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Real-Time Detection of Chemical Warfare Agents Using Multi-Wavelength Photoacoustics

by Kristan Gurton, Melvin Felton, and Richard Tober

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Real-Time Detection of Chemical Warfare Agents Using Multi-Wavelength Photoacoustics

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

We present a proof-of-concept study designed to investigate the utility of operating a conventional photoacoustic spectroscopy technique in a “multi-wavelength” mode applied to chemical vapor/aerosols for application of trace species detection and identification. The technique involves propagating three or more laser sources through a non-resonate, flow-through photoacoustic cell. Each laser source is modulated at a different frequency, chosen at some convenient acoustic frequency. A portion of each laser’s power is absorbed by a particular test gas/aerosol that is passing through the PA cell, resulting in a acoustic signal that is found to be proportional to the absorption cross section of the gas/vapor at the particular laser wavelength. A superposition of frequency component (equal to the number of laser wavelengths used), combines with the ambient acoustic noise spectrum and is recorded by an electret microphone housed in the photoacoustic cell. The signal is deconvolved using phase sensitive detection where each component (one corresponding to a particular modulation frequency for a particular laser) is amplified and recorded as function of species concentration. Ratios of the resultant absorption information are used to produce an identifiable metric that remains constant for all concentrations. For the study presented here, we used 3 laser wavelengths all lying in the spectrally rich long-wave infrared (LWIR), i.e., 8.72, 9.27, and 10.35 µm. Test nerve agents simulants include (but not limited to), diethyl phosphonate (DEMP), dimethyl methylphosphonate (DMMP), and diisopropyl phosphonate (DIMP). Measured photoacoustic absorption results compare well with Fourier Transform Infrared (FTIR) analysis that is conducted in situ with the photoacoustic portion of the measurement.

15. SUBJECT TERMS

photoacoustic, nerve agent, Chem/Bio detection, DEMP, DMMP, DIMP

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1. Background

Currently, there are no reliable means for accurate "real-time" detection and identification of poisonous chemical and/or biological substances that are airborne, either in gaseous or aerosol form. As a result, early-warning systems that are capable of *instantaneous* detection of such materials are badly needed. Because rapid detection and identification is desired, an optically based technique should be considered.

To this end, we propose a new approach based on the detection of the optical absorption measured in situ for various organophosphorus-based nerve agent simulants. The novelty of the proposed study is to modify a traditional ultra-sensitive spectroscopic technique, i.e., gaseous and aerosol photoacoustics, by incorporating multiple laser-line sources. Photoacoustic techniques that utilize laser sources routinely measure absorption characteristics of trace gases in the ppb, and are considered among one of the most sensitive spectroscopy methods available (*1, 2*). Unfortunately, conventional photoacoustic techniques have been greatly limited by the availability of particular laser sources (*3*). This has been particularly true for infrared (IR) photoacoustic spectroscopy, in which the researcher typically had only a hand full of wavelengths available that were usually produced by cumbersome carbon dioxide (CO_2) and lead salt (PbS/PbSe) lasers. However, with the advent of the newly developed Quantum Cascade IR laser diode substrates being developed at the U.S. Army Research Laboratory (ARL) and elsewhere, practically any wavelength within 3–14 μm is now readily available.

Our approach is simply to incorporate multiple Quantum Cascade (QC) laser sources in an ultra-sensitive spectroscopic method that has traditionally only used one laser source at a time. By doing so, we intend to measure multiple (three or more) absorption coefficients simultaneously of a given nerve agent simulant in vapor form. We intend to show that a reliable metric will result based on the relationships between the measured absorption parameters that can be used to detect and identify trace species of a given chemically based toxin.

