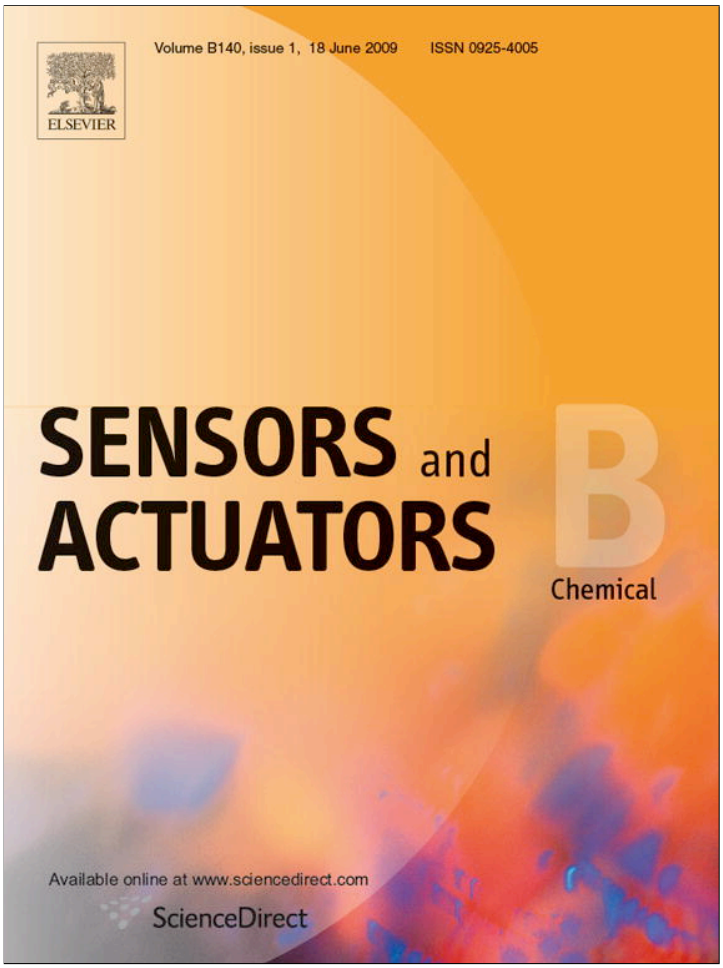

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External cavity widely tunable quantum cascade laser based hollow waveguide gas sensors for multianalyte detection

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ABSTRACT

In the study presented here, quantitative detection of ethyl chloride, dichloromethane, and trichloromethane individually and in mixture has been demonstrated using an external cavity broadly tunable quantum cascade laser (EC-QCL) based hollow waveguide gas sensor. The EC-QCL has been characterized by coupling into a FT-IR spectrometer documenting sufficient optical power output across a frequency tuning range from 1297 cm^{-1} to 1219 cm^{-1}. Concentrations as low as 4 ppb for ethyl chloride, 7 ppm for dichloromethane, and 11 ppb for trichloromethane were detected during exponential dilution experiments with the EC-QCL precisely tuned to selective absorption frequencies of the Q-branch for each constituent at 1287.25 cm^{-1}, 1262 cm^{-1}, and 1220 cm^{-1}, respectively.

1. Introduction

Mid-infrared (MIR; 3–20 μm) gas sensors are generally gaining momentum in trace gas sensing due to their intrinsic molecular selectivity [1], and specifically since the advent of the quantum cascade laser (QCL) [2] providing beneficial light source attributes such as compact dimensions, room-temperature operation, and an output power of up to 700 mW [3]. The detection of organic molecules in the MIR relies on the excitation of fundamental vibrational and rotational transitions, which provide distinct molecular signatures at detection limits ranging from the parts-per-million to the parts-per-trillion range [1,4].

The conventional light source used for mid-infrared spectroscopy of trace gases is the Fourier-transform infrared spectrometer (FT-IR); however, to date, power consumption for a portable, yet still bulky FT-IR can be as high as 140 W whereas miniaturized, hand-held devices, such as the QCL, typically consume 28 times less power, only 1.5–5 W [5]. Still, FT-IRs have a significant advantage over a laser light source due to broadband radiation in which multiple analytes can be measured simultaneously. However, widely tunable QCLs are quickly becoming a viable option for frequency tunable, hand-held, sensitive and selective trace gas sensors.

