

# Infrared Semiconductor laser based trace gas sensor Technologies: Recent Advances and Applications

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## ABSTRACT

Recent advances in the development of trace gas sensors based on the use of quantum cascade lasers (QCLs) for the sensitive, selective detection, quantification and monitoring of small molecular gas species with resolved spectroscopic features will be described. High detection sensitivity at ppbv and sub-ppbv concentration levels require detection sensitivity, enhancement schemes such as multipass absorption cells, cavity enhanced absorption techniques, or quartz enhanced photo-acoustic absorption spectroscopy (QEPAS). These three spectroscopic methods can achieve minimum detectable absorption losses in the range from  $10^{-8}$  to  $10^{-11}$  cm<sup>-1</sup>/√Hz. Two recent examples of real world applications of field deployable PAS and QEPAS based gas sensors will be reported, namely the monitoring of ammonia concentrations in exhaled human breath and major urban environments.

**Keywords:** Quartz enhanced photoacoustic spectroscopy, wavelength modulation, distributed feedback quantum cascade laser, trace gas ammonia detection, breath analysis, environmental monitoring

## 1. REALTIME DETECTION IN EXHALED HUMAN BREATH USING A QCL BASED SENSOR

Exhaled breath is a mixture of more than four hundred molecules, some of which are present at parts per billion (ppb) or even as low as parts per trillion (ppt) concentration levels [1]. These molecules provide a unique breath profile of a person's health conditions and have endogenous and exogenous origins. The sources of endogenous molecules are normal and abnormal physiological processes, whereas the sources of exogenous molecules are: inhaled air, digested food and beverages, or any exogenous molecules that have entered the body by other routes (e.g. dermal absorption) [2]. The concentrations of some exhaled molecules can be used as biomarkers for the identification and monitoring of human diseases or wellness states [3]. Therefore, a breath test is becoming increasingly important as a non-invasive procedure for clinical diagnostics [4]. The potential of breath in medicine was first recognized in ancient times. Hippocrates, considered to be the father of medicine, suggested that a specific breath odor might reflect a certain disease, such as diabetes. The earliest recorded studies of human breath, related to the role of oxygen in respiration, were performed more than 200 years ago by Lavoisier and Laplace [4-5].

Currently, the standard instrumentation for exhaled human breath analysis is based on gas chromatography and various detection methods such as flame ionization detection [6-7], mass spectrometry [8], ion mobility spectrometry [9], or selected ion flow tube mass spectrometry [10]. In recent years, several laser based breath analyzers, capable of sensitive and real time detection of

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molecular species in breath samples, were demonstrated with different laser spectroscopic techniques [11-13]. Promising results from previous studies have confirmed that optical sensors have a considerable potential for the detection, quantification, and monitoring of exhaled breath [14]. In this paper, a novel quantum cascade laser based optical breath sensor for ammonia detection will be described. By monitoring ammonia concentration levels in exhaled breath, a fast, non-invasive diagnostic method for treatment of human subjects with liver and kidney disorders is feasible.

## 2. AMMONIA BREATH SENSOR ARCHITECTURE

The block diagram of the ammonia breath sensor architecture is depicted in Fig. 1. The optical sensor uses a quartz enhanced photoacoustic spectroscopy (QEPAS) technique [15,16] that employs an ultra-small piezoelectric quartz tuning fork (QTF) as an acoustic transducer. A high resonance frequency of the QTF (in vacuum  $f=2^{15}$  Hz~32.7 kHz) results in immunity to low frequency environmental acoustic noise for QEPAS measurements. In addition, QEPAS possesses a large dynamic range of nine orders of magnitude of the acoustic signal, and its noise is limited by fundamental Johnson thermal noise of the QTF. The signal-to-noise ratio for QEPAS based trace gas detection measurements can be improved up to 30 times when the QTF is enhanced with two metal tubes acting as a micro-resonator. The optimum inner diameter and the length of each tube (for a ~32.8 kHz sound wave the tube length estimated to be between  $\lambda/4$  and  $\lambda/2$  of the acoustic wavelength) were experimentally determined to be 0.6 mm and 4.4 mm, respectively [17]. Moreover, the QEPAS based trace gas sensor is capable of ultra-sensitive trace gas detection and is suitable for real time breath measurements, due to the fast gas exchange inside a compact QEPAS gas cell, which acts as an absorption detection module (ADM) or “spectrophone”. The total volume of a typical QEPAS ADM is ~3.8 cm<sup>3</sup>. It can be made even smaller in an alternative cell design, because, the volume of the analyzed gas sample is limited by the dimensions of the QTF and the acoustic micro-resonator tubes to ~3 mm<sup>3</sup>.