2. Method

Detection of optical absorption using a photoacoustic method is fairly simple. For gaseous photoacoustic spectroscopy, a small-diameter laser beam is modulated at some convenient acoustic frequency, 1 kHz, for example, and is passed through a sealed cylindrical gas cell, often via two or more transmitting windows. The absorbed IR energy raises the absorbing molecules from the ground vibrational state to an excited vibrational-rotational state. Collisional processes then redistribute the energy into translation and rotation, with a resulting increase in the pressure of the gas. The time required for vibrational relaxation to occur at standard temperature and

pressure (STP) is on the order of 1 µs. The resultant rapid change in pressure at the modulation frequency of the laser results in an acoustic signal that is detected by an electret microphone usually with the aid of a lock-in amplifier. The measured acoustic, or pressure, signal is found to be proportional to the average power of the optical source, the absorption cross-section of the species, and the sensitivity of the electret. The last two parameters are usually known, and one is then interested in measuring the absorption response of the gas at the laser-line.

We have developed a modified flow-through photoacoustic cavity designed specifically to overcome the limited sensitivity inherent in closed-cell designs that use windows to transmit the laser radiation into a photoacoustic cell, as shown in figure 1* (*4, 5*).

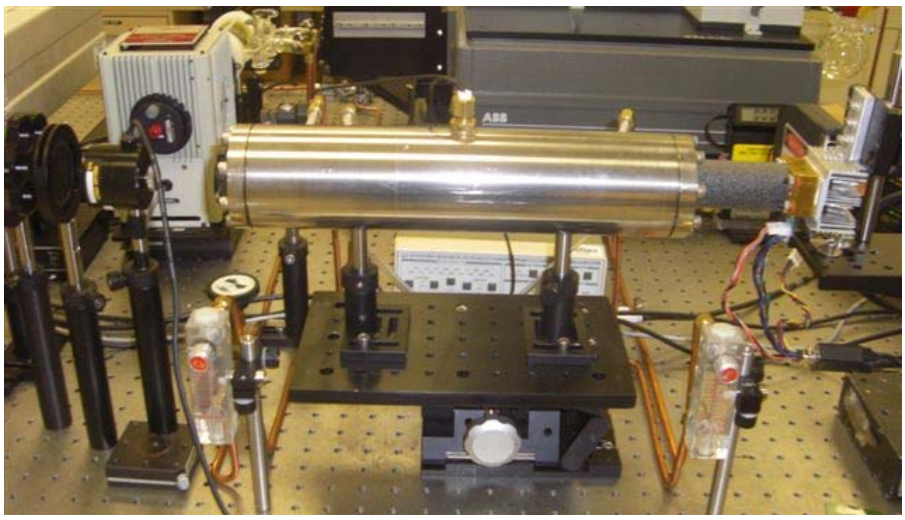


Figure 1. Flow-through photoacoustic cell.

Not seen in the photograph is a series of acoustic dampeners mounted inside the cell at both ends of the tube that serve to suppress any ambient noise. Situated in the center of the cell is a small field-effect transistor (FET) based electret microphone. The faint acoustic signal resulting from the absorbing gas is amplified and fed into a 24-Bit dynamic signal acquisition device that digitizes the analog signal. By accurately digitizing and processing the acoustic signal using a PC, we avoid having to use multiple lock-ins that are usually needed to deconvolve each signal. Instead we conduct a fast Fourier transform (FFT) on the signal and filter only frequency components that correspond to the modulation frequencies of our lasers. Using this approach, we are able to deconvolve up to eight separate laser-induced signals simultaneously with just a single PC.

Initially, we had hoped to use only QC IR laser diode sources that were to be provided by our corporate partner, Maxion Lasers Inc., College Park, MD, but due to production difficulties, we were only provided one QC source (operating at 8.72 µm with CW power 60 mW at 14 °C) at

*Often such system are noise limited as a result of residual absorption from the transmission windows that if often greater that the faint acoustic signal resulting from the absorbing species.

the time of this report. In order to move forward with our proof of concept, we procured two other conventional CO_2 laser sources operating at 10.54 and 9.27 µm. The three sources were made coincident and propagated axially through the cell. Each source was modulated at a different acoustic frequency, e.g., 10.35 µm at 1700 Hz, 9.27 µm at 1900 Hz, and the 8.72 µm QC at 1300 Hz.

