Fiber Optic Sensors for In-Situ Monitoring of Diesel Engine Exhaust Gas

FIBER OPTIC SENSORS FOR IN-SITU MONITORING OF DIESEL ENGINE EXHAUST GAS

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A THESIS

SUBMITTED TO THE DEPARTMENT OF ENGINEERING PHYSICS AND THE SCHOOL OF GRADUATE STUDIES OF MCMASTER UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF APPLIED SCIENCE

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Abstract

A fiber optic carbon dioxide sensing system was developed for in-situ monitoring of carbon dioxide within a diesel engine exhaust environment. The fiber sensor was based upon the encapsulation of pyranine paired with tetraoctylammonium hydroxide within a hydrophobic glass formed using the sol-gel process. The sensitivity of the sensor to carbon dioxide was shown to follow a non linear trend with the highest sensitivity in the 0 - 5% CO_2 range. The lower detection limit was experimentally determined to be better than $0.3 \% CO_2$. The fiber sensor's response was also characterized within an environment similar to that within an diesel engine exhaust stream. The fiber sensor was shown to be relatively unaffected by carbon monoxide and nitric oxide at concentrations which are typically found within a diesel engine exhaust gas. Nitrogen Dioxide, however, caused an effect in biasing the sensor response to erroneously report higher concentrations of carbon dioxide than were present. Higher concentrations of nitrogen dioxide were shown to permanently damage the fiber sensor and render it inoperative. The effects of increased environmental temperature and relative humidity were shown to decrease the sensitivity of the fiber sensor within the range of interest for carbon dioxide sensing within diesel exhaust gases. An experiment within the exhaust stream of a single cylinder 2.4 kW diesel engine demonstrated that the fiber sensor was capable of monitoring the carbon dioxide levels for 6 minutes, however, longer exposure to this exhaust environment caused the destruction of the fiber.

Acknowledgements

First, I would like to thank Dr. Chang and Dr. Xu for their help and support during the course of my studies at McMaster.

I would also like to thank Dr. Weidong Tao and Carmen Carrasquilla for their technical help and thoughtful advice with the experiments and preparation of the sensing materials. Your help has made the work more enjoyable and your technical experience greatly sped up the research.

I would also like to thank Sean Cianflone, Paul Bray, Leah Allen, Dr. Steve Kornic, for their technical advice. They helped me out of a few tight spots, for which I am grateful.

I would like to thank my family and friends for their love and support. It was greatly appreciated and helped me when I needed it the most.

To Rachie, Sarah, Sal, Paul: No one has known better friends, thank you for all your help and advice. Thank you for laughing at the cynicism and bitterness, keeping me grounded and generally making my life much more enjoyable.

And to most especially Anya. You kept me company on those very long nights in the lab, helped me through my anxiety and stress. You were there for me through all 2 years of this, and I hope one day to repay all that you have given me. Thank you.

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Chapter 1

Introduction

1.1 Carbon Dioxide and the Climate

It is widely known that carbon dioxide is a contributing factor to climate change, in its role as a greenhouse gas. Greenhouse gases are those which can contribute to global warming by absorbing some of the infrared energy that is being emitted from our planet and prevents it from being re-emitted into space contributing to the warming of the atmosphere (Jacob, 1999). The effects of global warming have and still are being studied extensively, with many undesirable projections being made as to the future state of the planet, including melting of the polar ice caps and an increase in the water level, warming of the atmosphere, acidification of the oceans and changes in global weather patterns (Solomon et. al, 2009).

Many human activities contribute to the production of large amounts of carbon dioxide, such as transport vehicles, manufacturing industries, power generation, etc. In recent times, there have been new political incentives to limit the generation of carbon dioxide. In 1998 the Kyoto Protocol was instated to achieve a limit on the amount of carbon dioxide produced to 5% below that of 1980 (United Nations, 1998). More recently the Copenhagen Climate Summit decided that gaseous emissions must be limited in order to prevent a rise in the global temperature by more than 2°C (United Nations, 2009).

There are new limitations and goals that countries are now placing on reducing the total greenhouse gas emissions and prevent temperature rise. It is in the interest of society and the environment to have a robust, accurate and inexpensive sensor for carbon dioxide in order to accurately monitor the output of this harmful greenhouse gas, in order to have proper estimates of the human impact to climate change, and also ensure that these goals are being met.

This work will focus on the measurement of carbon dioxide under diesel engine exhaust emission conditions. The characterization of the exhaust gases from vehicles is currently inferred through the oxygen levels, which is detected using an electrochemical sensor. The output of this sensor is mainly used for proper combustion feedback and limiting the emission of nitrogen oxides (NO_x) (Ivers-Tifée, 2001), not for measurement of the exhaust emissions to the environment. Currently, there are no commercially available carbon dioxide sensors which are capable of detecting carbon dioxide while surviving the harsh environment of diesel engine exhaust gases.

1.2 Objectives

The objective of this work is to develop a carbon dioxide sensor which is capable of withstanding the harsh diesel exhaust gas environment. The exhaust gas from a diesel engine is known to contain carbon dioxide (CO_2), carbon monoxide (CO), nitric oxide (NO) and nitrogen dioxide (NO_2) and particulate matter (PM), as well as to operate at an elevated temperature. The sensor that was developed was a fluorescent sensing material which was dip coated onto an optical fiber. This main objective is to determine the feasibility of using this type of carbon dioxide detection method within the diesel engine exhaust environment, and to determine if it is capable of operating under these harsh conditions, or if not, what specifically are the causes for failure in order to determine possible alterations in order to develop a low cost detection unit which could be placed in-situ for real time sensing.

The work done in this thesis follows from that which was done previously, during the course of my graduate studies, to determine a means of in-situ treatment of diesel engine exhaust gases. The detection of carbon dioxide was a second project, and this thesis is focussed upon the feasibility tests for this sensor.

This thesis first determines the optimal composition for the dipping onto the fiber. It then characterizes the fiber sensor's response in different environments; specifically the sensors response to CO_2 , CO, NO, NO_2 at levels present within a diesel engine, and also any interference effects which can occur from changes in environmental temperature and relative humidity, which are also possible in the actual sensing environment. Following this work, experiments were done to simulate reality, by placing the sensor within the exhaust loop of a diesel engine.

This work contains 6 chapters, the first being this introduction. The second chapter will explain the various other sensing mechanisms which are commercially available or in experimental stages in a critical review. The chapter will then follow to explain why the fluorescence sensor was chosen over the other options. Background information will then be given, explaining the fluorescence based sensor, as well as the sol-gel composition and the choice of materials, and a brief description of fluorescence and sol-gels. Chapter 3 will be a description of the experimental setup and procedures that were used to conduct the experiments of this study. Chapter 4 will contain the results of the experiments and a discussion regarding the performance of the sensor. Chapter 5 will contain the conclusion, summarizing the progress that was made, and Chapter 6 will be a recommendation for future work on the fiber sensor. Appendix A contains a brief summary, list of publications and conferences relevant to the first project of diesel engine exhaust treatment.

Chapter 2

Background Information

In this chapter, a literature review on different types of methods to detect carbon dioxide, resulting finally in the choice of a sensor for this study, i.e. a fiber optic sensing scheme involving suppression of a fluorescent signal. The following section will describe the sensing scheme in detail as well as present a review on pyranine, the fluorescent dye that was used for this study, and its behaviour in sol-gel materials. A brief qualitative explanation of fluorescence and characteristics of sol-gels will also be described, as they are pertinent to the fiber sensor which was employed in this work.

2.1 Literature Review of CO₂ Detection Methods

Carbon dioxide is a fairly difficult substance to detect since it is a fairly stable, nonreactive compound; very few materials beyond alkali metals and water react with it. Its presence in air can be associated with both beneficial and harmful effects; and so it follows that being able to accurately determine the quantity of such a substance would be very desirable. Carbon dioxide detection has its uses in many different scenarios of day to day life, such as in food packaging as well as climate control within buildings.

In the food packaging industry, the presence of oxygen in packaged food greatly increases bacterial growth. Generally the atmosphere of the food item is modified to contain only a mixture primarily of carbon dioxide, ozone and nitrogen. Since carbon dioxide is incapable of supporting life, it is an ideal solution for the packing industry. Implementing it into the atmosphere around the food would aid in minimizing the bacterial growth on food products and as a result, increase shelf life and minimize food loss due to spoilage. Too high a level of carbon dioxide can cause discolouration of food, especially in meats. Typically, a carbon dioxide value of 30 - 40% is desired, as well as 0.5 % carbon monoxide to minimize pathogen spread and keep the food item looking healthy.

Carbon dioxide levels are also of importance in heating and air conditioning ventilation systems (HVAC) and in mining scenarios. Levels of carbon dioxide as low as 1.5 - 5% have noticeable effects on health, with headaches, nausea and fatigue and possibly hyperventilation. At 6 - 10% CO₂, tremors, visual disturbances and unconsciousness may result [BP America, 2004]. Levels under 1000 ppm (0.001%) are considered to be safe for prolonged exposure and any higher levels require signalling to the ventilation system to increase the amount of fresh air being drawn to offset the rising carbon dioxide level. The ventilation systems require real time monitoring of carbon dioxide, typically within a resolution of detection of 10 ppm CO₂ and to an accuracy of 100 ppm CO₂ [Digital Control Systems, 2009].

The purpose of this review was to determine a suitable method for optical sensing for carbon dioxide for diesel exhaust conditions. Literature was reviewed on current sensing methods that already exist in the experimental stage, as well as those that are commercially available to discover alterations to present methods for a fiber-optic sensing scheme, or adapting optical sensors which are already patented. Analytical techniques for measuring carbon dioxide concentration, such as mass spectrometry or gas chromatography, were not included in this study as the cost for this application and the equipment required would not be practical. One idea for an optical sensor was to consider materials used for carbon capture as an optical sensing material, as the index of refraction of objects would change dependent on the carbonation of the species. However, this was abandoned due to the inability to find suitable regenerative materials. This review will only detail the different sensing schemes that are currently available.

2.1.1 Infrared Absorption Detection

All molecules present in the world consist of atoms which have different bond strengths and geometries. Depending on the degrees of freedom available to these bonds, the atoms can flex, bend, twist and vibrate according to different energy levels. This knowledge can be applied to determine which elements are present, as these energy levels are quite specific to each molecule and can be used to identify molecules based on their infrared radiation absorption spectra.

Non-dispersive Infrared absorption, or NDIR, is commonly used for the detection of carbon dioxide. Infrared light is shone upon a gas sample, in which case the molecules within the gas absorb the photons depending on their structure, causing the molecular bonds to bend, stretch or vibrate. There is generally insufficient energy to cause ionization, but instead to induce kinetic energy in the aforementioned ways [Hsu, 2009]. The wavelength absorbed corresponds to a specific bond, in this case the carbon - oxygen double bond in carbon dioxide. The carbon - oxygen double bond strongly absorbs light in the infrared spectrum at wavelengths of 4.26 μ m and 2.7 μ m [Zhang et. al, 2000]. The absorption peak at 4.26 μ m is very unique to carbon dioxide, while that of 2.7 μ m overlaps with some of the infrared absorption peaks of water [Hsu, 2009]. This overlap with the infrared absorption of water can cause interference effects when testing in uncontrolled environments.

