ARL-RP-0550 ● Sep 2015

US Army Research Laboratory

Toward the Realization of a Compact Chemical Sensor Platform using Quantum Cascade Lasers

by Ellen L Holthoff, Logan S Marcus, and Paul M Pellegrino

A reprint from Proc. of SPIE Vol. 9467 94672Q-1.

NOTICES

Disclaimers

ARL-RP-0550 ● SEP 2015

US Army Research Laboratory

Toward the Realization of a Compact Chemical Sensor Platform using Quantum Cascade Lasers

by Ellen L Holthoff, Logan S Marcus, and Paul M Pellegrino
Sensors and Electron Devices Directorate, ARL

A reprint from Proc. of SPIE Vol. 9467 94672Q-1.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
Sep 2015

2. REPORT TYPE
Reprint

3. DATES COVERED (From - To)

4. TITLE AND SUBTITLE
Toward the Realization of a Compact Chemical Sensor Platform using Quantum Cascade Lasers

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Ellen L. Holthoff, Logan S. Marcus, and Paul M. Pellegrino

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
RDRL-SEE-E
2800 Powder Mill Road
Adelphi, MD 20783-1138

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-RP-0550

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
A reprint Proc. of SPIE Vol. 9467 94672Q-1.

14. ABSTRACT

The Army is investigating several spectroscopic techniques (e.g., infrared spectroscopy) that could allow for an adaptable sensor platform. Traditionally, chemical sensing platforms have been hampered by the opposing concerns of increasing sensor capability while maintaining a minimal package size. Current sensors, although reasonably sized, are geared to more classical chemical threats, and the ability to expand their capabilities to a broader range of emerging threats is uncertain. Recently, photoacoustic spectroscopy, employed in a sensor format, has shown enormous potential to address these ever-changing threats, while maintaining a compact sensor design.

In order to realize the advantage of photoacoustic sensor miniaturization, light sources of comparable size are required. Recent research has employed quantum cascade lasers (QCLs) in combination with MEMS-scale photoacoustic cell designs. The continuous tuning capability of QCLs over a broad wavelength range in the mid-infrared spectral region greatly expands the number of compounds that can be identified. Results have demonstrated that utilizing a tunable QCL with a MEMS-scale photoacoustic cell produces favorable detection limits (ppb levels) for chemical targets (e.g., dimethyl methyl phosphonate (DMMP), vinyl acetate, 1,4-dioxane). Although our chemical sensing research has benefitted from the broad tuning capabilities of QCLs, the limitations of these sources must be considered. Current commercially available tunable systems are still expensive and obviously geared more toward laboratory operation, not fielding. Although the laser element itself is quite small, the packaging, power supply, and controller remain logistical burdens. Additionally, operational features such as continuous wave (CW) modulation and laser output powers while maintaining wide tunability are not yet ideal for a variety of sensing applications. In this paper, we will discuss our continuing evaluation of QCL technology as it matures in relation to our ultimate goal of a universal compact chemical sensor platform.

15. SUBJECT TERMS
photoacoustic spectroscopy, QCL, chemical sensor

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Ellen L. Holthoff
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (Include area code)
Unclassified	Unclassified	Unclassified	UU	18	301-394-0939

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Toward the Realization of a Compact Chemical Sensor Platform using Quantum Cascade Lasers

Ellen L. Holthoff, Logan S. Marcus, and Paul M. Pellegrino
U.S. Army Research Laboratory, 2800 Powder Mill Road, RDRL-SEE-E, Adelphi, MD, USA 20783

ABSTRACT

The Army is investigating several spectroscopic techniques (e.g., infrared spectroscopy) that could allow for an adaptable sensor platform. Traditionally, chemical sensing platforms have been hampered by the opposing concerns of increasing sensor capability while maintaining a minimal package size. Current sensors, although reasonably sized, are geared to more classical chemical threats, and the ability to expand their capabilities to a broader range of emerging threats is uncertain. Recently, photoacoustic spectroscopy, employed in a sensor format, has shown enormous potential to address these ever-changing threats, while maintaining a compact sensor design.

In order to realize the advantage of photoacoustic sensor miniaturization, light sources of comparable size are required. Recent research has employed quantum cascade lasers (QCLs) in combination with MEMS-scale photoacoustic cell designs. The continuous tuning capability of QCLs over a broad wavelength range in the mid-infrared spectral region greatly expands the number of compounds that can be identified. Results have demonstrated that utilizing a tunable QCL with a MEMS-scale photoacoustic cell produces favorable detection limits (ppb levels) for chemical targets (e.g., dimethyl methyl phosphonate (DMMP), vinyl acetate, 1,4-dioxane). Although our chemical sensing research has benefitted from the broad tuning capabilities of QCLs, the limitations of these sources must be considered. Current commercially available tunable systems are still expensive and obviously geared more toward laboratory operation, not fielding. Although the laser element itself is quite small, the packaging, power supply, and controller remain logistical burdens. Additionally, operational features such as continuous wave (CW) modulation and laser output powers while maintaining wide tunability are not yet ideal for a variety of sensing applications. In this paper, we will discuss our continuing evaluation of QCL technology as it matures in relation to our ultimate goal of a universal compact chemical sensor platform.

Keywords: Photoacoustic spectroscopy, sensor, quantum cascade laser, MEMS

1. INTRODUCTION

Monitoring trace gases is of great importance in a wide range of applications. Research and development in hazardous materials detection technology focuses on increasing speed, sensitivity, and selectivity, while reducing size and cost. Although the current state-of-the-art vapor detector (Joint Chemical Agent Detector (JCAD)) is lightweight, handheld, and easily attaches to a belt, it still provides added bulk to a soldier on foot patrol. Both the military and industry have expressed interest in the development of more sensitive, easily adaptable, and compact trace gas analysis equipment. In recent years, photoacoustic spectroscopy (PAS) has emerged as an attractive and powerful technique well suited for sensing applications. The development of high-power radiation sources and more sophisticated electronics, including sensitive microphones and digital lock-in amplifiers, has allowed for significant advances in PAS. Furthermore, photoacoustic (PA) detection of infrared absorption spectra using modern tunable lasers offers several advantages, including simultaneous detection and discrimination of numerous molecules of interest.

