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Ammonia Sensing and a Cross Sensitivity Evaluation with Atmosphere Gases using Optical Fiber Sensor

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Abstract

This paper describes an optical fiber sensor for the monitoring of ammonia gas. An open path optical technique is used to analyze the absorption lines of ammonia within the Ultra Violet region. The optical fibre sensor shows absorption lines comparable to the theoretical ammonia spectra. Cross sensitivity with carbon dioxide and oxygen gas has also been tested and clearly shows that these two gases have no effect on ammonia measurement in the ultra-violet region, between 200 nm and 230 nm.

Keywords: Optical fibre sensor, ammonia sensor, cross sensitivity

1. Introduction

The earth's atmosphere comprises 78.08% nitrogen, 20.95% oxygen, 0.93% argon, 0.038% carbon dioxide, and trace amounts of toxic gases such as NOx, NH_3 and SOx. It also contains around 1% of water vapour. Since the atmosphere contains a variety of gases, development of a gas sensing system which is uniquely sensitive to one particular gas is a significant challenge. Many gas sensors are susceptible to cross sensitivity issues. Therefore a number of different methods have been introduced to develop selective sensor systems, such as gas separation techniques using a membrane [1-3], principle component analysis [4] and artificial neural networks, also known as artificial nose [5-7]. In this paper, a cross sensitivity of ammonia gas mixed with O_2 and CO_2 will be studied.

According to the European Environmental Agency, EEA, Report 2003, 93% of EU15 ammonia emission in 2001 was caused by agriculture sector and it has been the main contributor to ammonia emission since 1990. Hence an ammonia sensor for the agriculture industry needs to be developed as an alternative to current sensing method. It must have the required baseline sensitivity (lower detection limit, LDL of 25 *ppm*) coupled with good selectivity. This is due to ammonia gas being toxic to human and its maximum safe level is 25 *ppm* for long term exposure (8 *hours*) and 35 *ppm* for short term exposure (15 *min*) [16]. In this investigation two atmospheric gases namely, CO_2 and O_2 were examined for potential cross sensitivity with ammonia gas.

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2. Theory

Each gas species has its own unique absorption spectrum i.e. a characteristic set of wavelength absorption values (pattern). A comprehensive collection of absorption theoretical absorption cross sections for gaseous molecules was accessed from the Max Planck Institute, *MPI Mainz* database including that for ammonia gas [8]. The data can vary from source to source and they depend on temperature and wavelength range. For ammonia gas concentration calculation, the Beer-Lambert Law was utilized. The Beer-Lambert law describes the relationship between absorbance and concentration of an absorbing species and its general form is shown in equation (1).

$$\frac{I}{I_o} = e^{(-\sigma.N.l)} \qquad (1)$$

$$\sigma = \frac{-[\ln\frac{I}{I_o}][T\times 22.4]}{ppm\times N_A \times l \times 273 \times P \times 10^{-9}} \qquad (2)$$

Where I is the transmitted intensity, I_o is the incident intensity, l (cm) is the distance that the light travels through the gas, σ ($cm^2/Molecule$) is the absorption cross section and N ($Molecules/cm^3$) is the concentration of the absorbing medium. Equation (2) is the derivation from the Beer Lambert Law and was previously described [17].

2.1. Cross sensitivity

For NH_3 gas sensing, it has been reported [9-12] that the cross sensitivity with humidity is a major problem and occurs in certain wavelength ranges. Cross sensitivity with humidity happens across many types of ammonia gas sensors including optical gas sensor. Optical sensors which detect in the Mid IR range are susceptible to interference with humidity where absorption due to water vapour is high as compared to NH_3 [18]. As there is no absorption due to water vapour in the UV region, cross-sensitivity with humidity is not an issue. Therefore, this investigation is limited to the cross sensitivity assessment of ammonia with CO_2 and O_2. Theoretically if UV light is used as the light source for NH_3 detection, the cross sensitivity effect with CO_2 and O_2 can be minimised. This is based on comparative absorption spectra shown in Fig. 1. The absorption amount for both gases are relatively small compared to ammonia in the region 200-230 *nm*. The data for O_2 spectrum are attained from M. Ackerman *et al* [13] and for CO_2, the details are referred from Shemansky [14].