It is possible to make NDIR sensors which are capable of reading up to 100% carbon dioxide dependant on the intensity of the infrared light in the absorption band. Typically for gas sampling, a minimum of 50 ppb is necessary to achieve a significant signal to quantitatively indicate the presence of carbon dioxide [Hsu, 2009]. Response time depends on the system involved and its various factors such as how the sample gas is collected, if filtering is present, the orientation of the emitter and detector, and the volume of the sample. The infrared radiation is produced using a radiation source such as a Nernst glower, Globar, or a Nichrome coil; these are inert solids which are heated to 1000 - 1800 °C where they then emit infrared radiation in conjunction with a filter which would remove all the light extraneous light frequencies except those centered about 4.26 μ m [Zhang et. al, 2000]. The nichrome coil or heated element used for the lamp must be fairly stable and consistent to give a regulated signal of known intensity. So for higher accuracy a robust and stable power supply must be used.

The absorbance follows the Beer-Lambert Law, $I = I_0 e^{-\mu pl}$, where μ is the absorptivity of the CO₂, p is the partial pressure and l is the length of the cavity containing the gas sample [Zhang et. al, 2000]. By calibrating the sensor to a known amount of CO₂ at temperature, it is possible to determine by the drop in intensity at the specific wavelength, the amount of CO_2 in the sample gas. In recent work, Quantum Cascade Lasers have been very recently been realized at the 4.26 μ m absorption peak of carbon dioxide, however their adaptation into a commercial product has not happend as of yet [Tuzon et. al, 2008; Bartalini et. al, 2009]. The light sources currently used are the broadband heated elements and so the intensity of the system will be inherently low at the desired wavelength. The sensor design requires an IR source and detector, a temperature detector to offset thermal noise, pressure sensing, signal amplifier and then a readout method using a computer to take into account the variations in the environment and calculate a carbon dioxide level.

An advantage of NDIR sensing is that there is no regenerative sensing material as it is absorption based, and only dependent on the gas characteristics such as pressure, volume and temperature. However, this also means that the sensor is also very dependent on thermal and pressure fluctuations, as the changing density of the sampling gas changes the absorptivity. Despite this advantage, complications arise when line of sight is obstructed, and as such cannot be used in sooty conditions. The sampled gas must be filtered, as any light loss due to scattering or absorbed by particles will give faulty readings of the carbon dioxide level. This requires a separate filter to remove particulates, as well as a strong pump to overcome the pressure drop the filter induces, and still be able to quickly purge the gas remaining the sensing chamber in order to have a quick enough response for real time sensing. In addition, NDIR methods have a large temperature dependence, though can be compensated for up to approximately 70 - 80 °C for most sensors [RAE Systems, 2009]. There is also fairly large power consumption in the heating of the infrared source. Also, pressure variations would cause changes in absorbance and the signal. Both soot and pressure



Figure 2.1: Block diagram of carbon dioxide sensing equipment based on NDIR, modified from [Zhang et. al, 2000]

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pulses are very common within engine exhaust environments.

Combustion gas analyzers also typically employ NDIR carbon dioxide sensing. The NDIR system used in this study is capable of giving real time results with a response time of 1 s, and is capable of detecting carbon dioxide for a range of 0 - 40% with a resolution of 0.3% for less than 10% CO₂ and 3% for a range of 10 - 40% CO₂. The on board NDIR sensor is incapable of detecting any carbon dioxide beyond this point, but relies on a calculated extrapolation for values above 40% CO₂, due to the IR signal strength [Eurotron, 2009]. This is sufficient in most automobiles since the carbon dioxide content of engine exhaust seldom reaches 10% CO₂.

Depending on the specifications needed, the cost can be as low as a few hundred dollars if accuracy can be sacrificed [Digital Control Systems, 2009]. The materials used in the construction are very robust, and typical sensors have a lifetime on the order of years, with minimal calibration, or self-calibrating devices.

A typical NDIR setup which can be used for combustion gas as in the analyzer used in this study has overcome these through a treatment procedure for the gases before they are to be analyzed. These sensors have overcome the sooty environment, temperature and pressure fluctuations and the interfering gases by typically siphoning off a portion of the exhaust gas, and allowing a long transit time to the sensing unit, allowing it to cool. It is drawn with a separate pump, into a larger cavity to smoothen out any pressure pulses, after passing through filters to remove any particulate, water vapour and interference gases. This significantly increases the price and size of the unit, as well as the long term usability; the filters need to replaced after only a few hours of operation.

2.1.2 Potentiometric Sensing

Potentiometric sensing is fairly new, and is still mainly in the experimental stages. There is currently a fair bit of research being done in this field to bring the advantages of solid state potentiometric sensing into the useable ranges where NDIR cannot go, such as directly within a combustion gas exhaust environment. Potentiometric sensing is based on electrochemistry; the voltage that is generated between two dissimilar compounds. The simplest sensing scheme involves using carbonates as electrolytes, where the reference electrode is immersed in a known gas and isolated from the sensing electrode. As the carbon dioxide concentration changes on the sensing side, it affects the equilibrium reaction of $CO_2 + \frac{1}{2}O_2 + 2e^- \rightleftharpoons CO_3^{2-}$. This increase in ions causes a change in the voltage, which can be measured. The voltage is given by the Nernst equation: $V = \frac{RT}{nF} \ln(\frac{[CO_3^{2^-}]_S}{[CO_3^{2^-}]_R})$, where R is the gas constant, T is the temperature in Kelvin, n is the charge of the ion (2 for carbonate) and F is Faradays constant. This expression can be simplified to $V = \frac{RT}{nF} \ln([CO_3^{2-}]_S) - b$, where b is the constant, $\frac{RT}{nF}\ln([CO_3^{2-}]_R)$. This yields a non-linear sensing regime, yielding some issues with the sensitivity over small concentrations of carbon dioxide [Salam and Weppner, 1999]. The sensing materials can be changed to non-carbonate based electrodes, usually an alkaline metal on the sensing region is used with another metallic compound of with the same alkaline metal in the reference electrode, such as the sensing electrode being $Li_2CO_3 - MgO$ and a reference electrode of $LiMn_2O_4$. As the carbon dioxide concentration changes on the sensing electrode, carbonate is formed or released, which changes the concentration of Li¹⁺ ions, which alters the voltage at the reference electrode [Fergus, 2008].

Sensors based on this type of sensing scheme suffer from a few setbacks. Currently, because of the carbon dioxide-carbonate equilibrium reaction shown above, or the carbonation of alkali metal compounds, very high temperatures are required, above 500-700 °C, which restricts their use [Fergus, 2008]. Another limiting factor is that most electrodes are susceptible to corrosion by acidic vapours, or even water. High humidity deteriorates the alkali metals quickly as they react easily with water. The advantages, however, are that they are capable of running in these elevated temperatures, and are not as easily influenced by the production of soot or other particulate within the gas stream. A second advantage is based upon the design. Potentiometric sensors do not need an external power source, but naturally emit an electrical signal, which for the high temperature ceramics falls in the 100-400 mV range [Fergus, 2008]. The accuracy of these devices however, is fairly low, typically around 2.5% and suffer greatly due to drifting signal from thermal effects.

Currently, there is ongoing research to bring the temperature down into a more usable range where it can fit into automotive testing. The literature tends to favour the use of lithium ion because of its ease of conduction at lower temperatures, as was proven by the battery industry. Issues there still remain with oxygen dependencies in some compounds, which increases the sensitivity loss due to the logarithmic signal output and finding materials which will operate at an optimal temperature range [Nszabo et. al, 2003]. Currently, there has been a potentiometric sensor which has been tested in an automotive exhaust environment, however it had to be heated to several hundred degrees in order to properly function [Nszabo et. al, 2003].

2.1.3 Gas Separation Techniques

A low-cost method to detect atmospheric carbon dioxide, such as for atmospheric experimental or HVAC systems was designed using a fluorinated polymer, Teflon AF2400. It was designed to replace the more costly NDIR methods used, since the components required are much simpler and there is no expensive light source or large power consumption. This increased the portability of the sensor, allowing for use in atmospheric balloon sensing [Kebabian and Freedman, 2006]. The sensor takes advantage of the sieve like properties of the Teflon AF2400 to filter out most types of gases, and then measure the capacitance caused by the difference in dielectric constants of gases. It is impermeable to volatile organic compounds (VOCs) such as toluene and n-butane, but permeable to gases such as nitrogen, carbon dioxide, oxygen etc [Pinnau and Toy, 1996]. The only known solvents for this material are perfluorinated solvents, making it ideal for gas sensing, as it is very unlikely to encounter significant amounts of fluorinated gases under normal conditions from diesel exhaust gas or in atmospheric conditions.

Work done by Pinnau and Toy [Pinnau and Toy, 1996] discussed the gas transport behaviour of Teflon AF2400 and its response to various gasses at room temperature and with a feed pressure of 50 psig. Their work showed that selectivity of carbon dioxide was 5 times higher than that of nitrogen, and that the teflon film was able to filter out substantial amounts of hydrocarbons [Pinnau and Toy, 1996]. The advantage of Teflon AF2400 over previously existing polymers, namely poly(1-trimethylsilyl-1propyne) [PTMSP] and polycarbonate is that filters out hydrocarbons more effectively, though its selectivity for carbon dioxide is slightly lower than that for PTMSP [Pinnau and Toy, 2996]. A CO₂ sensor was designed using this material as a capacitance sensor [Kebabian and Freedman, 2006]. It took advantage of the selective adsorption of CO₂ and sufficient diffusivity to create a sensor which measured the difference in capacitance in a circuit caused by the difference in dielectric constants of carbon dioxide and air. The researchers experimented by alternating blasts of 100% CO₂ onto the sensor and completely deficient CO₂ air. The gas was passed through a desiccant first to remove any water vapour. A typical transition from 0% CO₂ to 100% CO₂ showed a first order response signal for a transition from full CO₂ to air in approximately 50 seconds, and a transition from air to 100 % CO₂ in 20 seconds [Kebabian and Freedman, 2006].

However, employing this sensing scheme for diesel engine exhaust gases has its faults. Testing the permeability of Teflon AF 2400 with temperature, it was noted that permeability decreased slightly with temperature increase over a range of 25 -60 °C, though the temperature dependence over this range was shown to be very weak [Kebabian and Freedman, 2006]. Vapour activity (p/p_{sat}) has a much more significant impact, where upon reaching a vapour activity of 0.7 of VOCs, the polymer became VOC selective [Kebabian and Freedman, 2006]. Permeability follows an Arrhenius plot, indicating that as temperature increases, the permeability of carbon dioxide will increase, though it should vastly outweigh the permeability of other gases found in combustion gas. The main difficulty would be the effect of the water vapour and minimal amounts of nitrous oxide present in the system, as it is a part of the combustion reaction, it would be impossible to eliminate. The sensor response to water and nitrous oxide was found to be higher than that for carbon dioxide [Kebabian and Freedman, 2006]. There would be no feasible way to keep a desiccant within the diesel engine environment which would not saturate from water vapour which would be present from both the atmosphere and combustion. At the time of the paper, the sensor did not have any temperature compensation feedback, and was subject to some drift errors, however the paper reported an accuracy of 2.7% [Kebabian and Freedman, 2006]. However, it could be beneficial as a filter to use for hydrocarbons and potentially other gases which could be of use in the future.