Until recently, QCLs have been limited in their tuning range across molecular absorption features to approximately 3–4 cm^{-1} by adjusting the injection current, or up to approximately 20 cm^{-1} by controlling the temperature of the laser chip [6]; however, a wider laser tuning range is desirable for the simultaneous detection of multiple analytes, as encountered in many real-world gas sensing applications.

External cavity tunable quantum cascade lasers (EC-QCL) [7–11] offer a different approach to conventional QCL wavelength tuning yielding a significantly broader tuning range exceeding 100 cm^{-1} [12]. Here, wavelength tuning provided by coupling radiation emitted from the QCL to a grating usually in a first order direct feedback configuration, or a Littman-Metcalf configuration [4]. Consequently, adjusting the angle of the grating results in shifting the location of the resonant peak, thereby enabling to precisely overlap the QCL emission with the maximum of selective analyte absorption features in a broad spectral window for sensitive and selective molecular detection in the gas phase.

To date, EC-QCLs have been tested in a variety of sensing systems providing in part detection limits at the sub-ppb concentration level [13]. Pushkarsky et al. have used EC-QCLs and photoacoustic spectroscopy (PAS) to demonstrate the detection of

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2,4,6-trinitrotoluene (TNT) at approximately 0.1 ppb, and acetylene at approximately 2.5 ppb (1σ) [14]. Phillip et al. have used an EC-QCL quartz-enhanced PAS (QEPAS) system utilizing a quartz tuning fork as the transducer to determine the absorption spectra of two gases, pentafluoroethane and 1,1,1,2-tetrafluoroethane, which were in excellent agreement with reference spectra [15]. Likewise, Lewicki et al. have shown trace-gas detection of pentafluoroethane at 3 ppb (1σ), and acetone at approximately 520 ppb (1σ) using EC-QCL QEPAS. Both analytes were also quantitatively determined within a custom gas mixture at concentrations of 47.2 ppm for acetone and 4.4 ppm for pentafluoroethane [12].

This work reports a multianalyte sensing capability with a possibly smaller form factor and minute quantity of analyte used. To achieve this, a mid-infrared (MIR) absorption spectroscopy gas phase chemical sensing system with a state-of-the-arts broadly tunable external cavity quantum cascade laser (EC-QCL) and hollow core waveguide (HWG) [16] was used. The HWG simultaneously serves as a waveguide for MIR radiation as well as a miniaturized gas cell [17] with an internal volume on the order of a few milliliters [18]. Additionally, HWGs permit fast response times on the order of a few seconds and yield detection limits in the low ppm to low ppb concentration range [18–22] making these trace gas sensors ideal candidates for applications such as human breath diagnostics.

In the present study, the first EC-QCL based HWG gas sensor was demonstrated for the quantitative detection of individual molecules at trace levels, as well as for the discrimination of structurally related constituents within gas mixtures. A tuning range of ~80 wavenumbers was achieved, effectively providing functionality of a "miniaturized spectrometer" with wide tunability on a compact platform.

2. Experimental

The pulsed QCL was characterized using an Au coated off-axis parabolic mirror (OAPM) to focus the emitted radiation into the external port of a Bruker IFS 66 (Bruker Optics, Inc., Billerica, MA) Fourier transform infrared (FT-IR) spectrometer utilizing a liquid-nitrogen–cooled mercury–cadmium-telluride (MCT) detector (detector element: 1 mm × 1 mm, detectivity: $D^* = 3 \times 10^{10}$ cm Hz$^{1/2}$ W^{-1}, model: FTIR-16-1.0, InfraRed Associates, Inc., Stuart, FL). The laser was external cavity tuned across a range of 1297–1219 cm^{-1} at a spectral resolution of 1 cm^{-1}, and spectra were collected averaging 10 scans per measurement at a spectral resolution of 0.25 cm^{-1} across a spectral range of 4000–400 cm^{-1} using the Blackman–Harris 3-term apodization function [23]. In a separate measurement, the laser was refocused directly onto the same MCT detector to determine the output voltage evaluated with an oscilloscope (TDS3032, Tektronix, Beverton, OR).

