Hazardous exhaust gas monitoring using a deep UV based differential optical absorption spectroscopy (DOAS) system

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Abstract. A fibre-optic sensor for the monitoring of hazardous exhaust gases is described. The sensor based on Differential Optical Absorption Spectroscopy was developed to operate within exhaust environments, monitor several exhaust gases and demonstrate low susceptibility to interferences from other gases. Experimental results describing the calibration of the sensor against a commercial analyser and tests documenting the sensor's operating capabilities within the exhaust of an engine are presented. The lower limit of detection for the sensor was found to be 5ppm for nitric oxide, and 1ppm for both nitrogen dioxide and sulphur dioxide. Response times were found to be 3.4 seconds.

1. Introduction

Since the industrial revolution, worldwide energy consumption has been growing steadily. In developed countries historic air pollution problems were typically due to high levels of smoke and SO_2 arising from the combustion of fossil fuels such as coal for domestic and industrial purposes. However with the introduction and growth of modern passenger cars coupled with vastly increased demand for power, the twentieth century saw rapid increases in the use of fossil fuels. In effect oil consumption is expected to increase from an estimated 78.6 million barrels a day in 2003 to 119 million barrels a day by 2025 [1]. A growing source of concern associated with the increase in global oil consumption has been the effect of the combustion of these nitrogen-bearing fuels on our atmosphere.

Fuel combustion is in fact the primary source of a large number of damaging air pollutants, including fine and respirable particulate matter (PM), carbon monoxide (CO), oxides of sulfur (SO_X), oxides of nitrogen (NOx), hydrocarbons, ozone (O3), and atmospheric lead. Some of these pollutants are direct by-products of fuel combustion. However others such as ozone are formed in the air through chemical reactions with other agents in the atmosphere. These emissions can cause or add to many local and global environmental issues such as acid rain, the greenhouse effect, the destruction of the ozone layer and air pollution known as "smog". In addition to these, increased air pollution can have a serious impact on human health. Air pollution has been associated with many major health conditions including heart failure, arrhythmia and other cardiovascular causes of death. In some western countries it is estimated that motor vehicle emissions kill twice as many people as road traffic accidents [2].

2. Legislation

The European Automobile Manufacturers Association (ACEA) in conjunction with the EU has taken important steps over the past decade to reduce harmful emissions with the installation of several

modifications into their motor vehicles. These include fuel injection systems, catalytic converters, charcoal canisters, engine preheating, CFC-free air conditioning systems, and monitoring and warning systems. In addition to this anti-pollution and fuel consumption regulations are being introduced by environmental protection agencies throughout the world. In 1991 the European Union introduced the *EURO* directives [3-5] in which all new vehicles must comply with a set of emission regulations. The regulated emissions include particulate matter (PM), nitrogen oxides (NO_x), hydrocarbons (HC), and carbon monoxide (CO). The *EURO* directive for passenger cars (category M_1) is summarized below in Table 1. Protecting the atmosphere and environment is an issue that will dominate EU policies on transport for decades to come and even more stringent laws and regulations will be introduced in the near future. As a result a need has emerged for sensors capable of accurately monitoring low concentrations of these exhaust gases.

Table 1. European emission standards for passenger cars (g/km)

Tier	Date	CO	HC	HC+NO_X	NOx	PM
Diesel		**(g/km)**				
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08
Euro 2, DI	1996.01	1.0	-	0.9	-	0.10
Euro 3	2000.01	0.64	-	0.56	0.50	0.05
Euro 4	2005.01	0.50	-	0.30	0.25	0.025
Euro 5‡	mid-2008	0.50	-	0.25	0.20	0.005
Petrol (Gasoline)		**(g/km)**				
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-
Euro 2	1996.01	2.2	-	0.5	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-
Euro 4	2005.01	1.0	0.10	-	0.08	-
Euro 5‡	mid-2008	1.0	0.075	-	0.06	0.005

* Before Euro 5, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles
† Values in brackets are conformity of production (COP) limits
‡ Proposed

