Versatile, ultra-low sample volume gas analyzer using a rapid, broad-tuning ECQCL and a hollow fiber gas cell

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ABSTRACT

We describe a versatile mid-infrared (Mid-IR) spectroscopy system developed to measure the concentration of a wide range of gases with an ultra-low sample size. The system combines a rapidly-swept external cavity quantum cascade laser (ECQCL) with a hollow fiber gas cell. The ECQCL has sufficient spectral resolution and reproducibility to measure gases with narrow features (e.g., water, methane, ammonia, etc.), and also the spectral tuning range needed to measure volatile organic compounds (VOCs), (e.g., aldehydes, ketones, hydrocarbons), sulfur compounds, chlorine compounds, etc. The hollow fiber is a capillary tube having an internal reflective coating optimized for transmitting the Mid-IR laser beam to a detector. Sample gas introduced into the fiber (e.g., internal volume = 0.6 ml) interacts strongly with the laser beam, and despite relatively modest path lengths (e.g., L ~ 3 m), the requisite quantity of sample needed for sensitive measurements can be significantly less than what is required using conventional IR laser spectroscopy systems. Example measurements are presented including quantification of VOCs relevant for human breath analysis with a sensitivity of ~2 picomoles at a 1 Hz data rate.

Keywords: Mid-Infrared (Mid-IR), spectroscopy, quantum cascade laser (QCL), hollow fiber optic waveguide, gas analysis, volatile organic compound (VOC)

1. INTRODUCTION

Tunable laser absorption spectroscopy (TLAS) is a highly effective method for trace gas concentration and isotope analysis. Multipass gas cells are often used to increase the sensitivity of TLAS systems, but the volumes of such cells are typically 100 – 1000 mL, which can preclude their use in sample limited applications. In addition, relatively narrow tuning lasers are typical for TLAS sensors, but the limited tuning range makes such systems applicable to only 1 or 2 molecular species, significantly reducing the versatility and utility. The system described here combines two innovative technologies, see Figure 1: (1) a hollow fiber gas cell and (2) a rapidly-swept broad tuning laser, which are utilized together to overcome the limitations listed and enable sensitive measurements of a wide range of gas/vapor analytes.

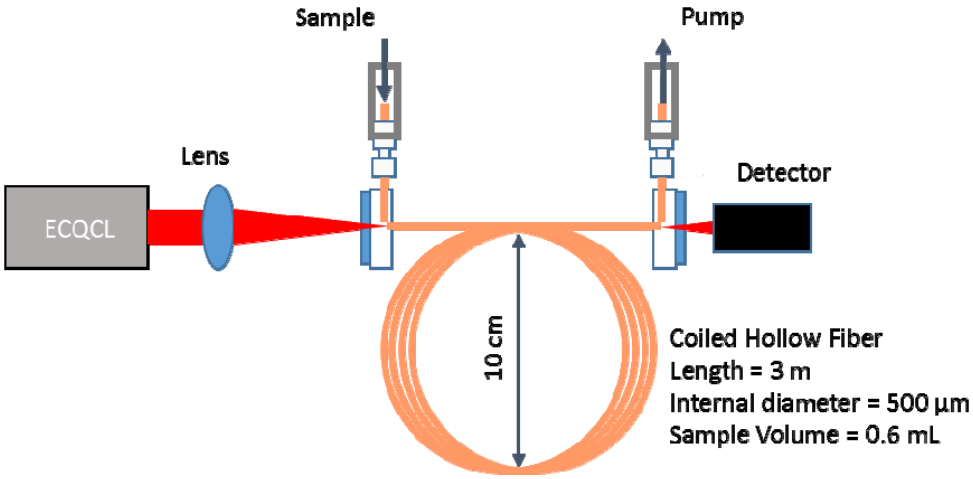

Figure 1. Diagram of versatile CAS+ECQCL system for the analysis of multiple gasses with an ultra-small sample volume.

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The hollow fiber gas cell concept, called a capillary absorption spectrometer (CAS), was developed by Dr. Jim Kelly and colleagues while at the Pacific Northwest National Laboratory (PNNL) [1]. Gas under analysis is drawn into the fiber, which has a reflective inner coating that guides a tunable laser beam to a detector. There is near unity overlap between the laser beam and the gas sample, leading to a highly sensitive system with an ultra-compact cell. The broad tuning external cavity quantum cascade laser (ECQCL) used here was developed by Dr. Mark Phillips and colleagues also at PNNL[2]. This laser has been used in systems to achieve ppb level concentration measurements of a wide-range of gas species at relatively high data rates (100 Hz). Both of these mid-infrared (Mid-IR) spectroscopy technologies are now being developed by OptoKnowledge and are discussed in more detail in the sections below, followed by example measurements taken using a combined (CAS+ECQCL) system.