2.1.4 Fiber Optic Carbon Dioxide Sensing using Fluorescent Dyes

An optical carbon dioxide detection scheme put forth for Modified Atomospheric Packaging (MAP) which involves using a acidic acid/base indicator which has fluorescence properties in conjunction with a quaternary ammonium ion to produce a detection system by embedding the acid base indicator into different types of transparent media which were capable of gaseous transport. The chemical reaction is described below with Q being a quaternary ammonium ion and D being the deprotonated form of the acid/base indicator.

$$HD_{(aq)} + QOH_{(aq)} \rightleftharpoons D^{-}Q^{+}.xH_{2}O$$
$$D^{-}Q^{+}.xH_{2}O + CO_{2(gas)} \rightleftharpoons D^{-}Q^{+}.xH_{2}O + CO_{2(aq)}$$
$$D^{-}Q^{+}.xH_{2}O + CO_{2(aq)} \rightleftharpoons D^{-}Q^{+}.(x-1)H_{2}O + H_{2}CO_{3(aq)}$$
$$D^{-}Q^{+}.(x-1)H_{2}O + H_{2}CO_{3aq} \rightleftharpoons HCO_{3}^{-}Q^{+}.xH_{2}O + HD_{(aq)}$$

The chemical reaction occurs with the quaternary ammonium ion attaching to deprotonated state of the acid creating a salt and water. When carbon dioxide is introduced into the system, it will dissolve into water in an equilibrium reaction, and also create H_2CO_3 , with a concentration dependant on the concentration of the CO_2 . The acid/base indicator should be chosen such that H_2CO_3 is a stronger acid. Another equilibrium reaction takes place which yields the deprotonated form of the acid/base indicator to capture a proton from the stronger acid, and the anion $HCO_3^$ to combine with the quaternary ammonium salt [Mills et. al, 1992].

For a fluorescent acid/base indicator dye, the emission wavelengths differ based upon whether the dye is in its protonated or deprotonated form, with emission. The protonated form of the dye emits light of a shorter wavelength than the deprotonated dye, due to the presence of the proton affecting the energy levels of the system [Weigl and Wolfbeis, 1988]. By monitoring the fluorescence intensity of the deprotonated form, it is possible to draw a correlation between the intensity of the emitted light and the concentration of carbon dioxide. As the carbon dioxide level increases, it is expected that the equilibria will shift towards more production of carbonic acid which will result in the protonation of the acid/base indicator. This will in turn diminish the fluorescence intensity of the deprotonated dye, and the loss in signal can then be used to determine the carbon dioxide levels [Weigl and Wolfbeis, 1988].

This method of sensing has been tested in multiple scenarios, involving illumination and detection from monoliths and by dip coating a sensing film onto an optical fiber. The procedure generally involves deposition of the dye within a hydrophobic material. The quaternary ammonium ion is generally a very large organic compound, with the hydroxide group attached to the tail of an organic string off of one of the 4 branches of the nitrogen [von Bültzingslöwen et. al, 2002]. Upon combination with the acid/base dye this allows the formation of a very large organic salt which, with the aid of a surfactant, can be combined to form reverse micelles of water and dye suspended into a hydrophobic layer. This creates little sensing droplets of the deprotonated dye in a large hydrophobic environment, which prevents the water from evaporating. Many different plastics, rubbers and sol-gels have been used depending upon the equipment setup, however, sol-gels have been found to have optimal characteristics for optical fibers. Basic sol-gel properties will be described later. Sensors using fluorinated xerogels (a type of sol-gel) resulted in a quick response time of 1.7 second to transfer from 100% nitrogen to 100% carbon dioxide, and a response time of 38.5 seconds to go in the other direction, from carbon dioxide to nitrogen with a resolution of 2.5% [Chu and Lo, 2008].

The sol-gel method was chosen for use in carbon dioxide sensing in diesel engine exhaust gases. The simplicity of the sensor design is appealing, as well as the ease of fabrication. The fabrication methods, which will be described later, indicate that the fiber sensor is capable of withstanding temperatures of at least up to 70°C, and humidity would damage the fiber, as per the potentiometric sensing scheme, and should have less interference effects from soot and combustion gases than the NDIR and gas separation methods. The effects of other gases should be minimal, as this sensor is mainly pH based and is dependant on the dissolution of gases into water, in which case the main concern is the NO₂ in combustion gases. The characteristics of diesel engine exhaust gases from the diesel engine that was used will be described in Chapter 3. In general, the nitrogen oxides found in diesel engines are treated by catalytic convertors, and air is injected into the exhaust line for this to take place, which will act to both reduce the temperature and NO₂ concentration. It was for these reasons, that the initiative was taken to further explore the use of optical fiber sensing of carbon dioxide using fluorescent dyes.

The materials that were used to develop this sensor were chosen with a purpose. The sol-gel used in this work was a fluorinated xerogel, the same as used by Chu and Lo (2008), due to the robustness and fast response time of the sol-gel composed of n-propyl trimethoxysilane and trifluoropropyl trimethoxyilane vs. cellulose and sol-gels composed of polydimethylsiloxane or tetraethylorthosilicate. The phase transfer agent was chosen based on the work done by von Bültzingslöwen et. al. Their work composed of a review of three of the mainly used phase transfer agents, cetyltrimethylammonium hydroxide, tetraocytlammonium hydroxide and tetrabutylammonium hydroxide. Of the three mentioned, it was found that the tetraoctylammonium hydroxide had the highest sensitivity and almost linear response in the 0%-1% CO₂ range [von Bültzingslöwen et. al, 2002]. Depending on the carbon dioxide concentrations of interest, the phase transfer agent can be switched for higher sensitivity in desired regions. However, for this work, high sensitivity was preferred in low concentrations of carbon dioxide. The dye which was chosen was pyranine. It is the most commonly used due to its very high quantum efficiency of 0.98, and very large emission peak difference between the protonated and deprotonated forms of the dye.

2.2 Sol-Gel Properties

Sol-gels are of interest because they allow a glassy material to be made with specific properties at room temperature. In the case of this work, silicates were used to create the sol-gel. Silicate gels are generally created by hydrolyzing precursors with a mineral acid or base as a catalyst [Brinker, 1990]. The general reaction at a functional group level is, for an alkyl group R C_xH_{2x+1} [Brinker, 1990]:

Hydrolysis $\equiv Si - OR + H_2O \rightleftharpoons \equiv Si - OH + ROH$ Esterification and Alcohol Condensation $\equiv Si - OR + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si + ROH$ Alcoholysis and Water Condensation $\equiv Si - OH + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv +H_2O$

The first step is the hydrolysis reaction where an alkoxide group (OR) is replaced with a hydroxyl group (OH). The condensation reactions then occur where the silanol (Si-OH) groups produce siloxane bonds (Si - O - Si) and additional alcohol (ROH) or water. This is either by a reaction with the initial alkoxide silane precursor (Si - OR) or between two silanol groups. This hydrolysis is most rapid when catalysts are employed, such as mineral acids, such as HCl. The acid catalyzation causes a decrease in the electron density of the silicon, allowing it to be more susceptible to hydrolization by water, this dipole created by the donated proton allows it to become more electrophilic. The water molecule then binds, and creates a slight positive charge, allowing for an easier formation of alcohol [Brinker, 1990]. As described above in the equations, these processes are reversible, allowing for bond breaking and reformation. This breaking and reforming of bonds is what eventually leads to the cross-linking of siloxane bonds to form a network, to form clusters. These clusters can then grow and collide to form gels. The links between the clusters will become entangled creating a continuous solid network [Brinker, 1990].

The sol-gel used in this work was composed of fluorinated organically modified silicates, the preparation of the sol-gel precursors will be described later. Due to the electrophilic nature of the silane during condensation, it is possible to embed fluorescent dyes within the silane while it is hydrophilic, and upon condensation the silane forms a hydrophobic network gel, the dye trapped within this matrix [Chu & Lo, 2008]. The sol-gel precursors that were used were of a type called xerogels. Upon condensation, the alcohol and water can be slowly evaporated, leaving a highly porous, glassy skeleton structure behind. This structure has a very high surface area, typically 500 to 900 m²/g. These high surface area glasses make wonderful sensing probes due to the large reaction area to take place in such a small volume. Upon the heating and evaporation (below the glass temperature, which would cause reorganization of the matrix and lose this skeletal structure) the sol-gel forms a highly transparent, photostable, chemically resistant and highly sensitive to the environment films.

2.3 Principle of Fluorescence

The majority of the information in this section is referenced from *Molecular Fluores*cence - *Principles and Applications* by B. Valeur, unless otherwise noted.

Fluorescence and phosphorescence mainly involve the electronic transitions of an electron within a π -bond or a non-bonding electron pair through excitation by an incident photon. A π -bond results from the overlap of p electron orbitals, causing a diffuse covalent bond between the atoms. The procedure for fluorescence begins with a molecule originally in its ground state, S₀. If light incident upon the molecule is of the correct frequency which corresponds to the energy difference between the ground state and a higher energy state, S₁ or S₂, the molecule absorbs this energy, and is placed into an excited state. This excitation involves the formation of an antibonding orbital from one of the two types of electrons mentioned earlier. This electron decays from higher level electronic states by shedding energy through by transitions

in vibrational energy levels. Transitions where energy is transferred from electronic states to vibrational states is radiation-less, and are known as internal conversions. It is possible that these radiation-less conversions yield a non-radiative inter-system crossing into a triplet state and this results in phosphorescence. In fluorescence, this radiation-less conversion occurs very quickly, until the electron decays to a lower state where it is more probable for a radiative process to occur. A photon is then emitted as the molecule decays to its ground state. Due to these radiation-less internal conversion between energy levels, the emitted light from the molecule is of a lower energy and longer wavelength than the incident light. This is depicted in Figure 2.2

Excitation to an anti-bonding state usually occurs on the order of 10^{-15} s, which is much faster than the characteristic time for molecular vibrations of $10^{-12} - 10^{-10}$ s. This indicates that it is much more likely for an electronic transition to occur without a change in position of the molecule that is being excited. Fluorescence occurs after some internal relaxation through the vibrational modes allowed, and occurs in a timescale of $10^{-10} - 10^{-7}$ s. Internal conversion will take precedence over a radiative process while the energy gap between the transition states is small. This type of transition becomes very inefficient at large energy differences, and it is in these cases where radiative processes becomes the dominant means of relaxation, usually to the ground state. Fluorescence usually occurs between the first excited state, S₁, and the ground state, S₀, as the band energies between higher level states usually tend to be much smaller, where non-radiative processes are more probable. According to the Boltzmann distribution, at room temperature, a large majority of the molecules present in a species are in fact in the ground state, so it is not unreasonable to expect excitations from the ground state to higher energy levels when stimulated, or



Figure 2.2: Energy transitions during the process of fluorescence. [Modified from B. Valeur, 2002].
decay from higher energy levels to the ground state. This would change with elevated temperature or other perturbation effects.

Due to fluorescence usually occurring from the decay of the first electronic excitation state to the ground state, except in very few special cases, the fluorescence emission wavelengths are independent of the exciting wavelength, providing that the exciting wavelength is close to an absorption peak of the molecule. It is normal that the absorption and emission spectra partially overlap, due to emission from electrons which are initially in a thermally excited state, as prescribed by the Boltzmann distribution. Generally the absorption and emission spectra are fairly broad. This is because in fluorescent molecules, the amount of electronic energy levels is very high, and at higher electronic energy levels, the energy gap between two states is greatly diminished. There are also fluctuating dipole moments within the molecule itself, which would alter the energy level system of the molecule, and allow for a small spread in the energy required to excite the molecule, which is a type of Homogenous Broadening, as it applies to every molecule equally [Milonni & Eberly, 1988].

The environment surrounding the fluorescing molecule also plays an important role in determining any changes in fluorescence. An increase in temperature can allow extra vibrational modes to become available, decreasing the probability of emission from the $S_1 - S_0$ transition. Also, with the increased energy in the system, the vibrational transitions occur much more rapidly and fluorescence decay times are also increased.