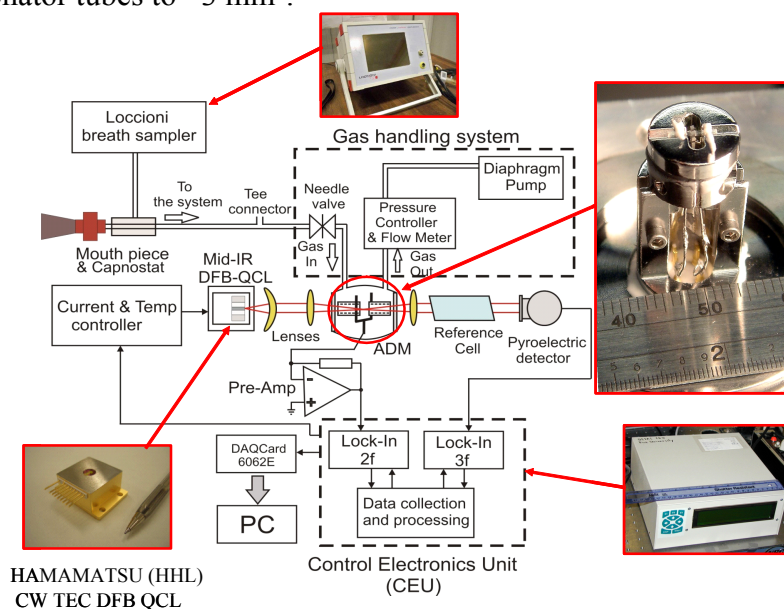


Fig. 1. Block diagram of ammonia breath sensor architecture.

The  $\text{NH}_3$  breath sensor employs a continuous wave (CW), room temperature (RT), distributed feedback quantum cascade laser (DFB-QCL) in a high head load (HHL) package from Hamamatsu ([www.hamamatsu.com](http://www.hamamatsu.com)). Such a DFB-QCL uses only air cooling, produced by a small electronics fan and a heat sink attached to the back of the QCL. A 4mm diameter ZnSe aspheric lens, with a working distance of 0.65 mm and clear aperture of 3.6 mm, was used to collimate the laser beam. In order to pass the beam through the micro-resonator a 0.5" diameter and 1.17" focal length ZnSe plano convex lens was employed. The laser power was found to be 22mW after being transmitted through the micro-resonator. This is ~90% of the initial power of the DFB-QCL operated at 17.5 °C. The photoacoustic signal is detected by the QTF, amplified by a low-noise trans-impedance preamplifier, and delivered to a control electronics unit (CEU) for further data processing. A 10 cm long reference cell, filled with 0.2% of  $\text{NH}_3$  in  $\text{N}_2$  at 130 Torr, and a pyroelectric detector were installed after the ADM module to lock the laser frequency to the center of the selected optimum  $\text{NH}_3$  absorption line.

