In-situ monitoring of ammonia gas using an optical fibre based approach

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Abstract. An optical fibre sensor for the monitoring of low level atmospheric ammonia concentrations is presented. The measuring technique employed is based on a differential optical absorption approach, rather than a semiconductor based technique which is generally exploited within comparable commercially available products. The sensor described herein demonstrates vast improvements in terms of sensitivity, selectivity and lifespan over ammonia sensors currently available commercially. Extensive laboratory-based experimental tests demonstrate the sensor’s ability to monitor concentrations as low as 1ppm without any notable cross-sensitivity issues to atmospheric gases such as nitrogen, oxygen and carbon dioxide. Furthermore, in-situ experimental tests within an agricultural cattle enclosure demonstrate sensor’s suitability to environments where low concentration monitoring of ammonia over extended periods of time is necessary.

1. Motivation

In 2008, the environmental protection agency in Ireland estimated that over 91% of all ammonia emissions in Ireland came from the agricultural farming sector as a result of animal manures. In fact it is estimated that 16% of all nitrogen contained within animal waste is released as ammonia gas into the atmosphere [1]. This amounted to 95.3 kilotonnes of ammonia gas from agricultural farming in Ireland being released into the atmosphere in 2008 [1].

After these emissions enter the earth’s atmosphere they can lead to many adverse affects including acidification and ground-level ozone. As a result, increasingly stringent European legislation such as the National Emissions Ceilings (NEC) Directive has been established in an effort to reduce the amount of ammonia emissions worldwide [2]. This has led to the demand for a sensitive sensor which for the monitoring of ammonia gas over the last number of years.

In addition, the concentration level of ammonia in an enclosed agricultural environment such as an agricultural cattle enclosure can be of high importance within an agricultural setting. Exposure to excessive levels of ammonia gas within an agricultural environment can lead to a wide range of health issues, both for livestock and agricultural personnel alike. This has also increased the demands for the development of an ammonia sensor. However a sensor capable of operating within the environment selectively and accurately with a relatively long lifespan is of preference.
2. Sensing Technique

The earth’s atmosphere comprises primarily of nitrogen, oxygen and carbon dioxide gases. It also contains around 1% of water vapor. This wide composition makes it difficult for sensors operating in such an atmosphere due to inherently challenging cross-sensitivity effects. Commercially available sensors capable of monitoring ammonia are often based on semi-conducting films [3] for detection. Sensors based on this technique can provide a relatively high level of sensitivity; however they can suffer from cross-sensitivity effects and can have a relatively low lifespan. Ammonia sensors have also been reported based on optical absorption within the Infrared region [4]. However due to relatively high absorption strengths for water vapor in this region, these sensors can exhibit cross-sensitivity to humidity.

Recently developed optical devices operating within the ultraviolet region of the spectrum has allowed for the development of low cost optical based sensors within this region. This has allowed for a low cost optical approach based on absorption in the ultraviolet region. This approach can provide an appropriate measurement solution to this issue with minimal cross-sensitivity effects. This technique, often referred to as differential optical absorption spectroscopy, allows for a significantly high selectivity response through the monitoring of absorption lines associated with ammonia gas molecules.

Sensors based on direct absorption spectroscopy utilize the fact that all gas specie absorbs optical light at different characteristic wavelengths. The absorption spectrum for ammonia gas demonstrates significant absorption coefficients within the ultraviolet region at wavelengths between 171nm and 216nm (reported previously by Chen et al) [5]. Through the analysis of similarly reported absorption coefficients for nitrogen, oxygen, carbon dioxide and water vapor (shown in figure 1), it was determined that cross-sensitivity effects within this region were negligible. Experimental tests confirming this relatively high rate of selectivity has been reported in previous published papers [6-7].

An extrinsic sensor based on an open path configuration is the basis for the sensor setup. The setup consists of a deuterium–halogen lamp (DH-2000 from Ocean Optics) for optical light emission and a high resolution spectrometer (Ocean Optics HR2000) for optical detection. Collimating lenses are located at either end of the gas cell to aid with the propagation of optical light across the open space, where it interacts and absorbs parts of the optical light.

Optical fibres for transmission to the sensing region allow for remote monitoring and online measurements, giving the possibility for data analysis on optical light recordings in real-time. The experimental setup for the sensor is shown in figure 2.

![Absorption Co-efficients](image)

**Figure 1.** Theoretical absorption line intensities for NH₃, O₂, CO₂ and N₂.

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A variation of the Beer-Lambert Law, given by equation 1, is used to relate the loss of optical light in the UV region and the concentration of ammonia gas in the gas cell. Where, $I$: Transmitted intensity; $I_0$: Incident intensity; $\sigma$: Absorption cross section for ammonia (cm$^2$/Molecule); $N_A$: Avogadro’s constant; $L$: Path length (cm); $T$: Temperature (K); $P$: Pressure (atm).

$$
ppm = \frac{-(\ln \frac{I}{I_0})[22.4]}{\sigma \times N_A \times l \times 10^{-9}} \times \frac{T}{273} \times \frac{1}{P}
$$

(1)

The spectrally resolved data from the spectrometer is interpreted in accordance with the equation 1 using a software based platform and development environment (LabVIEW$^\text{TM}$). The processed data is then displayed to the user in real-time.