Chapter 3

Experimental Apparatus and Procedures

This section will describe the method that was used in order to prepare and determine the optimal sol-gel coating for the sensor, as well as discuss the setup of the equipment used to characterize the fiber optic sensor. It includes a description of the optical equipment, environmental chamber setup, the sol-gel preparation and characterization procedure, the apparatus used for the interference effects of CO, NO, NO_2 , the effects of humidity and temperature and also explain the diesel test facility and the experiment using the diesel engine.

3.1 Optical Equipment, Environmental Chamber and Sensors

The optical fibers used had physical characteristics of 600 μ m core multimode optical fiber with a numerical aperture of 0.39, a core plus cladding diamater of 630 μ m and the fiber with core, cladding and jacket layers had a diameter of 1030 μ m diameter (ThorLabs). The 600 μ m core fibers were terminated with SMA905 connectors. The optical fiber setup included a bifurcated fiber (BIF-600-UV-VIS, Ocean Optics) with one end connected to a blue LED light source (LED-450 Ocean Optics), while the other was connected to a CCD spectrometer (USB-4000 UV-VIS, Ocean Optics Spectrometer). The common end was connected to the sensing fiber. The initial power output of the LED after coupling with an optical fiber was approximately 130 μ W. The light intensity that was transmitted to the sensing fiber was approximately 70 μ W. The LED emits light peaked at 462 nm, with a Full Width Half Maximum peak width from 455 nm - 472 nm. The spectral resolution of the CCD spectrometer was 1.5 nm. There were significant coupling losses between connections of the bifurcated fiber to the sensing fiber, as expected, since the common end of the bifurcated fiber is two optical fibers terminated into an SMA connector. Thus the alignment of the cores could not cover more than 50% of the surface area of any of the two fibers and so it is not possible to achieve a higher signal transmission than 50% from the sensing fiber. Also, large core fibers have larger losses due to bending when compared to smaller core fibers. The lengths of the fibers contributed to significant bending losses as the bifurcated fiber was fairly long (2 m), and when coupled to the sensing fiber, the length increased significantly to the point where it was not possible to avoid coiling the fiber, further reducing the intensity of the transmitted light. It is for this reason that the fibers were immobilized to minimize any changes in light intensity caused by movement or bending. Each experiment involved normalizing the output intensity of the fiber to the 0% CO_2 level (100 % N_2), and an integration time of 5 seconds for the spectrometer was used in order to ensure a high signal to noise ratio for the experiments.

In order to test the detection of carbon dioxide, it was necessary to conduct experiments within a sealed environmental chamber. The environmental chamber that was used in this experiment was a Pyrex glass 4 port connector chamber. Each port had a common circumference of 37 cm and the length of a straight segments were 40.5 cm. The chamber can be seen as two of these cylinders intersected at the middle and the chamber had an approximate volume of 7.78 L. The sides of the chamber were sealed with aluminum plates, approximately 1 inch thick, with an O-ring groove cut in each, where a viton O-ring coated with a thin layer of vacuum grease was inserted in order to ensure a proper seal. On the upper plate of the environmental chamber a 1" interior diameter hose was placed and was connected to a rotary vacuum pump. Adjacent to this was a 1/4" Teflon tube which was used as the inlet for the gases being injected into the chamber. One of the side panels contained two openings, one for the fiber coated with the sensing agent and a second in close proximity to the fibers sensing head, where a combustion gas analyzer (Greenline 8000) was placed in order to detect the gases being injected into the chamber. The combustion gas analyzer was capable of detecting carbon monoxide (CO), nitrogen dioxide (NO₂), nitric oxide (NO), sulfur dioxide (SO_2) , hydrogen sulfide (H_2S) and hydrocarbons. The accuracy for the detection of CO is $\pm 4\%$ of the reading in the range of 0 - 20000 ppm, $\pm 3\%$ of the reading for CO₂ in the range of 0-20%, for NO the accuracy is $\pm 4\%$ of the reading in the 0 - 2000 ppm range and for NO₂ the accuracy is ± 5 ppm in the range from 0 - 100 ppm. For detection of hydrocarbons, the uncertainty in the combustion gas analyzer was ± 10 ppm in the range 0 - 50000 ppm range. A vacuum pressure gauge was also inserted into this side. The base plate of the chamber had an opening which could be closed with a valve. This was used to control the opening for the exhaust and seal the chamber when necessary.

The gas cylinders used were connected to a mass flow controller (Edwards Model 825) which had controllers for 5 channels of varying air flow rates of 20 ml/min, 200 ml/min, 2 L/min, 5 L/min and 20 L/min which were used to mix the gases. The combustion gas analyzer was used as an external sensor to verify the concentration of the mixed gases, instead of proportioning the gases.

3.2 Sensing Material Characterization Procedure

To prepare the reagents for the sensing material, a similar method to that described in Chu and Lo was used (Chu and Lo, 2008). The fiber was initially stripped of its jacket and soaked in 0.1 M sodium hydroxide for 24 hours. The phase transfer agent was prepared by adding 0.7 mg of tetraoctylammonium bromide (TOA-Br) (Sigma-Aldritch) with 0.3 mg of silver (II) oxide (Sigma Aldritch) in 5 ml of methanol for 4 hours to form tetraoctylammonium hydroxide (TOAOH). This liquid was decanted, leaving the sediment behind and was stored in the refrigerator at 4°C until it was required. The sol-gel precursor solution was made using 0.750 ml of trifluoropropyltrimethoxysilane (Gelest Inc.) mixed with 0.345 ml of n-propyltrimethoxysilane (n-propyl-TriMOS) (Sigma-Aldritch) with 0.750 ml of Ethanol, 0.318 ml of deionized



Figure 3.1: Schematic of experimental setup for carbon dioxide sensing in environmental chamber

water and 0.04 ml of 0.1 M HCl to catalyze the ORMOSIL process. This mixture was sealed and stirred for 1 hour. 0.075 ml of Triton-X100 (Sigma-Aldritch) was added to the solution during mixing to improve the homogeneity of the sol-gel. The sensing dye material was made by first mixing 1 g of the 1-hydroxypyrene-8,3,3-trisulfonic acid (pyranine) (Sigma-Aldritch) with 10 ml of 0.1 M sodium hydroxide. Then separately, an organic layer was made by first dissolving 0.1 g of the TOA-Br in 2.5 ml of the n-propyl-TriMOS mixed with 0.15 ml of dichloromethane. This organic layer was then mixed with the pyranine in NaOH allowing the organic dye to mix in with the organic layer formed. After allowing the two liquids to separate into a hydrophobic organic layer and an aqueous layer, the organic layer was extracted and rinsed by injecting it into a container filled with deionized water. It was rinsed 3 times before it was extracted and mixed for an hour.

3.2.1 Experimental Procedure for Characterization within a Multiwell Plate

Previous work had mentioned the procedure for the chemical reagent preparation, but there was no mention of the proportion to mix these three solutions; (1) the phase transfer agent, tetraoctylammonium hydroxide (TOAOH); (2) the sol-gel precursor (which will be referred to as simply the sol-gel); and (3) the organic layer containing the dye, the pyranine in the n-propyl trimethoxysilane (which will be referred to as HPTS). In order to determine the correct ratio to mix these three components, a 96 well plate was used to determine the ideal mixture, by attempting various compositions. Initially, a plate was made with compositions of roughly equal parts of the sol-gel, TOAOH and HPTS. It was found that with the large quantity of liquid the mixture tended to separate into different layers before gelation could occur. This was not useful for testing; after gelation the signals were very erratic, and the fluoresence signal was very low. Due to this, the tests were repeated with less TOAOH, as the TOAOH was the only solution which did not contain any silane, and did not contribute to the glass forming reaction. The TOAOH caused dilution slowing down the condensation process, and allowing separation of the sol-gel into multiple layers. With this adjustment, it was expected for the fluorescence intensity to decrease, as the phase transfer agent was required for allowing the pyranine to become enveloped within the sol-gel. To monitor the effects of changing the TOAOH levels within the sol-gel composition, the experiment within the wells was done with two different TOAOH levels. The quantity of the surfactant Triton-X100 was also slightly increased from the procedure outlined by Chu & Lo (Chu & Lo, 2008), as the Triton-X100 is used to increase the homogeneity of the gel, in order to form a more uniform layer within the multi-well plate. Again, to determine if there were any effects from changing the Triton-X100 levels, the experiment was repeated with two levels of Triton-X100.

A description of the compositions are outlined in Table 3.1. The table shows a total of 28 different compositions. The sol-gel and organic dye amounts were varied from 42 - 78 μ l, the TOAOH amounts were 12 and 15 μ l, and the Triton-X100 amounts were 0.02 and 0.03 μ l, per well.

The different mixtures were repeated in 3 wells where the total volume of solution in a well was 120 μ l. The gels were then allowed to dry and were tested after a 48 hour drying period, and then again 2 weeks after in order to consider any stabilization effects due to hydrolysis of the sol-gel films. The plate was tested using a TECAN Safire plate reader, which is capable of individually testing each well for fluorescence.

Table 3.1: Composition of Sol-Gel Materials Tested in TECAN Safire

10010 0.11 0	composition of bor d	of materials rested .		
Composition	(Sol-gel μ l : HPTS μ	μ l : TOAOH μ l: Trit	ton-X100 μ l)	
78:42:12:0.02	78:42:15:0.02	78:42:12:0.03	78:42:15:0.03	
72:48:12:0.02	72:48:15:0.02	72:48:12:0.03	72:48:15:0.03	
66:54:12:0.02	66:54:15:0.02	66:54:12:0.03	66:54:15:0.03	
60:60:12:0.02	60:60:15:0.02	60:60:12:0.03	60:60:15:0.03	
54:66:12:0.02	54:66:15:0.02	54:66:12:0.03	54:66:15:0.03	
48:72:12:0.02	48:72:15:0.02	48:72:12:0.03	48:72:15:0.03	
42:78:12:0.02	42:78:15:0.02	42:78:12:0.03	42:78:15:0.03	

The TECAN plate reader illuminated each well individually with light at 450 nm, and the total fluorescence intensity was measured at 515 nm. The factors to consider were the strength of fluorescence as well as the standard deviation of the intensities between wells. A strong fluorescence signal is useful and is important when considering the signal losses that the system will endure from fiber coupling and bending losses. The standard deviation between wells is a measure of the repeatability and consistency of the sol-gel. It is desirable to have a film which is consistent in its fluorescence and not easily susceptible to small deviations in fabrication.

The results from these experiments would only be valid for gels within a plate, as the proper procedure would be the dip casting of these gels onto a fiber. It is possible that the different geometry and much higher surface area to volume ratio when dip coating onto a fiber could affect the drying and final composition, ultimately changing the fluorescence behaviour, when compared to gelation within wells. Another important factor to be recalled is that the amount of TOAOH was decreased in order to prevent separation of the compounds during gelation. The information from these experiments was useful for characterization of the sol-gel, but further characterization was necessary using an optical fiber.