A schematic of the experimental sensing setup including exponential dilution is described in Fig. 1. Radiation from the EC-QCL (relative temperature: 0 °C, pulse width: 0.50 μs, frequency: 100.0 kHz, duty cycle: 5%, current: 1500 mA, Daylight Solutions, Inc., Poway, CA) was focused into at custom-made hollow waveguide gas cell using two OAPMs. The hollow waveguide is a structural silica tube internally coated with an IR-reflective Ag/AgI layer. After absorption, radiation was then focused onto a liquid-nitrogen cooled MCT detector. A reference beam was generated by using a beamsplitter prior to focusing radiation into the hollow waveguide, and via an additional MCT detector, thereby allowing for signal normalization compensating for e.g., fluctuations in optical power as a function of frequency.

Gas samples were prepared by exponential dilution, and directly introduced into the EC-QCL HWG gas sensor, as previously demonstrated [18]. Nitrogen was used as inert carrier gas at flow rates in the range of 8–42 mL/min depending on the tested analyte, however, remained constant throughout an individual measurement.

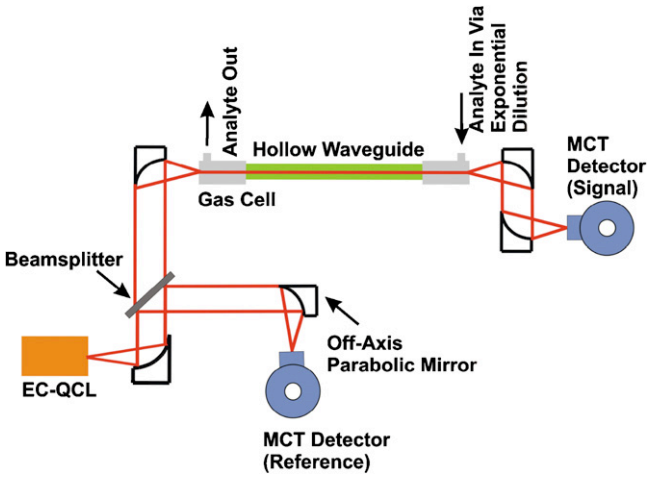

Fig. 1. Schematic of the experimental setup using exponential dilution.

For the determination of multivariate calibration samples, gas mixtures were prepared in sealed volumetric flasks, and injected into the hollow waveguide via needle valves available at the custom gas cells sealing off the HWG at both ends. While tuning the EC-QCL across its frequency range, molecularly selective damping of the laser radiation was determined as a function of decrease in voltage using an oscilloscope at a spectral resolution of 1 cm^{-1}.

3. Results and discussion

Fig. 2A shows the characterization of the EC-QCL emission with optical output power as a function of the emission frequency. As expected, the optical power decreases with increasing deviation from the native central emission frequency of the laser (1258 cm^{-1}). The deviation between the selected laser emission frequency and the measured emission frequency was determined to be below ±0.5 cm^{-1} of the selected EC-QCL emission frequency, as described in Fig. 2B. Fig. 2C depicts the correlation between expected and actual EC-QCL emission frequency. These performance parameters are essential for trace-gas sensing applications, as absorption lines may exhibit comparatively narrow bandwidths, thereby demanding precise overlap of the QCL emission frequency for ensuring maximized sensitivity and selectivity.

Univariate calibration of the gas sensing system was performed using exponential dilution, which is a commonly accepted method for preparing trace-level sample dilutions e.g., for calibrating gas chromatographs [24]. Using this procedure, the limit of detection for three individual analytes was determined at 1287.25 cm^{-1} (ethyl chloride), 1262 cm^{-1} (dichloromethane), and 1220 cm^{-1} (trichloromethane), respectively.