Photothermal spectroscopy encompasses a group of highly sensitive methods that can be used to detect trace levels of gases using optical absorption and subsequent thermal perturbations of the gases. The underlying principle that connects these various spectroscopic methods is the measurement of physical changes (i.e., temperature, density, or pressure) as a result of photo-induced change in the thermal state of the sample. Photothermal methods are classified as indirect methods for detection of trace optical absorbance because the transmission of the light used to excite the sample is not measured directly. Examples of photothermal techniques include photothermal interferometry (PTI), photothermal lensing (PTL), photothermal deflection (PTD), and photoacoustic spectroscopy (PAS). In comparison to other photothermal techniques,

Micro- and Nanotechnology Sensors, Systems, and Applications VII, edited by Thomas George,
Achyut K. Dutta, M. Saif Islam, Proc. of SPIE Vol. 9467, 94672Q · © 2015 SPIE
CCC code: 0277-786X/15/$18 · doi: 10.1117/12.2178533

which measure the refractive index using combinations of probe sources and detectors, PAS measures the pressure wave produced by sample heating. This is accomplished using modulated or pulsed excitation sources.[1-3] The pressure waves detected in PAS are generated directly by the absorbed fraction of the modulated or pulsed excitation beam. Therefore, the signal generated from a PA experiment is directly proportional to the absorbed incident power. However, depending on the excitation source (i.e., modulated or pulsed), the relationship between the generated acoustic signal and the absorbed power at a given wavelength will differ.[4] Recent research suggests that PAS is a particularly sensitive technique, capable of trace gas detection at parts-per-trillion (ppt) levels.[5, 6] Although these studies demonstrate the sensitivity capabilities of photoacoustic sensors, the total system size represents a large logistics burden in terms of size, cost, and power consumption. To date, limited research has been done to demonstrate the feasibility of a miniaturized photoacoustic sensor.[7-13] Initial examination of the scaling principles associated with PAS in respect to microelectromechanical systems (MEMS) dimensions indicated that photoacoustic signals would remain at similar sensitivities or even surpass those commonly found in macro-scale devices.[8-13]

The first step in a PA experiment is the introduction of light. The main criterion for the starting point of PAS is that the molecules of interest need to be excited electronically, vibrationally, or rotationally. In the broadest sense, this light can be at many different wavelengths, and even span large differences in imparted energy (e.g., ultraviolet through the infrared). Light sources can take various forms, depending on the application at hand. There are two main categories of light sources used for PAS: broadband sources and narrow band laser sources. Although lamp-based PAS is still common, modern PAS research has been mainly carried out using laser sources. Some of the key advantages of laser sources are their large spectral brightness, collimated output, ease of modulation, and narrow spectral linewidth. Disadvantages include expense and limited tunability; however, these are not a generic quality of every laser architecture.

In 1994 the introduction of the quantum cascade laser (QCL) by Bell Labs[14] changed the prospects of laser photoacoustics and, in general, infrared spectroscopy. Since that time, continuing and aggressive evolution has been occurring. There have been numerous government programs run by different agencies (e.g., Defense Advanced Research Projects Agency) that have addressed many aspects of QCL performance, including thermal management, overall optical efficiency, beam handling, and other advances in gain media production. This funding has provided investment to various researchers and companies to increase the QCL's capability and availability during this time period. The QCL has matured to a level at which numerous companies can produce gain material for laser systems both in the United States and abroad. Along with this production, several companies have produced laser systems that are suitable for spectroscopic purposes (e.g., Daylight Solutions, Inc. and Pranalytica, Inc.). The current state of the art for external-cavity (EC) grating-tunable QCL systems has been shown by Daylight Solutions, Inc. (San Diego, California), which has demonstrated tuning capability of a QCL system producing upward of 350 and 500 cm^{-1} tuning spans using a single element in the 8-12 μm and 3-5 μm regions, respectively. Spectroscopically, these sources have had a dramatic impact on PA research due to their wide tuning over pertinent regions in the infrared.

Over the past 8 years, we have evaluated QCL technology in the implementation of these sources in our PA gas sensor platforms. To date, we have demonstrated that widely tunable QCL sources can achieve full spectroscopic discrimination of gas analytes, due to their large tuning ranges.[15] Furthermore, these sources operating in low-duty cycles, have demonstrated that PAS based on lock-in amplification can still be performed and indeed shows great promise. Here, we review our PA sensing research employing a variety of QCLs as excitation sources and discuss the unique capabilities and challenges we have encountered with this technology.

2. EXPERIMENTAL

Figure 1 depicts a block diagram of the basic elements required for a photoacoustic gas sensor.

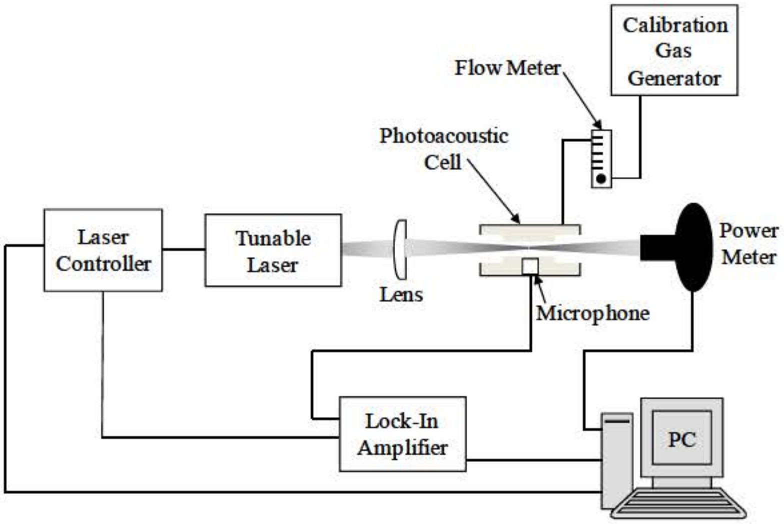

Figure 1. Schematic diagram of a general laser-based photoacoustic gas sensor system.

2.1 Quantum Cascade Lasers

Daylight Solutions, Inc. We evaluated 4 different QCL models from this vendor. A broadly tunable, ***pulsed*** EC-QCL (Daylight Solutions, model: 10080) was employed as an excitation source for the sensing system. The laser was powered by an external controller (Daylight Solutions, model: TLC 1001). The QCL was continuously tunable from 1032 cm^{-1} to 1070 cm^{-1} (9.69 μm–9.34 μm) and had a spectral resolution of 1 cm^{-1}. The pulsed source operated at room temperature with convective cooling. Current pulses of 1650 mA with a 500 ns duration and 20.9 kHz pulse rate corresponded to a 1.0% duty cycle and provided an average optical power of 1.35 mW. A KBr planoconvex lens (ISP Optics, model: custom) was utilized for focusing purposes.

A second broadly tunable, ***pulsed*** EC-QCL (Daylight Solutions, model: 11088) was employed as the excitation source for the sensing system. The laser was powered by an external controller (Daylight Solutions, model: TLC 1001). The QCL was continuously tunable from 1015 cm^{-1} to 1240 cm^{-1} (9.85 μm–8.06 μm) and had a spectral resolution of 1 cm^{-1}. The pulsed source operated at room temperature with convective cooling. Current pulses of 1600 mA with a 500 ns duration and 21.6 kHz pulse rate corresponded to a 1.1 % duty cycle and provided an average optical power of 1.32 mW. A BaF_2 plano-convex lens (ISP Optics, model: BF-PX-12-25) was utilized for focusing purposes.

A broadly tunable, ***modulated continuous wave (CW)*** EC-QCL (Daylight Solutions, model: 21096) was employed as the excitation source for the sensing system. The laser was powered by an external controller (Daylight Solutions, model: TLC 1001). The QCL was continuously tunable from 1032 cm^{-1} to 1070 cm^{-1} (9.69 μm–9.34 μm) and had a spectral resolution of 1 cm^{-1}. The modulated CW source required a compact chiller (Solid State Cooling Systems, model: Oasis 150) for operation at 15 °C. An injection current of 725 mA provided an average optical power of 11.97 mW. A function generator (Stanford Research Systems, model: DS340) was connected to the laser head via a subminiature version A (SMA) connector to allow for external current modulation. A 17.2 kHz sine wave with a peak amplitude of 2.5 V resulted in 65% amplitude modulation. Beam focusing was accomplished using a CaF_2 plano-convex lens (ISP Optics, model: custom).