3.2.2 Experimental Procedure for Characterization a Coated Optical Fiber

The mixtures that were tested for the characterization upon the fiber had compositions of (sol-gel (μ l) : HPTS (μ l) : Triton-X100 (μ l)) amounts of (60 : 60 : 0.03), (66 : 64 : 0.03), (72 : 48 : 0.03) and (78 : 42 : 0.03). These solutions were mixed into 1 mL capsules and then mixed using a vortex mixer. The final preparation for

the optical fibers prior to dip coating involved removing the fibers from the sodium hydroxide and rinsing them with copious amounts of deionized water. After mixing the different compositions of the sol-gel mixture, it was necessary to wait until there was a condensation of the gel within the capsule. This could be noted by the liquid gradually turning cloudy. It was necessary to wait for this to occur, as it was found that dip coating prior to this resulted in very thin films initially that did not remain upon the fibers after incubation. If the fiber was dip coated too late after this, the gel film upon the fiber was very uneven and resulted in a droplet of gel instead of a film. This wait time differed per composition. Once the condensation was noticed the fibers were cleaned with ethanol to remove any oils or dust from handling. Previous protocols involved the fibers being dip coated at a speed of 25 mm/s in order to ensure an even thickness over the fiber. There was no apparatus available to duplicate this, instead a dip coating speed of 10 mm/s was attempted. However, it was determined that the thickness of the film was too thin and the gel did not survive the incubation within the oven. Instead the fibers were dip coated by hand, and though it was impossible to duplicate the thicknesses of the sol-gel films exactly, the normalized emission intensities and response times were similar. The fibers were then placed into an oven at 70° C with multiple containers of water to ensure an environment with high humidity. It was found by von Bültzingslwen et. al that by incubating the gel in a high humidity environment it may be possible to avoid a one week stabilization period of the fiber as the gel becomes hydrolyzed by the ambient moisture [C. von Bültzingslwen et.al, 2004]. By incubating in a high humidity environment, and letting it cool slowly in this same environment, the hydrolization occurs much more rapidly and stabilizes the sol-gel film. The fibers were then ready for use. They were stored

in ambient temperature and humidity, within an enclosed box.

3.3 Experimental Procedure for Carbon Dioxide Sensitivity Experiment

The gas cylinders used for carbon dioxide detection were 99.99% carbon dioxide 99.99% nitrogen obtained from VitalAire. Before beginning an experiment it was necessary to remove any gaseous impurities, such as air or humidity from within the environmental chamber. The chamber was sealed and then evacuated using the rotary vacuum pump for a total of 1 min, until the reading on the vacuum gauge was 30 Torr. Once that was attained, the values of the mass flow controller were opened and a nitrogen purge was then used while the vacuum was still in operation. Once the pressure within the chamber returned to slightly above atmospheric levels, the vacuum pump was turned off. The valve leading to the exhaust was then opened and the gas mixture was allowed to flow for an additional 5 minutes. The pressure inside the environmental chamber was allowed to be higher than atmospheric to ensure that no gas would back-flow from the exhaust line once the valve was opened. The flow rates of the input gas were maintained above 15 L/min during the testing. Given that the residence time of gas within the cylinder at this flow rate is approximately 30 seconds, the combination of the 1 minute evacuation using the vacuum pump and the constant purge at a flow rate of 15 L/min for 5 minutes allowed for impurity levels to be reasonably low. The tests were then conducted by slowly introducing carbon dioxide into the environmental chamber using the mass flow controller. The data was collected by recording of the fluorescence emission from the optical fiber with the CCD spectrometer and personal computer in a continuous manner and synchronizing this with a data logger for the combustion gas analyzer. The response time for the combustion gas analyzer is on the order of milliseconds, with a reading being given every second. The fiber sensor had an integration time of 5 seconds to ensure a high signal to noise ratio for intensity measurements, and as such only gave a reading every 5 seconds. All experiments were performed at room temperature.

3.4 Experimental Procedure for Interference Effects of Carbon Monoxide, Nitric Oxide, Nitrogen Dioxide

The experimental studies of potential interference gases generated by combustion was similar to that of carbon dioxide. In this case, the gases were mixed to be slightly higher concentrations that are typically seen within diesel engine exhaust gas as will be described later. The gas cylinders that were used were: a premixture of 300 ppm of nitrogen dioxide with balance nitrogen (BOC Gases); 10% carbon monoxide with balance nitrogen (BOC Gases); and a cylinder with 0.1% of nitrous oxide with balance nitrogen (Air Liquide). The same procedure of first evacuating the environmental chamber for 1 minute, and then allowing the gas mixture to flow into the chamber for 5 minutes to act as a purge for any residual traces of air at a flow rate of 15 L/min. Tests were taken first with nitrogen and carbon dioxide as previously described; first evacuating the chamber and then purging with nitrogen and then conducting the test. After the nitrogen/carbon dioxide test was done, a second test was done with a mixture of the interference gas. The environmental chamber was evacuated and then purged with one of : a) 5000 ppm of carbon monoxide in nitrogen, b) 550 ppm of nitrous oxide in nitrogen or c) 35 ppm of nitrogen dioxide in nitrogen. After the gas mixture stabilized, then again, carbon dioxide was slowly allowed to enter the chamber in this new mixture, and the carbon dioxide flow rate was slowly increased. After this test, to ensure that no permanent effects transpired with the fiber chemistry, the fiber was once again tested in only nitrogen and carbon dioxide to reproduce the original results, and show no change.

The typical concentration levels of these interference gases were found in literature (Adler et. al, 1993), and were referenced with the exhaust gas composition found in the single stroke diesel engine that was used in this work. Typical concentrations of diesel exhaust gas are shown in Table 3.2. The characteristics of the diesel exhaust gas of the single stroke diesel engine for this thesis is shown in Figure 3.2.

It was found that nitrogen dioxide had an effect on the fiber sensor's response, and this was explored further. In order to determine the effects of higher concentration of nitrogen dioxide, experiments were conducted by first monitoring the response of the optical fiber to 0% and 5% Carbon Dioxide (VitalAire) in balance nitrogen, to 0% and 5% carbon dioxide in 300 ppm of nitrogen dioxide and balance nitrogen. The gas was changed in the environmental chamber by first evacuating for one minute and following this, a 5 minute purge was performed using the new gas. Once this was completed, the readings were taken.

3.5 Interference Effects of Relative Humidity

The studies for the interference effects of relative humidity only included two different humidity values, near 0% by direct injection from the gas cylinders, and near 100%

Table 3.2: Typical Diesel Engine Exhaust Characteristics from Adler et. al, 1993

Exhaust Gas Component	Units	At Idle	At Maximum Output
Nitrogen Oxides (NO_x)	ppm	50 - 250	600 - 2500
Hydrocarbons	ppm	50 - 500	150
Carbon Monoxide	ppm	100 - 450	350-2000
Carbon Dioxide	Vol. %	< 3.5	12 - 16
Water Vapour	Vol. %	2 - 4	<1
Oxygen	Vol. %	18	2 - 12
Particulate Matter	$ m mg/m^3$	20	200
Temperature	°C	100 - 200	550 - 750



Figure 3.2: Concentrations of CO, NO, NO₂, O_2 in diesel engine exhaust gas from the single stroke diesel engine used in this study under an operating load of 2.4 kW.

as was measured by a relative humidity detector (VWR Digital Humidity and Temperature Monitor). The humidity monitor had an uncertainty of $\pm 4\%$ of the reading, over the range from 25%-95%. The 0% relative humidity level was obtained by using gas directly from the cylinder, where moisture levels are less than 300 ppm. In order to achieve high relative humidity conditions, the gas was first bubbled through 300 ml of distilled water before it was injected into the chamber. By passing carbon dioxide through water, the water was made more acidic and as such the water needed to be replaced between tests in order to limit the effects of the dissolved carbon dioxide being released back into the gaseous stream and altering the signal. The tests were again conducted as before, by evacuating the chamber for 1 minute, followed by a 5 minute nitrogen purge at 15 L/min and then gradually increasing the carbon dioxide injection rate. The test using the dry gas was done first, as it was difficult to remove humidity or condensation from the chamber once in place.

3.6 Effect of Environmental Temperature on

Fluorescence Signal

The studies for environmental temperature effects were conducted using the same method as the other tests. In order to increase the temperature, the gas was preheated before entering the chamber by passing it through stainless steel tubing which was wrapped in heating tape. The environmental temperature was measured using a K-type thermocouple placed in close proximity to the fiber. The temperature reading from the K-type thermocouple was taken using a Fluke 50 Series II thermometer, which had an uncertainty of $\pm 3^{\circ}$ C. The energy input to the heating tape was controlled using a VARIAC variable transformer, and the temperature was maintained at 55 °C.

3.7 Diesel Engine Exhaust Gas Monitoring Study

The final test for the fiber was to place it in as close to an approximation to a realistic situation as possible. In this endeavour, the fiber optics sensor was placed into a diesel engine exhaust test facility where its performance under real diesel exhaust conditions was measured.

3.7.1 Near Zero Emission Diesel Exhaust Test Facility

The diesel engine in the Near Zero Emission Diesel Exhaust Test Facility is a 2.4 kW Lombardini 15LD350 single cylinder diesel engine generator. The characteristics of the diesel engine are given in Table 3.3. A 500 ml graduated cylinder was used as the fuel tank for the diesel engine, in order to monitor the fuel consumption throughout the experiment. Due to provincial law in Ontario, all diesel fuel is low sulphur fuel, with less than 30 ppm sulphur content. This is not typical in other countries. The exhaust system was split into two branches, using 1 inch diameter piping. One branch was used as a by-pass to allow some of the flow to be diverted using gate valves so it would be possible to regulate the flow rate that the fiber optic carbon dioxide sensor would interact with. The by-pass branch consisted of a Venturi flow meter and gate valves to control the flow. The test branch where the fiber sensor was located consisted of a Diesel Particulate Filter (DPF) located 2 m upstream of the location

of the fiber sensor, capable of removing 99.9% of the particulate greater than 10 nm in size from the diesel exhaust gas. However there is still non-negligible nanosized particulate which flows through DPF and agglomerates. A schematic of this setup is shown in Figure 3.4. There was also a K-type thermocouple in close proximity of the fiber sensor, followed by the combustion gas analyzer (Greenline 8000) and a particulate sensor (Hazdust-1003). The temperature from the thermocouple was again taken using the thermometer described previously. Downstream of these systems was another Venturi flow meter. The pressure differential across the Venturi flow meters were measured using a pressure transducer (Validyne DP15TL).

3.7.2 Diesel Exhaust Gas Experiment Procedure

The experiment was conducted by starting the diesel engine with all of the exhaust gas being bypassed around the carbon dioxide sensor until the engine could warm up, which took approximately 5 minutes. After this period, the combustion analyzer, particulate sensor and fiber optic sensor began their data logging. The gate valve was then opened to allow flow through the test leg, which was set to divert approximately 68% of the flow from the by-pass. The length of the experiment was 20 minutes, and the only parameter which was altered was the flow rate through the test branch. The experiment was conducted at idle power for the diesel engine. The exhaust gas concentrations and soot measurements after the DPF for the diesel engine that was used were previously mentioned in Figure 3.2 and Figure 3.4.



Figure 3.3: Schematic of experimental setup for carbon dioxide Sensing in diesel engine exhaust gas test facility



Figure 3.4: Single stroke diesel engine exhaust particulate matter concentration after DPF at 2.4 kW load

Table 3.3: Lombardini 15LD350 Engine Specifications from Kohler Company, 2009.

Cylinders	Displacement	Bore & Stroke	Max Power	Min. Idling Speed
(No.)	(cm^3)	$(mm \ x \ mm)$	(kW/HP)	(rpm)
1	349	$82 \ge 66$	5.5/7.5	950 - 1000

Chapter 4

Experimental Results and Discussion

This section will present the results of the experiments that were previously outlined. The order will follow those presented in the Experimental Apparatus and Procedures section. First the results of the sensing layer characterization will be discussed, as well as the key points that were discovered for proper fabrication of an optimal fiber. The second section will contain the results of the characterization of the fiber sensor's response to various levels of carbon dioxide between 0% and 30% CO_2 will be discussed. Following this, the focus will be carbon dioxide sensing within the diesel engine environment, beginning with the results of the tests for interference effects of gases commonly found in diesel combustion exhaust. In the final section, a presentation will be given of the results and discussion of the test within the Near Zero Emission Diesel Engine Exhaust Gas Test Facility, where the fiber sensor's performance within real diesel engine exhaust is demonstrated and evaluated.