Examples of the organophosphorus nerve agent simulants considered include diethyl phosphonate (DEMP), dimethyl methylphosphonate (DMMP), and diisopropyl phosphonate (DIMP). Simulant vapor was generated by heating the liquid (low vapor pressure materials), where residual particles were removed by passing the vapor through a condenser that was cooled with liquid nitrogen (LN_2). Simulant concentrations were varied by mixing with dry air that was pumped through the system at differing flow-rates.

Complete IR absorption spectral for each simulant was simultaneously measured from 3–13 µm by passing the gas sample through a Fourier Transform IR (FTIR) spectrometer monitored transmission cell. This allowed for direct comparison with the three measured absorption coefficients that result from the photoacoustic portion of the study. A simplified schematic of the experiment can be seen in figure 2.

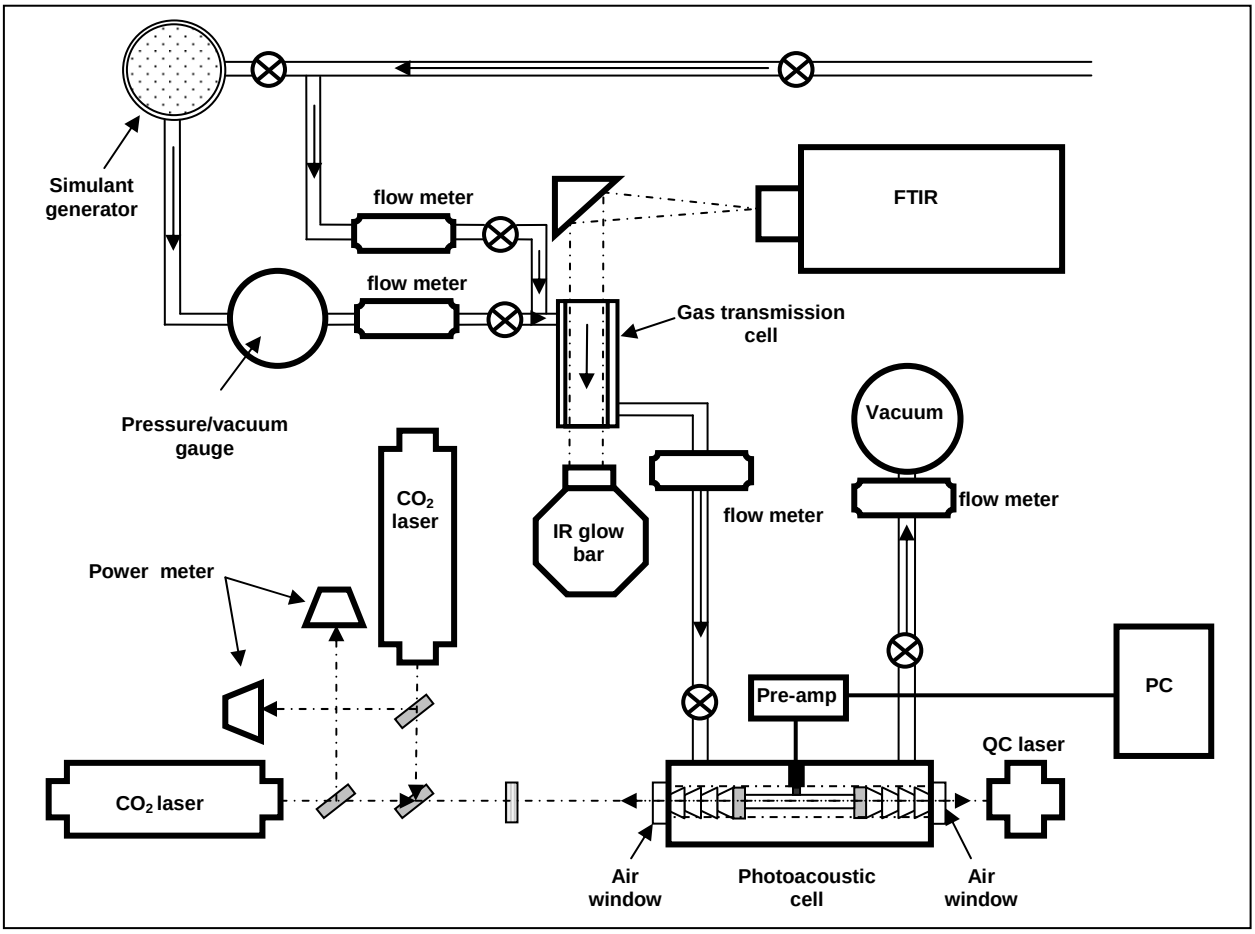


Figure 2. Multi-wavelength photoacoustic test bed.

3. Preliminary Result/Conclusions

At the time of this report we had just begun testing the specified nerve agent simulants, e.g., DMMP, DEMP, DIMP, etc., and results from those runs must still be analyzed. However, we will show data based on our "practice" vapor, i.e., isopropyl alcohol, in which optimum operating procedures were established. The following figures show the evolution of the raw photoacoustic signal for 8.72 µm, 9.27 µm, and 10.35 µm laser lines, as varying concentrations of isopropyl alcohol are released into the cavity. Figure 3 shows the magnitude of alternating current (AC) component of the acoustic signal for the lock-in synced at 2.5 kHz, i.e., the modulation frequency of the QC laser operating at 8.72 µm. Region 1 highlighted in the figure shows the period just prior to the release of the vapor, and the subsequent signal increase as the simulant enters the active region of the photoacoustic cell. During this portion of the measurement, simulant is heated to about 80 °C (dependent on the vapor pressure), and a pressure of about 2–3 psi is allowed to build in the system. This high concentration of vapor is then leaked at a rate of about 100 ml/min into the FTIR transmission cell and continues to flow into the photoacoustic sample region. A maximum saturation is reached in region 2, at which point we begin to mix the simulant flow with varying concentrations of dry air which reduces the overall concentration, as shown in region 3. The large signal spike seen in region 2 corresponds to opening of valves for the fresh air mixture. We intentionally chose this particular curve to highlight the obvious appearance of acoustic noise seen in the trailing end of the signal in region 3. This noise is apparent in much of the acoustic frequency spectrum above 2 kHz and results from the fluid flowing in the lines. We merely had to adjust our modulation frequencies to avoid the high frequency noise region. Figure 4 shows the corresponding raw acoustic signal for the 10.35 µm CO_2 laser line modulated at 2.1 kHz, where the noise is still present. Figure 5 shows the 9.27 µm signal modulated at 1.7 kHz and a much better noise profile as we move down in frequency.

