

Agricultural ammonia sensor using diode lasers and photoacoustic spectroscopy

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Abstract

A trace-gas sensor based on fibre-amplifier enhanced photoacoustic spectroscopy has been developed for measuring ambient ammonia in agricultural settings. The sensor was built in an enclosure for continuous, unattended operation in dusty and humid conditions. Lab testing yielded benchmark results of sub-ppm sensitivity with a measurement time of 1 min and a linearity of 99.99%. Field testing was performed in environmental chambers at UC Davis where the excreta from three Holstein cows were allowed to accumulate, providing a source of ambient ammonia. The photoacoustic sensor measured the ambient ammonia in the room as it increased from below the detection threshold, up to 8 ppm, operating over a three-day period. Intercomparison measurements with the Federal reference method (EPA 40 CFR, using sulfuric acid filled impingers to trap ammonia and subsequent analysis using ion chromatography) yielded good to excellent correlation.

Keywords: ammonia sensors, agricultural ammonia emissions, photoacoustic spectroscopy

1. Introduction

The problems of extensive agricultural emissions have gained recent notoriety as a pressing public health issue due to the subsequent effects of these emissions on odour and air quality [1–3]. Ammonia is considered an important pollutant species due to its role as a precursor in fine particulate matter formation (with attendant health effects) and its impact on ecological nitrogen balance. As a result, various federal and state agencies such as the Environmental Protection Agency (EPA), United States Department of Agriculture (USDA), California Air Resources Board (CARB) and the Iowa Department of Natural Resources, have shown strong interest and support to develop, test and verify appropriate ammonia monitoring instrumentation.

Such sensors must be able to measure ammonia over a large concentration range, covering sites such as:

- (a) poultry houses, where the concentration can be as high as 150 ppm,
- (b) dairy wastewater lagoons, where the concentration can be less than 10 ppm,
- (c) at property fence lines, where regulatory reports [2] mandate maximum ammonia concentrations of 500 ppb.

As such, sensors need to have a sensitivity better than 150 ppb to resolve concentrations at the fence line, yet also require more than three orders of magnitude linearity in order to be deployed within the facilities, all with a measurement time of approximately 1 min. Moreover, agricultural sensors must be able to withstand the ambient conditions, which include heavy dust loading, moisture from humidity, condensation and rain and vibrations from instrument use.

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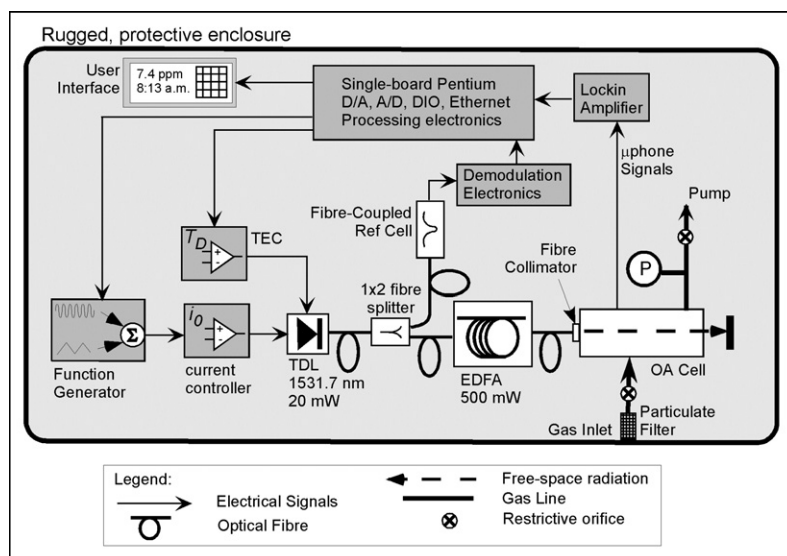


Figure 1. Instrumentation schematic of the portable photoacoustic sensing platform contained within a protective enclosure. (EDFA = erbium-doped fibre amplifier; OA cell = optoacoustic cell; TDL = tunable diode laser; TEC = thermo-electric cooler; μ phone = microphone; A/D = analogue-to-digital converter; D/A = digital-to-analogue converter; DIO = digital inputs and outputs; P = pressure gauge; T_D = nominal diode temperature; i_0 = nominal injection current)

This paper reports on the development and testing of an enclosed portable ammonia sensor, based on near-infrared (NIR) diode lasers and fibre-amplifier enhanced photoacoustic spectroscopy that was designed to address the problem of monitoring ambient agricultural ammonia.