A broadly tunable, ***ultracompact pulsed*** EC-QCL (Daylight Solutions, model: SpriteIR)[16] was employed as the excitation source for the sensing system. The laser was powered by an external controller (Daylight Solutions, model: custom). SpriteIR is a prototype laser developed during an Army Small Business Innovation Research (SBIR) Phase II Development program. The compact source built for this program offers performance in a small package (a 2 in. cube) that is typically achieved with larger, bench-top laboratory lasers. The packaged laser prototype contained a voice coil motor-based tuning mechanism that allowed both sweeping and stepping motions for rapid wavelength tunability. The SpriteIR was tunable from 1000 cm^{-1} to 1205 cm^{-1} (10.0 µm–8.30 µm) and had a spectral resolution of 1 cm^{-1}. The prototype source was mounted on a cooling tower (Daylight Solutions, model: custom) and required a compact chiller (Solid State Cooling Systems, model: Oasis 150) for operation at 17 ºC. Current pulses of 500 mA with a 500 ns duration and 20.0 kHz pulse rate corresponded to a 5% duty cycle and provided an average optical power of 1.08 mW. A BaF_2 plano-convex lens (ISP Optics BF-PX-12-25) was utilized for focusing purposes.

Pranalytica, Inc. We evaluated one QCL model from this vendor. A broadly tunable, ***quasi-continuous wave*** (QCW) (i.e., high duty cycle pulsed operation, typically ~50%) EC-QCL (Pranalytica, model: MonoLux-80-CW) was employed as the excitation source for the sensing system. The laser was fully self-contained and required only standard AC power and external computer control to operate. The QCL was continuously tunable from 1145 cm^{-1} to 1434 cm^{-1} (8.733 µm–6.974 µm) and had a spectral resolution of 0.2 cm^{-1}. The QCW source operated with a compact chiller (Solid State Cooling Systems, model: Oasis 150) for operation at 17 ºC. The laser output could be modulated by an externally supplied transistor-transistor logic (TTL) signal. The modulation was imposed on the internal high frequency (1 MHz) drive signal. A function generator (Stanford Research Systems, model: DS340) was connected to the laser head via a Bayonet Neill–Concelman (BNC) connector to allow for external modulation. A 5.0 V, 21.5 kHz TTL signal resulted in 50% modulation of the high repetition frequency pulse and provided an average optical power of 39 mW. The laser system was equipped with a red guide laser for ease of alignment.

In all cases, the transmitted laser power was measured with a power meter (Ophir Optronics Nova II) equipped with a thermal head (Ophir Optronics 3A). These measurements allowed for normalization of the photoacoustic signal for any residual drift associated with the excitation source.

2.2 MEMS-Scale Photoacoustic Cells

MEMS-scale differential photoacoustic cells were fabricated to meet our design specifications[17] by Infotonics Technology Center, Inc. The differential technique employs two resonator tubes, both housing a microphone (Knowles FG-23629), but with radiation directed through only through one to generate a photoacoustic signal. The microphones possessed similar responsivities, which allowed for subtraction of the reference microphone signal from the photoacoustic microphone signal. This allowed for the removal of noise elements that were present in both resonant chambers, such as external vibrations.

The influence of cell geometry on the photoacoustic signal has been discussed elsewhere.[5, 18, 19] Briefly, cell design #1 (Figure 2(A) and (B)) consisted of two 8.5 mm long open resonators having square cross sections, each with a diameter of 0.93 mm. Cell design #2 (Figure 2(C) and (D)) consisted of two 10 mm long open resonators having square cross sections, each with a diameter of 0.864 mm. In both cell designs, the resonators were flanked on both sides by a buffer volume (acoustic filter), which provided noise suppression. The resonator length was twice that of the buffer volume and the diameter of the buffer volume was at least three times that of the resonator. To further suppress gas flow noise, the buffer volumes were each connected by a tube to gas input and output acoustic filters (Figure 2(A) and (C)).

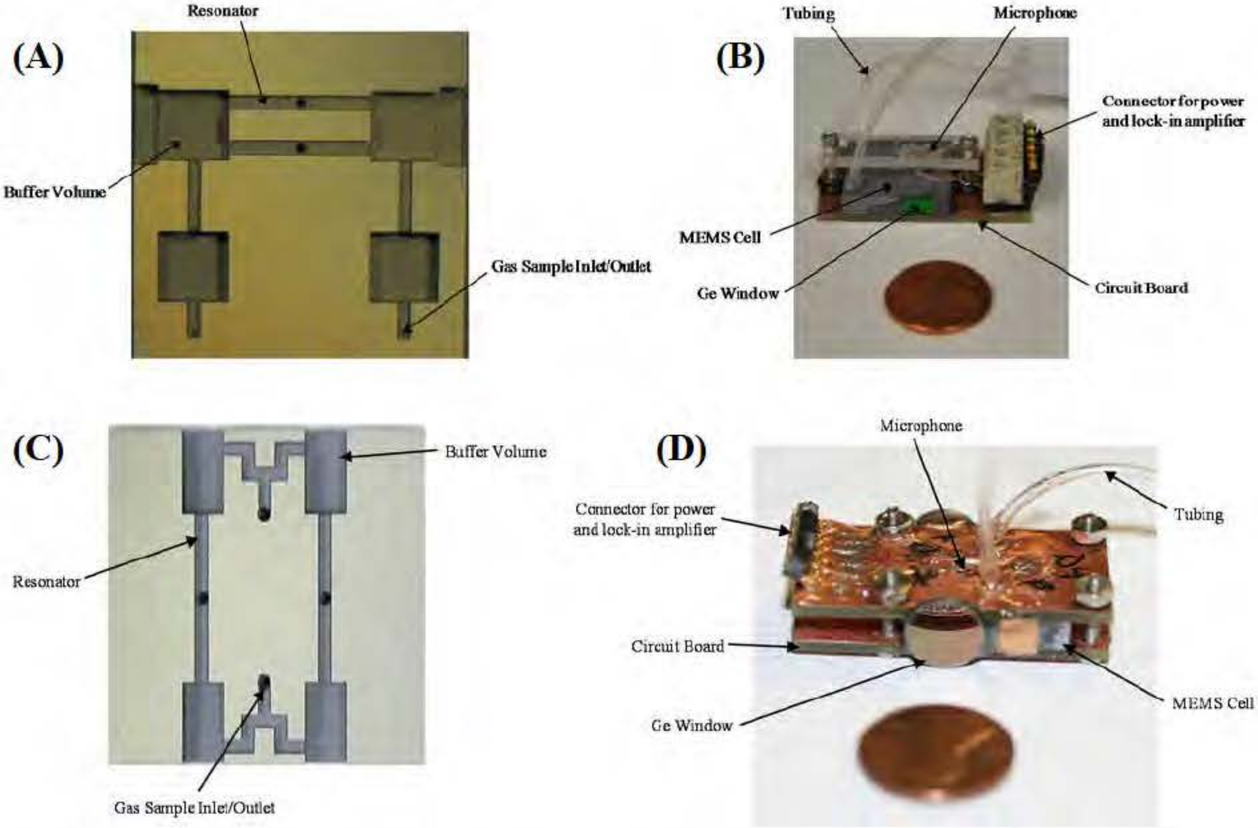

Figure 2. (A) Photograph of the internal structure of the MEMS-scale photoacoustic cell design #1. (B) Photograph of the MEMS-scale photoacoustic cell design #1 used when collecting data. (C) Photograph of the internal structure of the MEMS-scale photoacoustic cell design #2. (D) Photograph of the MEMS-scale photoacoustic cell design #2 used when collecting data.

