Laser Absorption of Atmospheric Ammonia for Mobile Measurements

ABSTRACT

Researchers from Colorado State University and Surprise, AZ have developed an ammonia sensor based on wavelength modulation spectroscopy (WMS) utilizing a quantum cascade laser (QCL) at 10.33 µm for mobile applications. The ammonia sensor was deployed on a ground vehicle for ammonia concentration measurements in a city for automobile combustion and on a fixed-wing plane for measurements in air for feedlot ammonia emissions. This compact (~20 L), lightweight (~3.5 kg), and battery-powered (<30 W) design operates autonomously to achieve a sensor accuracy of <~2% and precision of ~4 ppb in 1 s. This mobile sensing approach provides a scalable solution for detecting and quantifying anthropogenic emissions of ammonia in the atmosphere in industrial and agricultural settings.

NITROGEN EMISSIONS

Anthropogenic emissions contribute to greenhouse gases and gases that are significant risks to human health and the environment. Among these emissions are nitrogen (N) compounds, which add to climate change and reduce the overall ecological quality of life. The most abundant nitrogen compound containing atmospheric species, due to anthropogenic emissions, is ammonia (NH_3).[1] Around 55% of these compounds are comprised of ammonia while oxides of nitrogen and nitrous oxide make up the rest.

A majority of nitrogen emissions from human activity come from agricultural sites. Ammonia makes up a majority of this emission from fertilizer and animal waste. This is a result of ammonification: decomposition from micro-organisms (bacteria or fungi) to convert organic nitrogen to ammonia. Ammonia in the air is converted from over half of the nitrogen fed to cattle in feedlots and dairies. This is directly related to the increased ammonia concentrations around feeding areas which can be over 100 times larger than typical background concentrations.

Figure 1. Cattle feedlot – one of the largest sources of anthropogenic ammonia emissions.

Because of the potential adverse effects of ammonia emission on the environment, human health, plant growth, aquatic health, and air quality, regulations toward reducing atmospheric ammonia are increasing as well as new best practices for agricultural sites to reduce atmospheric ammonia. Atmospheric ammonia needs to be well quantified in these areas to better regulate and reduce nitrogen anthropogenic emissions.

PROBLEMS AND GOALS

Accurately and precisely detecting and quantifying nitrogen emissions, particularly ammonia emissions, can lead to solutions for potential adverse effects on the ecosystem and air quality. While some emission sources have much higher ammonia concentrations (animal waste and fertilizer) and are easily detectable in ranges of 500 to 1200 parts-per-billion (ppb)[1], other sources have much lower impacts (industrial and vehicular) and are more difficult to measure. Although agricultural ammonia emissions are much higher, industrial and vehicular ammonia emissions still contribute to the total impact of ammonia on the environment and can be monitored and recorded for further regulation or reduction.

Concentrations of atmospheric ammonia can vary widely even in short ranges. Ammonia is also a "sticky gas", meaning it tends to absorb or adsorb with surfaces, making typical closed-path instruments difficult to use. Point sensors are more applicable to mobile use which is better suited for a versatile study of different locations and sources on the ground and in the air.

Chemical ionization mass spectrometry achieves adequate sensitivity and time resolution, but it is too complex and large for mobile applications. Optical techniques provide a more compact instrumentation solution. Methods, such as direct absorption spectroscopy, photoacoustic spectroscopy, integrated cavity output spectroscopy, differential absorption spectroscopy, cavity ring-down spectroscopy, and wavelength modulation spectroscopy (WMS) with multi-pass cells have been utilized in near-infrared or mid-infrared devices. However, very few of these sensors are capable of sensitive, mobile measurements of atmospheric ammonia. A successful, mobile, atmospheric ammonia sensor achieves high sensitivity (<~1 ppb) while having a fast temporal response (<~1 s), is compact, has low mass, and has low power consumption for use on ground or aerial vehicles.[1]

A previous wavelength modulation spectroscopy (WMS) design satisfies all of these requirements but is used at ~9.0 μm output wavelength.[1] Although the size, weight, and packaging are all favorable, the system could be improved upon for better atmospheric ammonia detection with an alternative wavelength selection to access stronger absorptions.

METHOD

Researchers from Colorado State University and Surprise, AZ have developed an open-path WMS atmospheric ammonia sensor that is relatively lightweight, low power, and achieves ppb sensitivity using a quantum cascade laser. This design is powered by a battery, making it applicable to mobile measurements on a ground or aerial vehicle. The mobile sensor allows access to hard-to-reach or dangerous locations for ammonia detection.