Exponential dilution theory enables that at any given point of time the instantaneous concentration of analyte can be calculated if the initial concentration, the volume of the dilution flask, and flow rate of carrier gas are known as follows:

$$C = C_0 e^{-at},$$

where C is the calculated instantaneous concentration of the analyte, C_0 is the initial concentration of the analyte, α is flow rate of the carrier gas divided by the volume of the dilution flask, and t is the time at which the concentration is calculated during exponential dilution [24]. Practically, a known amount of analyte is injected into the exponential dilution flask [25], while a stir bar constantly and continuously mixes and dilutes the analyte gas with the carrier

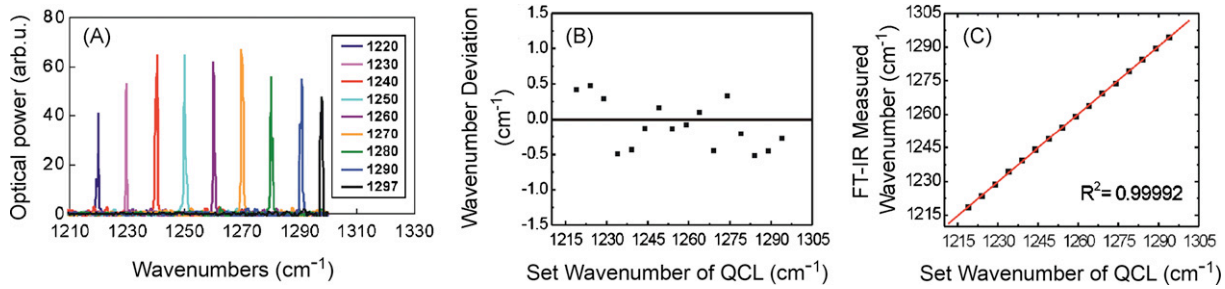

Fig. 2. FT-IR characterization of EC-QCL emission: (A) raw data FT-IR spectra over a range of wavenumbers. (B) Calculated deviation of set wavenumber from measured wavenumber. (C) Correlation between measured emission versus expected emission.

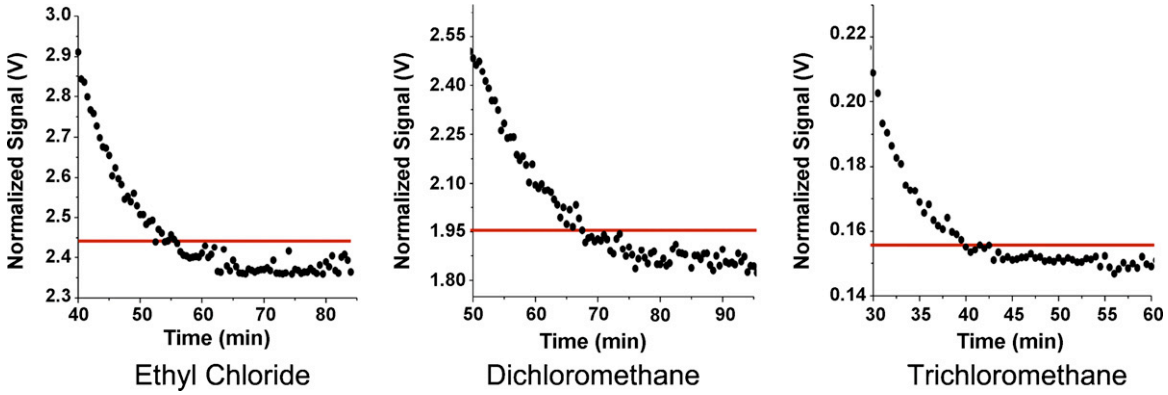

Fig. 3. Exponential dilution of ethyl chloride, dichloromethane, and trichloromethane. The red line indicates the noise level derived as noise average + 3σ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

gas at a constant flow rate. The limit of detection for this sensing system was derived from the smallest detectable analyte concentration using exponential dilution theory, which could be discriminated against the background noise level.