Both photoacoustic cell designs had two germanium windows (Edmund Optics NT47-685), which were attached to the buffer volumes on either side of the photoacoustic resonator with epoxy. On design #2, small aluminum squares were attached to the buffer volumes on either side of the reference resonator with epoxy. Tygon® tubing was connected to the buffer volumes to allow for gas sample inlet and outlet flow. The MEMS-scale photoacoustic cell was mounted on a printed circuit board, which allowed for wiring the microphones to a power supply (AA battery) and a lock-in amplifier (via modified BNC cables). Figure 2(B) and (D) are photographs of the complete MEMS-scale photoacoustic cell package designs #1 and #2, respectively.

2.3 Sample Generation

The trace gases were generated using calibration gas generators (Owlstone Nanotech OVG-4 and VICI Metronics Dynacalibrator 190). Nitrogen was used as the carrier gas. The gas sources were gravimetrically certified permeation tubes (KIN-TEK Laboratories, Inc. model: HRT-010.00-3026/40 (acetone); HRT-007.00-3047/40 (vinylacetate), HRT-002.00-3045/100 (1,4-dioxane); VICI Metronics, model: Dynacal 107-150-7845-C100 (dimethyl methyl phosphonate (DMMP)), length: 15 cm). The acetone and vinyl acetate tubes were placed in a calibration oven held at a constant temperature of 40 °C. The permeation rates at this temperature for acetone and vinyl acetate were 1,114 ng/min and 1,986 ng/min, respectively. The 1,4-dioxane tube was placed in a calibration oven held at a constant temperature of 100 °C. The permeation rate at this temperature was 1,715 ng/min. The DMMP tube was placed in a calibration oven held at a constant temperature of 100 °C. The permeation rate at this temperature was 1,180 ng/min. Varying calibrated flow rates of the nitrogen carrier gas from 50 mL/min to 1000 mL/min governed the concentration of the analytes of interest. The concentration range for each analyte is limited by the permeation tube and the permissible flow rates of the calibration gas generators. Poly (tetrafluoroethylene) (PTFE) tubing was used to connect the gas generator to the sample inlet of the photoacoustic cell. A flow controller and a relief valve were placed in line between the gas generator and the photoacoustic cell to ensure a constant flow rate of 60 mL/min through the cell. This was done to reduce flow noise.

2.4 Data Acquisition

The signals detected by both the photoacoustic and reference microphones were extracted using the differential voltage input on a lock-in amplifier (Stanford Research Systems SR530) with a time constant of 3 s operating at the pulse frequency of the laser or the external modulation frequency of the function generator. LabVIEW (National Instruments, version 2012) was used to create a virtual instrument (VI) to read and record the voltage outputs from the lock-in amplifier under various conditions directly to a personal computer (PC). The VI was programmed to collect the X (in-phase), Y (quadrature), R (amplitude) and θ (phase angle) components of the photoacoustic signal. Photoacoustic spectra were obtained by holding the laser pulse frequency constant while scanning the laser wavelength range. This allowed for the determination of the wavelength having the maximum analyte absorbance in this region. 200 measurements were made at each increment, and a mean value was calculated and recorded for the subsequent construction of a photoacoustic spectrum. To estimate the limit of detection (LOD), the laser pulse frequency or external modulation frequency and wavelength having the maximum photoacoustic absorbance signal were held constant and the gas generator flow rate was ramped, which produced decreasing sample concentrations. Mean values and standard deviations of 200 points at a given concentration were calculated. The background signal, attributed to the absorbance of laser radiation by the cell windows and walls, was also measured. This background signal was subtracted from the mean photoacoustic signal measured at each concentration. These values were used to prepare a linear regression with which the LOD could be calculated by taking three times the standard deviation (3σ) of the background and dividing it by the slope of the linear function.

2.5 Instrumentation

All Fourier transform infrared (FTIR) absorbance spectra were collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a potassium bromide (KBr) beamsplitter and a mercury cadmium telluride (MCT)-A (narrow band – 650 cm^{-1} cutoff) detector. Each spectrum was acquired at a resolution of 1.0 cm^{-1} averaging 100 scans.

3. RESULTS

Laser photoacoustic spectra and limits of detection (LOD) of various analytes of interest (e.g., DMMP, 1,4-dioxane, and vinyl acetate) were determined for the MEMS-scale photoacoustic sensor platforms employing a variety of QCLs as excitation sources. The analytes were chosen based on known absorption features within the wavelength tuning ranges of each evaluated laser. The majority of these results have been discussed previously[20-22]; however, it is important to highlight them again for the purpose of this paper.

3.1 Daylight Solutions Pulsed EC-QCL (model 10080)

A laser photoacoustic spectrum was collected for DMMP using photoacoustic cell design #2. The spectrum was collected as the laser was continuously tuned from 990 cm^{-1} to 1075 cm^{-1} (10.10 μm–9.30 μm), in 1 cm^{-1} increments. This analyte has known absorption features in this region, assigned to phosphorus—oxygen—carbon stretching vibrations.[23] There is very good agreement between the photoacoustic and FTIR spectra (see Figure 3(A)). Figure 3(B) illustrates the sensor response as a function of DMMP concentration. The 3σ limit of detection was determined to be 54 ppb for DMMP. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9996. As a measure of the effectiveness of this sensing platform, we considered the recommendations for protecting human health from potential adverse effects of exposure to relevant nerve agents.[24] For a 30 min exposure, the lethal concentration is approximately 575 ppb, with the first noticeable health effects occurring at 5.8 ppb. While we have not achieved the necessary detection limits employing this laser in our PA sensor platform, we are confident that sensor optimization, including an excitation source with higher output power, will yield the desired results.