A commercially available breath sampler (Loccioni, Italy) was employed to monitor and maintain the pressure of the exhaled breath within an acceptable range and to measure the breath  $\text{CO}_2$  concentration level. After a human subject breathes into a mouth piece, the collected breath gas sample simultaneously enters the Loccioni breath sampler and the laser-based breath sensor. The breath passes through the ADM, a pressure controller (MKS Instruments), followed by a mass-flow meter (see [www.mksinst.com](http://www.mksinst.com)) and is then released into the atmosphere by means of a compact oil free diaphragm pump (KNF model UN816.3 KTP). The flow rate through the  $\text{NH}_3$  sensor is fixed by a needle valve to 220 ml/min and the pressure value was set and controlled at 130 Torr. When a breath sample is acquired, both the  $\text{NH}_3$  and  $\text{CO}_2$  concentration profiles as well as the airway pressure are simultaneously displayed in a graphical format by the Loccioni breath sampler display. At the same time the  $\text{NH}_3$  breath profile and the maximum breath  $\text{NH}_3$  concentration level in ppbv acquired by the breath sensor are plotted in real-time on a laptop screen. Furthermore, the ADM, needle valve and the mouth piece connected to the Loccioni breath sampler pipe line were heated to  $\geq 38^\circ\text{C}$  to avoid  $\text{NH}_3$  adsorption on the various sensor component surfaces as well as to prevent condensation of the water vapor inside the  $\text{NH}_3$  sensor. The  $\text{NH}_3$  breath sensor system consists of 6 main components, which includes the  $\text{NH}_3$  laser-based sensor contained in a 14" x 10" x 12" enclosure, a separate QCL current controller, a CEU, a Loccioni breath sampler, a laptop and a power supply (Acopian) for powering self adhesive heaters of the ADM and the heating cord covering the needle valve.

The Hamamatsu CW RT DFB-QCL was selected to emit radiation at 10.34  $\mu\text{m}$  wavelength, within the  $\nu_2$  fundamental absorption band of ammonia. The laser can be operated from 0 to 50°C with a spectral shift of 0.1  $\text{cm}^{-1}/^\circ\text{C}$ . For the QCL operating at 18°C, single mode operation between 966.7 and 968.7  $\text{cm}^{-1}$  was achieved resulting in spectral shift of 0.017 $\text{cm}^{-1}/\text{mA}$ . Two  $\text{NH}_3$  absorption lines free from  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and methanol interferences can be selected at 967.35  $\text{cm}^{-1}$  and 965.35  $\text{cm}^{-1}$  within the available DFB-QCL tuning range. The  $\text{NH}_3$  absorption line located at 967.35  $\text{cm}^{-1}$  can be accessed with the laser operating temperature set to 17.5°C. This results in a laser output power of > 20 mW. To access the 965.35  $\text{cm}^{-1}$   $\text{NH}_3$  line, a much higher laser operating temperature of ~30°C is needed, which results in a significant decrease of the DFB-QCL optical output power to ~5 mW. Therefore when using the QEPAS technique, where the detected signal scales linearly with optical power, the optimum selection for the  $\text{NH}_3$  absorption line position is at 967.35  $\text{cm}^{-1}$ . HITRAN simulated spectra at 130 Torr depicting  $\text{NH}_3$  absorption lines are illustrated in Fig. 2 together with potentially interfering  $\text{CO}_2$  and  $\text{H}_2\text{O}$  absorption lines in the ~ 966  $\text{cm}^{-1}$  spectral region

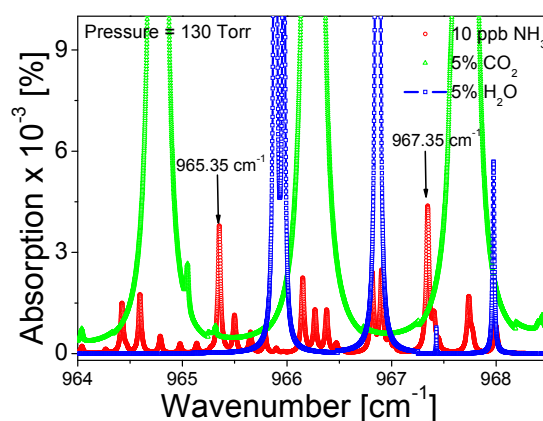


Fig. 2 HITRAN simulated spectra at 130 Torr indicating two potential  $\text{NH}_3$  absorption lines for exhaled breath measurements.