This optical system yielded several innovations:

- self-contained laser-based ammonia-sensing instrument that can be deployed in agricultural settings for unattended long-term (many days) operation,
- fibre-coupled permanently-sealed ammonia gas reference cell for wavelength locking,
- fibre amplifier for generating enhanced photoacoustic signals in a non-laboratory environment.

2. Theory

Photoacoustic spectroscopy is a particularly suitable technique for the requirements of agricultural sensing because of its simplicity, ruggedness and sensitivity. This technique is well known and its application for ammonia detection with near-infrared lasers [4, 5], field measurements [6] and fibre amplifiers has been described in previous work [7]. In brief, it is an optical technique that involves absorption of the laser radiation (modulated either in frequency or amplitude) at a wavelength that overlaps with an absorption feature of the target species, followed by deactivation of the excited molecule via collisions, during which the absorbed radiation energy is converted into periodic local heating at the modulation frequency, and thereby inducing acoustic waves that can be monitored with a low-noise microphone. Figure 1 shows the basic instrumental layout, wherein the photoacoustic (PA) cell is designed to be an acoustic resonator and the microphone is embedded inside.

The photoacoustic signal, S , in volts, at a particular operating frequency is

$$S = S_m P C \alpha, \quad (1)$$

where the microphone sensitivity at the activation frequency, S_m , is in units of volts per Pascal; the power, P , is in watts; the absorption coefficient, α , is in inverse centimetres; and the cell factor, C , which includes the acoustic resonant enhancement quality factor, Q , has units of Pascal per inverse centimetres per watt. The signal is therefore linearly proportional to the incident laser power and absorption coefficient. Thus, photoacoustic instrumentation for trace gas detection derives sensitivity benefit from the use of as much laser power as is reasonably available, hence the value of the fibre amplifier.

Though photoacoustic spectroscopy is considered a ‘zero baseline signal’ strategy because signal is generated only if the target molecules are present, for implementations that use amplitude modulation of the laser, background ‘noise’ that is coherent with the signal, though small, often emerges due to window absorption. Moreover, broadband absorption from gas constituents other than the target species in addition to ambient noise, flow noise, and so forth, may also contribute toward degrading the sensitivity. Perhaps the most robust technique for eliminating the contributions from broadband background absorbers and $1/f$ noise is wavelength modulation spectroscopy (WMS). When modulating the wavelength of the laser at a frequency f about the centre of the absorption transition, the acoustic signals from wavelength-independent sources such as window absorption and other broadband absorbers (for example continuum spectra and the wings from interfering species) show up as an offset and thus are eliminated when evaluating the derivatives of the signal via $2f$ demodulation [7].

For WMS, the laser frequency is described by

$$\omega_i(t) = \omega_c + a \cos(ft), \quad (2)$$

where $\omega_i(t)$ is the instantaneous frequency of the laser, ω_c is the laser’s mean frequency, a is the modulation depth and f is the sinusoidal modulation frequency [8].

3. Instrumentation details

The design of the ammonia sensor prototype was based on a platform of laser-based photoacoustic spectroscopy because of its reliability, ruggedness and sensitivity. A prior photoacoustic sensor based on CO₂-lasers (with an optical output >1 W) demonstrated a sub-ppb ammonia detection sensitivity [9], which is satisfactory for agricultural settings, but this sensor does not meet the desired criteria for size, weight, power consumption, ruggedness, portability and suitability for dusty environments. However, because the ammonia buildup levels in agricultural settings are typically greater than 1 ppm, and the recommended regulations are for a concentration level at the property fence line of 500 ppb and at neighbouring properties 150 ppb, a sensitivity in the range of 50–150 ppb is a reasonable target for a sensor to be used in agricultural emissions-monitoring. As a result, the focus of this work was to relax the sensitivity requirement of the sensor in exchange for an instrument that would satisfy the remaining criteria. Prior work demonstrated the utility of near-infrared telecommunications-grade fibre-coupled diode lasers combined with fibre amplifiers for the detection of ammonia in this sensitivity range [7], and therefore that benchtop platform was used as a starting point for the work contained in this paper.