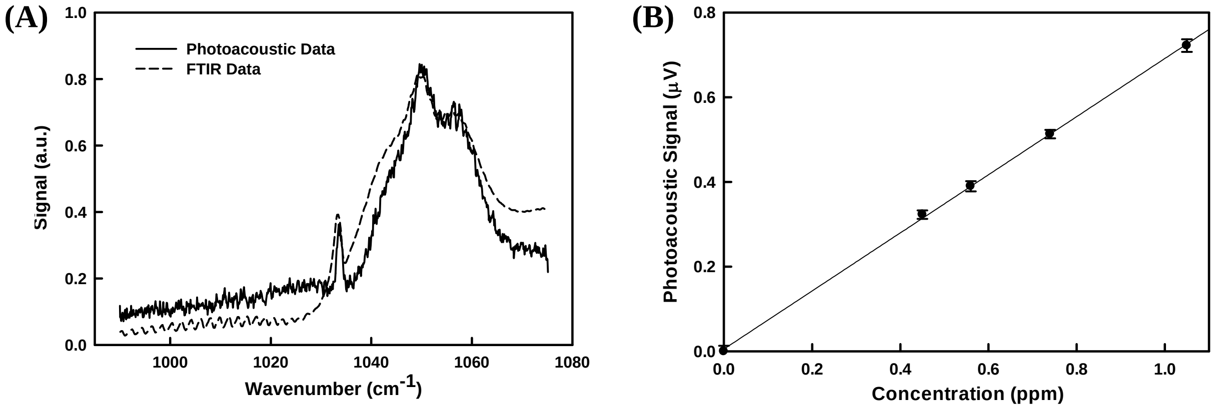

Figure 3. Daylight Solutions pulsed EC-QCL (model 10080) results. (A) Measured laser photoacoustic spectrum of DMMP compared to FTIR reference spectrum. (B) Photoacoustic sensor response as a function of DMMP concentration. Error bars represent one standard deviation. A linear function has been fit to the data.

3.2 Daylight Solutions Pulsed EC-QCL (model 11088)

Laser photoacoustic spectra were collected for 1,4-dioxane and vinyl acetate using photoacoustic cell design #1. The spectra were collected as the laser was continuously tuned from 1,100 cm^{-1} to 1,240 cm^{-1} (9.09 µm–8.06 µm), in 1 cm^{-1} increments. These analytes have known absorption features in this region, assigned to carbon—carbon and carbon—oxygen stretching vibrations.[5, 25] For 1,4-dioxane and vinyl acetate, there is excellent agreement between the photoacoustic and FTIR spectra (see Figure 4(A) and (B), respectively). Figure 4(C) illustrates the sensor response as a function of 1,4-dioxane concentration. The 3σ limit of detection was determined to be 180 ppb for 1,4-doixane. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9945. Figure 4(D) illustrates the sensor response as a function of vinyl acetate concentration. The 3σ limit of detection was determined to be 224 ppb for vinyl acetate. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9986. As a measure of the effectiveness of this sensing platform, we considered the National Institute for Occupational Safety and Health (NIOSH) recommended airborne exposure limits for 1,4-dioxane[26] and vinyl acetate[27]. Employing this laser in our PA sensor system, we have achieved detection limits well below the suggested value of 1 ppm (Threshold Limit Value, 20 min exposure) for 1,4-dioxane and 4 ppm (Threshold Limit Value, 15 min exposure) for vinyl acetate.

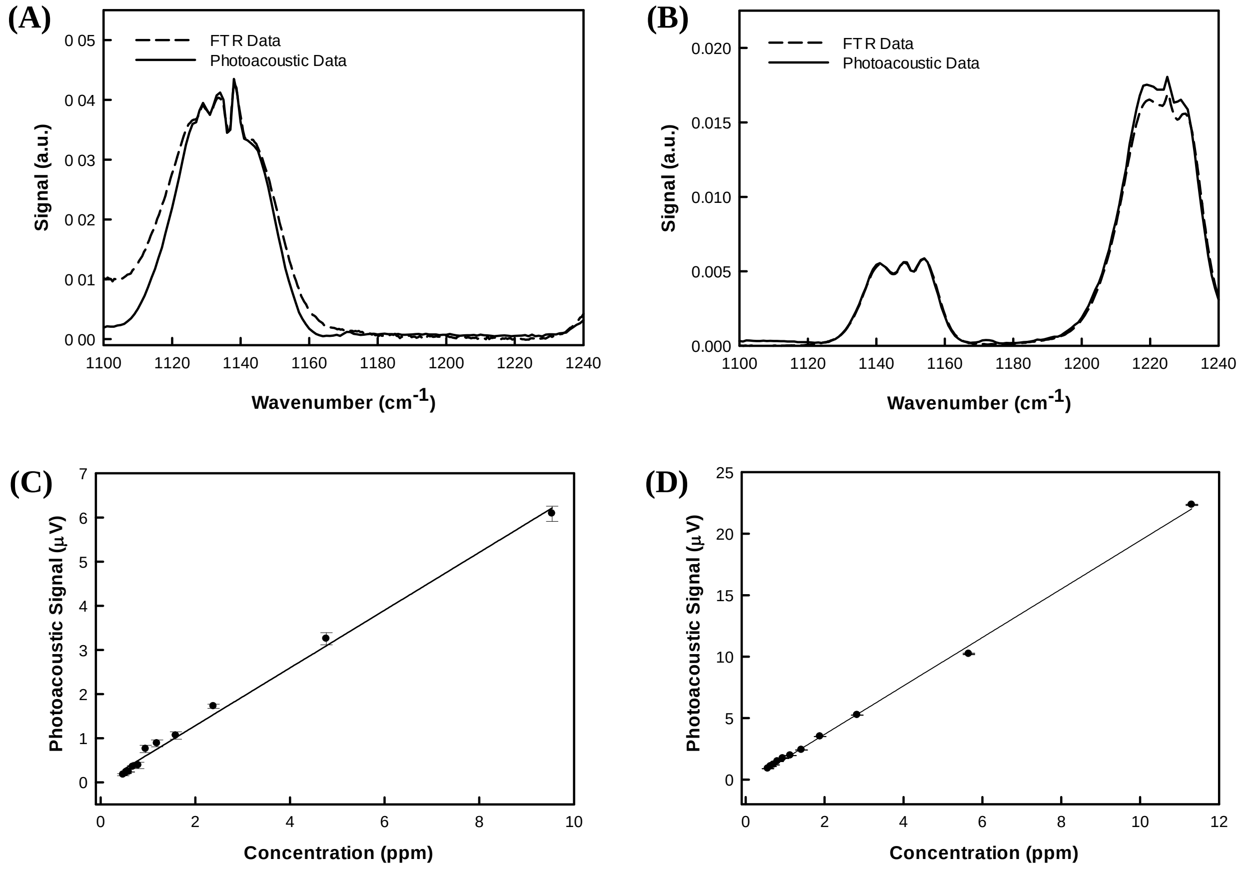

Figure 4. Daylight Solutions pulsed EC-QCL (model 11088) results. (A) Measured laser photoacoustic spectrum of 1,4-dioxane compared to FTIR reference spectrum. (B) Measured laser photoacoustic spectrum of vinyl acetate compared to FTIR reference spectrum. (C) Photoacoustic sensor response as a function of 1,4-dioxane concentration. Error bars represent one standard deviation. A linear function has been fit to the data. (D) Photoacoustic sensor response as a function of vinyl acetate concentration. Error bars represent one standard deviation. A linear function has been fit to the data.