1.1 Hollow Fiber Gas Cell / Capillary Absorption Spectrometer (CAS)

Hollow core fiber optic waveguides, as utilized here, were developed and pioneered by Prof. Jim Harrington at Rutgers [3]. The basic structure consists of a wavelength tuned dielectric mirror (silver + silver-iodide) deposited on the inside of a glass capillary tube, see Figure 2. These hollow fibers are highly effective for delivery of Mid-IR laser beams, and are particularly appealing for spectroscopy applications given that (1) there are no end reflections from the hollow core, which could potentially cause feedback to the laser, (2) broadband options enable coverage of essentially the entire Mid-IR wavelength range (e.g., λ = 2-16 µm), and (3) single-mode operation is possible with a relatively large core ($\geq$ 200 µm) [4][5]. The technology developed at Rutgers was transferred to OptoKnowledge in the early 2010's, and since then OptoKnowledge has been producing hollow fiber based products [6], as well as advancing the technology specifically for spectroscopy applications [7].

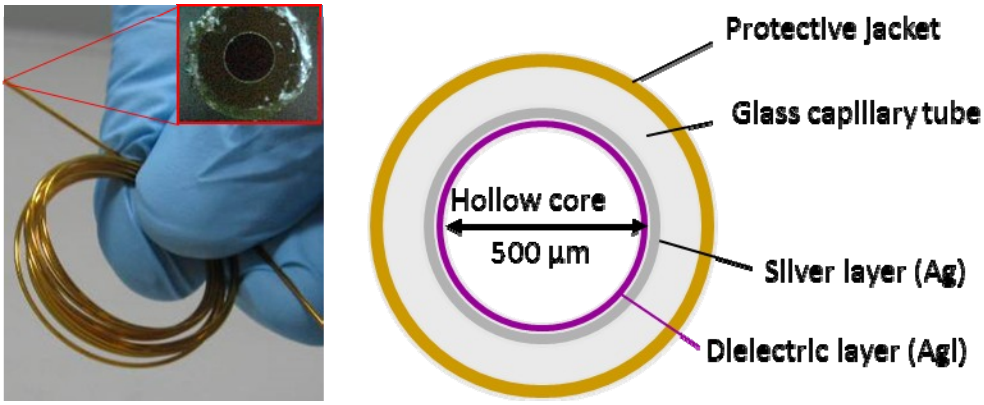

Figure 2. Picture of tightly coiled hollow fiber alongside cross-sectional diagram.

Back in the early 2000's PNNL began to utilize hollow core fibers as a low-volume gas cell for Mid-IR laser absorption applications [8]. More recently, PNNL began a collaboration with OptoKnowledge to take advantage of the hollow fibers being produced there [9]; this collaboration has since morphed into a transition of the CAS technology from PNNL to OptoKnowledge for a range of commercial and government applications including work on isotope analysis being done in collaboration with NASA/JPL. However, all of these prior and current CAS systems utilize relatively narrow tuning lasers, e.g., distributed feedback (DFB) lasers, which are typically limited to a tuning range of 1-2 cm^{-1} wavenumbers, thus limiting the applicability of any such system to a few molecular species with relatively narrow absorption features.

1.2 Broad-tuning, rapidly-swept external cavity quantum cascade laser (ECQCL)

PNNL began utilizing QCLs for spectroscopy [10] soon after the advent of the QCL, and quickly began to develop their own ECQCL for field sensor applications. The PNNL ECQCL differs from most commercial ECQCLs in that it utilizes a Litmann-Metcalf cavity design (Figure 3), rather than the more typical Littrow design. The trade-off is that the power out of the PNNL ECQCL is relatively low (e.g., ~ 1 mW); however, the tuning speed (200 Hz) and spectral resolution (0.2 cm^{-1}) that has been achieved over a relatively wide tuning range (110 cm^{-1}) is unmatched in the literature [11]. PNNL and OptoKnowledge have been collaborating over the last few years on transitioning this ECQCL technology [12].