3.1. Optical system

A resonant photoacoustic system as described above was built into a rugged, man-portable enclosure, as shown in figure 1, to protect the instrument from dust, water and other physical damage such as that from rough handling. The photoacoustic cell was designed to act as an acoustic resonator, with the first longitudinal resonance at approximately 1830 Hz and a quality factor, Q , of approximately 50. The laser's wavelength was modulated at 915 Hz, such that the $2f$ signal overlapped with the acoustic resonance. A fibre-coupled diode laser with approximately 20–30 mW of output power operating near 1531.7 nm was used to interrogate an ammonia transition that is isolated from standard atmospheric interferences, including H₂O and CO₂ [10]. The laser was scanned across the transition at approximately 0.8 Hz. A computer-controlled erbium-doped fibre amplifier (EDFA) was used to increase the photoacoustic signal as needed by boosting the laser's output power to between 50 and 500 mW, while maintaining the wavelength and linewidth of the seed laser source.

The optical train was designed to maintain optical alignment despite instrument vibrations and avoid dust contamination by use of fibre-optic components throughout, including, a fibre-coupled diode laser, 1×2 fibre splitter, fibre-coupled permanently sealed gas reference cell, fibre amplifier and fibre collimator. The 1×2 fibre splitter is a standard telecommunications component that sends 90% of the optical power into one output fibre, and 10% into the other output fibre. This splitter permits simultaneous use of the seed laser to interrogate a gas reference cell for wavelength-stabilization and as the input to the EDFA.

The gas reference cell was fibre-coupled to eliminate air gaps between the fibre tip and the cell. The cell itself is a 3 cm long permanently sealed glass tube filled with approximately

5 Torr of pure ammonia gas. Several fill/purge cycles of pure ammonia were used to condition the cell in order to avoid adsorption effects and maintain a stable signal over long periods of time. The cell has an embedded photodiode for monitoring absorption of the laser light by ammonia gas within it. To our knowledge, this is the first use of a fibre-coupled permanently sealed ammonia gas reference cell. The fibre collimator was a custom designed mechanical piece that attached directly to the photoacoustic cell and contained a collimating lens for sending the output of the fibre amplifier through the centre of the cell and onto a beam dump. The mount was designed to keep air and dust from between the cell's lens and input window.

3.2. Electronics

Custom board-level electronics circuits were designed for this sensor in order to accomplish a variety of control and sensing tasks. A waveform synthesizer was designed and built that combined a triangle wavefunction generator (for sweeping the laser's wavelength across the ammonia transition), a sine wave (for modulating the laser) and bias voltages for controlling the laser wavelength via the nominal diode temperature and injection current. These generators were built using high-precision voltage-controlled oscillator (VCO) chips and had computer control for the following parameters: sine wave amplitude (modulation depth), sine wave frequency (modulation frequency), triangle wave amplitude (scan depth), triangle wave frequency (scan frequency) and laser bias.

A narrow-bandwidth bandpass filter for demodulating harmonic signals from the reference cell photodiode was designed with a 6-pole Butterworth bandpass filter (1820 Hz centre frequency, 100 Hz bandwidth) and comprised three high-precision capacitor chips with op-amp buffers and 1% precision resistors. A board-level computer-controlled lock-in amplifier was used to demodulate the photoacoustic cell's microphone signals at $2f$. The laser control circuitry for temperature and current were designed using miniaturized controllers and protection to limit the laser and TEC current and control gain.

The waveform generator, bandpass filter and laser control circuitry were combined into a custom-designed two-layer printed circuit board (PCB) along with signal conditioning for the pressure gauge, temperature sensors, voltage regulators and numerous breakout headers for custom cable harnesses to connect with the computer, components and power supplies. In addition to the embedded electronics, the PCB included discrete components such as a controller for the photoacoustic cell temperature, user interface via a 4-line 40-character liquid crystal display (LCD) for instrument readings and a 4×5 keypad for user inputs, EMI/RF filtering of the ac input power, and a dust- and water-proof power entry module. The overall system consumes approximately 85 W of power (comparable to a laptop computer).