3.3 Daylight Solutions Modulated CW EC-QCL (model 21096)

A laser photoacoustic spectrum was collected for DMMP using photoacoustic cell design #2. The spectrum was collected as the laser was continuously tuned from 1,005 cm^{-1} to 1070 cm^{-1} (9.95 μm–9.34 μm). Due to the mode hopping[28], nature of this source, continuous wavelength tunability over the entire tuning range required simultaneous control of the laser current and wavelength. While necessary for source stabilization, this process resulted in longer data acquisition times. However, high resolution may not be necessary to accurately record spectral detail of analytes having broad absorption features, such as DMMP. Therefore, a reduction in the number of measured wavelengths will maintain the structure of the DMMP absorption spectrum and decrease measurement times. We chose to investigate 102 wavelengths in the range of 1,032 cm^{-1} to 1,070 cm^{-1} (9.69 μm–9.34 μm). An important feature of this range is that the measurements were performed without any change in the laser current. Although mode hopping still occurs in this wavelength region, there is agreement between the laser photoacoustic data and the FTIR spectra (see Figure 5(A)). Figure 5(B) illustrates the sensor response as a function of DMMP concentration. The 3σ limit of detection was determined to be 20 ppb for DMMP. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9996. As a measure of the effectiveness of this sensing platform, we again considered the recommendations for protecting human health from potential adverse effects of exposure to relevant nerve agents (see above discussion for Daylight Solutions, Inc. model 10080).

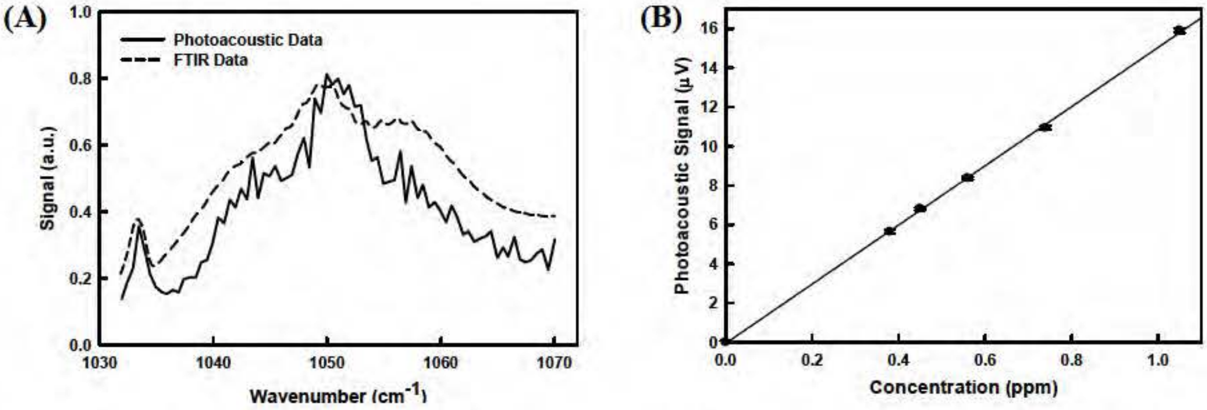

Figure 5. Daylight Solutions modulated CW EC-QCL (model 21096) results. (A) Measured laser photoacoustic spectrum of DMMP compared to FTIR reference spectrum. (B) Photoacoustic sensor response as a function of DMMP concentration. Error bars represent one standard deviation. A linear function has been fit to the data.

3.4 Daylight Solutions Ultracompact Pulsed EC-QCL (model SpriteIR)

A laser photoacoustic spectrum was collected for 1,4-dioxane using photoacoustic cell design #1. The spectrum was collected as the laser was tuned from 1,100 cm^{-1} to 1,170 cm^{-1} (9.09 µm–8.55 µm), in 1 cm^{-1} increments. There is excellent agreement between the photoacoustic spectrum collected using the SpriteIR laser and the FTIR spectrum (see Figure 6(A)). A photoacoustic spectrum of 1,4-dioxane collected using a commercially available EC-QCL is also provided in Fig. 6(A) for comparison.[15] Figure 6(B) illustrates the sensor response as a function of 1,4-dioxane concentration. The 3σ limit of detection was determined to be 133 ppb for 1,4-dioxane. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9960. As a measure of the effectiveness of this sensing platform, we considered the NIOSH recommended airborne exposure limit for 1,4-dioxane. Employing this laser in our PA sensor system, we have achieved a detection limit well below the suggested value of 1 ppm (Threshold Limit Value, 20 min exposure).

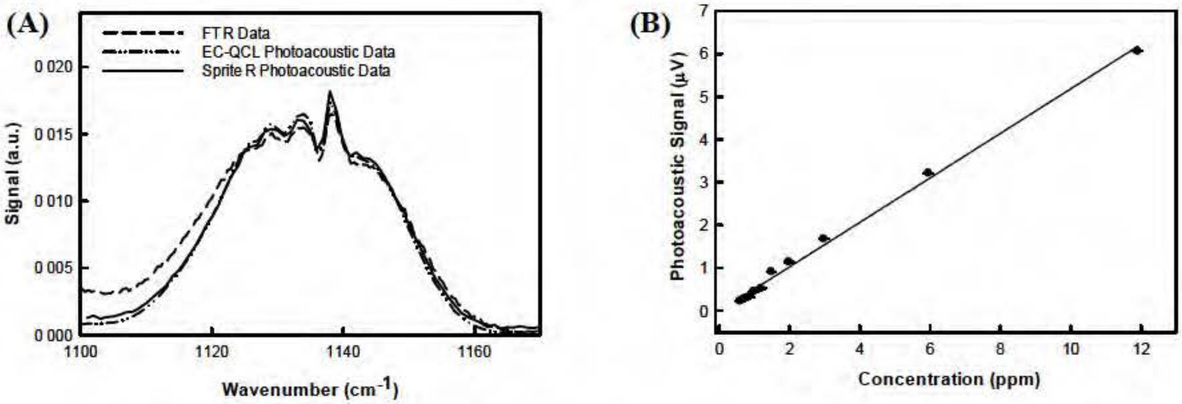

Figure 6. Daylight Solutions ultracompact pulsed EC-QCL (model SpriteIR) results. (A) Measured laser photoacoustic spectrum of 1,4-dioxane compared to FTIR reference spectrum and commercially available EC-QCL photoacoustic spectrum. (B) Photoacoustic sensor response as a function of 1,4-dioxane concentration. Error bars represent one standard deviation. A linear function has been fit to the data.

3.5 Pranalytica QCW EC-QCL (model MonoLux-80-CW)

A laser photoacoustic spectrum was collected for vinyl acetate. The spectrum was collected as the laser was from tuned from 1,176 cm^{-1} to 1,265 cm^{-1} (8.50 µm–7.90 µm), in 1 cm^{-1} increments. There is good agreement between the photoacoustic and FTIR spectra (see Figure 7(A)); however, the photoacoustic spectrum is slightly shifted. This is an interesting result and will be investigated further as we continue to employ this laser in our photoacoustic sensor platform. Figure 7(B) illustrates the sensor response as a function of vinyl acetate concentration. The 3σ limit of detection was determined to be 20 ppb for vinyl acetate. The results exhibit excellent linearity with a correlation coefficient (R^2) of 0.9986. As a measure of the effectiveness of this sensing platform, we considered the NIOSH recommended airborne exposure limits for vinyl acetate. Employing this laser in our PA sensor system, we have achieved detection limits well below the suggested value of 4 ppm (Threshold Limit Value, 15 min exposure) for vinyl acetate.