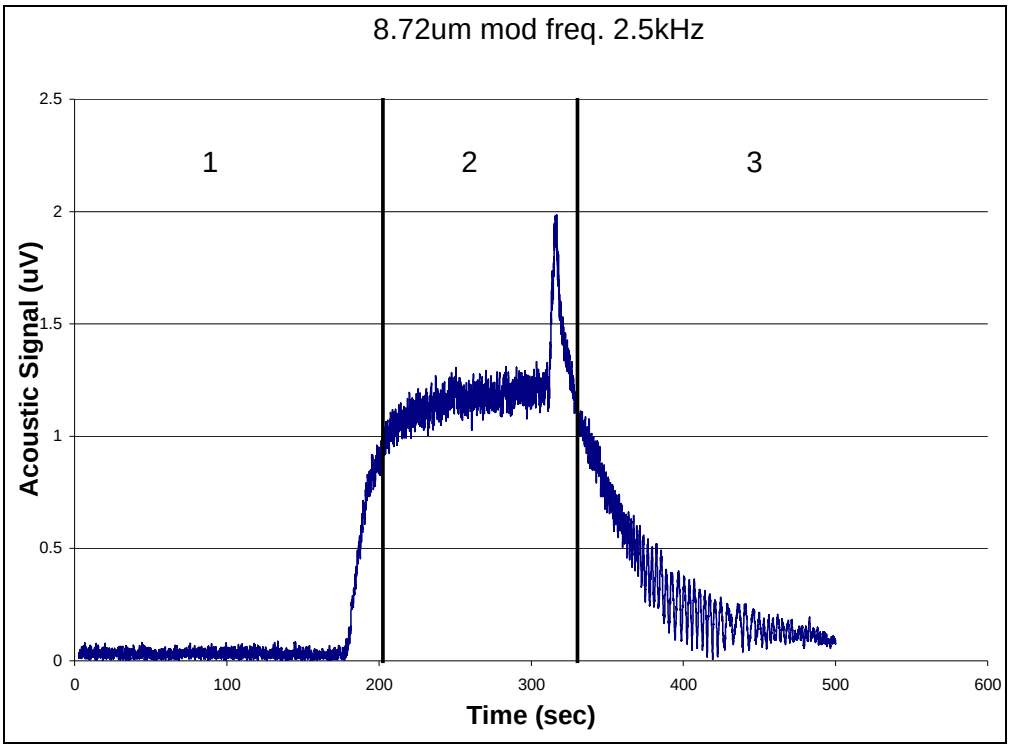
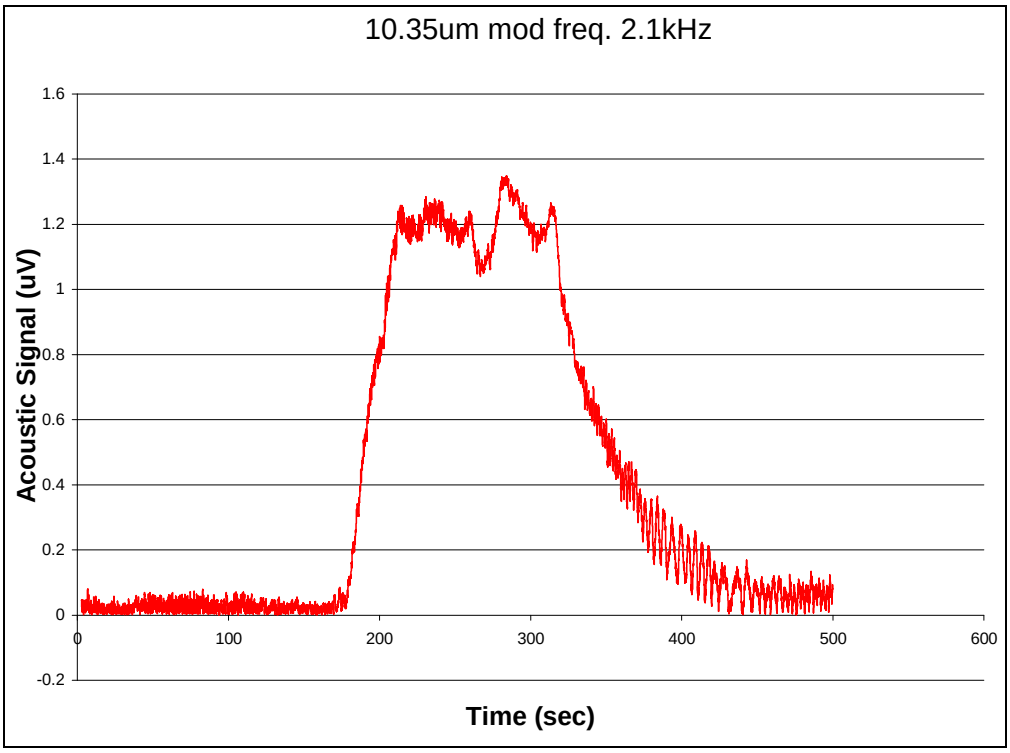


Figure 3. AC component of the electret signal sampled at 2.5 kHz while isopropyl vapor is drawn through the photoacoustic cavity.