With this open-path system, researchers utilized a Herriot multi-pass cell to increase the effective path length of the laser beam to 19.88 m with 28 round trips and, therefore, increase the sensor's sensitivity. The laser source is a distributed feedback quantum cascade laser (QCL) with a center wavelength of 10.33 μm and a total output power of 30 mW. The developed ammonia sensor system, including QCL, photodetector, multi-pass cell, and relative size, can be seen in **Figure 2**.

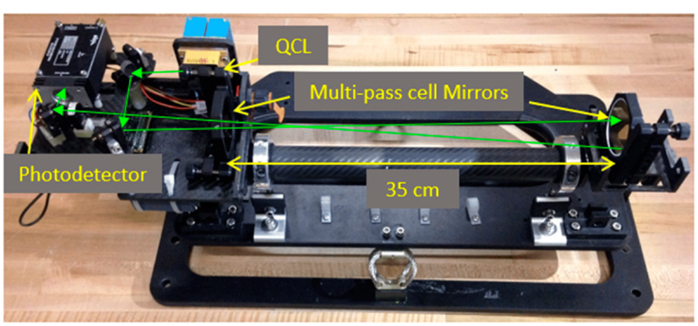

Figure 2. Open-path WMS based ammonia sensor. Green arrows show the approximate beam path (neglecting the multiple cell passes).[1]

Wavelength modulation for WMS and the wavelength scan are both controlled by the current which is set by Wavelength Electronics' FL500 laser driver. With WMS, the first (1*f*) and second (2*f*) harmonic signals closely resemble the first and second derivatives of the absorption spectrum. By normalizing the 2*f* signal with the 1*f* signal, absorption measurements are more immune to laser power and atmospheric-induced fluctuations. With the 2*f*:1*f* measurement of ammonia, other absorption lines of other species (H_2O and CO_2) are negligible, isolating the ammonia absorption and solving isolation problems with most open-path configurations.[1]

The ammonia sensor is designed for both terrestrial ground vehicles and unmanned aerial vehicles (UAVs). **Figure 3** shows the mounting setup on a truck for ground deployments. The power draw of the system is low (30 W) enabling battery operation from a standard automotive battery seen at the bottom of **Figure 3**. With the sensor mounted on the roof of the truck, the open-path design can sample ambient air during vehicle movement. With robust mounting clamps and fasteners, the sensor is protected from misalignment from driving on paved and gravel roads and standard vibrations while driving. All experiments with the ground-based setup lasted over 20 hours proving the reliability of this technique. Typical tests lasted approximately 1 hour capturing elevated ammonia concentrations of automobile combustion and of cattle and agricultural sources at the ground level.

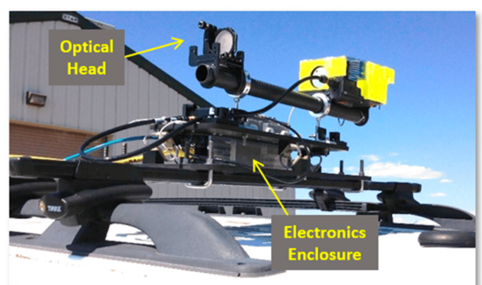

Figure 3. (Top): Photograph of sensor vehicle roof mount. (Bottom): Pictorial view of components used to power the sensor for vehicle deployments.[1]

The ammonia sensor was also mounted to a wing of a fixed-wing UAV for elevated ammonia measurements at higher altitudes. Similarly to the ground setup, the sensor can collect measurements in air with the open-path system. **Figure 4** shows the UAV ammonia sensor mounting.

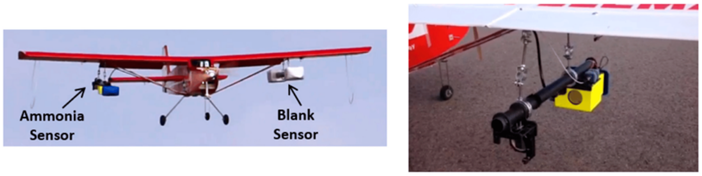

Figure 4. (Left): Sensor on flying UAV. (Right): Zoom-in (rear) view of ammonia sensor mounting.[1]

The runway used for the plane was hard-packed ground, showing the versatility of the setup and the durability of the sensor. Flights were relatively short - the ammonia concentration from a flight shown later in this paper had a duration of approximately three minutes. Altitude and latitude/longitude can also be recorded by the sensor from GPS. With flight paths and measured ammonia concentrations, sources with elevated ammonia quantities can be identified in the air in a variety of places that may be inaccessible at ground level.