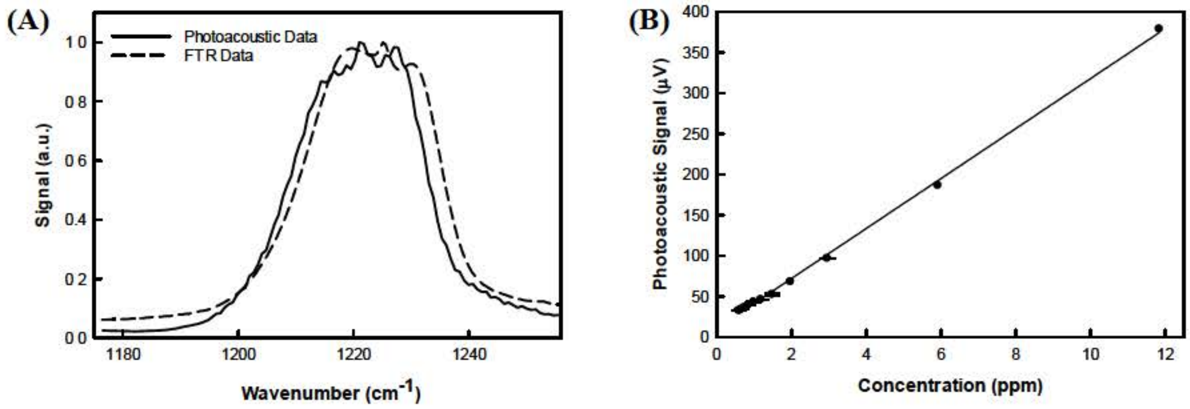

Figure 7. Pranalytica QCW EC-QCL (model Monolux-80-CW) results with cooling at 17°C. (A) Measured laser photoacoustic spectrum of vinyl acetate compared to FTIR reference spectrum. (B) Photoacoustic sensor response as a function of vinyl acetate concentration. Error bars represent one standard deviation. A linear function has been fit to the data.

4. DISCUSSION

As demonstrated by the results summarized above and published previously, our chemical sensing research has benefitted from the broad tuning capabilities of QCLs. However, each laser system we have employed in a PA sensing platform has exhibited limitations. Although the laser element itself is quite small (typically 3 mm to 6 mm) in each of the systems discussed here, the packaging, power supply, and controller remain logistical burdens. The evaluated laser systems are shown in Figure 8. This figure provides a side-by-side comparison of the systems in terms of overall size and components. The Daylight Solutions pulsed/modulated CW EC-QCL system (models 10080, 11088, and 21096) is by far the largest package, and the modulated CW system necessitates a chiller, which adds additional bulk. The Pranalytica MonoLux laser system is attractive in that it does not have a separate controller; however, depending on the mode of operation, this system also requires a chiller. The Daylight Solutions SpriteIR is one tenth the size of commercially available Daylight Solutions QCL systems; however a cooling tower and chiller are required. Given that photoacoustic sensor miniaturization requires light sources of comparable size, the Daylight Solutions SpriteIR is a successful demonstration of the ability to package a QCL on a smaller scale.

Figure 8. Photograph showing a size-by-size comparison of the various evaluated laser systems. (A) Daylight Solutions ultracompact SpriteIR pulsed EC-QCL system (laser and controller); (B) Daylight Solutions pulsed/modulated CW EC-QCL system (laser and controller); (C) Pranalytica QCW EC-QCL system (complete).

As stated earlier, the signal generated from a photoacoustic experiment is directly proportional to the absorbed incident power. This power is dependent on the wavelength and output format of the excitation source, which is normally restricted to CW or low-duty cycle pulsed operation. This restriction is directly associated with the inefficiency of the laser source (<10%) and its thermal effect on the feedback mechanisms. The localized heating of the element will change output wavelength and "pull" the laser to mode-hop unless it is pulsed short enough to avoid large heating or operated in a continuous fashion, which establishes thermal equilibrium. In general, both pulsed and CW Daylight Solutions QCLs specify (wavelength dependent) >100 mW power (CW)/peak power (pulsed) and >5 mW average power (pulsed). For the pulsed sources evaluated in our laboratory (Daylight Solutions models 10080, 11088 and SpriteIR), the duty cycles were as low as 1% and no higher than 5%. These values were dictated by the pulse frequency, which in our PA experiments was slow compared to the manufacturer's optimized specifications (100 kHz). This factor greatly reduced the average power available for our PA sensing experiments. A higher average optical power was achieved using the Daylight Solutions modulated CW source (model 21096); however, amplitude modulation was not optimal and we were limited to specific current settings due to the mode-hopping nature of the source. These factors reduced our ability to attain a higher average power with this QCL model. In all cases, there was no discernable power drift from the Daylight Solutions QCLs. The specifications (wavelength dependent) for the Pranalytica QCW laser are >100 mW average power and >400 mW peak power, which resulted in significantly more average optical power for our PA sensing experiments compared to the Daylight Solutions QCLs. However, when operated at room temperature with passive cooling, the power was not stable and decreased with time (15% drift over 2 h). When the QCL was cooled to 17°C (chiller limited), the power could be better stabilized (3% drift over 3 h). Although Pranalytica only specifies the use of a chiller for CW operation at 14°C, cooling of the laser to some degree in QCW mode resulted in power stabilization. Although the modulated CW/QCW sources provided increased output power compared to that obtained using pulsed sources, consideration of heat management may favor the use of a pulsed QCL for future sensor development.

Due to the variety of wavelength tuning ranges for the evaluated QCLs, we are not able to make a LOD comparison for a single analyte; however, we have been able to make sensitivity comparisons between different Daylight Solutions laser models as well as between Daylight Solutions and Pranalytica sources employed in our PA sensor platform. For the detection of DMMP, both the Daylight Solutions modulated CW QCL and a Daylight Solutions pulsed QCL were evaluated. The average optical power of the modulated CW QCL was significantly greater than the pulsed model. Therefore, it was expected that the PA sensor employing the modulated source would produce improved DMMP detection limits compared to the pulsed laser. For the detection of 1,4-dioxane, both a Daylight Solutions pulsed QCL model and the Daylight Solutions ultracompact pulsed QCL (SpriteIR) were evaluated. An improved LOD was achieved using the SpriteIR laser. Although the average power output of the SpriteIR laser was less than that of the commercial pulsed source, less noise or background signal was observed using the SpriteIR laser, which allowed for an improved detection limit. Finally, for the detection of vinyl acetate, both a Daylight Solutions pulsed QCL model and the Pranalytica QCW laser were evaluated. Based on the optical power, it was expected that the PA sensor employing the Pranalytica QCW source would produce improved detection limits for vinyl acetate compared to the Daylight Solutions QCL. Although the average power output of the Pranalytica laser was much higher than that of the Daylight Solutions pulsed QCL, higher noise or background signal was observed using the Pranalytica source. Further PA experiments are needed employing this source to fully understand the capabilities. Additionally, in order to achieve a better comparison between the Pranalytica and Daylight Solutions QCLs, operation of the Pranalytica source in pulsed mode is needed. Compared to the pulsed sources, the modulated CW/QCW sources provided increased output power and therefore, allowed for better PA sensor figures of merit; however, the results were not as improved as we had expected. Further investigations are needed to determine the ideal operating mode of these sources when they are employed in a PA sensor platform. Perhaps a pulsed QCL with increased optical output power at the appropriate pulse repetition frequency will result in detection limits comparable to or better than those realized with the modulated CW/QCW QCLs.