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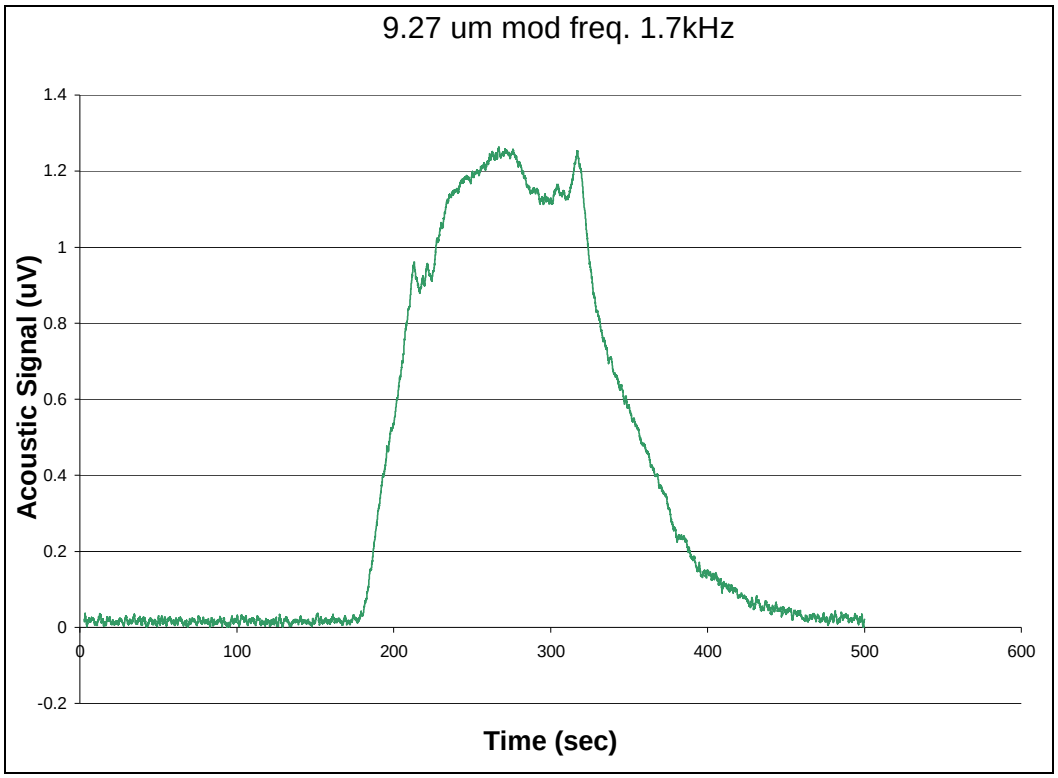


Figure 5. AC component of the electret signal sampled at 1.7 kHz while isopropyl vapor is drawn through the photoacoustic cavity

It is only in region 3 (see figure 3), in which uniform concentrations are acquired, where absorption information is most reliable.

At first glance we were somewhat surprised to see that the relative magnitude for the three signals was about the same (after normalizing for the differing laser powers), i.e., peaking around 1.2 µV. However, after reviewing the absorptance spectra measured by the FTIR, the relative relationships between the three photoacoustics signals appear to be justified, (figure 6).

