Selective real-time detection of gaseous nerve agent simulants using multiwavelength photoacoustics

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An optical detection method is presented that is designed to detect and identify the presence of macromolecular gas species (e.g., organophosphate-based nerve agent simulants) at trace level concentrations. The technique is based on a modified version of conventional laser photoacoustic (PA) spectroscopy, in which optical absorption is typically measured using a single laser source. We demonstrate the ability to simultaneously measure multiple absorption-related parameters that serve as a concentration-independent identifier. Three continuous wave mid-infrared laser sources, operating at 8.68, 9.29, and 10.35 μm, are combined and propagated axially through a specially designed flow through PA cell. Each laser is modulated at a different frequency and the resultant acoustic signal(s) are detected and deconvolved using a PC-based 24 bit dynamic signal acquisition device. Species detection and identification is achieved by tabulating independent ratios of the acoustic response for each laser source. Quantitative absorption measured is verified using a Fourier transform infrared spectrometer. Results show good detection and species separation/identification at moderately low ppm concentrations.   © 2012 Optical Society of America

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Currently, there are no reliable means for accurate real-time detection and identification of harmful vapors that is effective over a wide range of chemical species at low concentrations. Much research has been devoted to the detection and identification of gaseous chemical materials and can be generally categorized by two distinctly different approaches, i.e., a material science method in which species-specific substrates are developed that change electrical characteristics when exposed to a particular gas, and the more conventional, laser-based spectroscopic approach [1–4].

One of the more direct methods to implement in practice (without sacrificing sensitivity) is laser photoacoustic spectroscopy (LPAS) [5]. We have worked with both gas and aerosol photoacoustic (PA) systems for many years but have been disappointed by the lack of convenient laser sources spanning the spectrally rich mid-infrared (MidIR) spectral region. Similarly, traditional LPAS is usually limited to measuring a "single" absorption cross-section at a time. In addition, traditional LPAS typically requires cumbersome and expensive signal processing instrumentation, e.g., data acquisition systems, preamplifier/lock-in amplifiers, etc. Taking these factors into consideration, conventional LPAS seems poorly suited as a viable gas "detection" technique.

However, recent advancements in IR laser technology and signal processing instrumentation have allowed us to reconsider using a modified version of LPAS for selective gas detection. First, the limitation imposed by a lack of convenient MidIR laser sources has been all but eliminated by the recent advancement of commercially available quantum-cascade (QC) lasers. These solid-state devices are custom made to produce practically any MidIR wavelength the user desires. In addition, advancement in PC-based "virtual" instrumentation has eliminated the need for expensive and bulky analog signal processing devices. For example, we use a single National Instruments, Inc., PCI dynamic signal acquisition board (model PCI-4472) which, when programmed appropriately, effectively functions identically as eight separate lock-in amplifiers.

With readily available MidIR sources and greatly simplified signal processing electronics, it now seems reasonable to consider a "multiwavelength" LPAS approach. By propagating multiple laser sources through a single, untuned, flow through PA cell in which each sources is modulated at a different acoustic frequency, one can deconvolve the resultant absorption-related signals by using a multichannel virtual lock-in. This effectively allows for a real-time measurement of multiple absorption-related coefficients that can be used to identify the presence of a particular gas species. Although the approach described here is relatively straightforward, we have found no similar studies in the literature in which multiple lasers sources are combined in a single PA cell, allowing for the simultaneous measure of multiple absorption cross-sections.

In order to develop a reliable detection scheme, a metric that is insensitive to fluctuations in vapor concentration must be developed. Since the raw acoustic response from the PA cell is proportional to the absorption cross-section (where the constant of proportionality is related to the cell path length and concentration), a simple concentration-independent metric can be formed by simple ratios of the deconvolved PA signal for each laser source. For this proof-of-concept study we used three MidIR wavelengths. However, in principle, there is no fundamental limitation on the number of laser-lines one could consider. In fact, species specificity increases greatly as the number of wavelengths considered are increased [i.e., the number of independent ratios goes as $n(n-1)/2$, where n are the number of wavelengths available]. For our case here, three laser sources produce the corresponding signals $S_{\lambda 1}$, $S_{\lambda 2}$, and $S_{\lambda 3}$ which, in turn, generate a set of three independent ratios $S_{\lambda 1}/S_{\lambda 2}$, $S_{\lambda 1}/S_{\lambda 3}$, and $S_{\lambda 2}/S_{\lambda 3}$. However, for systems with 4 or 5

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14. ABSTRACT

species (e.g., organophosphate-based nerve agent simulants) at trace level concentrations. The technique is based on a modified version of conventional laser photoacoustic (PA) spectroscopy, in which optical absorption is typically measured using a single laser source. We demonstrate the ability to simultaneously measure multiple absorptionrelated parameters that serve as a concentration-independent identifier. Three continuous wave mid-infrared laser sources, operating at 8.68, 9.29, and 10.35 μm, are combined and propagated axially through a specially designed flow through PA cell. Each laser is modulated at a different frequency and the resultant acoustic signal(s) are detected and deconvolved using a PC-based 24 bit dynamic signal acquisition device. Species detection and identification is achieved by tabulating independent ratios of the acoustic response for each laser source. Quantitative absorption measured is verified using a Fourier transform infrared spectrometer. Results show good detection and species separation/identification at moderately low ppm concentrations.