QCL system size and power output are key factors in the continued development of a miniaturized photoacoustic chemical sensing platform; however, we have also considered the ease of use of each of the sources we have evaluated. All of the laser systems were easy to set up. The Daylight Solutions modulated CW and pulsed models (10080 and 11088) were easily controlled using the laser controller. Settings including wavelength, pulse frequency, pulse width, current, and temperature were all able to be modified by the user with the controller interface. The user was also provided the appropriate programming language to control the laser settings with a computer running instrument control software (i.e., LabVIEW), allowing for all data collection to be automated. The Daylight Solutions ultracompact SpriteIR laser and the Pranalytica QCW laser both included software for computer control. The software allowed the user to control basic functions, including turning the laser emission on, changing the wavelength setting, and, in the case of the SprtieIR, controlling the pulse frequency; however, these laser control software programs were not easily modified by the user and data collection could become tedious.

5. CONCLUSION

We have successfully demonstrated the use of a MEMS-scale photoacoustic sensing platform for trace vapor detection. We have evaluated a variety of QCLs in this platform allowing for detection limits in the ppb range. We believe that this sensor platform is an important step toward the development of a man-portable prototype. The availability of continuously tunable QCLs having a broad wavelength tuning range makes this an attractive approach for a variety of applications. Employing multiple continuously tunable QCLs having different center wavelengths in a PA sensor would provide a broad wavelength tuning range, allowing for increased molecular discrimination and simultaneous detection of several molecules of interest; however, power consumption and thermal stability must be considered. Although each QCL we have evaluated to date offers certain attractive features, we have yet to encounter a single laser system that fulfills all of the desired capabilities (i.e., low cost, small system package, high average power (>5 mW), broad tuning range) for the continued development of our miniaturized chemical sensor platform.

6. REFERENCES

[1] J. B. Kinney, R. H. Staley, Applications of photoacoustic spectroscopy. Ann. Rev. Mater. Sci. 12, 295 (1982).
[2] C. K. N. Patel, A. C. Tam, Pulsed optoacoustic spectroscopy of condensed matter. Rev. Mod. Phys. 53, 517 (1981).
[3] A. C. Tam, Applications of photoacoustic sensing techniques. Rev. Mod. Phys. 58, 381 (Apr, 1986).
[4] A. Miklos, P. Hess, Modulated and pulsed photoacoustics in trace gas analysis. Anal. Chem. 72, 30A (2000).
[5] F. G. C. Bijnen, J. Reuss, F. J. M. Harren, Geometrical optimization of a longitudinal photoacoustic cell for a sensitive and fast trace gas detection. Rev. Sci. Instrum. 67, 2914 (1996).
[6] M. Nagele, M. W. Sigrist, Mobile laser spectrometer with novel resonant multipass photoacoustic cell for trace-gas sensing Appl. Phys. B 70, 895 (2001).
[7] U. Bonne, B. E. Cole, R. E. Higashi. (US Patent 5886249, 1999).
[8] S. L. Firebaugh, K. F. Jensen, M. A. Schmidt, Miniaturization and integration of photoacoustic detection with a microfabricated chemical reactor system. JMEMS 10, 232 (2001).
[9] S. L. Firebaugh, K. F. Jensen, M. A. Schmidt, Miniaturization and integration of photoacoustic detection. J. Appl. Phys. 92, 1555 (2002).
[10] D. A. Heaps, P. Pellegrino, Examination of a quantum cascade laser source for a MEMS-scale photoacoustic chemical sensor. Proc. SPIE 6218, 621805 (2006).
[11] D. A. Heaps, P. Pellegrino, Investigations of intraband quantum cascade laser source for a MEMS-scale photoacoustic sensor. Proc. SPIE 6554, 65540F (2007).
[12] P. Pellegrino, R. Polcawich, Advancement of a MEMS photoacoustic chemical sensor. Proc. SPIE 5085, 52 (2003).
[13] P. Pellegrino, R. Polcawich, S. L. Firebaugh, Miniature photoacoustic chemical sensor using micorelectromechanical structures. Proc. SPIE 5416, 42 (2004).
[14] J. Faist *et al.*, Quantum Cascade Laser. Science 264, 553 (1994).
[15] E. Holthoff, J. Bender, P. Pellegrino, A. Fisher, Quantum Cascade Laser-Based Photoacoustic Spectroscopy for Trace Vapor Detection and Molecular Discrimination. Sensors 10, 1986 (Mar, 2010).
[16] E. Fotheringham, M. J. Weida, W. B. Chapman, T. Day, Progress towards compact broadly tunable laser modules for high-resolution mid-IR spectroscopy and commercial applications. Proc. SPIE 8268, 82682I (2012).
[17] R. G. Polcawich, P. M. Pellegrino. (US Patent 7304732, 2003).
[18] A. Miklos *et al.*, Improved photoacoustic detector for monitoring polar molecules such as ammonia with a 1.53 mu m DFB diode laser. AIP Conf. Proc., 126 (1999, 1999).
[19] J. F. Schill, E. L. Holthoff, P. M. Pellegrino, Predicting the resonant frequency of photoacoustic cells with side branches. IEEE Sens. J. 15, 1336 (2015).
[20] E. L. Holthoff, J. S. Bender, P. Pellegrino, A. Fisher, Quantum Cascade Laser-Based Photoacoustic Spectroscopy for Trace Vapor Detection and Molecular Discrimintaion. Sensors 10, 1986 (2010).
[21] E. L. Holthoff, D. A. Heaps, P. M. Pellegrino, Development of a MEMS-Scale Photoacoustic Chemical Sensor Using a Quantum Cascade Laser. IEEE Sens. J. 10, in press (2010).
[22] E. L. Holthoff, L. S. Marcus, P. M. Pellegrino, in *2013 IEEE Sensors*. (IEEE, Baltimore, MD, 2013), pp. 1-4.
[23] E. Brunol, F. Berger, M. Fromm, R. Planade, Detection of dimethyl methylphosphonate (DMMP) by tin dioxide-based gas sensor: Response curve and understanding of the ractional mechanism. Sens. Actuators, B 120, 35 (2006).
[24] Final recommendations for protecting human health from potential adverse effects of exposure to agents GA (Tabun), GB (Sarin) and VX. Fed. Regist. 68, 58348 (2003).
[25] J. McMurry, *Organic Chemistry*. (Brooks/Cole, Pacific Grove, CA, ed. 5th, 1999).
[26] Chemical Sampling Information: Dioxane. Available online: www.OSHA.gov (accessed on February 25, 2010).
[27] Chemical Sampling Information: Vinyl Acetate. Available online: www.OSHA.gov (accessed on February 26, 2010).
[28] T. A. Heumier, J. L. Carlsten, in *ILX Lightwave Corporation*. (Bozeman, MT, 2003).

1 (PDF)	DEFENSE TECH INFO CTR DTIC OCA
2 (PDF)	US ARMY RSRCH LAB IMAL HRA MAIL & RECORDS MGMT RDRL CIO LL TECHL LIB
1 (PDF)	GOVT PRNTG OFC A MALHOTRA
4 (PDF)	US ARMY RSRCH LAB RDRL SEE G WOOD RDRL SEE E E HOLTHOFF L MARCUS P PELLEGRINO