tests, the detectors were tested against potential interference from commonly found substances under field conditions. These tests were conducted in M-Field at the Edgewood Area of Aberdeen Proving Ground. The interferents were disseminated upwind of the detectors in an open field. The ranges of detector readings recorded during the exposure are presented in Table 5. It should be noted that the concentration of the

interferent cloud reaching the detectors fluctuated with wind direction and velocity. Therefore, the detector readings should only be considered an indication of the qualitative effect of the interferents on the detectors. To avoid excessive contamination of the detectors, many of the burning material smokes were not tested.

The ambient temperature and relative humidity levels during these tests were in the range of 83-92°F and 49-79%RH with gentle wind. The detector readings reported in Table 5 are corrected by subtracting the background reading obtained for the ambient air away from the interferent plume, hence the negative values for some conditions.

**Table 5. Field Interference Testing Summary**

| Interferent               | Detector Readings, PPM |             |                                    |              |              |                            |
|---------------------------|------------------------|-------------|------------------------------------|--------------|--------------|----------------------------|
|                           | RAE                    | Passport    | HNU                                | TV PID       | TV FID       | Draeger Tubes <sup>a</sup> |
| Gasoline Exhaust, at Idle | No Response            | No Response | No Response                        | No Response  | No Response  | Not Tested                 |
| Gasoline Exhaust, Revved  | 23 to 24               | 25 to 29    | No Response                        | 27 to 29     | 64 to 86     | Negative                   |
| Diesel Exhaust, Revved    | No Response            | No Response | -2 to 0                            | -1.7 to +1.0 | 0.47 to 0.66 | Negative                   |
| Gasoline Vapor            | 300 to 316             | 2000        | All Detectors have strong Response |              |              | Not Tested                 |
| Burning Gasoline Smoke    | Not Tested             | Not Tested  | Not Tested                         | Not Tested   | Not Tested   | Negative                   |
| Diesel Vapor              | No Response            | No Response | No Response                        | -0.1 to +0.2 | -1 to +4     | Not Tested                 |
| Burning Diesel Smoke      | Not Tested             | Not Tested  | Not Tested                         | Not Tested   | Not Tested   | Negative                   |
| JP8 Vapor                 | 2.4 to 3.3             | 12 to 28    | 0 to 2                             | 12 to 13     | 43 to 50     | Negative                   |
| Burning JP8 Smoke         | Not Tested             | Not Tested  | Not Tested                         | Not Tested   | Not Tested   | Negative                   |
| Burning Wood Fire Smoke   | 0 to 4.5               | 0 to 0.4    | 0 to 4                             | 0.2 to 0.5   | 0.3 to 0.53  | Negative                   |
| Doused Wood Fire Smoke    | 10 to 11.4             | 3.9 to 4.8  | 0 to 5                             | 7            | 18 to 90     | Negative                   |
| Kerosene Vapor            | 0 to 3.8               | 4 to 5.7    | 0 to 4                             | 3            | 9 to 10      | Negative                   |
| Burning Kerosene Smoke    | Not Tested             | Not Tested  | Not Tested                         | Not Tested   | Not Tested   | Negative                   |
| Diluted AFFF Vapor        | No Response            | No Response | No Response                        | No Response  | No Response  | Negative                   |
| Bleach Vapor              | No Response            | No Response | No Response                        | No Response  | No Response  | Negative                   |
| 10% HTH Vapor             | No Response            | No Response | No Response                        | No Response  | No Response  | Negative                   |
| Burning Cardboard Smoke   | 0.3 to 0.4             | No Response | No Response                        | No Response  | 2.6 to 4.9   | Negative                   |
| Burning Cloth Smoke       | 1.3 to 2.5             | 0 to 1.3    | No Response                        | No Response  | 6.7 to 7     | Negative                   |
| Burning Tire Smoke        | 0.5 to 0.9             | 0.1 to 0.5  | No Response                        | 1.4 to 2.1   | 3.1 to 6.3   | Negative                   |

<sup>a</sup>Negative Draeger Tube reading means no persistent color change.

### 3.4 LABORATORY INTERFERENCE

None of the detectors would calibrate correctly after the field tests. All detectors required disassembling and cleaning before they could be properly calibrated in order to continue laboratory testing. However, after the first series of Laboratory Interference testing, they failed the routine calibration once again. The interferents appear to adversely affect the sensitivity of the detectors. Table 6 presents the results of testing the detectors and the Draeger Tubes with conditioned air containing HD or GB and/or one percent by volume of 20°C air saturated with diesel fuel vapor or AFFF vapor. The test was truncated before all combinations of detectors, interferents and concentrations were tried because of the extensive time required to clean the detectors after each test and the overall erratic readings from the detectors.