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Fig. 1. Schematic of the multiwavelength LPAS experiment.

Fig. 2. Representative measured absorbance spectra for the five nerve agent simulants, where the arrows identify the three laser wavelengths at 8.68, 9.29, and 10.35 μm.
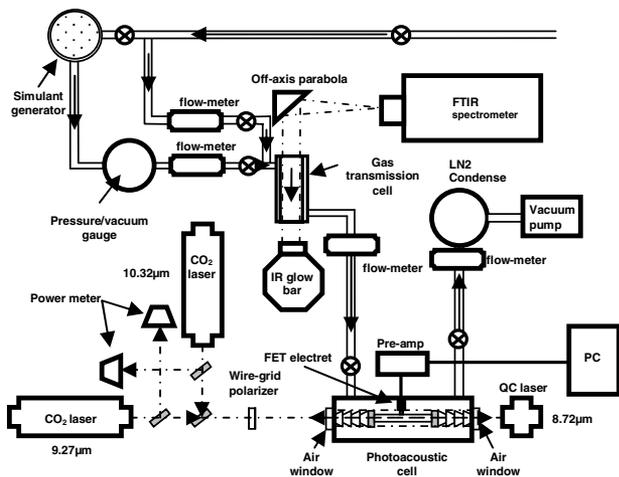
different wavelengths, the number of independent ratios becomes 6 and 10, respectively.

A schematic of the multiwavelength LPAS experiment is shown in Fig. 1, and a detailed description of the PA cell can be found in Gurton *et al.* [6,7]. Varying concentrations of simulant vapor and dry air are volumetrically controlled and combined inline via a series of calibrated pressure gauges, mass-flow meters, and needle valves. Vapor is fed into a 10 cm long Fourier transform infrared (FTIR) transmission cell that is used as a quantitative reference for the multiwavelength LPAS study. The spectral absorption is measured from 3 to 12 μm using a Bomem MR Series FTIR spectrometer operating with a spectral resolution of 4 cm^{-1}. A radiometrically stabilized IR Nernst glow-bar serves as the broadband source for the FTIR measurement. The simulant–air mixture exits the FTIR transmission cell and is passed through a flow through PA cell at predetermined flow rates.

Three CW MidIR laser sources were used for the study, which consisted of two Universal Inc., CO_2 lasers (operating at 9.27 and 10.54 μm) and one Maxion Inc., QC laser (operating at 8.72 μm). For uniformity, all lasers were attenuated to the same value of 50 mW. In order to separate the acoustic response for the different wavelengths, each laser was modulated at a different acoustic frequency, i.e., 10.35 μm at 1700 Hz, 9.27 μm at 1900 Hz, and 8.72 μm at 1300 Hz. Choice of specific laser modulation frequencies is usually dictated by the response of the electret and the acoustic spectrum of the ambient noise. However, for multiwavelength operation, care should be taken to avoid choosing frequencies with overlapping harmonics to avoid mixing of the signals.

For conventional LPAS, the amplitude of the acoustic signal is related to the absorption via a calibration process [8,9]. However, due to the qualitative nature of this particular study, no calibration was necessary, i.e., we are not interested in measuring absolute absorption cross-sections, but are merely attempting to determine sufficient information in order to identify the presence of a particular nerve agent simulant species.

The acoustic signal(s) resulting from laser line absorption is detected by the electret and amplified using a low-noise preamplifier. Analog-to-digital conversion of the amplified acoustic signal is accomplished using an
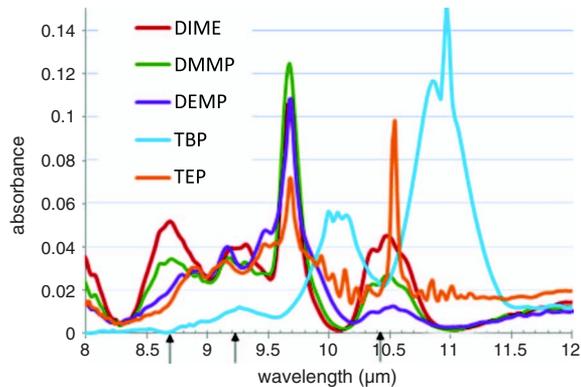
8 channel National Instrument 24 Bit dynamic signal acquisition PCI card. Once digitized, the signal is deconvolved (much like a conventional analog lock-in amplifier) and individual AC components for each of the three modulation frequencies are recorded as a function of time.