Tests were conducted for both gases to prove that in practice there were no discernible cross sensitivity effects on ammonia measurements. However, it is not possible to test the cross sensitivity for every atmosphere gas as there are too many of them and outside CO_2 and O_2, the concentrations of those gases are small and their impact can be ignored. In the laboratory, a reference measurement is performed prior to every ammonia test cycle in order to establish the correct calibration and thus yield the correct values of ammonia measurement.

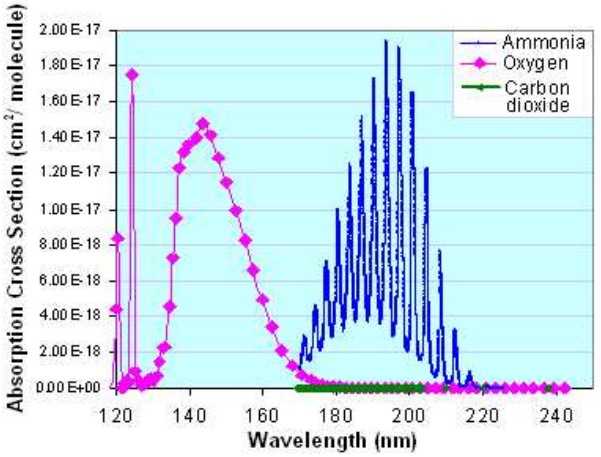

Fig. 1. O_2 and CO_2 absorption lines as compared to ammonia gas.

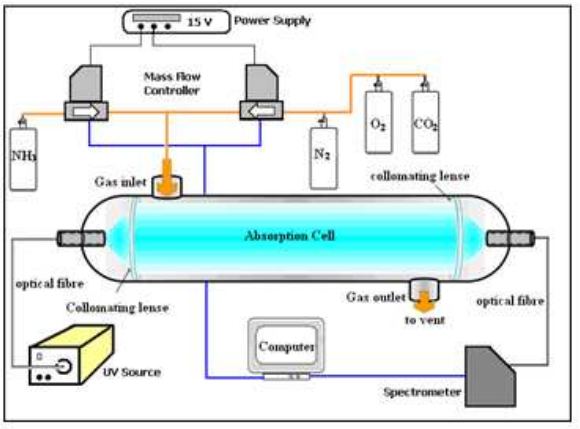

Fig. 2. Experimental setup.

3. Experimental Setup

The experimental arrangement is shown in Fig. 2. A Deuterium-Halogen lamp (DH-2000 from Ocean Optics) was used as a light source. The light was transmitted through UVNS fiber (Ultra Violet Non Solarising) with 644.4 *nm* core size. Two collimating lenses were placed at either ends of the gas cell and were used to focus the incident and transmitted light. The transmitted light interacts with the ammonia gas in the cell prior to being coupled to another (receiving) optical fibre at the other end of the gas cell to the light detector. The light detector was an Ocean Optics *HR2000* spectrometer. The spectrometer has a range from 200 to 650 *nm* and it provides a spectral resolution to 0.65 *nm*. The spectrometer was interfaced with the computer using *SpectraSuite* software. *SpectraSuite* is a specifically designed program provided by Ocean Optics in order to acquire the data from the spectrometer in real time. The transmitted intensity, I and the incident intensity, I_o were recorded and equation (2) is used to obtain the absorption cross section. These absorption values were plotted against the wavelength and compared with theory. Two mass flow controllers, (MFC) model *F-201CV* by Bronkhorst High-Tech, were used to control the flow rate of the test gas and provide the amount of test gas needed. The MFCs were powered by 15 V power supply and were operated at the gas pressure above 1 bar. They were controlled by software (*FlowDDE V4.58)* provided by Bronkhorst. The maximum flow rate of each MFC is 1 *l/min.* Each gas has its own flow rate and the gas mixing calculations are based on the flow constant provided by Bronkhorst.