In order to verify if the wing of a neighboring  $\text{CO}_2$  line centered at  $967.71 \text{ cm}^{-1}$  can interfere with the selected  $\text{NH}_3$  absorption line, two 2f wavelength modulation (WM) scans were performed within spectral range of interest. The initial 2.5 ppm  $\text{NH}_3$  in a  $\text{N}_2$  mixture was flushed through the sensor system and a 2f QEPAS spectrum for ammonia was recorded by Labview software. Then the same measurement was repeated for a 5%  $\text{CO}_2$  in  $\text{N}_2$  and 1% water vapor mixture. The results of this test are illustrated in Fig. 3 which shows that there is no overlap between the  $967.35 \text{ cm}^{-1}$   $\text{NH}_3$  and the adjacent  $\text{CO}_2$  absorption lines when using the 2f WM technique. Furthermore when a  $\text{CO}_2$  measurement is made, a signal related to the remaining ammonia in the system is also detected. This effect is due to  $\text{NH}_3$  molecules sticking to the wall which can be eliminated by increasing the temperature of the sensor system to  $> 38^\circ\text{C}$ , keeping the tubing length as short as possible, and maintaining a flow at  $> 200 \text{ ml/min}$  inside the sensor.

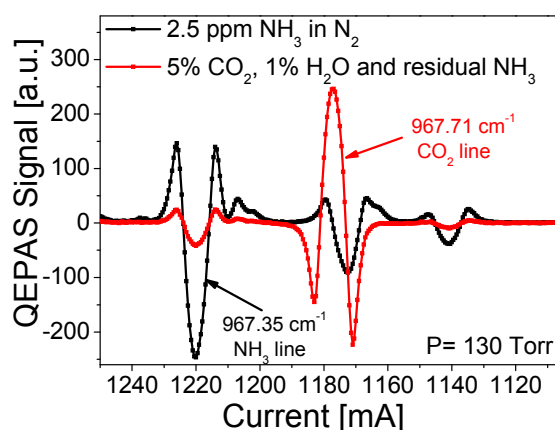


Fig. 3 2f wavelength modulation QEPAS signals for a 2.5 ppm  $\text{NH}_3$  in  $\text{N}_2$  mixture and 5%  $\text{CO}_2$  in  $\text{N}_2$  and 1%  $\text{H}_2\text{O}$  mixture recorded within the  $967\text{--}968 \text{ cm}^{-1}$  spectral region.

### 3. EXPERIMENTAL RESULTS FOR A DFB-QCL QEPAS BASED $\text{NH}_3$ SENSOR

Sensitive detection of ammonia at low parts per billion (ppb) concentration levels was performed with a 2f WM technique, which is intrinsically a zero background technique. An optimum  $\text{NH}_3$  sensor pressure value of 130 Torr and modulation depth of 15mA were experimentally determined to maximize the QEPAS signal. The  $1\sigma$  minimum detectable concentration of ammonia for a calibrated mixture of 5ppm  $\text{NH}_3$  balance  $\text{N}_2$  is achieved at  $\sim 8$  ppb when the laser frequency is tuned by varying the current over the  $967.35 \text{ cm}^{-1}$   $\text{NH}_3$  absorption line (see black plot in Fig. 4a). However, for line scanning, additional noise related to the current frequency tuning process can be introduced into the sensor system. Each scan lasts  $\sim 2$  minutes which is too long for some applications where a fast system response is required. For a background free sensor system, where no significant baseline drift is observed, a more convenient method is to acquire data only at one selected laser frequency corresponding to the peak of the investigated  $\text{NH}_3$  absorption line. Therefore, a line-locking scheme was implemented to always keep the laser frequency at a fixed position. A 3f pyroelectric detector signal with a zero crossing point exactly at the maximum of the 2f WM QEPAS signal was used as a reference for the line-locking technique. A 3f signal was also demonstrated in Fig. 4a as a red plot. An example of continuous measurements after locking a laser frequency to the  $967.35 \text{ cm}^{-1}$   $\text{NH}_3$  absorption line is demonstrated in Fig. 4b. In this case the analyzed gas medium was alternately switched between two cylinders; an ultra high purity  $\text{N}_2$  and a certified 5ppm  $\text{NH}_3$  in  $\text{N}_2$ . The  $1\sigma$  minimum detectable concentration of ammonia for a line locked laser frequency was achieved at  $\sim 6$  ppb. The data points for all measurements demonstrated in Fig. 4 were acquired with a 1 sec time resolution.