3.3. Embedded programming and algorithm development

Achieving reliable remote, unattended and turnkey operation in the field required a software platform and algorithms that would remain stable over extended periods. Moreover, for a portable system, it was necessary to design a computing system that could be moved frequently and subject to vibrations

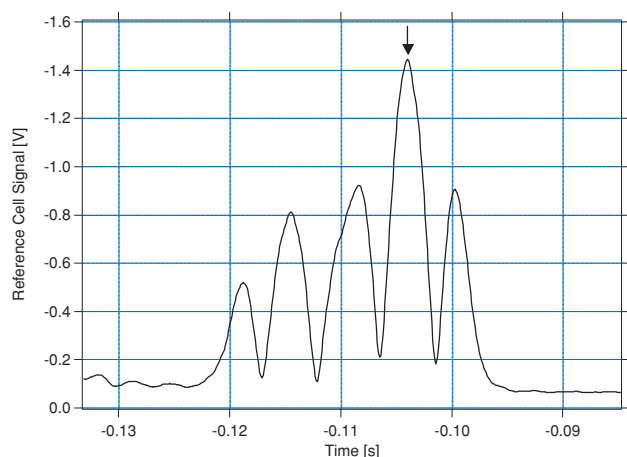


Figure 2. Demodulated reference cell signal of the blended ammonia doublet near 1531.7 nm (0.8 Hz sweep, 40 averages). The largest peak, marked by the arrow, was used for calibration and field measurements of ammonia.

during use. To meet this latter need, solid-state storage devices rather than a conventional spinning-disk storage device were used for the computer operating system, program and data files. Storing the entire operating system, program and collected measurements onto compact solid-state disks, which typically have far less storage space than conventional drives, required switching from a large-scale operating system with extensive overhead typically found on desktop computers to a compact system. To do so, a Linux operating system with a full installation size of 2 GB, was stripped down to its bare essentials, eventually requiring only 60 MB for its final installation on a single compact flash hard disk, while retaining USB, ethernet, keyboard, video and other capabilities.

In addition to the operating system requirements, the entire computer program was written in C for maximum stability. To increase speed, device drivers for direct memory access 16-bit A/D sampling were written as a Linux Kernel level implementation, improving the overall system data digitization, collection and transfer speed to 3 kHz. This fast sampling with 16-bit accuracy was required for acquiring and analysing high-precision spectroscopic lineshapes. A single-board computer with a Pentium® microprocessor was used for controlling the instrument and analysing the data.

After the instrument is turned on, the Kernel module drivers and program boot up automatically, the program begins a warm-up sequence, and the measurements begin. Therefore, the only action required of the user is to turn on the instrument. Auto-initialization in the case of irreconcilable errors and automatic re-initialization occur to avoid software freezes.

The system algorithms include extensive triggering and timing to make sure data for the reference cell and sample cell are collected simultaneously during the 0.8 Hz laser scan. The demodulated data from the lockin amplifier were collected, parsed, averaged and then aligned with each other based on the location of the largest absorption peak (the second peak from the right in figure 2, marked by the arrow) as determined by the reference cell information. Data analysis was performed by use of a singular-value decomposition routine to determine a best-fit concentration of the gas. In addition, the computer used the reference cell signals to control the laser wavelength to

centre the absorption feature in the measurement window. The measurement data (date, time stamp, ammonia concentration, system temperature and other internal instrument diagnostics) are stored in log files that can be easily downloaded over an ethernet cable for post-sampling analysis.

3.4. Mechanical, thermal and gas handling design

The greatest challenges during instrument development were related to isolation of the photoacoustic cell from vibrations (e.g. from flow noise in the sample lines, or from the vacuum pump) and cooling of the sealed instrument. A standard hand-portable hard-sided dust- and water-proof briefcase was used for the enclosure, and all the components were contained inside, leaving only the power cord and gas inlet as connections external to the instrument. Opening the lid reveals a panel with an LCD readout (with updates on instrument status, last measurement reading and last measurement time), an input keypad (for changing instrument settings, controlling the instrument, etc), power switch, fuse and connectors (ethernet jack for downloading data from the internal computer, debugging signals, video output, etc). Thermal control was established by use of two vents on the side of the case with cooling fans and dust covers attached, and custom ventilation pipe inlets for the fibre amplifier.