4.1 Sensing Material Characterization

4.1.1 Characterization within a Multiwell Plate

As described in Chap.3 the first step towards development of this sensor was to characterize the sol-gel material which would be placed onto the tip of the fiber for carbon dioxide sensing. The 28 different concentrations were repeated in 3 different wells and were tested with the TECAN Safire plate reader. The plate reader gave an intensity for each well, and from this data the average intensity of the 3 wells of the same composition was taken, as well as the standard deviation. Figure 4.1 shows a graph of the standard deviation vs. average intensity. Ideally, the optimal gel composition would be located in the upper left quadrant of the graph, indicating that the gel is easily reproducible and the emission is stable and has a very high intensity output. The plate read after 1 day after the gelation of the wells shows a grouping of 6 different compositions in this quadrant, namely 78:42:15:0.03, 72:48:15:0.03, 66:54:15:0.03, 78:42:12:0.03, 72:48:12:0.03, and 78:42:12:0.02. The results also show that an increased concentration of HPTS generally results in a lower fluorescence emission.

In order to monitor any effects which may arise from stabilization, a second reading was taken of the multiwell plate, and it showed somewhat different results. Figure 4.2 shows again a plot of Standard Deviation vs. Fluorescence Intensity for the multiwell plate after a 2 week stabilization period. This time period allowed for hydrolization of the films, and the plate read showed that generally the sol-gel compositions with the higher amount of Triton-X100 and higher silane amounts have a higher fluorescence intensity. There is some repetition in the gels in the upper left quadrant, namely 78:42:15:0.03, 72:48:15:0.03, 78:42:12:0.02 but also 78:42:12:0.03, 72:48:12:0.03, 66:54:12:0.03 are new to this region. It is important to note that in each of these compositions the amount of HPTS is lower than that of the sol-gel precursor and generally, the increased amount of Triton-X100 does contribute to a smaller standard deviation of fluorescence signal of repeated samples.

The results that were obtained from the multiwell plate suggest that the sensing layer composition should contain a slightly higher amount of Triton-X100 than previously reported and the amount of HPTS dye should be less than the amount of the sol-gel precursor.

4.1.2 Characterization Upon Coated Optical Fibers

From the results from the plate reading study, it was determined that high concentrations of HPTS were not favourable, and it was desirable to use a higher Triton-X100 amount than prescribed in the protocol by others. Therefore, the next phase was to try different compositions upon the fibers themselves, with varying levels of TOAOH to determine the optimal composition, in terms of creation as well as signal. Fibers were tested with compositions of (sol-gel : HPTS : Triton-X100) amounts of (60 μ l : 60 μ l : 0.03 μ l), (66 μ l : 64 μ l : 0.03 μ l), (72 μ l : 48 μ l: 0.03 μ l) and (78 μ l : 42 μ l : 0.03 μ l). As mentioned in Chap.3, there was a wait time prior to dipping the fiber in order to allow the sensing material to condense. For high amounts of TOAOH, above 90 μ l, it was found that the condensation time to wait before dipping was well over 150 minutes, and at that point still showed no signs of condensation. For compositions below 40 μ l of TOAOH, the condensation times were very rapid on the order of a few minutes, yielding very brittle gels after incubation, which were



Figure 4.1: Standard deviation vs. fluorescence intensity for various compositions of sol-gel, 24 hours after drying





too fragile and easily broken during handling. Finally, compositions with 0.03 μ l of Triton-X100 and (sol-gel : HPTS : TOAOH) amounts of (72 μ l : 48 μ l :48 μ l), (72 μ l : 48 μ l :72 μ l), (72 μ l : 72 μ l :48 μ l), (60 μ l : 60 μ l :90 μ l), (60 μ l :60 μ l :60

The figure shows the emission from multiple compositions of the sensing layer upon optical fibers and the data was obtained from the CCD spectrometer. The plot shows the intensity given in arbitrary units and the wavelength given in nanometers. The peak at 462 nm corresponds to the emission from the LED as well as the emission from the protonated form of the pyranine. It is the peaks above 500 nm that are of interest. As is shown, the fiber compositions of roughly equal parts of the sol-gel precursor and the pyranine-silane mixture (HPTS) show higher emission from the deprotonated version of the pyranine. The fiber with 80 μ l of the phase transfer agent (TOAOH) shows the highest emission, and stability. Though all of these fibers had shown some ability to detect carbon dioxide, the much higher emission is best suited for real applications. The fluorescence of deprotonated forms slightly differ from each other with varying compositions. This is most evident in the case of the (60 μ l : 60 μ l : 90 μ l) composition, where the increased concentrations of the TOAOH generally results in blue shifting of the emission from the deprotonated form.

The results of these experiments show that the ideal fiber to use was a fiber dipped into a mixture with 60 μ l of the sol-gel precursor with 0.03 μ l of Triton-X100, 60 μ l of the silane with pyranine and 80 μ l of the tetraoctylammonium hydroxide. This fiber yielded the best fluorescence in the appropriate region and did not require long wait times for gelation to occur and created a gel that was not extremely brittle or fragile.



Figure 4.3: Optical emission intensity vs. wavelengths between 300 - 700 nm from different sol-gel compositions

4.2 Experimental Results for Carbon Dioxide Sensitivity

Typical optical emission spectra are shown in Fig 4.4, showing the change of the fluorescence response with increasing carbon dioxide levels from the HPTS embedded in the sol-gel based film. The plot shows a figure of the intensity vs. wavelength at varying levels of carbon dioxide concentration. The curves are labelled according to the carbon dioxide concentration at which the reading was taken. The peaks above 500 nm are of interest, and correspond to the emission from the deprotonated pyranine. The intensity of these peaks are diminished as the carbon dioxide concentration increases. This figure shows a definitive blue shift of the emission of the deprotonated pyranine as the carbon dioxide concentration increases, while there is no such shifting or change in the shape of the emission from the protonated version of the dye, beyond the increase in intensity.

Using the information from this figure, it is possible to determine the carbon dioxide concentration in the environment surrounding the sensor. By monitoring the peak emission intensity of the peaks above 500 nm, it is possible to calibrate this sensor to determine carbon dioxide concentration. Also, it is possible to utilize the integrated intensity of the emission spectrum of the deprotonated dye as a sensing scheme. The integrated data is an approach which has not been used in literature for optical carbon dioxide sensors before. It is considered to be more relevant than that based on the maximum peak intensity, which was the method shown by many of the references found [Chu and Lo, 2008; Mills et. al, 1992; Burke et. al, 2006; Mülleran and Hauser, 1995; He and Rechnitz, 1995; Mills et al, 1997]. By choosing a



Figure 4.4: Optical emission spectra for various carbon dioxide concentrations from the fiber sensor

detection method that was based on the integration of the emission over the emission wavelengths the sensor becomes much simpler to produce: it would suffice to use optical filters and a photodiode rather than a much more costly spectrometer. In this study it also has the benefit of a much higher signal and also being less influenced from white noise than peak intensity measurements, as any random white noise within the emission spectra over the wavelengths would effectively be integrated to 0. Table 4.1 displays the noise measurements for a few fibers, and shows the improvements in signal quality from the spectral intensity method when noise is a significant factor. In most cases there is a significant decrease in the error, with the exception of when the error is already small. The measured signal, be it emission peak intensity or integrated intensity, was normalized to the 0% carbon dioxide level, i.e. the measured signal was I/I_o , where I is the measured intensity at a carbon dioxide level and I_o is the intensity at 0% carbon dioxide.

Figure 4.5 shows the normalized peak intensity and also the normalized integrated intensity vs. carbon dioxide concentration. The error was experimentally determined by repeated measurement at a condition of 0% CO₂. Sixty measurements were taken and the error bars determined by 3 times the standard deviation of these measurements. The curves for the two different sensing methods show a close agreement. The results from this study over this range show a trend which is different from the linear trend given by the authors mentioned above. Both sets of data concur that in a range of 0 30% carbon dioxide, the data sets follow very closely to fifth-order polynomials. The best fit curve for the normalized peak intensity over this range follows $y = (-4.449e - 7)x^5 + (3.843e - 5)x^4 - (1.269e - 3)x^3 + (2.034e - 2)x^2 - 0.1688x + 0.9868$ with a correlation of $r^2 = 0.9919$. The best fit for the normalized integrated intensity

Table 4.1: Table of Noise Measurements for Multiple Fibers			
	Emission Peak Intensity	Integrated Intensity	
	Noise Measurement	Noise Measurement	
Fiber Sensor 1	4.55%	4.02%	
Fiber Sensor 2	1.75%	1.16%	
Fiber Sensor 3	0.836%	0.845%	
Fiber Sensor 4	4.18%	1.30%	



Figure 4.5: Normalized intensity vs. carbon dioxide concentration. a) normalized emission peak intensity, b) normalized integrated intensity

transient follows the curve $y = (-2.82e - 7)x^5 + (2.375e - 5)x^4 - (7.692e - 4)x^3 + (1.245e - 2)x^2 - 0.1151x + 0.9879$ with a correlation constant of $r^2 = 0.9951$. The deviation from this trend in the range between 1.2% - 4% can be explained by the use of the mass flow controller. In order to attain higher concentrations of carbon dioxide, a different channel capable of a higher flow rate was used, and this change occurred at this point. When changing the channels, there was a noticeable delay between when the signal was sent to the micro-controller and the commencement of flow from the channel. Due to this lag, the flow rate was not able to be kept constant during changes in concentration. Altering the flow rate creates changes in the partial pressure of gases within the chamber, and also affects the solubility of the gases in the droplets of water formed within the sensor, altering the signal. The successive smaller deviations are also attributed to changes in the incoming injection rate. The curves show a very high correlation to the data, and demonstrate the equivalence of considering the integrated intensity over the peak emission intensity.

Figure 4.6 shows the results for the carbon dioxide concentration range of 0% 0.5%. For low concentrations of carbon dioxide, again we can see the clear agreement between the two methods of detection, though the integrated emission signal shows higher tolerance for error. The results follow a linear trend; the normalized emission peak intensity has a best fit line of y = -0.265118x + 1.00908 with a correlation coefficient of $r^2 = 0.985067$. The normalized integrated intensity transient has a best fit line of y = -0.18232x + 1.0037 with an $r^2 = 0.993248$. The normalized integrated integrated integrated integrated integrated integrated. The normalized integrated integrated integrated integrated integrated. The smallest detectable concentration was determined to be less than 0.3%,

which was the limit of the capability of the combustion gas analyzer.

The linear curve is to be expected for the smaller concentration levels, less than 0.5%. This is due to the aforementioned very high sensitivity of fluorescent dye sensors using TOAOH as the phase transfer agent in the region of 0 - 1% CO₂. The high sensitivity and linear relationship follows from previously observed results in monoliths with different sol-gel compositions [von Bültzingslöwen et. al, 2002]. Over the larger concentrations up to 30%, the 5th order polynomial is appropriate, as it matches the decrease in sensitivity over this region, which is to be expected with this phase transfer agent.