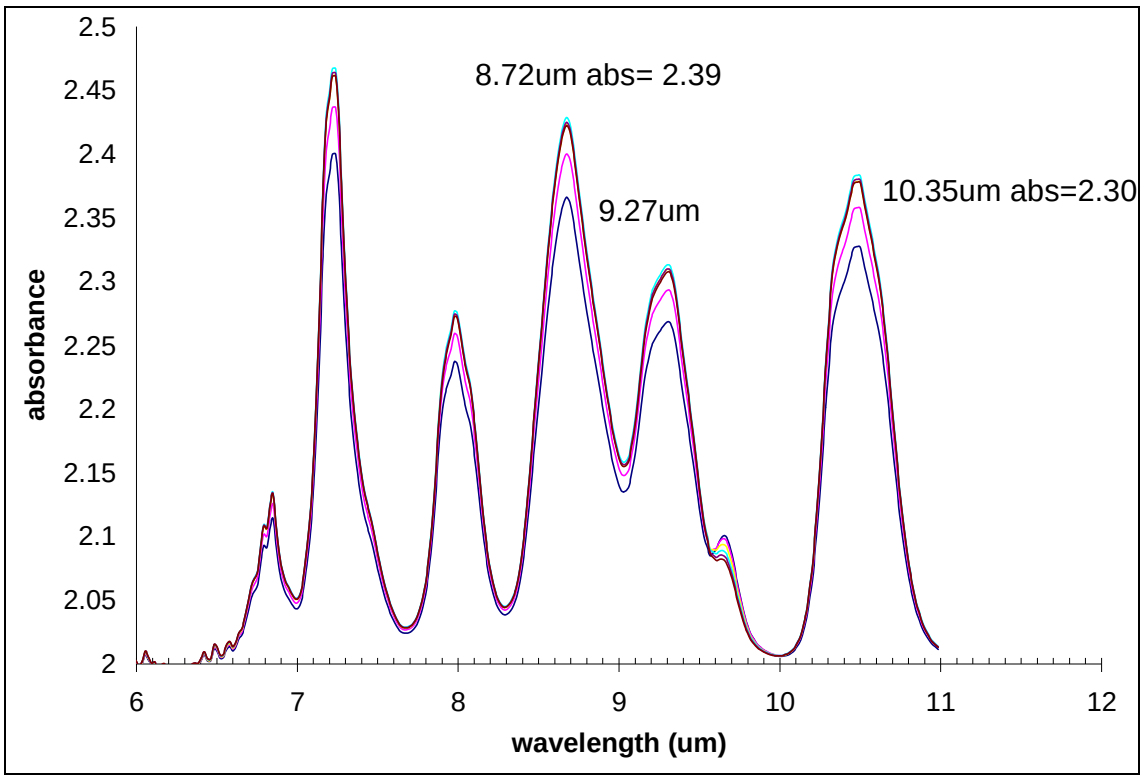
Currently, by using the muti-wavelength photoacoustic method as described previously, we are accurately measuring the absorption response for a variety of nerve agent simulants. We are investigating several new photoacoustic cell designs to improve optical energy density in the cavity by inducing multiple reflections of the laser beams (figure 7). Similarly, these new approaches will boost signal by reducing unwanted attenuation of the lasers by keeping the laser-gas interaction region small and in close proximity to the electret.

It is our intent to replace the two CO_2 lasers with QC laser diodes chosen to operate at 10.10 µm and 9.62 µm during the winter of 2009.

Additional work is needed to better quantify simulant concentrations to establish ultimate detectability. Similarly, we need to establish the best metric to use in the detection/identification of a given agent.

A possible "concentration invariant" metric would involve ratios of the integral of the electret signal for a predescribed period of time for each wavelength. For example, during the sampling of a suspect species, we measure three different acoustic signals (one for each of the three wavelengths chosen), and the integral over a time period Δt results in the three independent quantities, $S(\lambda 1)$, $S(\lambda 2)$, and $S(\lambda 3)$. A three-number metric associated with the species would then be $\{S(\lambda 1)/ S(\lambda 2),\ S(\lambda 2)/ S(\lambda 3),\ S(\lambda 1)/ S(\lambda 3)\}$.

It is our hope to expend testing to incorporate particulate matter and aerosols, and attempt to distinguish various biological particles based on documented absorption spectra in the mid- and long-wave IR (LWIR) (6, *7*).