Testing continued using only the Draeger tubes for the completion of the interference screenings. Neither the P nor T tubes showed any positive reaction to the interferent vapors tested. The laboratory interferents used were as follows: 1% saturated vapor of diesel, AFFF, gasoline, JP8, household chlorine bleach, Windex, Spray 9 cleaner, and floor wax vapor, and ammonia vapor (NH<sub>3</sub>) at 25 PPM.

**Table 6. Results of Laboratory Interference Tests with Agents**

| Chemical Agent and Concentration, mg/m <sup>3</sup> (PPM) | Interferent, 1% of Saturation | Detector Reading, PPM <sup>a</sup> |            |            |            |            | Indication <sup>b</sup> |            |
|---|-------------------------------|------------------------------------|------------|------------|------------|------------|-------------------------|------------|
|   |                               | RAE                                | Passport   | HNU        | TV PID     | TV FID     | Draeger Tubes           |            |
|   |                               |                                    |            |            |            |            | P                       | T          |
| HD at 8.3 (1.25)  | Diesel Vapor                  | 0                                  | 1.8        | 3.5        | 2.5        | 1.9        | Not Tested              | Not Tested |
| No Agent  | Diesel Vapor                  | 0                                  | 0          | 0.7        | 0.4        | 1.0        | Negative                | Negative   |
| HD at 8.3 (1.25)  | AFFF Vapor                    | 0                                  | 0          | 3.2        | 2.5        | 1.1        | Not Tested              | Not Tested |
| No Agent  | AFFF Vapor                    | 0                                  | 0          | 0          | 0          | 0          | Negative                | Negative   |
| HD at 5.1 (0.77)  | Diesel Vapor                  | Not Tested                         | Not Tested | Not Tested | Not Tested | Not Tested | Negative                | Positive   |
| HD at 5.1 (0.77)  | AFFF Vapor                    | Not Tested                         | Not Tested | Not Tested | Not Tested | Not Tested | Not Tested              | Positive   |
| GB at .03 (0.005)   | None                          | Not Tested                         | Not Tested | Not Tested | Not Tested | Not Tested | Positive                | Negative   |
| GB at .03 (0.005)   | Diesel Vapor                  | Not Tested                         | Not Tested | Not Tested | Not Tested | Not Tested | Positive                | Not Tested |
| GB at .03 (0.005)   | AFFF Vapor                    | Not Tested                         | Not Tested | Not Tested | Not Tested | Not Tested | Positive                | Not Tested |

<sup>a</sup>(Corrected Reading) = (Detector Reading) – (Background Reading)

<sup>b</sup>Negative Draeger Tube reading means no persistent color change.

#### 4. DISCUSSION

The PID and FID detectors were tested under varied temperature and humidity conditions to assess their responses. No consistent response factor for any detector could be determined. All detectors developed symptoms of contamination that seemed to cause the erratic detection of the CW agents tested.

The required calibration of the detectors before use was believed to have caused the differences in observed response factors for the CW agents. The calibration process re-established the sensitivity of the detector using the highly volatile span gases. The different response factors observed indicated that these detectors responded differently to CW agent than to the calibration gases, perhaps due partly to the volatility differences.

Occasionally, the detectors were rechecked with the calibration gas after the agent challenges to observe residual effects and/or calibration drift. The responses usually were somewhat lower than the initial calibrated values. This suggests that the detector sensitivity may have been degraded by exposure to the CW agent vapor.

A malfunctioning MiniRAE unit was disassembled and cleaned when it failed to respond to the calibration gas during calibration. The detector functioned normally after a thorough cleaning. While cleaning the RAE, it was noticed that the lamp surface was clouded. The other PID detectors were then inspected and all detectors showed similar cloudiness. All PID and FID detectors (lines, lamps, or lenses) were then cleaned. After the cleaning, the detectors functioned properly using the appropriate calibration gas.



The fact that these detectors required frequent cleaning even when operated in the clean laboratory environment indicates that the detectors would require more frequent cleanings when operated in the damp, dusty, and smoky field environments common during emergency response situations such as highway spills, railroad accidents, fires and explosions. Detection capability, if CW agents were also present, would be questionable. It appears that the CW agent vapors in combination with the humidity also coated the lamp surfaces. This affects the sensitivity of the detector. These changes in sensitivity were masked by the repeated calibration and sensitivity adjustments using the highly volatile calibration gas. Consequently, responses to the less volatile CW agent vapor varied. Test results confirmed what was stated in the operational manuals provided by the manufacturers that many compounds, as well as, moisture and oxygen will quench the PID signal causing the instrument to under report the vapor concentration.