Following the shape of the emission spectra in Figure 4.4, it can be seen that the emission peak wavelength blue shifts with an increase in the carbon dioxide concentration. Therefore, it is possible to take advantage of the blue-shift phenomena as a third sensing scheme. Figure 4.7 shows a plot of the wavelength vs. carbon dioxide concentration. As the concentration of carbon dioxide increases, the deprotonated version of the pyranine dye observes a substantial shift of the in its emission peak wavelength, as much as 14 nm over the tested range of 0 - 30% CO₂. As mentioned in Chapter 3, the spectral resolution of the CCD spectrometer that was used was only 1.5 nm, so there was a diminished capability of detecting carbon dioxide this way with our equipment as the experimental uncertainty is large. However, the total shift from 0 - 30% CO₂ is well outside of the emission peak shift and carbon dioxide concentration.

In order to compensate for the limitations in resolution, a smoothing algorithm involving the convolution of the signal data with a Hann window of width of 76



Figure 4.6: Normalized optical intensity as a function of CO_2 concentration below 0.5%. a) normalized emission peak intensity, b) normalized integrated intensity

points (10 nm), the approximate width of the largest peak. The Hann window that was used is given by $y(n) = \frac{1}{2} - \frac{1}{2}\cos(\frac{2\pi n}{M-1})$ for 0 < n < M-1, where M is the width of the window. In Figure 4.7, the shifting of the emission peak with increasing carbon dioxide is shown. The best fit curve for the wavelength is given by $y = (2.95642e - 5)x^4 - (3.04049e - 3)x^3 + 0.122472x^2 - 2.38666x + 521.377$ with an $r^2 = 0.985139$. The initial readings between 0-4% are not very clear and show a jump, which could be a combination of the error discussed above with the channels of the flow controller as well as that of the decreased resolution capability.

An explanation for this shift can be found when considering the environment of the pyranine within the sol-gel. It is known that the shape and intensity of the absorption and emission spectra are very dependant upon the proton affinity of the medium that contains the pyranine [Prayer et. al, 1996, Schulman et. al, 1995]. Thus the pH of the gel material plays an important role in determining the emission spectrum. As carbon dioxide is introduced into the system, it acidifies the environment through reaction with the water that is generated by the combined pyranine and TOAOH. This created a less proton receptive environment, due to the acidification and higher concentration of positive charge within the sensing material. Work done by Wittouck et. all has shown that a decrease in the proton affinity of the environment around pyranine will cause a blue shift of the emission when encased within an organically modified silicate [Wittouck et. al, 1997]. This effect then causes the blue shift of the emission peak, which can be used to detect carbon dioxide levels. This is beneficial for real time sensing because integration times can be smaller as the noise to overcome is spectral in nature, as opposed to intensity, and a spectral range of a few 10s of nm can be quickly detected using current optical spectral analyzing equipment. This



Figure 4.7: Emission peak intensity wavelength shift as a function of carbon dioxide concentration

also has the possibility to be more accurate, as spectral shifts can already be resolved to a very high accuracy, yielding potentially even higher resolution and a smaller lower detection level limit than is currently reported with intensity measurements. However, this is dependent on whether the initial plateau in the results shown in Figure 4.7 between 0 - 4% is an artifact from the poor spectral resolution of the equipment, or if there is in reality minimal change in the peak emission wavelength until the 4% level. If this is the case then this sensing scheme is only practical in the regime of higher sensitivity above 4% CO_2 .

4.3 Interference effects of Carbon Monoxide, Nitric Oxide, Nitrogen Dioxide

4.3.1 Carbon Monoxide Interference Effects

The results from this experiment show that there are no interference effects from the introduction of carbon monoxide to the fiber sensing system. By comparing the response of the fiber sensor towards carbon dioxide in an environment with pure nitrogen as the dilution gas and comparing to its response in 5000 ppm of carbon monoxide as the dilution gas on a single plot, the interference effects of carbon monoxide, if any, would be visible. In Figures 4.9 and 4.8 the the experimental results of the normalized intensity emission as a function of carbon dioxide concentration is shown. The error was again calculated by 3 times the standard deviation of 60 repeated measurements at the 0% carbon dioxide level. Each figure shows the signal response for the fiber sensor at various carbon dioxide concentrations in different balance gases. The
balance gases used to dilute the carbon dioxide concentration are, in order of experimental procedure: (1) nitrogen, (2) 5000 ppm carbon monoxide in balance nitrogen, and (3) nitrogen. The numbering is the order the tests were conducted. Figure 4.8 shows the fiber sensor response using the normalized emisison peak intensity, and Figure 4.9 shows the response when the signal is the normalized integrated intensity.

The results show that, within the experimental uncertainty, the plots of the carbon dioxide within the carbon monoxide/nitrogen mix (2) and purely nitrogen (3) are the same. There is a deviation in the plot of the first test in the nitrogen only (1) environment, where it demonstrated a slightly decreased sensitivity in relation to the other two. It was later discovered to be caused by residual moisture left within the fiber, which could only be removed by flowing dry gas over the fiber for over 20 minutes. The evacuation and purge was not sufficient in removing this effect. As carbon dioxide concentration increases, the data points for all three curves begin to group more closely. This suggests that the interference effects of carbon monoxide, if any, are below the detectable limits for concentrations higher than that within a diesel engine, and has no significant effect on the performance of this fiber sensor.

4.3.2 Interference Effects of Nitric Oxide

Figure 4.10 and 4.11 show the plots of normalized intensity vs. carbon dioxide concentrations for both emission peak and integrated intensities, respectively, for this experiment. Again the plots of the fiber sensor response with a dilution gas of pure nitrogen is compared to the response with the dilution gas of 550 ppm of nitric oxide to take note of any deviations. The balance gases that were used to lower the concentration of the carbon dioxide are, numbered in order of experimental



Figure 4.8: Normalized emission peak intensity vs. carbon dioxide concentration in nitrogen and 5000 ppm carbon monoxide



Figure 4.9: Normalized integrated intensity vs. carbon dioxide concentration in nitrogen and 5000 ppm carbon monoxide

procedure: (1) nitrogen, (2) 550 ppm nitric oxide (NO) in balance nitrogen, and (3) nitrogen. The error was experimentally obtained as described previously. The integrated intensity and emission plots are again in very close agreement. When considering the plots of the sensor response to pure nitrogen and 550 ppm nitric oxide in nitrogen there is a minor discrepency but very similar behaviour in the situation where nitric oxide is used in the dilution gas. Again, the curve of the initial plot with nitrogen deviates from the second and third plots due to the lingering moisture embedded in the sensor due to inadequate purging, as was described in the experimental results of carbon monoxide above. The response in 550 ppm nitric oxide demonstrated a slight deviation from the trends shown in pure nitrogen until approximately 0.8% CO_2 where significant overlap of the data points begins. There is shown to be minimal effects of nitric oxide upon the fiber sensor at very low concentrations of carbon dioxide. Above levels of 0.8% CO₂ this discrepancy vanishes. In most cases for diesel engine exhaust gas, the carbon dioxide concentration is above the 2% level, and it is unlikely that the nitric oxide would have an effect in sensor performance given that the deviation seems to vanish. The data sets being marginally outside of the experimental error also indicates that it is possibly a result of the experimental conditions of the day. It was expected that nitric oxide would not have a substantial effect, which is explained later and this experiment should be repeated to ensure that the deviation is correct.



Figure 4.10: Normalized emission peak intensity vs. carbon dioxide concentration in nitrogen and 550 ppm nitric oxide



Figure 4.11: Normalized integrated intensity vs. carbon dioxide concentration in nitrogen and 550 ppm nitric oxide

4.3.3 Interference effects of Nitrogen Dioxide

The results for the interference effects of nitrogen dioxide are shown in Figures 4.12 and 4.13 for the normalized emission peak intensity and normalized integrated intensity, respectively. The plots are ordered according to the order of experiments in which the gases were used to dilute the carbon dioxide: (1) nitrogen, (2) 35 ppm nitrogen dioxide in balance nitrogen and (3) nitrogen. The integrated intensity and emission peak intensity plots are in agreement that the introduction of nitrogen dioxide into the system does have an effect on the fiber sensor. Nitrogen dioxide causes a decrease in the emission signal, causing a deviation from the control curve of carbon dioxide in nitrogen. However, after conducting the test with the nitrogen dioxide and repeating the test using pure nitrogen as the dilution gas shows that the fiber is able to recover from the nitrogen dioxide, and the gas is not noticeably damaging the fiber, it seems to be an interference source for carbon dioxide detection.

As nitrogen dioxide is the only gas to have had a substantial interference effect, this phenomena was explored in depth. Raw emission plots are shown in Figure 4.14. This figure shows that the nitrogen dioxide does not effect the shape of the emission. A second experiment was conducted at a concentration of 300 ppm, 10x higher than that found within diesel exhaust gas. This was conducted as a very rough approximation to lifetime testing, and to note the effects of culmulative exposure to nitrogen dioxide. Simply applying a higher concentration is not ideal. However, it could yield some insight into the long term behaviour of the sensor. At the concentration level of 300 ppm NO₂, it was observed that the nitrogen dioxide caused a reduction in the sensitivity of the fiber. However it was still capable of detecting changes in carbon dioxide concentrations. This is demonstrated in Figures 4.15, 4.16. In this figure,



Figure 4.12: Normalized emission peak intensity vs. carbon dioxide concentration in nitrogen and 35 ppm nitrogen dioxide



Figure 4.13: Normalized integrated intensity vs. carbon dioxide concentration in nitrogen and 35 ppm nitrogen dioxide

the horizontal axis shows the experiment number, where the data represented is in chronological order of the gases being tested. The vertical axis shows the normalized intensity. The graph depicts how initially, the fiber sensor is able to detect a change in the atmospheric gas to 5% carbon dioxide, and it is able to recover. It then shows that introducing 300 ppm of nitrogen dioxide causes a decrease in signal strength and that the sensor is unable to recover after removal of all the nitrogen dioxide and reintroducing nitrogen. The nitrogen is then replaced again by nitrogen dioxide and there is no further decrease in the sensitivity of the fiber, and it is still capable of carbon dioxide detection.

It was observed that there was no lasting damage from repeated testing at the small concentration level of 35 ppm over the span of 2 weeks. However, at the higher concentration of 300 ppm, the sensing film on the optical fiber changed colour after a single day's exposure to this concentration, and was no longer able to fluoresce, indicating that the fiber had been irreversibly damaged. The film on the fiber is generally a green colour, however after the interaction with the nitrogen dioxide, it had turned a maroon colour.

4.3.4 Discussion of Interference Effects of Carbon Monoxide, Nitric Oxide, Nitrogen Dioxide

The lack of interference from carbon monoxide and minimal interference from nitric oxide is to be expected. The basis of the sensor involves a reaction with small droplets of water formed within the fiber sensor, which effects an increase in the pH of the sol-gel. The pyranine reacts to this change in pH by accepting a proton, and undergoing a decrease in the intensity of the deprotonated species of the pyranine, as



Figure 4.14: Selected emission spectra of fiber sensor response at various levels of carbon dioxide and nitrogen dioxide.