RESULTS

Ammonia concentrations were measured in the laboratory, by ground vehicle, and by plane using the WMS, QCL-based, open-path, ammonia sensor. To validate the WMS method with the designed sensor, the WMS spectrum for the case of 150 ppb is compared to an example of the data. **Figure 5** shows the scan range of the sensor in an actual experiment as well as the comparison of simulated and experimental spectra of ammonia concentration.

The peak amplitude and overall spectral shape are in excellent agreement with the simulated data, showing the validity and potential of the developed ammonia sensor.[1]

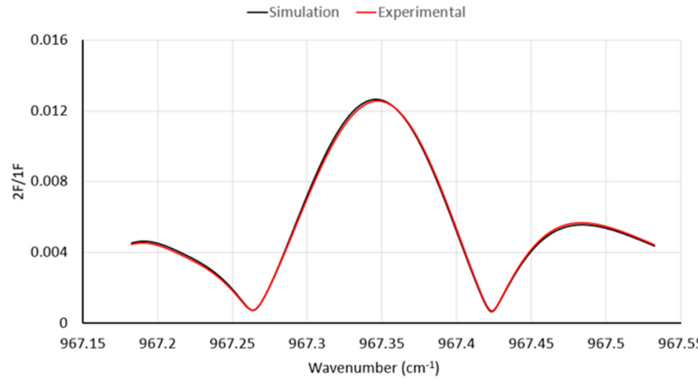

Figure 5. Comparison of simulated and experimental spectra for NH_3 concentration of 150 ppb.[1]

To measure the accuracy and precision of the sensor, a closed-path configuration was used. **Figure 6** shows a test characterizing the ammonia sensor accuracy with good agreement between measured and expected ammonia concentrations. The average discrepancy is <2%, and the Allan variance study yielded a sensitivity of ~4 ppb at 1 s.[1] While this sensitivity isn't as low as other WMS designs, it is very adequate, achieving single-digit ppb sensitivity, for many ammonia sensing applications while providing a compact setup for mobile measurements.

For in-field experiments and tests, researchers deployed the sensor on a UAV 1.5 km away from the target location: a nearby agricultural feedlot. **Figure 7** shows the aerial view of the flight path and the measured ammonia concentration time series. In the ~3-minute flight, ammonia concentration data showed elevated readings over 200 ppb associated with the emission from the feedlot taking into account the local wind direction during the measurements.[1]

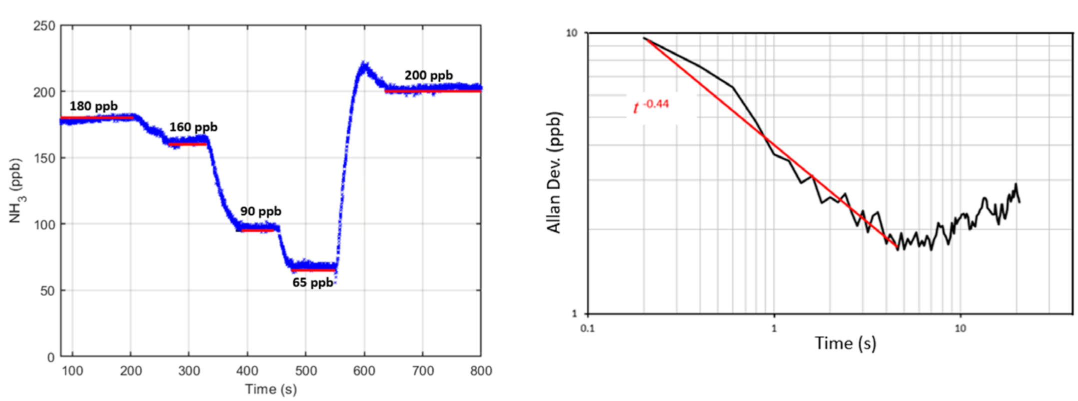

Figure 6. (Left): Comparison between measured and expected ammonia concentrations with closed-path configuration. Red bars show the fix delivered concentrations. (Right): Allan variance analysis shows the sensitivity of ~4 ppb (at 1 s).[1]