Systems based on the PNNL laser have been proven to offer the following benefits:

- Simultaneous measurement of several different species with a single laser scan
- Ability to measure relatively "large" molecules with broad absorption features (e.g., VOCs)
- Accurate measurement of "smaller" molecules with relatively narrow absorption features including "background" species (e.g., water) for effective removal and more precise fit to other species
- Ability to operate at atmospheric pressure, avoiding issues with high vacuum, including need for large pumps
- Relatively high dynamic range through the ability to use different spectral features depending on the concentration
- Full sweep data rates as high as 200 Hz with the ability to time average the data for higher precision if needed
- Unattended, long-term monitoring – systems have run continuously (24/7) for months with no maintenance or calibration required.

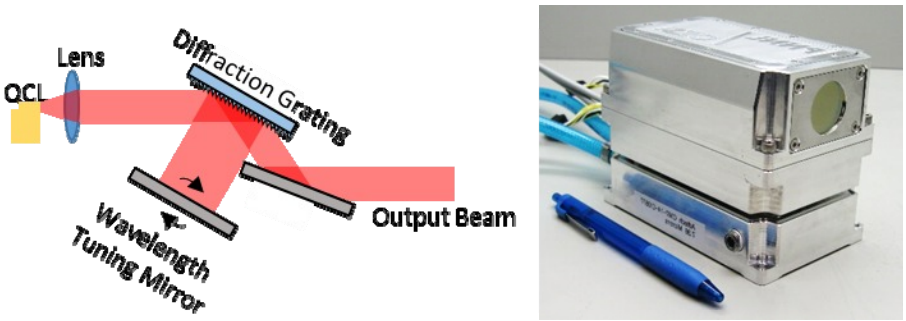

Figure 3. Diagram of PNNL ECQCL Littmann-Metcalf cavity, alongside a picture of an ECQCL produced jointly by OptoKnowledge and PNNL.

2. CAS+ECQCL DEMONSTRATION

2.1 Experimental Setup

We assembled a combined CAS+ECQCL system for a proof of concept, specifically demonstrating simultaneous measurement of multiple gasses with an ultra-small sample volume. A simple diagram of the experimental setup is shown above in Figure 1. The fiber cell was made from a hollow fiber waveguide coated at OptoKnowledge for optimal transmission from λ = 4-12 µm, and having an inner diameter, ID = 500 µm, and length, L = 3 m, for a total internal volume, V = 0.6 mL. The specific ECQCL used in this system was jointly produced by OptoKnowledge and PNNL and covers the tuning range from about λ = 7.0 – 7.8 µm (1425 – 1285 cm^{-1}). Quantitative library spectra from the PNNL Northwest Infrared database [13] are shown in Figure 4 for various test gases/vapors used in this study.

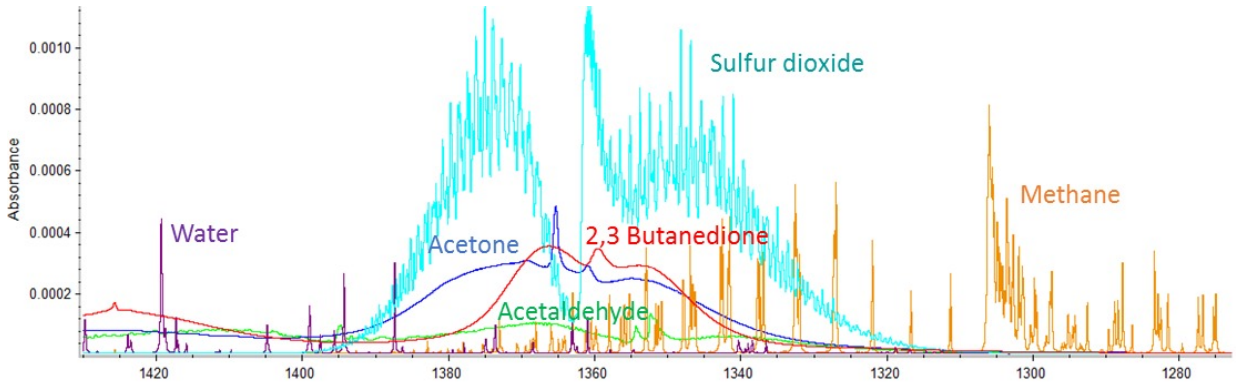

Figure 4. Spectral library of molecular species of interest in the tuning range of the ECQCL used in this study.