Typical results for such exponential dilution experiments indicating the recovery of the background signal, as the analyte is increasingly diluted within the HWG gas cell are given in Fig. 3. For experiments at individual gases, the EC-QCL was tuned to the center Q-branch of the CH_2 wagging mode for each analyte. Efficient overlap of the laser emission with the appropriate analyte absorption yielded limits of detection (according to the 3σ criteria) at 4 ± 3 ppb for ethyl chloride, 7 ± 6 ppm for dichloromethane, and 11 ± 15 ppb for trichloromethane, respectively.

Fig. 4 shows an exemplary spectrum of a mixture containing the three analytes, as recorded with the EC-QCL HWG gas sensor at a spectral resolution of 1 cm^{-1}. As any changes of the hollow waveguide response function and fluctuations in optical power are taken into account during absorption experiments, distinct and selective vibrational features of all three analyte are discriminated within the wavelength tuning range of a single EC-QCL.

Quantitative multivariate data analysis of gas mixtures was demonstrated by using a partial least squares model, which was built on a limited data set of manually prepared gas standards prepared by an experimental design approach for deliberately varying the concentrations per calibration sample while avoiding collinearity. The trainings set consisted of 11 calibration samples, each

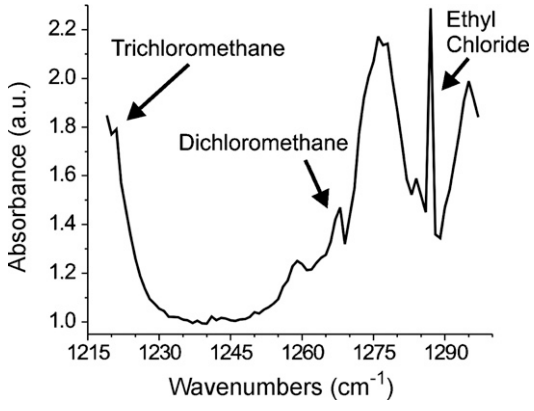

Fig. 4. Spectrum of all three analytes within a gas mixture recorded with EC-QCL HWG gas sensor.

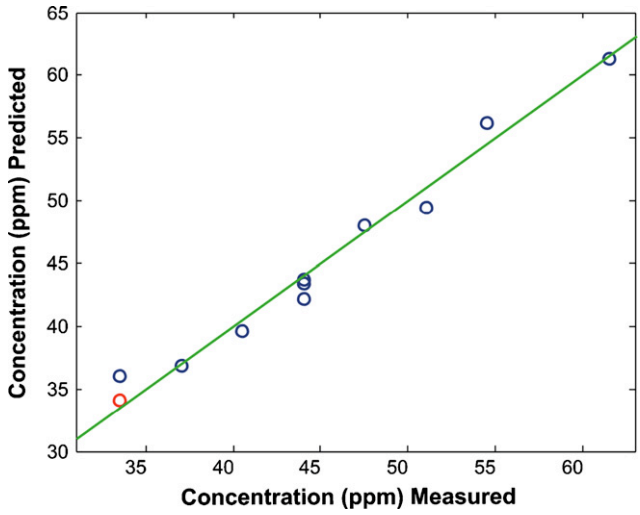

Fig. 5. PLS model validation for predicting the concentration of dichloromethane in mixture. The blue circles denote standards used to build the model. The red circle represents the standard left out as quasi unknown and the predicted value based on the established model. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

comprising all three analytes present within concentrations ranges: ethyl chloride 2000–9000 ppm, dichloromethane 30–70 ppm, and trichloromethane 40–100 ppm. The multivariate calibration model was built using PLS toolbox (Eigenvector Research, Inc., Wenatchee, WA). The prediction capability of the model was tested using cross-validation with each calibration sample randomly left out once and treated as quasi-unknown, after the model was generated using autoscaling for data preprocessing and selecting seven latent variables. The results are shown in Fig. 5; the validation of the model resulted in a coefficient of determination of 0.977, and a root mean square error of calibration of 1.294 for predicting the dichloromethane concentration within such gas mixtures characterized by considerable peak overlap between the constituents. It is expected that the robustness of the PLS model will further improve by substantially expanding the calibration data set using automated gas mixing routines.

