High-sensitivity, high-selectivity detection of chemical warfare agents

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We report high-sensitivity detection of chemical warfare agents (nerve gases) with very low probability of false positives (PFP). We demonstrate a detection threshold of 1.2 ppb (7.7 µg/m³ equivalent of Sarin) with a PFP of <1:10⁶ in the presence of many interfering gases present in an urban environment through the detection of disopropyl methylphosphonate, an accepted relatively harmless surrogate for the nerve agents. For the current measurement time of ~60 s, a PFP of 1:10⁶ corresponds to one false alarm approximately every 23 months. The demonstrated performance satisfies most current homeland and military security requirements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2166692]

Optical spectroscopy has long been used for identifying chemical compounds and is a relevant technique because the CWAs have strong optical absorption features in the infrared in the 9–11.5 μm region (Fig. 1, top panel), with absorption strengths of (1–6) × 10⁻³ (ppm meter)⁻¹. Detection of these gases at ppb levels of interest will necessitate absorption coefficient measurements of (1–6) × 10⁻⁸ cm⁻¹. Laser photoacoustic spectroscopy (L-PAS) permits such measurements in short optical pathlengths. Because high-power (>1 W) CO₂ lasers are available with wide tunability (Fig. 1, bottom panel) throughout the 9–11.5 μm where the CWAs absorb, they are ideal laser sources for L-PAS systems for the detection of the CWAs.

For the detection the CWAs in real environments, however, high sensitivity alone is not sufficient. Sensor must have very few false alarms to avoid unacceptable social and economic disruptions. The problem of interference rejection is severe because the broad absorption features of many interferents overlap with the broad absorption features of the target CWA. In normal indoor or outdoor environments, hundreds of gases are present, of which a few dozen need special consideration because of their ambient concentrations, absorption magnitudes, and spectral overlap with the CWAs. A simulation model has shown that L-PAS in this wavelength region could detect the CWAs at very low concentrations with very low PFP by using multiple wavelengths of the CO₂ laser to map the spectral signature of the target gas in a “soup” of background species.

Principles of L-PAS have been described in many papers. Our photoacoustic spectrometer includes a ¹³CO₂ laser that is tuned across 34 laser transitions in the P and R branches of the 0⁰⁰⁻¹⁻⁰ [0⁰⁰, 0²⁰⁰] band, covering 9.6 to 10.2 μm in ~40 seconds. The normalized PA on a laser transition is proportional to the cumulative optical absorption caused by all of the gases present in the cell including CWAs. The individual contribution from CWAs and the other species is extracted using the spectral libraries recorded with the spectrometer and a linear pattern recognition algorithm embedded in the analyzer. Disopropyl methylphosphonate (DIMP), an accepted and a relatively harmless surrogate for CWAs, was used to demonstrate the performance of the L-PAS for CWA detection.

Figure 2 shows the spectral libraries used to evaluate the absorption coefficient of species i at wavelength λj. Three additional vectors were added to account for the offset, slope, and curve of the background signals. When a mixture of trace gases is present in the photoacoustic cell, the total absorption α_j at a specific wavelength λ_j is given by

\[ \alpha_j = \sum_{i} \alpha_{ij} \]

FIG. 1. (Color) Spectral absorption features of Tabun (GA), Sarin (GB), Somant (GD), Cyclosarin (GF), VX, triethyl phosphate (TEP), dimethyl methylphosphonate (DMP), and disopropyl methylphosphonate (DIMP) in the 9–11.5 μm region (top panel); positions and relative power levels of the ¹³CO₂ laser output on the lasing transitions as a function of the wavelength (bottom panel). The left group of transitions corresponding to the P and R branches of the 0⁰⁰⁻¹⁻⁰ [0⁰⁰, 0²⁰⁰] band are used in the present studies to evaluate the performance of the L-PAS spectrometer for the detection of CWAs.