The test materials include the following six nerve agent simulants in vapor form: dimethyl methyl phosphonate (DMMP), diethyl methyl phosphonate (DEMP), diisopropyl methyl phosphonate (DIMP), dimethylpolysiloxane (DIME), triethyl phosphate (TEP), tributyl phosphate (TBP), and two volatile organic compounds (VOCs), acetone (ACE) and isopropanol (ISO). Figure 2 shows absorbance spectra measured using the FTIR spectrometer for the five nerve agent simulants.

Test runs were conducted over multiple days for each simulant and VOC. Prior to switching out a particular simulant, all vapor/liquid handling glassware and transport tubes were thoroughly cleaned and baked to remove any residual material. PAS electret signals were continuously recorded and amplified as a function of changing simulant concentrations, which was evident by a three order change in magnitude in the electret signal. However, ratios of the three absorption-related signals showed little variance over the test period.
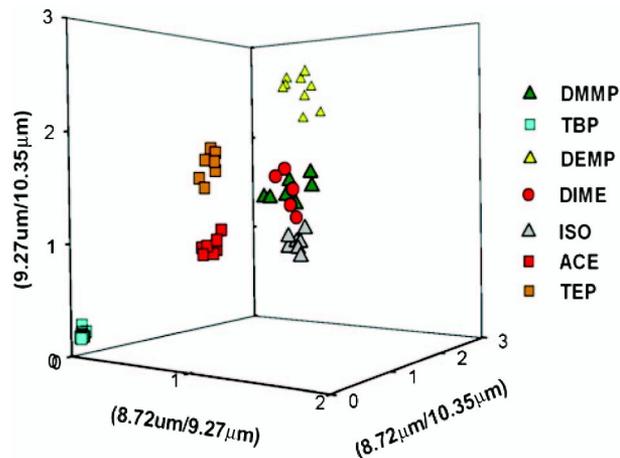

Fig. 3. Ratios of the absorption response for the three wavelengths are shown for the five nerve agent simulants and two volatile organic compounds.

Response ratios of the three wavelengths for the five nerve agent simulants and two VOCs are plotted in Fig. 3. As seen in this Figure, there is reasonable separation between different regions designating the various gaseous compounds. The only exception exists between the materials DMMP and DIME, in which the separation is more difficult to define. Unfortunately this problem will occur for spectroscopically similar compounds, but may be overcome with the introduction of an additional laser line wavelength. Minimum volumetric detection limits were approximated to be in the ppm using 50 mW laser power illumination. For example, 1.0 μl of saturated simulant vapor, TEP, when combined with 1.0 liter dry air, maintained the detection metric range shown in Fig. 3, but became unstable with further reduction in concentration.

In conclusion, we have shown that a novel application of a modified LPAS technique can be used to selectively detect and distinguish various nerve agent simulant compounds in gaseous form. This was accomplished by simultaneous operation of multiple laser line sources in the MidIR, each modulated at a distinctly different acoustic frequency and propagated through a conventional flow through PA cell. Separation and amplification of the various acoustic components is conducted and the resultant ratios of the absorption related acoustic response is shown to be a useful detection and identification metric. Only three wavelengths were used in this proof-of-concept study, which resulted in three independent metric ratios, but greater specificity is expected as the number of wavelengths is increased.

References

1. J. P. Novak, E. S. Snow, E. J. Houser, D. Park, J. L. Stepnowski, and R. A. McGill, Appl. Phys. Lett. **83**, 4026 (2003).
2. S. Chopra, K. McGuire, N. Gothard, and A. M. Rao, Appl. Phys. Lett. **83**, 2280 (2003).
3. K. A. Joshi, M. Prouza, M. Kum, J. Wang, J. Tang, R. Haddon, W. Chen, and A. Mulchandani, Anal. Chem. **78**, 331 (2006).
4. T. Topfer, K. Petrov, Y. Mine, D. Jundt, R. F. Curl, and F. K. Tittel, Appl. Opt. **36**, 8042 (1997).
5. M. W. Sigrist, Rev. Sci. Instrum. **74**, 486 (2003).
6. K. P. Gurton, M. Felton, R. Dahmani, and D. Ligon, Appl. Opt. **46**, 6323 (2007).
7. K. P. Gurton, R. Dahmani, D. Ligon, and B. Bronk, Appl. Opt. **44**, 4096 (2005).
8. X. T. Lou, G. Somesfalean, B. Chen, Y. G. Zhang, H. S. Wang, Z. G. Zhang, S. H. Wu, and Y. K. Qin, Opt. Lett. **35**, 1749 (2010).
9. A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy* (John Wiley & Sons, 1990).