3. Laboratory tests

Laboratory based experimental tests were carried out in order to comprehensively quantify the capability of the sensor. A series of mass flow controllers was used to provide a varying concentration of each of the gases during the testing procedure. In addition, a widely used commercially available sensor from Crowcon [4] was used for comparison throughout the testing procedure. Concentration measurement using a commercial sensor is carried out manually. The readings from LCD display from the commercial sensor are noted down for every 60s and the data compared with the optical sensor system, as shown in figure 3.
Laboratory based experimental test results demonstrate the sensor’s ability to provide accurate measurements compared to the commercial sensor. Calculated ammonia concentrations from the mass flow controllers and the optical sensor are in close agreement with each other, with an averaged error of 1.22% over the whole of the experimental test being recorded. However, the commercial sensor only demonstrates an accurate concentration measurement at 10ppm, above this the error rate increases significantly. In addition it is clear that the response of the optical sensor is significantly better than that of the commercial sensor. Response and recovery times throughout the test were recorded at an average of less than 4s.

4. In-situ tests

In-situ experimental tests were required to assess and fully quantify the performance of the optical sensor within the required environment. These experimental tests were carried out in an agricultural cattle enclosure in the Republic of Ireland, with 22 cattle accommodated across four fenced sections. The experiments were carried out during the peak winter season where ammonia is believed to be existing at a very low concentration \[8\]. The weather was foggy with some snow and the temperature was recorded at 0°C.

The optical sensor was placed at one corner of the enclosure, approximately 3m from the fenced section where a group of cattle was located. A cylinder of nitrogen gas was used in order to flush the absorption cell prior to the experimental test, while a vacuum pump was used to pump the surrounding air into the cell during the testing procedure. A photograph of the experimental test is shown in figure 4 and the experimental test results are shown in figure 5.

![Figure 4. Photograph of experiment setup for in-situ ammonia monitoring in an agricultural cattle enclosure.](image)

![Figure 5. Experimental results from in-situ experimental tests.](image)

To begin the in-situ experimental test, the nitrogen gas was turned off and pump was initiated. Although concentration levels recorded by the optical sensor are significantly low, approximately 1ppm, the sensor is able to accurately determine the presence of ammonia in the surrounding atmosphere. Following a period of approximately 10 minutes, the pump was turned off and the absorption cell is flushed with nitrogen. Once this occurs, the concentration readings from the optical sensor quickly return to zero. Upon the initiation of the pump (and deactivation of nitrogen) for the second time, the sensor once again records a concentration of approximately 1ppm, demonstrating a strong level of repeatability. Although the commercial sensor was operated throughout the testing procedure, it did not record any concentration levels of ammonia, indicating that it was incapable of measuring such low concentrations.
5. Conclusions
A novel optical fibre sensor for the detection of low concentrations of ammonia gas has been described. To achieve a high level of selectivity a technique based on differential optical absorption spectroscopy was developed and relatively low cost components were employed. Experimental tests were carried out using varying concentrations of ammonia as well as other atmospheric gases. Further tests were carried out in-situ within an agricultural cattle enclosure in the republic of Ireland in conjunction with a commercially available ammonia sensor.

Experimental tests were found to be very encouraging, with the lower limit of detection recorded to be at least 1 ppm, response times found to be under 4s and no recordable cross-sensitivity issue noted. These results show a marked improvement over commercial available ammonia sensors in terms of sensitivity, selectivity and response times.

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References
[1] “Trends in NH3 emissions”, Environmental Protection Agency, Ireland, http://www.epa.ie
[2] Directive on national emission ceilings for certain atmospheric pollutants, European Parliament and Council Directive 2001/81/EC of 23rd October 2001. More references
[3] A. Galdikas, A. Mironas, V. Strazdiene, A. Setkus, I. Ancutiene and V. Janickis, “Room-temperature-functioning ammonia sensor based on solid-state Cu$_x$S films” Sensors and Actuators B: Chemical, Volume 67, August 2000, Pp. 76-83
[4] “Tetra: A personal monitor you can trust”, Crowcon Detection Instruments, http://www.crowcon.com/
[5] F.Z. Chen, D.L. Judge, C.Y.R. Wu, J. Caldwell, "Low and room temperature photoabsorption cross sections of NH3 in the UV region". Planet. Space Sci., 1999. 47: p. 261-266.
[6] Manap H., Dooly G., O’Keeffe S., Lewis E., “Cross-sensitivity evaluation for ammonia sensing using absorption spectroscopy in the UV region”. Sensors and Actuators B: Chemical. In Press, Corrected Proof.
[7] S O’Keeffe, H Manap, G Dooly, E Lewis, “Real-time Monitoring of Agricultural Ammonia Emissions Based on Optical Fibre Sensing Technology”, IEEE Sensors Conference, Waikoloa, Hawaii, November 2010.
[8] N Yamamoto, H Nishiura, T Honjo, Y Ishikawa, K Suzuki, “A long-term study of atmospheric ammonia and particulate ammonium concentrations in Yokohama, Japan”, Journal of Atmospheric Environment, 1995. 29(1): p. 97-103.