4. Conclusions

Sensitive and selective trace gas detection of three analytes ethyl chloride, dichloromethane, and trichloromethane were demonstrated using an external cavity tunable quantum cascade laser hollow waveguide gas sensor tuned to the maximum absorption feature of each analyte. Gas mixtures were analyzed via a partial least squares model using the hollow waveguide as a miniaturized gas cell and tuning the EC-QCL across the frequency range from 1297 cm^{-1} to 1219 cm^{-1} at a spectral resolution of 1 cm^{-1}. As the development of QCL chips toward longer wavelengths progresses, it is anticipated that a wide range of relevant gaseous analytes could be determined with such compact gas sensing systems.

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Biographies

C. Young received her Bachelor of Science in Chemistry from the University of South Carolina, Columbia, South Carolina in 2005. She is currently a Ph.D. candidate at Georgia Institute of Technology, Atlanta, Georgia and recipient of the 2008 Society for Applied Spectroscopy Graduate Student Award. Her primary research interests include the development and application of sensitive and selective mid-infrared FT-IR and QCL based gas sensors as well as the fabrication, characterization, and optimization of photonic materials and devices for the integration of optical sensing systems.

B. Mizaikoff received his Ph.D. in Analytical Chemistry at the Vienna University of Technology in 1996. From 2000 to 2007 he was tenured faculty member at the Georgia Institute of Technology, School of Chemistry and Biochemistry, heading the Applied Sensors Laboratory (ASL). In Fall 2007, he joined the faculty at the University of Ulm, Germany, as a Chaired Professor heading the Institute of Analytical and Bioanalytical Chemistry. His research interests focus on optical sensors, biosensors and biomimetic sensors operating in the mid-infrared spectral range, quantum cascade lasers, system miniaturization and integration based on micro- and nanofabrication, multifunctional scanning nanoprobes and nano(bio)sensors, focused ion beam techniques, development of chemical recognition layers for separation and sensing applications, chemometric data evaluation, environmental analytical chemistry, process analytical chemistry, and biomedical diagnostics. He is author/co-author of over 120 peer-reviewed publications, 13 patents, and numerous invited contributions at scientific conferences.

S.-S. Kim received his Ph.D. in Physics from Northwestern University, Evanston, IL in 2003. Afterwards, he joined Lightbit Corporation, Mountain View, CA, where he developed wavelength converter and dispersion compensation devices based on periodically poled lithium niobate for fiber optic telecommunication for 3 years. Currently, he is a research scientist with Applied Sensors Laboratory at the Georgia Institute of Technology where he develops mid-infrared optical sensors.

M. Weida earned his Ph.D. in Chemical Physics at the University of Colorado in Boulder. After completing his Ph.D., he performed post-doctoral research in gas phase collisions using time resolved fluorescence studies at Indiana University, and femtosecond spectroscopy of surface electron dynamics in metals under a prestigious NSF fellowship at the Hitachi Advanced Research Laboratory in Japan. He brings five years of business experience to Daylight Solutions as well, having worked as a senior scientist at Wyatt Technology Corporation, a company specializing in laser-based scientific instrumentation for characterizing macromolecules in solution.

D. Arnone received his B.S. in Mechanical Engineering and his M.S. in Manufacturing Systems from Stanford University. Upon leaving Stanford, he joined New Focus Inc., as a senior engineer and business manager where he oversaw the development and commercialization of many high-precision mechanical and optomechanical products, including compact, rugged, tunable lasers in the visible and near-IR. He is presently a senior mechanical engineer at Daylight Solutions. He has 16 patents in the area of laser systems, optomechanics, and precision mechanisms.

T. Day received his B.S. and M.S. degrees in Physics from San Diego State University in 1985 and 1987 and his Ph.D. in Electrical Engineering from Stanford University in 1990. The same year, he co-founded New Focus Inc., which pioneered and manufactured many new photonics products including near infrared tunable external cavity lasers. He is presently the CEO and CTO of Daylight Solutions Inc., a company focused on the development of molecular detection and imaging products using laser-based technologies in the mid- to far-IR region of the electromagnetic spectrum. He has published more than 25 scientific papers and has issued and pending patents in the fields of tunable lasers and fiber-optic passive components.