The erratic behavior of these detectors could also have resulted from performing calibrations using bottled air with zero humidity and then testing the detectors at higher humidity. The response factor obtained for a given set of tests varied even between the two test units of the same detector type. Negative response factors were observed at high RH conditions when the background readings were higher than the readings from the CW agent challenges.

The failure of the detectors in the calibration process after the agent sensitivity tests, field interference tests, and interference testing in the laboratory, plus the wide range of response factors and the low CW agent detection sensitivity, suggests that these detectors cannot be relied upon for CW agent vapor detection. Detection of the CW agent vapor was unreliable even when the detectors were calibrated successfully.

Of the PID/FID detectors tested, the results of CW agent challenge can be summarized as follows:

- MiniRAE Plus responded to GA and HD, but failed to detect GB.
- TVA 1000B PID responded to GA and HD, but failed to detect GB.
- TVA 1000B FID responded to GB and GA, but not as well for HD.
- HNU units responded to GB, GA and HD, however, they frequently had trouble achieving proper span adjustments during calibrations.
- Passport II responded to HD only.
- The quantitative effects of interferent contamination on CW agent detection could not be determined with useful precision.

The Draeger tubes, both the phosphoric acid ester tube for nerve agent detection and the thioether tube for mustard detection, showed excellent results. None of the potential interferents tested caused them to falsely report the presence of CW agent. Their CW agent detection capability was unaffected by the presence of diesel or AFFF vapors. Detection thresholds were not severely affected by the humidity and temperature conditions tested. The phosphoric acid ester tube detected GA and GB at a minimum concentration of approximately 0.01–0.03 mg/m<sup>3</sup>. The thioether tube detected HD at a minimum concentration of approximately 3-5 mg/m<sup>3</sup>.

## 5. CONCLUSIONS

The UV lamps used by the photoionization detectors (PID) to ionize the vapor samples for detection become contaminated easily by dust, dirt, moisture and residue during use. Frequent and thorough cleaning was required to maintain the "factory level" performance of all four PID type detectors evaluated. The frequent lamp cleaning required to retain performance is impractical. There was no assurance that the response to CW agent would remain the same even when they were calibrated with the calibration gas successfully.

The flame ionization detector (FID) uses a flame instead of a lamp. However, the single FID design tested showed a much slower response time. Perhaps, this was due to longer sampling lines and the lower sampling flow rate. The FID detectors also required cleaning. The results showed that The FID was strongly affected by interferents.

Neither the PID nor the FID detectors tested can be relied upon for CW agent detection and warning. Exposure to vapors of CW agents and many other substances significantly degrades the overall performance of the detectors.

The current Joint Services Operational Requirement (JSOR) for point sampling CW agent detectors is  $0.1 \text{ mg/m}^3$  for the G (nerve) agents and  $2 \text{ mg/m}^3$  for the H (blister) agents. Neither the MiniRAE Plus, the HNU, the Passport II, the TVA PID, nor the TVA FID could detect any of the agents at the JSOR level, even under ideal conditions. Although they demonstrated some detection capability toward the CW agent vapor given sufficient concentration, the sensitivities were considered too low and too non-specific to provide the needed warning.

The Draeger tubes performed well in all tests and the results were consistent. The interferents did not affect their performance. However, Army regulation AR 385-61, Table 2-1, dated 28 February 1997, established that personnel conducting emergency operations in unknown CW agent concentrations or in CW agent concentrations exceeding  $0.2 \text{ mg/m}^3$  of GA or GB, or  $0.003 \text{ mg/m}^3$  of HD must wear the chemical protective ensemble. The phosphoric acid ester type Draeger tube will provide the necessary GA and GB sensitivity needed to support a potential decision to remove protective equipment except for the mask. Mask removal requires G concentrations less than or equal to  $0.0001 \text{ mg/m}^3$ . The indications would be definitive at the required  $0.2 \text{ mg/m}^3$  concentration level given its MDL at approximately  $0.03 \text{ mg/m}^3$ . The thioether type Draeger tube, however, will not provide the needed HD sensitivity to allow removal of any protective equipment.

UNIVERSITY OF  
Maryland  
National Criminal Justice Reference Service (NCJRS)  
Box 0000  
Pomona, MD 20849-6000