The gas handling was designed to maintain sample integrity, protect the optics and achieve a response time better than 1 min. The biggest obstacles include the dusty environment and ammonia's adsorptive or 'sticky' nature, which makes it likely to adsorb to most surfaces, thereby slowing down the instrument response time and potentially compromising the integrity of the flowing gas samples. To minimize ammonia adsorption, only chemically inert coatings were used on all the gas handling surfaces from the instrument inlet to the exit of the photoacoustic cell. Dust was removed from the samples by use of a particulate filter with a chemically passivated sintered block that allowed the gas through, but no particles greater than 7 μm . The cell pressure and flow rate were established to be approximately 175 Torr and 40–60 standard cubic centimetres per minute by use of restrictive orifices proximate to the inlet and exit of the cell. This pressure was selected to maximize WMS $2f$ signal from the blended ammonia doublet optical absorption feature at 1531.7 nm, and the flow rate was selected such that laminar conditions were maintained, thereby limiting flow noise. Note that at these conditions (temperature, humidity, pressure, flow rates and gas handling materials) the presence of water vapour has no impact on the concentration of ammonia in the samples due to chemical reaction or other means.

The overall system weighed 37 lbs and occupied less than 1.5 cubic feet.

4. Laboratory testing results

The completed sensor, constructed as described above, was tested extensively in the laboratory to establish its benchmark performance parameters. A sample reference cell trace during these tests for the blended ammonia absorption feature near 1531.7 nm is shown in figure 2. The largest peak (second from the right in figure 2, marked by the arrow) was used for centring the laser wavelength.

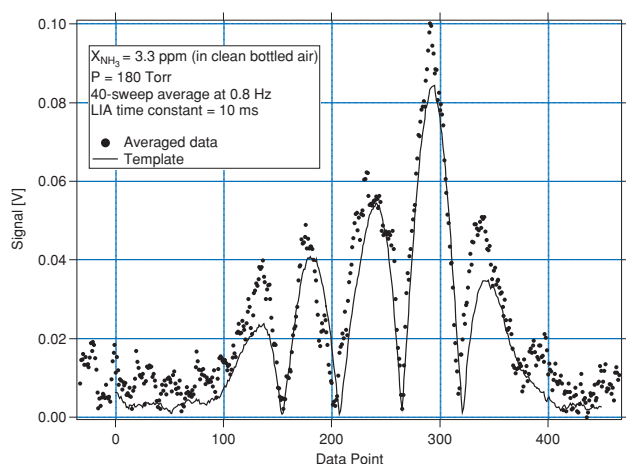


Figure 3. Sample lineshape measured for 3.3 ppm ammonia, overlaid with the scaled template used for determining concentration. Cell pressure is 180 Torr.

The instrument was characterized on the benchtop with ammonia mixtures that were generated by carefully diluting NIST-traceable sources of approximately 100 ppm NH_3 (supplier-specified accuracy of $\pm 2\%$) in air via dynamic mixing with a flow of zero-air. NIST-traceable mass flow controllers with absolute accuracies of $\pm 1\%$ were used for the dynamic dilution.

The cell pressure is maintained at approximately 175–185 Torr to keep the ambient water concentration low at standard conditions, and the cell temperature is maintained constant to minimize the artefacts arising from changing Doppler and collisional broadening. Maintaining these conditions constant therefore obviates the need for complicated temperature and pressure dependent curve fits to deduce the concentration. Rather, a template for the ammonia absorption pattern can be collected at concentrations that yield good signal-to-noise ratios (e.g., 10 ppm or above) and then scaled linearly to deduce the concentration of subsequent gas samples. Sample data for a measured absorption transition of ammonia are shown in figure 3. Note that the raw data trace is shown before its offset from zero was removed for data analysis, leaving a mismatch in peak amplitudes that appears larger than was used for the calculations. The remaining mismatch in overall shape, peak amplitude and peak location produces a measurement error as large as 10% when ammonia is present. The template was collected at 10 ppm and is shown with the solid trace, while the raw data (averaged 40 times) for 3.3 ppm ammonia are shown with markers and overlaid with a scaled template.

To determine the system's accuracy, linearity, sensitivity and precision, the prototype was tested with a 'staircase' of different ammonia concentrations. The results for one such staircase are partially shown in figure 4, with pertinent statistics listed in table 1. The accuracy at each plateau is within 10%, except for near 0 ppm ammonia concentration. The replicate precision (1σ) varies between 120 ppb and 1.07 ppm, and typically is 1–2% of the measured value. The sensitivity is approximated as the replicate precision for measurements near zero, thus in this case the sensitivity is 120 ppb or better. The staircase also reveals that the rise and fall times are less than a single measurement, which is approximately 1 min.