We studied 6 different species in the experiments presented here. **(1)** 2,3 Butanedione (also known as Diacetyl) and **(2)** Acetaldehyde (also known as Ethanal) are both VOCs of interest for medical breath diagnostics; **(3)** Acetone, which is also related to breath, but in addition has application to defense and security, being associated with illicit drugs and improvised explosives; **(4)** Sulfur dioxide (SO_2), which is an environmental pollutant significant both in earth science

(e.g., volcanos) and energy production (e.g., coal-fired power plants); **(5)** Methane (CH_4), which is the leading component of natural gas and a significant factor in climate change; and **(6)** water vapor (H_2O), which is a ubiquitous "background" gas with a relatively high concentration. This collection of molecular species represents a broad range of measurement challenges including overlapping spectral signatures with both broad and narrow features.

For the set of experiments described here, the hollow fiber gas cell was open to atmosphere and a continuous flow through the fiber was generated using a small diaphragm pump (Parker/Hargraves part#L008C-11), producing a pressure in the cell of about 0.95 Atm. We conducted a set of experiments by mixing up multiple gases/vapors diluted with room air. We would then inject 0.1 to 1.0 mL of this diluted mixture into an open sample chamber, which has a volume ~ 1 mL. The pump would draw the sample (along with additional room air) into and through the hollow fiber. The concentration of the sample gas would typically peak about 10 s after being injected into the chamber and gradually decrease with a time scale on the order of 100s as the gas remaining in the chamber was either pumped through the fiber and/or gradually diffused out of the chamber.

The ECQCL was operated with a 10 Hz full spectral scan rate and the resulting transmission spectrum through the gas sample was recorded with an MCT detector. Results presented below are an average of 10 scans each, giving a measurement update of 1 Hz. Note: the laser can indeed operate at much higher rates with data rates exceeding 100 Hz [11], and we will operate at such a rate in future studies.

2.2 Simultaneous multi-species concentration measurements

Sample data is shown in Figure 5. A measured "background" transmission spectrum (I_o), Figure 5(a), exhibits relatively strong absorption features due to the water vapor in the room air. After the sample is introduced, the resulting measured spectrum (I), Figure 5(b), still includes the water features, but also includes additional features due to the sample gases. Absorbance is calculated as $-Log_{10}(I/I_o)$ (note: Log base 10 is used to match the PNNL spectral library).

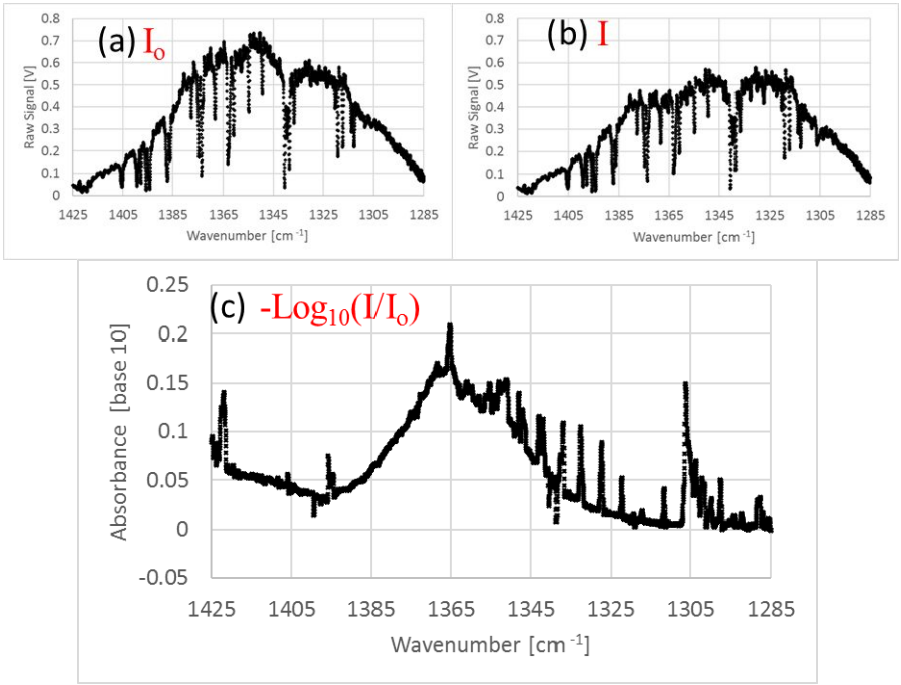

Figure 5. Sample data: (a) "Background" transmission spectrum (I_o) taken with room air circulating through cell, the strong absorption features are due to water vapor, (b) measurement spectrum (I) taken after a sample was introduced into the fiber gas cell, (c) Absorbance spectrum calculated as $-Log_{10}(I/I_o)$.