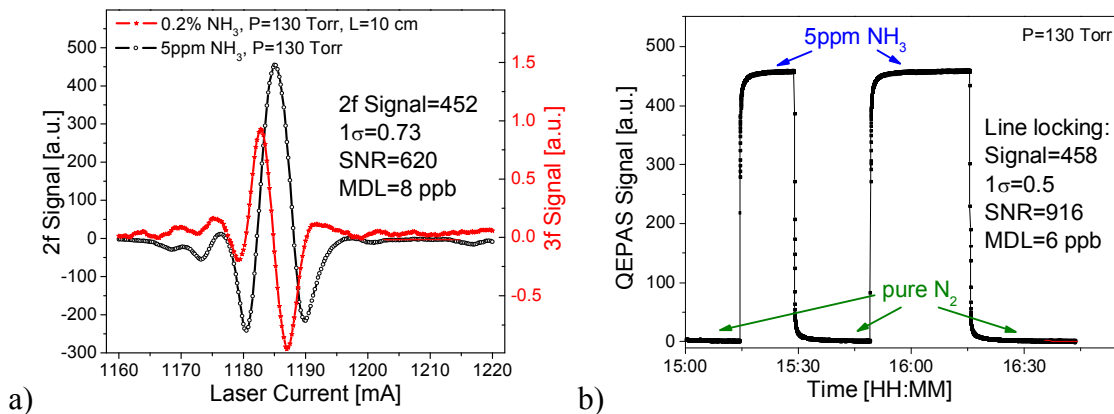


Fig. 4 a) 2f QEPAS signal (black) and reference channel 3f signal (red) when DFB-QCL is tuned across the  $967.35 \text{ cm}^{-1}$  line; b) 2f QEPAS signal when laser was locked to the  $967.35 \text{ cm}^{-1}$  line.

A similar detection limit of  $\sim 6$  ppb ( $1\sigma$ ) was obtained after diluting a calibrated mixture of 5ppm  $\text{NH}_3$  in  $\text{N}_2$  to a level of  $\sim 160$  ppb. This proves a linear response of the QCL based QEPAS based sensor platform. A higher discrepancy between the targeted and measured  $\text{NH}_3$  concentrations were observed with an increasing dilution ratio most likely resulting from the precision of the gas dilution system during the dilution process.

#### 4. REAL TIME HUMAN BREATH DATA

An  $\text{NH}_3$  sensor system for the real time monitoring of ammonia concentration levels in exhaled breath was designed to collect breath samples multiple times in  $\sim 3$  min intervals between each sample. These intervals allow the removal of the adsorbed ammonia from the sensor system. An example of the breath ammonia profile is depicted in Fig. 5a, where the ammonia concentration level, representing both a normal and an abnormal physiological body processes, is at  $\sim 450$  ppb (at the plateau point). The first part of the breath profile shown in Fig 5a, associated with highest detected  $\text{NH}_3$  concentration of  $\sim 650$  ppb, reflects the ammonia concentration in the oral cavity. This concentration is mostly related to oral bacterial processes of digested food and beverages. For each  $\text{NH}_3$  breath measurement, the  $\text{NH}_3$  profile is displayed in real time on a laptop and on a Loccioni breath analyzer and subsequently saved and stored on a laptop and the Loccioni memory stick for later data processing.