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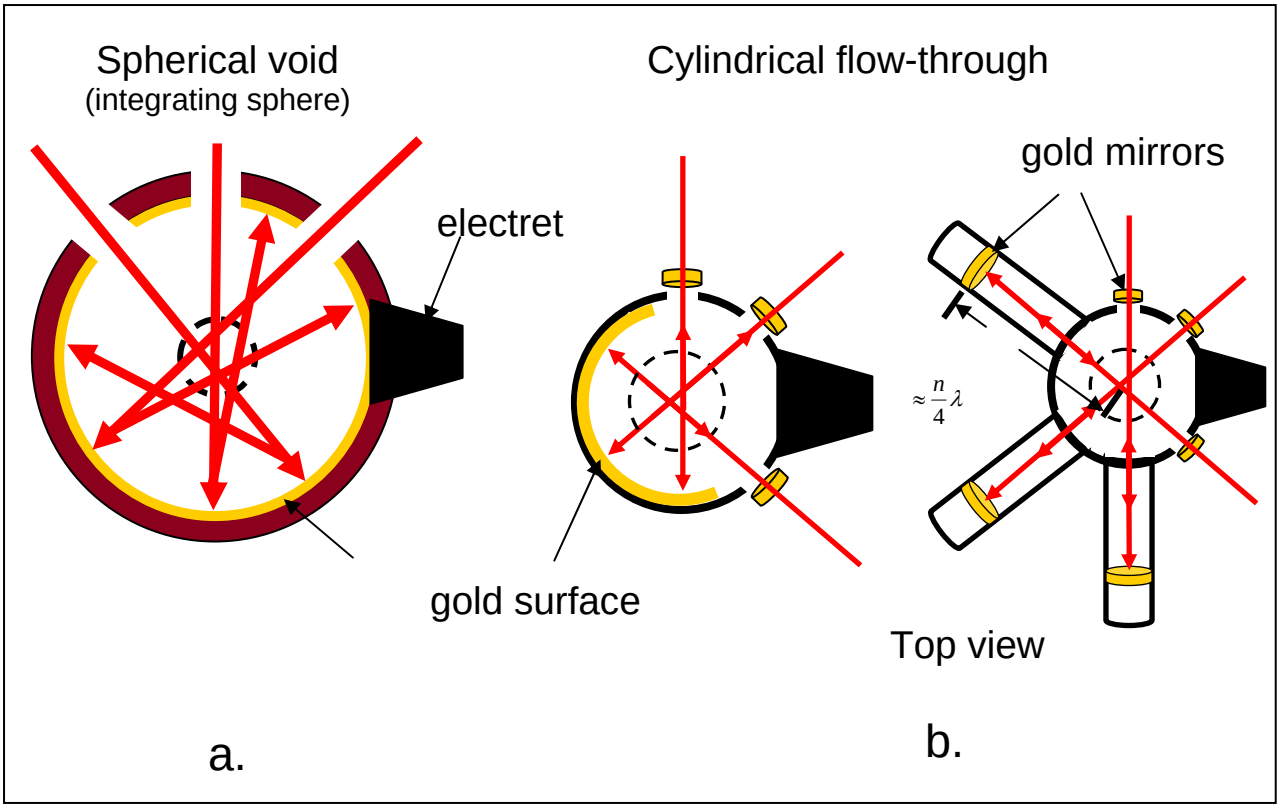

Figure 7. New photoacoustic cell design(s). Design a is based on the multiple reflections inherent in integrating spheres. Design b maintains a cylindrical column of vapor (into the page) but now the lasers are brought into the cell perpendicular to the flow in order to limit unwanted laser attenuation. In addition, the right cell shows possible enhancement of the signal by incorporating resonate effects by spacing opposing mirrors at distances on the order of quarter-multiples of the wavelength of sound associated with each modulation frequency.

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List of Symbols, Abbreviations, and Acronyms

AC	alternating current
ARL	U.S. Army Research Laboratory
CO_2	carbon dioxide
DEMP	diethyl phosphonate
DIMP	diisopropyl phosphonate
DMMP	dimethyl methylphosphonate
FET	field-effect transistor
FFT	fast Fourier transform
FTIR	Fourier Transform IR
IR	infrared
LN_2	liquid nitrogen
LWIR	long-wave IR
PbS/PbSe	lead salt
QC	Quantum Cascade
STP	standard temperature and pressure

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