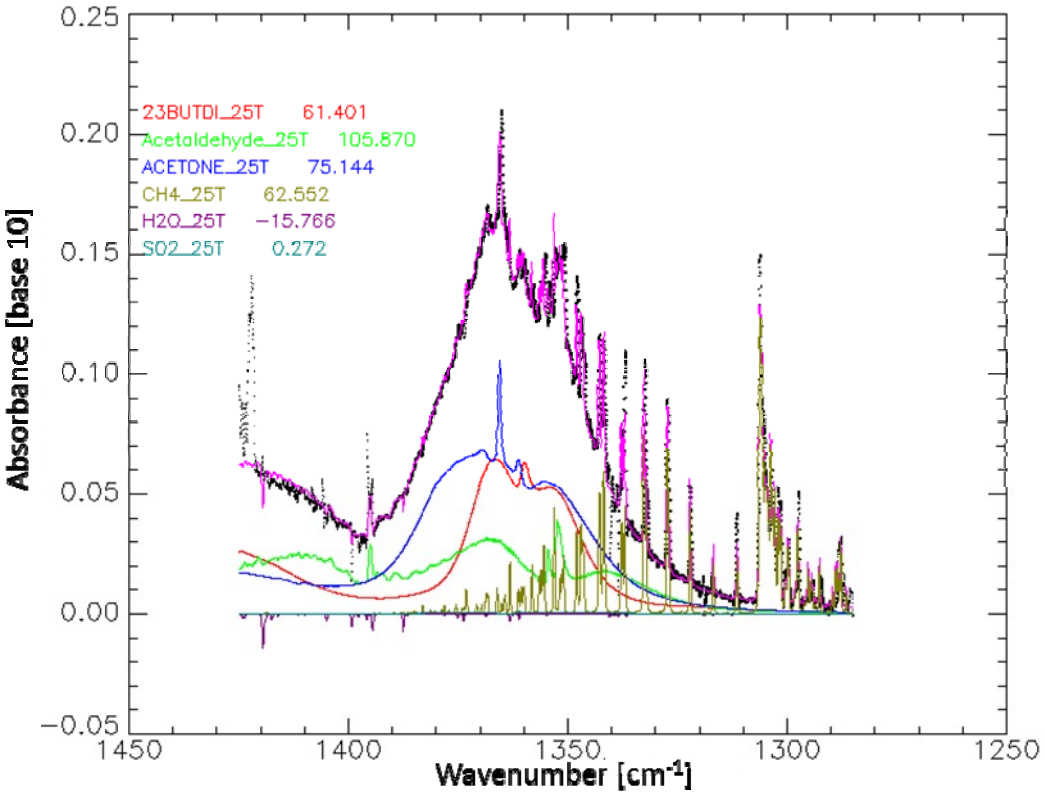

Figure 6. Example library fit to the sample spectral data that is shown above in Figure 5. Measured absorption is shown as black points and the composite quantitative fit is shown with the overlaid magenta line. Also shown is a representation of the contributing parts to this fit for the different library species with the legend listing the calculated concentration in ppm.

Using a technique previously described by PNNL[14], measured absorbance spectra were fit to library spectra using a linear regression analysis. To deemphasize points with low transmission and thus higher noise (e.g., regions associated with strong water lines) the raw transmission spectrum was used as a weighting function. For the measurements presented here, we used the library spectra shown in Figure 4 as the basis vector space for the fit.

An example demonstrating simultaneous concentration measurement of multiple species is shown in Figure 6 displaying the measured absorbance and the resulting fit, along with additional curves representing the relative contribution of the various species. The fitting technique is able to essentially deconvolve the measured spectrum and determine the contribution of the various molecular species. We emphasize that the PNNL spectral library is quantitative (ppm-m) and by scaling the result by the known path length (L = 3m), this is a quantitative fit with the result being a determination of the concentration of the various species in parts-per-million (ppm). We also note that the fit has a very low computational overhead and has no difficulty being utilized for real-time field analysis [14].

The fit shown in Figure 6 includes water vapor, which in the example shown in Figure 6 is calculated to have a negative concentration (-15.766 ppm). A negative concentration is indeed feasible since the measurement is relative to the baseline “room air” condition, and the sample, which actually displaces some of this air, naturally has a reduced water vapor content.