4. Results and Analysis

Initially, N_2 gas was released into the test gas cell. The integration time in the *SpectraSuite* software was set to 2000 *ms*. Intensity (counts) was measured and this was considered as the incident intensity, I_o. CO_2 gas was then released into the test gas cell. Intensity was measured again and this measurement was regarded as the transmitted intensity, I. The recorded data was entered into equation (2) to obtain the absorption cross section of the CO_2. The experiment was repeated using 100 *ppm* NH_3 in N_2.The absorption lines for both gases were plotted and are shown in Fig 3. The result shows the absorption line for measured NH_3 is in similar pattern but a bit lower compared to theoretical at the early of *x*-axis. This is due to high attenuation of the optical fiber used at the lower wavelength of UV light transmitted, resulting in a low signal-to-noise ratio. The experiment was repeated for 100 *ppm* NH_3 gas mixed with 1% of CO_2. 1% was chosen to create the similar atmosphere environment as this was a much higher value than the atmospheric concentration (380 *ppm*) and thus represents a much more stringent test. The absorption cross section for the mixing gas was calculated and the resulting mixed gas absorption spectrum is shown in Fig. 3. It shows that the present of CO_2 has no effect on NH_3 measurement.

The above method was repeated to check the cross sensitivity with 21 % of O_2. The absorption spectrum was monitored and the result is shown in Fig. 4. It also shows that the shape for NH_3 + 21% O_2 spectrum is almost the same as NH_3 spectrum. This indicates that O_2 has no significant effect on NH_3 measurements in the region of 200-230 *nm*.

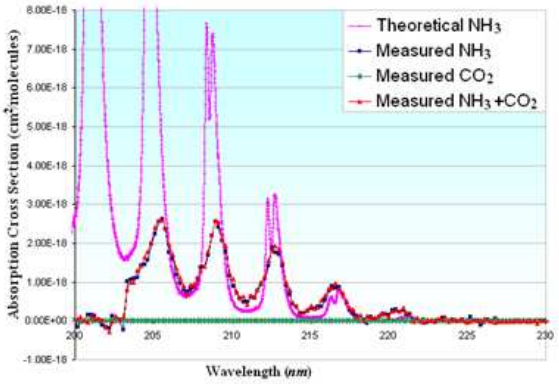

Fig. 3. Ammonia spectrum with the presence of 1% of CO_2.

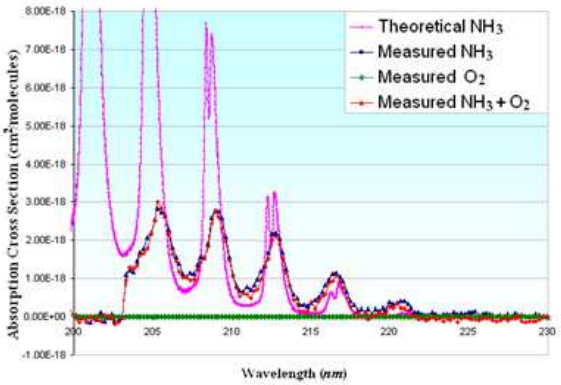

Fig. 4. Spectrum of ammonia in the presence of 21% of O_2.

5. Conclusion and future work

A novel optical fibre sensor for NH_3 gas has been described and reported. The optical sensor for ammonia shows its capabilities to detect 100 *ppm* ammonia in the deep UV region based on the absorption lines are similar to the theoretical spectrum. The cross sensitivity with CO_2 and O_2 gas has also been tested and it clearly shows that these two gases have no impact on the NH_3 measurement in the region of 200-230 *nm*. Thus, it has been demonstrated that the UV range is well suited for the measurement of NH_3. Future work will focus on measurement of NH_3 at various concentrations and the lowest detection level that the sensor is capable. A commercial NH_3 reference sensor will be integrated as a more accurate and efficient verification of NH_3 gas concentration.

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