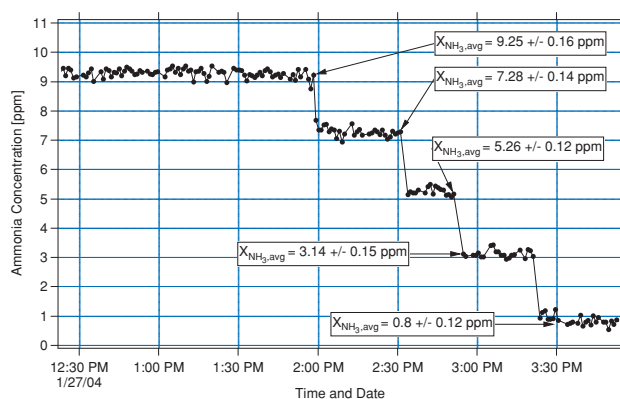


Figure 4. Instrument performance when exposed to ammonia mixtures with a 'staircase' of concentrations.

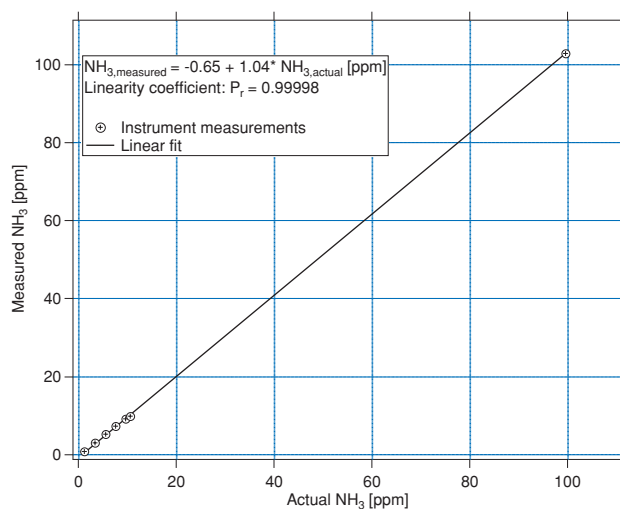


Figure 5. System linearity from 1 to 100 ppm is better than 99.99%, with a projected zero value of -0.65 ppm.

Table 1. Measured and actual values for ammonia, along with measurement error and replicate precision (1σ) at each plateau.

Measured NH_3 (ppm)	Actual NH_3 (ppm)	Error (%)	Replicate precision (ppm)
0.81	1.17	44.7	0.12
3.14	3.43	9.4	0.15
5.26	5.60	6.4	0.12
7.28	7.66	5.2	0.14
9.25	9.64	4.2	0.16
9.93	10.60	6.7	0.26
102.9	99.6	3.3	1.07

The values for measured ammonia concentration plateaus of the staircase were plotted against the actual ammonia concentration in figure 5. By performing a curve fit, the linearity was determined to be better than 99.99% for a range of 1 to 100 ppm, and the projected zero-value is -0.65 ppm.

5. Field testing

The prototype instrument was field-tested during two experiments at UC Davis. The UC Davis agricultural air quality research facility, which was used for this purpose, is equipped with two new and identical environmental exposure

Table 2. Comparison between measurements with the laser-based sensor and ion chromatography from the field-testing, showing excellent agreement.

Date	Time period (for IC measurements)	Prototype sensor (ppm)	IC (ppm)
29/1/04	12:32 to 13:38	6.00 ± 0.32	4.5
29/1/04	13:53 to 14:58	6.50 ± 0.36	6.4
29/1/04	15:03 to 16:02	6.30 ± 0.33	6.0
30/1/04	11:20 to 11:50	136.0 ± 6.4	145.6

chambers, each measuring H 10.7 m × W 4.8 m × H 3.1 m (159 m³). The chamber ceiling has two inlet air ducts and one outlet air duct. Fresh air (396 m³ min⁻¹) is supplied through the inlets air ducts to each chamber and the same amount of room air exited from the outlet air duct. The chamber has a total volume of 141 584 l, and a controlled and continuous airflow of 37 369 l min⁻¹, suggesting a total air turnover rate of approximately 4 min. Room temperatures were automatically kept at 22 °C.