A plot of measured species concentration versus time is shown in Figure 7, along with two inserts showing the transmission measurements at two instances in time during the measurement sequence. These measurements help illustrate the high dynamic range available with the system, with measured concentrations of some of the species varying over more than 3 orders of magnitude. The inserts show the measured transmission spectrum before the sample was introduced (i.e., “background”) and also at a time near the peak of the concentration spike. The latter shows nearly complete absorption over portions of the spectrum, yet reasonable (although unverified) concentration values are still obtained due to the ability to fit other portions of the spectrum.

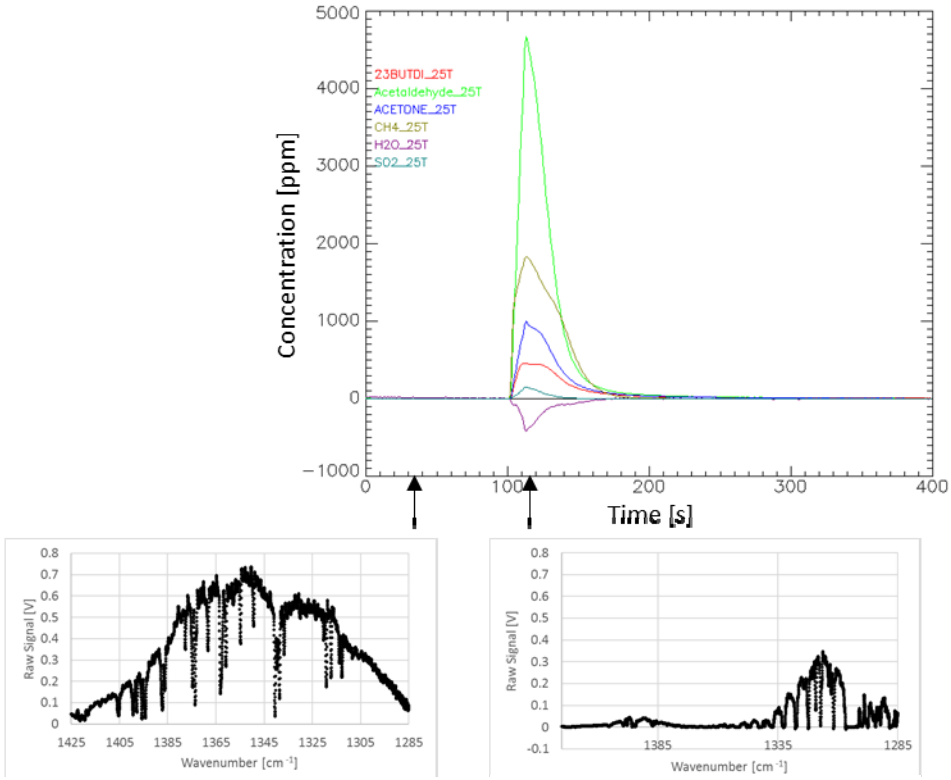

Figure 7. Measured concentration versus time demonstrating the high dynamic range and ability to determine concentration in the presence of strong absorption. Inserts show transmission spectra before and at peak concentration.

3. DISCUSSION

By simply fitting to the case with no sample gas (just room air), the noise equivalent concentration of the demonstration system was estimated and ranged from about 100 ppb to 1 ppm at a 1 Hz update rate for the gases studied here. We note that given the sample volume of the fiber (V = 0.6 mL), 100 ppb roughly corresponds to only 2 picomoles of gas at 0.95 Atm and room temperature (i.e., 22°C). Thus, in terms of the requisite amount of sample needed, the system is extremely sensitive. This low sample volume can be useful in human breath analysis by taking full advantage of a pre-concentrator to generate a low volume sample of VOCs. For example, consider that a typical breath sample is 0.5 liters, and a gas originally in breath at 0.1 ppb is equivalent to about 2 picomoles. By accumulating over several breath cycles and averaging spectral data over the equivalent period, extremely sensitive VOC measurements are possible.

The system demonstrated here is intended to provide a general proof of concept for the versatile CAS+ECQCL concept. There are myriad ways in which the system could be optimized for a specific application, including laser tuning range, hollow fiber ID / length, update rate, and system size, weight, power. While we recognize there have been prior uses of an ECQCL with a hollow fiber cell [15][16], to our knowledge the work presented here is the first demonstration of simultaneous measurement of multiple species in such a system, as well as being the first demonstration of a system able to quantify both smaller molecular gases (e.g., methane and water vapor) and larger vapors (e.g., acetaldehyde and 2,3 butanedione).

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