3. Current Technologies

A number of commercially available gas sensors are currently being used on a global basis by automotive industries. These include an electrochemical NO_X sensor for the monitoring of nitrogen oxides and the well known lambda sensor for O_2 monitoring. The NO_X sensor was designed to detect the presence of NO and NO_2 in an exhaust environment down to ppm concentration levels. However this sensor is not capable of distinguishing between the gases NO and NO_2 and in addition is prone to cross sensitivity to other gases within the exhaust environment. The Lambda sensor measures the oxygen content of the exhaust which is input into a control device for air-to-fuel ratio. This control increases the efficiency of the engine thus reducing the amount of pollutant gases. This sensor can also be used to give an indication of the concentration of CO_2 within the exhaust environment. Both the lambda and NO_X sensors can have a relatively short lifespan due to the chemical effects of other reactive gases present in the exhaust on the sensor element itself.

Many optical approaches to gas sensing have also been investigated over the years which include luminescent [6] and absorption based sensors. Luminescent sensors often have long delay times and so are not suited to exhaust gas sensing where the concentrations change rapidly. A wide range of absorption based techniques exist including a whole range of evanescent wave gas sensors [7], singlepass cell sensors [8] and multipass cell sensors [9]. Evanescent wave gas sensors can have sensitivity issues as the interaction between the optical light and the test gas is often very limited. Also multipass cell sensors depend on reflective surfaces which can get contaminated within an exhaust environment resulting in increased reflection losses. A potential solution to the above problems is to use a differential singlepass absorption technique as it has a high sensitivity and is not prone to contamination.

Many of the exhaust gases have strong absorption lines within the UV range including NO_2, NO and SO_2 [10]. Therefore it is proposed to use a UV based singlepass absorption sensor to detect low concentrations of these particular gases.

4. Theory

4.1. *Absorption Theory.* Gas species absorb light at characteristic wavelengths and each molecule has a unique absorption spectrum. This paper looks specifically at three gases namely, NO_2, SO_2 and NO which all have absorption lines in the ultraviolet region. The absorption spectra of these gases have been well documented in the Hitran database [10]. However, the data varies somewhat from paper to paper. The course taken then was to average all the data sets similar in temperature (298K) to the experiments carried out in the development of this sensor. The resulting theoretical absorption spectrum of each of the gases is shown in figure 2. NO_2 has a relatively wide absorption band from 250nm to 650nm centered on 413nm, while SO_2 has a band from 240nm to 330nm centered on 287nm. NO has several sharp absorption lines between 190nm and 230nm with its strongest line being located at 190nm.

4.2. *Concentration Calculations.* The Beer-Lambert law defines the relationship between absorbance and concentration of an absorbing species. At low concentrations (up to many tens of ppm) the Beer-Lambert law approximates to linear. A variation of the Beer-Lambert Law was utilised by a specifically designed LabVIEW program to calculate the concentration of the gases present as follows:

$$ppm = \frac{-\left[\ln \frac{I}{I_0}\right][w \times d]}{\sigma \times 10^6 \times N_A \times l} \quad (1)$$

Where I is the transmitted intensity, I_O is the incident intensity, l *(cm)* is the optical path length, , w *(amu)* is the molecular weight of the species, d *(kg/m^3)* is the density of the species, N_A is Avogadro's constant and *ppm* is the gas concentration in parts per million.

The program was designed to interrogate the highest absorbing wavelengths for each of the gases, documented at wavelength 190nm, 287nm and 413nm for NO, NO_2 and SO_2 respectively. However, due to the limited availability of light intensity available from the system within the deep UV region a higher wavelength absorption line for NO at 226nm resulting in a better signal-to-noise ratio was chosen. The resulting spectral power distribution from the sensor system which is a combination of the deuterium/halogen light source, the UV fibre and the high resolution spectrometer is shown in figure 1. This system is described in more detail in section 5.

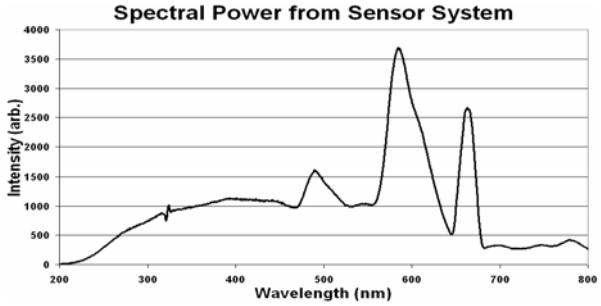

Figure 1. Spectral power distribution from the sensor system.