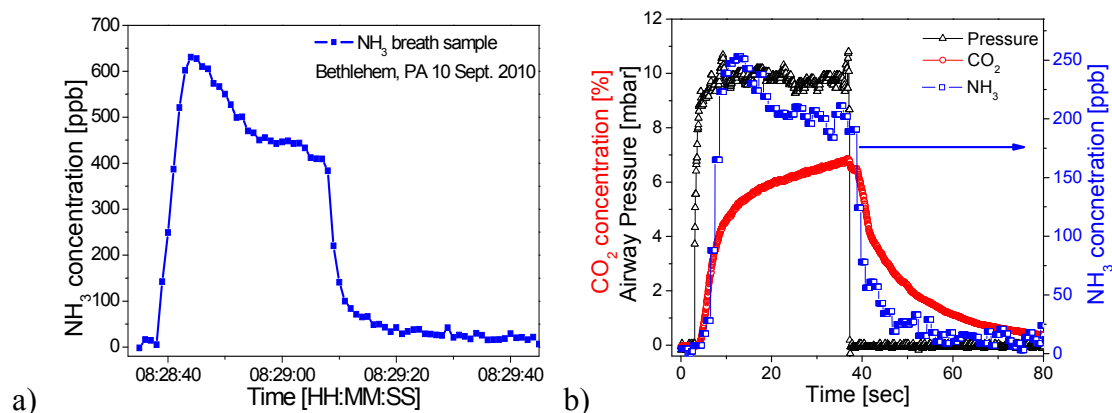


Fig. 5a) An example of the breath ammonia profile, taken at the Bethlehem, PA clinical testing site; b)  $\text{CO}_2$  concentration [%], airway pressure [mbar] and  $\text{NH}_3$  concentration [ppb] profiles of the same single breath exhalation.

Single breath exhalation profiles for  $\text{CO}_2$  concentration [%], airway pressure [mbar] and  $\text{NH}_3$  concentration [ppb] are depicted in Fig. 5b. It is clearly visible that no significant delay between airway pressure and breath ammonia profile is observed, which confirms that the  $\text{NH}_3$  sensor has an extremely fast response, as desired. In addition, after the breath sampling process is completed, fast ammonia decay from the system is also observed.

#### 5. EC-QCL PAS BASED ATMOSPHERIC AMMONIA SENSOR

Ammonia ( $\text{NH}_3$ ) is normally present in the atmosphere at trace concentration levels at the ppb level and like other nitrogen-containing trace gases, such as  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{HNO}_3$ , plays a significant role in atmospheric chemistry. The largest emission of  $\text{NH}_3$  to the atmosphere is caused by anthropogenic sources such as animal waste, poultry, mineral fertilizers, agricultural crops, and biomass burning. Other significant sources of  $\text{NH}_3$  emission are natural, including animals, oceans, vegetation, and the decomposition of plants [18]. Moreover, for highly developed urban areas, an



additional increase of atmospheric  $\text{NH}_3$  concentration levels can be observed as a result of industrial and motor vehicle activities.

From the perspective of environmental concern,  $\text{NH}_3$  is a precursor of particulate matter due to its chemical reaction with sulfuric and nitric acids to produce different ammonium salts such as ammonium sulfate  $((\text{NH}_4)_2\text{SO}_4)$ , ammonium nitrate  $(\text{NH}_4\text{NO}_3)$ , and ammonium bisulfate  $(\text{NH}_4\text{HSO}_4)$ . As a result, the abundance of  $\text{NH}_3$  in the atmosphere has a great impact on aerosol nucleation and composition. Moreover, for low  $\text{SO}_2$  environments, oxidation of  $\text{NH}_3$  is a potential source of atmospheric  $\text{NO}$  and  $\text{N}_2\text{O}$ .

Despite the importance of  $\text{NH}_3$  in atmospheric chemistry, it currently is not regulated by the U.S. Environmental Protection Agency (EPA) as an air pollutant. In addition, there are no governmental air quality monitoring network sites that regularly measure ambient  $\text{NH}_3$  concentration levels. The atmospheric  $\text{NH}_3$  concentrations for urban areas vary between 0.1 and 10 ppbv, depending on the proximity to the source [19]. For the Houston area the modeled  $\text{NH}_3$  concentration is estimated to range between 1 and 15 ppbv [20].