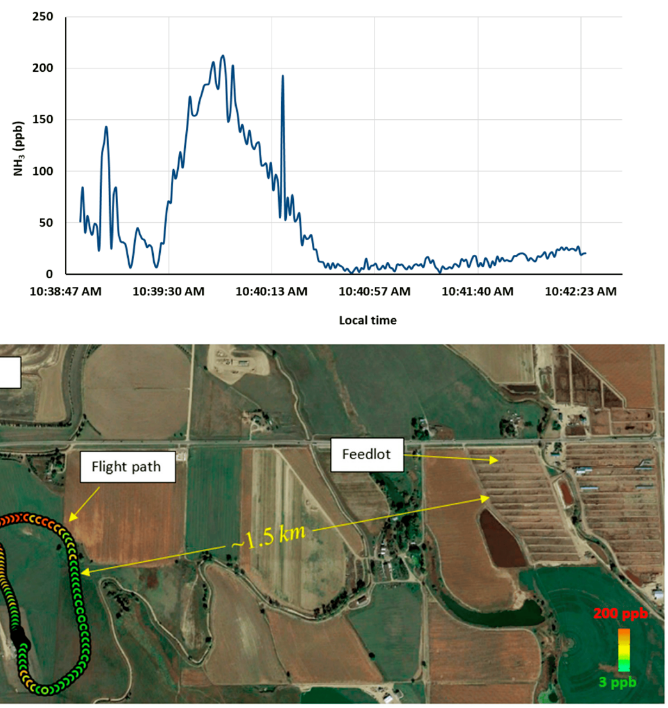

Figure 7. (Top): The measured ammonia concentration timeseries. (Bottom): The aerial view of the flight path and the feedlot.[1]

For mobile detection, size, weight, and power consumption are major concerns, yet the performance of the sensor is critical for in-field ammonia detection applications. The developed open-path ammonia sensor achieves a detection limit of ~2.5 ppb in 3 s using WMS. The packaging is far smaller and less power-hungry than previous methods. With a mass of ~3.5 kg and a power draw of 30 W, the sensor is perfectly designed for mobile deployment where previous systems were too large and needed too much power for battery operation. Using the laboratory and field experiments as proof, the designed WMS ammonia sensor using a QCL can open the door for a vast range of mobile applications for ammonia detection in ambient conditions on the ground and in the air.

Future work includes multiple measurement possibilities for ammonia and methane detection, particularly in the aerial deployment field.[1] Additional sensors and data could determine source location as well as quantity. This ties well into plume dispersion studies of different compounds and tracking sensitive species concentrations for managing air quality problems.

WAVELENGTH'S ROLE

Laser absorption spectroscopy requires high precision and accuracy, and researchers used high-performance electronics to drive the laser system for ammonia gas detection. Wavelength Electronics' laser driver enabled the sensitive measurements and analysis required for ammonia gas detection for mobile deployment.

Laser stability is critical for sensing low concentrations of harmful gases in the air. Wavelength Electronics' low noise laser diode driver, the FL500, can precisely deliver up to 500 mA of current and a compliance voltage of up to ~11 V to the laser, a QCL in this study. Because laser power stability or any fluctuations of the laser affect the spectra data and linewidth of the QCL, the FL500 achieves current stability at ambient temperature of 50 - 75 ppm for 24 hours, ensuring accurate and reliable results with the QCL. The FL500 also has noise as low as 3 µA RMS at full scale with a bandwidth of up to 500 kHz for current modulation or wavelength scanning. The driver enabled easy and precise wavelength scanning through the modulation of the supplied current.

Laser safety features include slow start, brownout protection, TTL-compatible shutdown pin, and current limit. For mobile deployment, researchers not only needed a reliable and safe laser driver - they also needed a compact and lightweight design. The FL500 is approximately 19 x 11.5 x 6.5 mm and weighs only 0.08 oz. (2.23 g). The small and compact design of the FL500 allows operation in mobile deployment in ground and aerial vehicles for battery-powered ammonia detection using WMS with a QCL.

REFERENCES

1. Shadman, S.; Miller, T.; Yalin, A.P. Open-Path Laser Absorption Sensor for Mobile Measurements of Atmospheric Ammonia. *Sensors* **2023**, 23, 6498. https://doi.org/10.3390/s23146498

USEFUL LINKS

- FL500 Product Page

PERMISSIONS

Figure 2 was cropped and the caption was adapted. No changes were made to the other captions or images. They are presented here in their original form.

PRODUCTS USED
FL500

KEYWORDS
Ammonia, open-path sensor, laser absorption sensor, wavelength modulation spectroscopy, quantum cascade laser, FL500, laser driver, nitrogen, unmanned aerial vehicle, mobile

REVISION HISTORY

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REVISION	DATE	NOTES
A	July 2024	Initial Release