The concentration of the gases present can therefore be calculated using equation 1 with all other factors shown in the equation known. The required factors are accessible during testing and therefore the program was developed to access this data in real time and output the concentration in ppm to the user every four seconds (response time of the sensor). This will be discussed further in section 6.3.

4.3. *Cross Sensitivity.* Cross sensitivity between other gases within an exhaust environment such as NO_2 and SO_2 was an issue due to their absorption spectra. A LabVIEW program was designed and tested to combat this cross sensitivity effect [11] and it proved capable of sustaining a low susceptibility to interferences from the other gases present in the exhaust system. The program was utilised in the development of this sensor for the monitoring of gas concentrations from laboratory based cylinder sources and within exhaust environments.

5. Experimental Set-Up

The experimental set-up used for the detection of the hazardous exhaust gases is similar to the one used previously in [11]. However as discussed in section 4.2 the optical light intensity at the wavelength of interest (226nm) is very limited. Therefore the spectrometer used was upgraded in order to increase its light capturing capabilities and improve the signal-to-noise ratio. The spectrometer used for detection was the Ocean Optics HR2000 with an input slit of 25um, range of 194nm to 645nm and an overall spectral resolution of 0.7 nm (FWHM).

6. Results

6.1. *Calibration / Full Spectrum Results*. The spectrum was analysed before and after the gas (NO_2) was allowed into the cell and from this data the percentage absorption due to the gas was calculated. The commercial gas analyser (Quintox KM9106 from Kane-May) gave a simultaneous reading of the concentrations present in the gas cell; these figures were then used to formulate the measured absorption line intensities i.e. based on the Beer-Lambert law calculations of equation 1. The measured absorption line intensities recorded from this experiment for each of the gases can be utilised by the LabVIEW program in future tests. In this way the sensor will be calibrated against readings recorded from the commercial gas analyser and initial indications are that our sensor is accurate to within a small error of that recorded by commercial gas analyser. Figure 2 shows the actual line intensities measured compared to the theoretical line intensities from previously published works for (a) NO_2, (b) SO_2 and (c) NO.

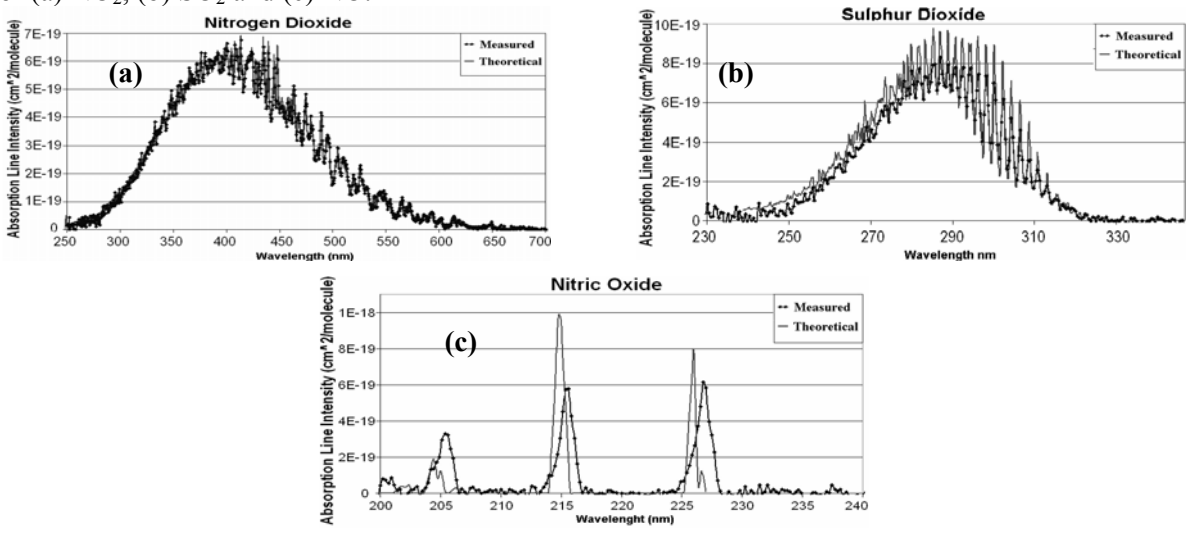

Figure 2. Measured absorption Line Intensities for (a) NO_2, (b) SO_2 and (c) NO compared to theory.