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of sensitivity, accuracy, and selectivity (low false alarms when the target gas is not present). Four different measurement scenarios were used:

1. 0 ppb DIMP in synthetic clean air to determine best-case sensitivity,
2. 0 ppb DIMP in real outdoor Santa Monica air to establish a benchmark for sensitivity and selectivity in nominal urban conditions,
3. 0 ppb DIMP in synthetic, highly contaminated air to establish sensitivity and selectivity under extreme conditions,
4. 14.3 ppb DIMP in synthetic contaminated air to establish accuracy.

The results of these four test cases are plotted in Fig. 3 with five different test segments (case 3 is conducted twice), and summarized in Table II. Case 1 is used to establish a benchmark for sensitivity with synthetic clean air (O₂, N₂, 1% H₂O, 500 ppm CO₂) and no DIMP present; the analyzer produced an average DIMP reading of −0.09±0.07 ppb (1σ) over 120 successive measurements (Fig. 3, segment 1). Thus, the best-case sensitivity for the system is approximately 70 ppt (0.51 µg/m³) and the zero-level is within 100 ppt of true zero.

Testing the L-PAS under nominal urban contamination levels was achieved in case 2 by measuring daytime outdoor Santa Monica air with no DIMP present (see Table I). For this test (Fig. 3, segment 2) 110 successive measurements yielded an average DIMP reading of −0.04±0.37 ppb corresponding to a sensitivity of 2.7 µg/m³. The cumulative effect of the interferences is a degradation of the sensitivity by a factor of ~6, but with no effect on the zero level, which remained within 100 ppt of true zero.

### Table I. Components and concentrations used in the present study for synthetic clean air, outdoor Santa Monica air, and synthetic contaminated air.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentrations for synthetic clean air</th>
<th>Concentrations for Santa Monica air</th>
<th>Concentrations for synthetic contaminated air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>79%</td>
<td>79%</td>
<td>79%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>20%</td>
<td>20%</td>
<td>20%</td>
</tr>
<tr>
<td>Water</td>
<td>1%</td>
<td>1%–2%</td>
<td>1%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>500 ppm</td>
<td>300–550 ppm</td>
<td>500 ppm</td>
</tr>
<tr>
<td>n-propanol</td>
<td>None</td>
<td>Unknown</td>
<td>730 ppb</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>None</td>
<td>Unknown</td>
<td>360 ppb</td>
</tr>
<tr>
<td>Toluene</td>
<td>None</td>
<td>Unknown</td>
<td>3.6 ppm</td>
</tr>
<tr>
<td>Methanol</td>
<td>None</td>
<td>Unknown</td>
<td>830 ppb</td>
</tr>
<tr>
<td>Ammonia</td>
<td>None</td>
<td>Unknown</td>
<td>700 ppb</td>
</tr>
<tr>
<td>Ethanol</td>
<td>None</td>
<td>Unknown</td>
<td>330 ppb</td>
</tr>
<tr>
<td>All others</td>
<td>None</td>
<td>Unknown</td>
<td>None</td>
</tr>
</tbody>
</table>

### Table II. Measurement results for each test segment.

<table>
<thead>
<tr>
<th>Segment</th>
<th>Test Conditions</th>
<th>Actual DIMP concentration</th>
<th>Measured DIMP concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthetic clean air</td>
<td>0 ppb</td>
<td>−0.09±0.07 ppb</td>
</tr>
<tr>
<td>2</td>
<td>Santa Monica outdoor air (daytime)</td>
<td>0 ppb</td>
<td>−0.04±0.37 ppb</td>
</tr>
<tr>
<td>3</td>
<td>Synthetic contaminated air</td>
<td>0 ppb</td>
<td>0.91±0.45 ppb</td>
</tr>
<tr>
<td>4</td>
<td>Synthetic contaminated air</td>
<td>14.3 ppb</td>
<td>14.1±0.69 ppb</td>
</tr>
<tr>
<td>5</td>
<td>Synthetic contaminated air</td>
<td>0 ppb</td>
<td>0.97±0.36 ppb</td>
</tr>
</tbody>
</table>
A performance test in highly contaminated conditions was conducted by analyzing a synthetic air mixture shown in Table I, the components of which are expected to be significant interferences. The concentration for each species was picked to be at levels exceeding those expected to be found in indoor contaminated air to serve as a strict test. The results, shown in the segments 3 and 5 (Fig. 3) reveal that the interferences cause the zero-level increase to an average reading of 0.91 and 0.97 ppb DIMP for the two respective segments, and degrade the 1σ value to 0.45 and 0.36 ppb (3.3 and 2.7 μg/m³), respectively.