## 6. EXPERIMENTAL RESULTS FOR AN EC-QCL PAS BASED $\text{NH}_3$ SENSOR PLATFORM

Environmental determination of ammonia concentration levels was performed with a  $10.4\text{-}\mu\text{m}$  external cavity quantum cascade laser (EC-QCL)-based sensor platform employing an amplitude modulated photo-acoustic spectroscopy (AM-PAS) technique (see Fig. 6a). A CW TEC EC-QCL system from Daylight Solutions (Model 21106-MHF) can be tuned from  $933$  to  $1006\text{ cm}^{-1}$ , emitting a maximum optical power of  $72\text{ mW}$ . Within this EC-QCL tuning range an optimum  $\text{NH}_3$  absorption line at  $965.35\text{ cm}^{-1}$  in the  $\nu_2$  fundamental absorption band of  $\text{NH}_3$  was selected in terms of available laser power, absorption coefficient, and lack of interfering species such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The laser beam was modulated by a mechanical chopper at  $1.8\text{ kHz}$ , and a  $9.1\text{ cm}$  long differential resonant photo-acoustic cell, with two balanced electret microphones, was used as the state-of-the-art photo-acoustic detector [21]. In order to achieve  $\text{NH}_3$  detection at single ppbv concentration levels, which is required for sensitive atmospheric measurements, the optical beam was passed through the cell three times. A pyro-electric detector placed after a  $10\text{-cm}$  reference cell, filled with  $0.2\%$  of  $\text{NH}_3$  at  $30\text{ Torr}$ , was used for frequency locking as well as monitoring the QCL power.

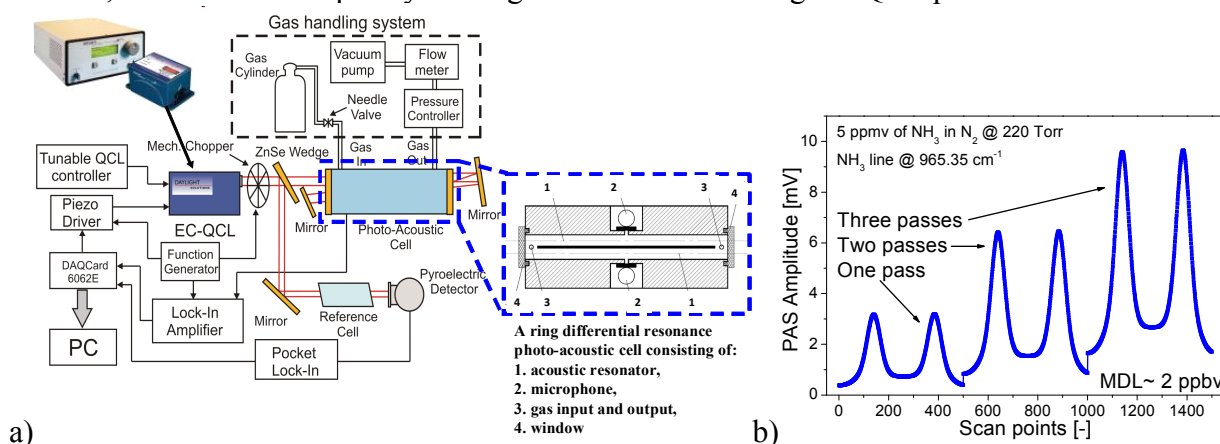


Fig. 6 a) Mid-infrared AM-PAS-based sensor platform for  $\text{NH}_3$  atmospheric detection, b) AM-PAS signal for reference mixture of  $5\text{ ppmv}$   $\text{NH}_3$  in  $\text{N}_2$  after one, two, and three laser beam passes through the photoacoustic cell.

The pressure inside the system was kept at 220 Torr while the flow was maintained at 150 ml/min. In order to minimize  $\text{NH}_3$  losses to surfaces and to prevent water vapor condensation in the sensor, the sensor enclosure was heated to  $38^\circ\text{C}$ . The minimum detectable concentration of  $\text{NH}_3$  for the sensor, when the laser beam passes three times through the photo-acoustic cell, was  $\sim 2$  ppbv for a 5-second data acquisition time (Fig. 6b). After averaging the data over 100 seconds, a sub-ppbv  $\text{NH}_3$  concentration level of  $\sim 0.6$  ppbv was achieved.