6.2. *Wavelength Specific Results.* Looking specifically at the wavelength with the highest absorption for each of the gases and using a reference wavelength of 645nm, it is possible (utilising the measured absorption line intensities of section 6.1) to calculate the concentrations of the gases present in the gas cell. Using this method the concentration of the gases present can be calculated immediately eliminating the need for processing the data after testing. Figure 3(a) shows one such test over time recording varying concentrations of NO_2 (mixed with N_2) using the ratio of intensity values at

413nm/645nm wavelengths. Also shown are the numerical average of the concentrations from the optical sensor during the step interval and their equivalent readings from the commercial gas analyser.

Similar tests can be seen in figure 3(b) showing absorption due to varying concentrations of SO_2 using the ratio of 287nm/645nm. Figure 3(c) shows absorption due to varying concentrations of NO by using the absorption ratio 226nm/645nm. Averaged concentrations from the sensor closely match the measured concentration from the commercial gas analyzer with an average error of less than 0.9% for NO_2, 0.8% for SO_2 and 1.9% for NO. The resolution for the sensor has shown to be as small as 1ppm for SO_2 and NO_2 and 5ppm for NO.

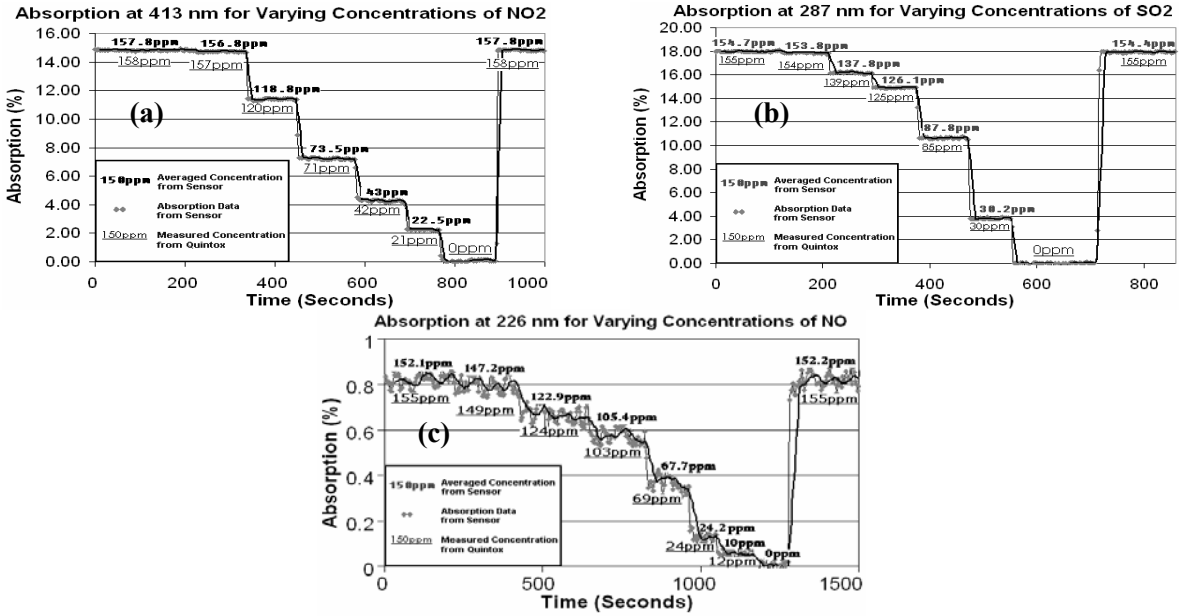

Figure 3. Recorded absorption levels for varying concentrations of (a) NO_2, (b) SO_2 and (c) NO. Also shown are the averaged concentrations from the optical sensor during the step interval and their equivalent readings from the commercial gas analyser.