In the first experiment, three non-lactating Holstein dairy cows were housed inside the environmental chambers. During the three days of ammonia measurements, faeces and urine were allowed to accumulate during the test period to generate a large source of ambient ammonia emissions.

The instrument was operated continuously during both of the first two days to measure ambient room air ammonia in the presence of the cows. On the third day cows were removed from the chamber and measurements were made using a 64-liter surface emissions flux chamber that was placed over a mixture of feces and urine, where ammonia concentrations were expected to be high. Ammonia measurements were made with (a) the continuously measuring prototype and (b) the federal reference method EPA 40 CFR (ion chromatography) at discrete times. The reference method EPA 40 CFR is the recognized standard method for ammonia sampling from area surfaces. As part of this method, air from inside the chamber was sampled through a sampling train, which contained sulfuric acid. The atmospheric ammonia was trapped in the sulfuric acid and later analysed in the laboratory using ion chromatography (Dionex ICS90, Dionex Corp., Sunnyvale, CA).

The comparison between both technologies/techniques yielded excellent agreement as summarized below.

On day 1, the cows were introduced into the environmental chamber at 11:30 a.m. Initial ammonia concentration was <0.2 ppm, and therefore below the instrument sensitivity. After several hours, the excreta accumulated and mixed (a precondition for ammonia formation is mixing of urine and faeces) on the floor and the ammonia subsequently increased to 3 ppm by the end of day 1 (see figure 7). On day 2, the ambient ammonia continued to increase to 8 ppm.

On day 2, comparative measurements between the optical prototype sensor and the reference ion chromatography method were undertaken. The results are overlaid in figures 6 and 7 and tabulated in table 2, revealing excellent agreement for three of the four measurements. The source of disagreement for the first measurement is unclear, but might be the result of calibration irregularities or start-up issues with the sample collection. It must be emphasized that the reference IC measurements did not provide results in real-time or with

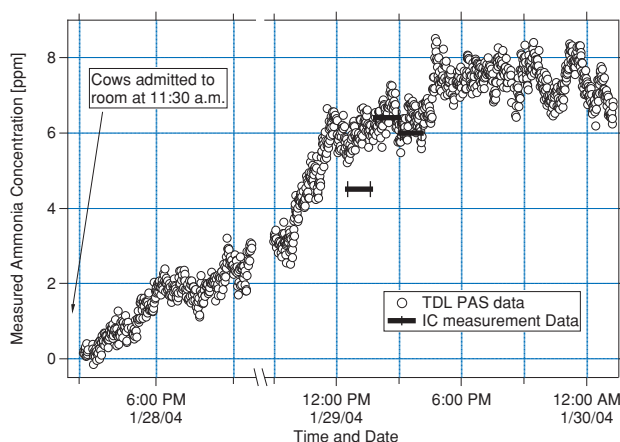


Figure 6. Ammonia measurements over two days in the environmentally controlled chamber with three Holstein cows and accumulating faeces and urine. Three measurements from the reference standard ion chromatography are overlaid for comparison. (TDL PAS = tunable diode laser photoacoustic spectroscopy).

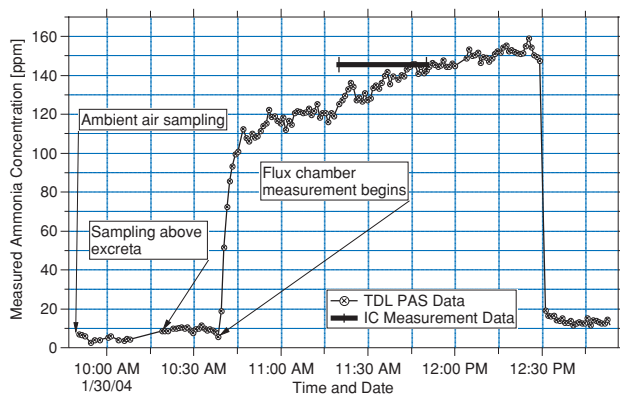


Figure 7. Ammonia measurements from a flux chamber (shown in figure 8) placed over Holstein excreta. One measurement from the reference standard ion chromatography is overlaid for comparison. (TDL PAS = tunable diode laser photoacoustic spectroscopy).

discrete time resolution. Rather, IC samples were collected in sulfuric acid over 30–60 min during the day then subsequently transported and analysed in a laboratory with results available several days later.