For reference, a typical CWA (Sarin) exposure that causes the first noticeable health effect (miosis) is 1 mg/min/m²; that is, a permissible concentration

\[ \text{CWA} \] of about 33 μg/m³ (5.8 ppb) for an exposure of 30 min, and 16 μg/m³ (2.9 ppb) for an exposure of 60 min. The L-PAS accuracy in the presence of interferences was established by adding 14.3 ppb DIMP to the synthetic contaminated air mixture. The L-PAS gave an average reading of 14.1±0.69 ppb (Fig. 3, segment 4), yielding excellent accuracy and a precision.

The experimental data for apparent DIMP values when it is not present permis us to estimate PFP for a particular alarm threshold. The PFP is the number of times the sensor indicates that DIMP is present above the alarm threshold when no DIMP is present. The PFP is evaluated using the statistical noise characteristics of the observed “zero DIMP” signal. The statistical variation of sensor readings over 12 h of measurements for the cases 2 and 3 are shown in Fig. 4. The average of sensor readings for synthetic contaminated air over the 12 h period on day 2 and for Santa Monica outdoor air over the 12 h period on day 3 were 1.45±0.47 ppb (the offset is the result of interferences, rather than from residual DIMP) and 0.02±0.43 ppb, respectively.

Histograms for each of the two cases, with >700 data points, are shown as insets. The PFP is calculated by performing a Gaussian fit to the histograms and then comparing the area under the curve above the alarm level with the total area under the curve. Figure 5 shows a plot of alarm threshold versus PFP (receiver operation characteristic, ROC) evaluated from the data in Fig. 4. For synthetic contaminated air, a false alarm will occur once every million measurements for an alarm threshold of 3.5 ppb (20 μg/m³ equivalent of Sarin), while for Santa Monica outdoor air the results are much better, and a PFP of 1:10⁶ is achieved with a lower threshold of 0.95 ppb (6.1 μg/m³ equivalent of Sarin). A PFP of 1:10⁶ leads to one false alarm every ~23 months (measurement time of 1 min). Both alarm settings are lower than the 30 min exposure threshold for miosis (33 μg/m³ or 5.8 ppb), and are satisfactory for the 60 min threshold (16 μg/m³ or 2.9 ppb) and should be adequate for warning the population at large about a CWA attack. It should be noted that the ROC curves (Fig. 5) permit a user to optimize the alarm threshold and the PFP depending on specific applications.

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\[ \text{Detection threshold (ppm)} \]

\[ \text{Probability of False Alarms} \]

\[ \text{Sarin exposure threshold} = 33 \text{ μg/m}^3 \]

\[ \text{Sarin equivalent} = 20 \text{ μg/m}^3 \]

\[ \text{PFP of 1:10}^6 = \text{1 false alarm every } 23\text{ months} \]

\[ \text{PFP of 1:10}^6 = \text{1 false alarm every } \text{measurement time of 1 min} \]

\[ \text{Sarin exposure threshold for miosis} = 33 \text{ μg/m}^3 \]

\[ \text{Sarin equivalent for 30 min} = 16 \text{ μg/m}^3 \]

\[ \text{Sarin equivalent for 60 min} = 2.9 \text{ μg/m}^3 \]

\[ \text{Sarin exposure threshold for 60 min} = 5.8 \text{ μg/m}^3 \]

\[ \text{PFP of 1:10}^6 = \text{1 false alarm every } 23\text{ months} \]

\[ \text{PFP of 1:10}^6 = \text{1 false alarm every } \text{measurement time of 1 min} \]

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