6.3. *Engine Test Results.* Measurements were recorded on a Kubota V1505-E diesel engine in the engine test laboratory at the University of Liverpool. The engine was maintained at constant speed recorded as 2950 revolutions per minute (rpm). The spectrum received at the spectrometer was initially recorded while the gas cell was being flushed with N2 and again when the engine was running. This data was used to calculate the total amount of measured absorption recorded across the UV-VIS spectrum as shown in figure 4(a). The commercial gas analyser was used to record an accurate reading for each of the gases in the exhaust which were used to form the theoretical absorption spectrum shown also in figure 4(a).

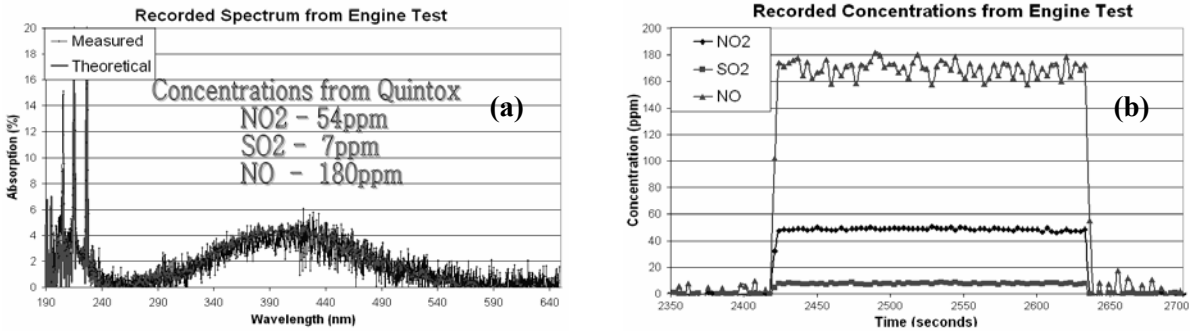

Figure 4. (a) Measured absorption across the UV-Vis spectrum for an engine test compared to theory. (b) Measured concentrations output to the user from the sensor for an exhaust engine test cycle.

The engine was again maintained at constant speed of 2950 revolutions per minute (rpm). The gas cell was flushed with N_2 before the engine was started and again immediately after the engine was stopped. Concentrations from the sensor for NO_2, SO_2 and NO in the exhaust for the engine test cycle were recorded as shown in figure 4(b).

These results show that the sensor is capable of operating within the harsh environment of an exhaust and capable of accurately measuring the concentration of the gases namely NO_2, SO_2 and NO. Current commercially available NO_X sensors are not capable of distinguishing between NO_2 and NO.

7. Conclusions and Future Work

A novel optical fibre sensor for the detection of hazardous exhaust gases in road vehicles has been described to achieve a high level of sensitivity. A singlepass open path cell based on differential optical absorption spectroscopy (DOAS) was used.

The sensor was calibrated using laboratory based cylinder gases of NO_2, NO and SO_2 against a commercially available gas analyser and optical spectra were recorded for each of the three gases. A LabVIEW program was developed to output the concentrations of the gases to the user and a novel approach to negating the effect of cross sensitivity between each of the gases within the exhaust was established. Tests were carried out using varying concentrations of each of the gases and the sensor reading agreed closely to that of the commercial gas analyser (average error of less than 0.9% for NO_2, 0.8% for SO_2 and 1.9% for NO). Further tests were carried out in the exhaust of a diesel engine and results showed the sensor performed correctly and was capable of fast response times (3.4 seconds).

The lower limit of detection for the sensor was found to be 5ppm for NO and 1 ppm for both NO_2 and SO_2. Although it is not possible to compare these emission levels to regulations discussed in Table 1 without knowing other factors such as total gas flow, our industry partners Centro Ricerche Fiat have confirmed these levels to be within the levels required by European Union legislation.

Acknowledgements

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