To improve our understanding of the dynamics of  $\text{NH}_3$  in an industrial and urban area such as Greater Houston, where atmospheric  $\text{NH}_3$  data are limited, the EC-QCL-based  $\text{NH}_3$  sensor platform was deployed on the roof of the 60 m high North Moody Tower, located on the University of Houston main campus, between November 2009 and October 2010. This experimental location is a perfect sampling site due to proximity to potential  $\text{NH}_3$  emission sources such as the Houston Ship Channel and several highways (I-610, US 59, I-45). In addition our atmospheric  $\text{NH}_3$  data will be compared directly with data simultaneously acquired by other advanced gas sensing instruments also installed at the Moody Tower air quality monitoring site.

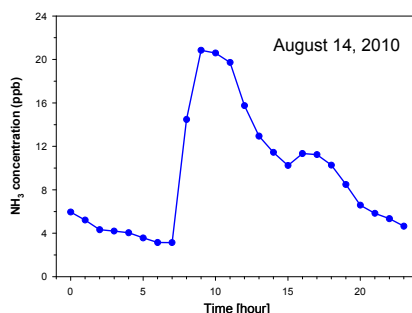


Fig. 7 Accidental ammonia release from a chemical fire resulting from a collision of 18-wheeler trucks on the Houston-Gulf Freeway (I-45) only 2 miles from the sampling site.

Fig. 7 shows a significant increase of the  $\text{NH}_3$  concentration ( $\sim 21$  ppb) on August 14, 2010, when a major accident occurred during the same time period on the Houston-Gulf Freeway (I-45) only two miles from the sampling site. The observed elevated concentration levels were found to be associated with  $\text{NH}_3$  generation from a chemical fire resulting from a collision of two 18-wheeler trucks, one of which was carrying dimethylamine, a liquid pesticide.

## 7. SUMMARY

Monitoring of ammonia concentration in exhaled breath using laser spectroscopy techniques provides a fast, non-invasive diagnostic method for human subjects with liver and kidney disorders. The achieved minimum detectable concentration of  $\text{NH}_3$  ( $1\sigma$ ) with DFB-QCL based QEPAS sensor was 6 ppbv with a 1 sec time resolution. This sensitivity is sufficient for detecting exhaled breath ammonia concentrations, which are estimated to be between 0.01 and 1 ppm in healthy humans. A fast sensor response time was obtained by shortening the length of the breath sampler tube and by keeping the metal components of the sensor at  $38^\circ\text{C}$  to minimize ammonia adsorption effects. By using a commercial breath sampler (Loccioni, Italy) with a built-in capnograph device, the  $\text{CO}_2$  concentration measurements can be performed independently. In addition, the breath sampler helps to standardize the breath collection process by monitoring and maintaining the pressure of exhaled



breath within a certain acceptable range. Laser spectroscopy with a mid-infrared, room temperature, continuous wave, high performance DFB QCL is a promising analytical approach for real time breath analysis and the quantification of breath metabolites. Moreover the QEPAS sensor technology is a robust technology for the development of sensitive, compact sensor systems that might be used in a doctor's office for non-invasive evaluation of a patient's medical condition.

The second application that is reported involves the monitoring of atmospheric  $\text{NH}_3$  in the metropolitan Houston area. A 67mw, 10.34  $\mu\text{m}$  EC-QCL source, targeting a  $\text{NH}_3$  absorption line centered at 965.35  $\text{cm}^{-1}$  resulted in a sub-ppb ammonia detection limit with a 1 s data acquisition time using an EC-QCL amplitude modulated photo-acoustic spectroscopy technique.

## Acknowledgment

The Rice University group acknowledges financial support from a National Science Foundation ERC MIRTHE award and a grant C-0586 from The Welch Foundation.

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