On day 3, comparative measurements between prototype and reference technologies/methods were made using a sealed 64-litre flux chamber (see figure 7) that was placed over a pile of excrement that we considered to be the best source of ammonia volatilization. The chamber had a flush rate of 1 l min⁻¹ with fresh air, and the measured ammonia concentration exceeded 100 ppm. A comparative measurement with ion chromatography was performed on the third day as well and is summarized in table 2, again showing good agreement.

In the second experiment, 24 piglets were housed in the same environmental chambers, in which they were exposed to 50 ppm ammonia for gas exposure studies. The ammonia concentration was monitored using three instruments: (1) prototype, (2) Draeger Pac III ammonia gas monitor (1 ppm accuracy; Draeger, Pittsburgh, PA), which was used three times per day; and (3) Dionex (Dionex ICS90,

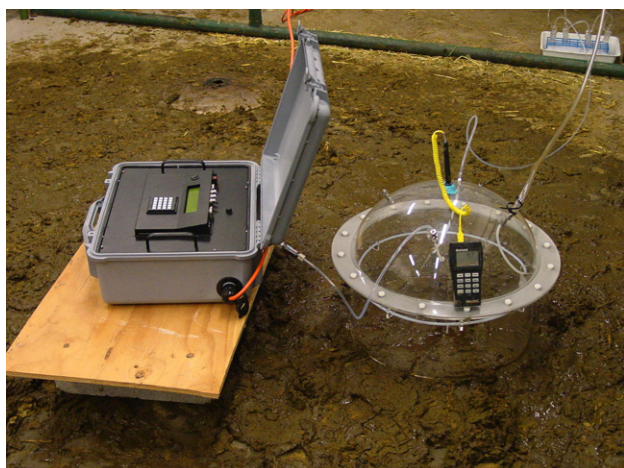


Figure 8. Photo of the prototype instrument sampling air from a 64 l flux chamber.

Table 3. Comparison between measurements with the laser-based sensor, ion chromatography and the Draeger IMS system from the field-testing, showing general agreement.

Date	Time period (for IC measurements)	Prototype sensor (ppm)	IC (ppm)	Draeger (ppm)
11/3/04	11:26–11:56	65.7 ± 2.3	60.23	47
25/3/04	10:47–11:17	50.6 ± 2.0	45.28	36
01/4/04	13:46–14:16	53.2 ± 2.0	54.37	50
08/4/04	14:38–15:08	39.3 ± 0.6	45.72	50

Dionex Corp., Sunnyvale, CA) ion chromatograph (EPA reference method, EPA 40 CFR).

Further intercomparison tests between these three technologies/methods were performed over eight weeks. For these tests, the air inlets for the sealed environmental chambers were filled with a steady flowing mixture of 50 ppm ammonia in air to test the health effects on animals. The photoacoustic instrument was operated many days throughout that period, and comparison measurements were available intermittently from the IC system, and from a Draeger IMS sensor. The results are listed in table 3, again showing good agreement.

6. Conclusions

We have developed a portable photoacoustic sensing platform for detecting trace concentrations of ambient ammonia in agricultural settings using NIR diode lasers and EDFAs for signal amplification. The entire system was contained within an enclosure for protecting the system from environmental conditions such as vibrations, dust and moisture.

This agricultural ammonia sensor was approximately the size of a briefcase and was designed to meet the requirements of the agricultural community (e.g. low power consumption, man-portable, rugged, resistant to dust, etc). This prototype was tested extensively in a laboratory to

quantify its performance, and subsequently tested in the field in environmental chambers occupied by three Holstein cows and 24 piglets to prove its feasibility. Comparison measurements were made by the federal reference standard (impingers and ion chromatography), yielding excellent results. Overall, the instrument worked consistently to yield measurements updated on minute-by-minute increments. The verification of those measurements with ion chromatography confirms the instrument's accuracy, which combined with the multi-day operation verifies the instrument's utility. These results represent the first application of diode-laser based optical sensors or fibre-amplifier enhanced photoacoustics for measuring ambient ammonia in agricultural settings.

Acknowledgments

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