Figure 4.15: Normalized emission peak intensity vs. carbon dioxide concentration in nitrogen and 300 ppm nitrogen dioxide



Figure 4.16: Normalized integrated intensity vs. carbon dioxide concentration in nitrogen and 300 ppm nitrogen dioxide

its concentration is diminishes within the sol-gel. Both carbon monoxide and nitric oxide have extremely poor solubility in water. The solubility of carbon monoxide in water is 2.095×10^{-5} , and that of nitric oxide is 4.163×10^{-5} , while that of carbon dioxide is a full order of magnitude higher at 8.21×10^{-4} , at room temperature and atmospheric pressure [Lide, 2010]. Nitrogen dioxide, however, is highly reactive with water. It readily forms nitric acid, HNO₃, which is a strong acid. The nitric acid readily protonates the pyranine and causes the decrease in the emission intensity. It is believed that long term exposure to nitrogen dioxide may have some detrimental effects to the fiber sensor. As described above, the smaller concentration tests showed no short term detrimental effects to the fiber sensor, however the much higher concentration caused a noticeable colour change, and the sensor was rendered inoperative. Figure 4.17 shows a photograph of (a) what the sol-gel should look like, and what occurs hours after (b) 1 and (c) 10 μ L of nitric acid is added to 2 mL of the solgel sensing layer. Initially there is no change, but after 3 hours, a very clear colour change has occured and the film became transparent in most places, with only a few areas where there was a maroon colouration. This colour change is indicative that the nitric acid is breaking down the pyranine into a different compound, which lacks the same fluorescent properties. This suggests that an accumulation of nitric acid from exposure to nitrogen dioxide will result in rendering the sensing layer inoperative, though for small concentrations in the short term the sensor is able to function.

4.4 Interference Effects of Relative Humidity

The effects of humidity on the behaviour of the fiber sensor is portrayed in Figure 4.18. The figure shows that initially, in concentrations below 5% CO₂ the signal decrease



Figure 4.17: a) 2 ml of Sol-Gel Sensing Layer, b) 2 ml of Sol-Gel Sensing Layer with 1 μ L of HNO₃, c) 2 ml of Sol-Gel Sensing Layer with 10 μ L of HNO₃

is much more rapid for dry gas measurements versus that for humid conditions, indicating that for lower concentrations, the interference effect of humidity is to cause a decrease in sensitivity. Above 12%, the sensitivity of the humid gas is higher than that of the dry gas. In the period of 5% to 12% the responses for both dry and humid gas are similar. This trend is found in both emission peak intensity measurements and integrated intensity measurements. It is possible that the decreased emission strength is a result of scattering within the sol-gel material caused by the high concentration of gaseous water molecules within the pores of the sol-gel, causing light to be lost. However, the decrease in sensitivity is not very large, and considering that this change occurred over a shift from no humidity to full humidity, small fluctuations in humidity level should not cause great errors in the sensors capabilities.

4.5 Effects of Environmental Temperature on Fluorescence Signal

The results of the experiment demonstrating the effect of temperature on the sensor response is shown in Figure 4.19. The two plots shown in the graphs are the sensor response to various carbon dioxide levels at a temperature of 55°C and at room temperature. The plots for normalized integrated emission and normalized emission peak intensity are shown. The signal response shows that the sensor is still capable of differentiating between various carbon dioxide levels at the two temperatures, though there is a decrease in sensitivity as the temperature increases.

This decrease in sensitivity arises from the decrease in emission intensity of the



Figure 4.18: Comparision of fiber sensor signal response in a dry and humid environment. a) Normalized emission peak intensity vs. CO_2 concentration. b) Normalized integrated emission intensity vs. CO_2 concentration

fluorescence as temperature increases. As the temperature increases, different vibrational relaxation modes become more probable and efficient due to the thermal excitation of the pyranine, i.e. energy can be lost more easily through vibrations between particles or through internal conversion within the excited pyranine molecule. This decreases the probability of a photon emission, and as such, a decrease in fluorescence intensity occurs. This makes it more difficult to distinguish between points, as the intensity differences between points approaches the fluctuation levels of the white noise associated with the equipment, a decrease in sensitivity and resolution is observed.

4.6 Diesel Engine Exhaust Gas Test Facility Experimental Results

Data obtained from the diesel engine exhaust gas experiment is shown in Figure 4.20 and Figure 4.21. Measurements of carbon dioxide, carbon monoxide, nitric oxide, nitrogen dioxide and the fluorescence emission intensity were observed and plotted against time and are shown in plots a) and b) of Figure 4.20. Figure 4.21 shows the temperature, hydrocarbon concentration and dust particulate measurements as a function of time. The volumetric flow rate of the gas through the test leg was 63 - 73.6 L/min, as determined by the Venturi flow meters. It is important to note that the diesel engine was already in operation for 10 minutes before data logging began in order to allow for the engine to warm up to a steady value. The diesel engine was in operation for the entirety of the time shown. The previous calibration curve obtained from the characterisation of the sensor could not be used to determine the



Figure 4.19: Comparision of fiber sensor response at room temperature and at 55° C. a) Normalized emission peak emission vs. CO₂ concentration. b) Normalized integrated emission intensity vs. CO₂ concentration

carbon dioxide levels and reference against the combustion gas analyzer. This was due to the totally new environment all the equipment had to be moved into. This experimental environment would contain varying levels of humidity, bursts of gas flow, different coupling losses, especially with the vibration and many other factors. The objective of this experiment was to determine the feasibility of developing this sensor further into a potential candidate for a diesel engine. It is unlikely to expect a perfect behaviour from the initial run, especially given what has been previously observed.

From Fig. 4.20 a), it is shown that the carbon dioxide levels within the exhaust gas decreased with time. The fiber sensor response reflected this as well, with an initial signal increase in this time period from t = 0 to t = 300. However, past this point the carbon dioxide levels continued to decrease, and the signal from the fiber sensor also decreased, contrary to the expected behaviour of fluorescence emission increasing. There was still fluorescence occuring, indicating that the sensor was still capable of detection and had not been completely destroyed, but the signal response continued to decrease for the duration of the experiment. ==

The concentrations of CO, NO and NO₂ remained mostly constant during the entirety of the experiment to the certainty of the detection error of the equipment. The temperature of the exhaust gases increased from 35° C when data logging began to 50° C in the first 300 seconds, and eventually peaked at a value of 74° C. The concentration of hydrocarbons within the exhaust stream also remained constant within experimental error at a value of 150 ppm. The particulate density initially was very high, as is typical for diesel engines, especially at idle, while they achieve a proper operating temperature, and eventually settled to 0.2 mg/m³. The H₂S and



Figure 4.20: Experimental data for diesel engine exhaust gas: a) Fiber optic sensor response vs time and CO_2 concentration vs time. b) Gas concentrations of CO, NO, and NO_2 as a function of time.



Figure 4.21: Experimental data for diesel engine exhaust gas: a) Temperature and hydrocarbon concentration progression with time, b) dust particulate measurements over time

 SO_2 concentrations were 0 ppm, confirming that low sulphur diesel fuel was used.

As the temperature continued to increase, we see the sensor response continue to diminish. It is noted that as the temperature reached approximately 50 °C, we see the beginning of the decrease in the emission intensity of the fiber sensor. The signal from the sensor continued to decrease for the duration of the experiment, and upon retesting the fiber the following day in the environmental chamber, it was discovered that the sensing layer had been damaged, and resembled those that had been damaged through contact with high levels of nitrogen dioxide.

Concentrations significantly higher than those measured of carbon monoxide and nitric oxide were tested with no adverse effects to the fiber sensor. As a temperature of 55° C had been tested before, and the fibers are incubated at 70° C without any damage. It is unlikely that temperature alone is the source of sensitivity loss and damage. Also nitrogen dioxide was tested at similar levels without the lasting damage and constant decrease in the signal.

The effects of hydrocarbons on the fiber sensor had not been tested, and as such the sensor's response to them is unknown. However, it is unlikely that they could directly effect the sensor response as they are not soluble in water and it is unlikely that they would have had an effect on the pyranine and TOAOH within the sensing layer. This is consistent with the initial sensor response to the changes in the carbon dioxide content of the surrounding gas, as the expected behaviour of the initial rise of the fiber response with decreasing carbon dioxide concentration. The silane that was used to create the sensing layer, however, was organically modified. The silica itself is formed a glass with a hydrophobic cage of the organics used to entrap the pyranine and the tetraoctylammonium hydroxide. It is possible that the small traces of gaseous hydrocarbons were able to gradually dissolve this hydrophobic cage which could have caused an evaporation of the water made by the reaction of the pyranine and tetraoctylammonium hydroxide. This is unlikely to be the case, as retesting in air with ambient humidity should have been able to garner some fluorescence from the sensor and this was not noticed the following day. It is also unlikely that the hydrocarbons were able to dissolve the sol-gel material, as they contain a silane matrix, which is very resilient, and there were no noticeable pitting upon the sensing tip or appreciable degradation of the film.

A more likely scenario is the effects of nitrogen dioxide at the temperature of 50° C and above. It is well known that an increase in temperature causes most chemical exothermic reactions to occur more rapidly and easily due to the extra kinetic energy available for the molecules. This knowledge with the discovered effects of high concentration of nitrogen dioxide in disabling the sensor from earlier in this work could be the explanation for the behaviour in the diesel engine. It is possible that the continual increase in temperature alone could cause the continual decrease in signal, however comparing the amount of signal that was lost with the temperature alone in the temperature test above against the magnitude of the signal drop that is experienced in this experiment, it is unlikely. A possibility is that at the elevated temperature above 50° C, the higher flow rate of gases in the diesel exhaust stream and the known effects of nitrogen dioxide in creating nitric acid and altering the effects of the fiber caused a continual decrease in the sensor response. It is likely that the degradation of the sensor that was previously noted at high concentrations does occur at low concentrations as well but takes a much longer time. At an elevated temperature, this degradation could occur much more rapidly, potentially at a rate which would be noticeable after 20 minutes. Thus the degradation of the pyranine by the increased rate of nitric acid formation within the sol-gel, coupled with the known effects of temperature inhibiting fluorescence would result in the signal decreasing, and eventually the destruction of the fiber, as was observed.

Chapter 5

Conclusions

In this study, a fiber optic carbon dioxide sensor was developed by optimizing the sol-gel material that would act as a sensing layer on an optical fiber. The fiber sensor sensitivity to carbon dioxide was first studied, and then the potential for interference effects from common gases and environmental changes that would be found within a diesel engine exhaust stream were investigated. The conclusions that can be drawn from the results of these experiments are:

• The optimal composition for the sensing layer described earlier in this work was discovered to be: 60 μ l of the sol-gel precursor, 60 μ l of the pyranine dye encased in a silane and 80 μ l of the phase transfer agent. This yielded a solution which could easily be dip casted upon the optical fibers. After gelation, this composition yielded the highest fluorescent signal output of those studied, and the sensing layer that was created was sufficiently robust to survive moderate handling without any change in capability.

• The fiber sensor showed that it was capable of detecting carbon dioxide within the range of 0 - 30% and was shown to have a lower limit of detection better than 0.3%, which was confirmed by the detection limit of a NDIR CO₂ detector in the combustion gas analyzer which was used. There was a fifth order polynomial relationship between carbon dioxide and the fluorescence emission over the span of 0-30% CO_2 , and a linear response in the range of 0 - 1% CO_2 as was predicted given the choice of the phase transfer agent (tetraoctylammonium hydroxide).

• The interference effects of gases which are typically found within diesel engines were also tested. Carbon monoxide and nitric oxide in balance nitrogen were found to have no significant effect on carbon dioxide sensing with the fiber within the detectable limits of the experiment. Nitrogen dioxide, at low concentrations, was found to cause a signal decrease, indicating higher than expected carbon dioxide levels using the fiber sensor. At higher concentrations of nitrogen dioxide, the fiber sensor suffered a permanent drop in fluorescence emission, and eventually led to the destruction of the sensing capabilities of the fiber sensor.

• Both environmental temperature and humidity were found to have an effect in decreasing the sensitivity of the fiber sensor by decreasing the overall fluorescence signals. For the case of temperature, this is believed to be caused by an increase in the probability of vibrational modes of relaxation of the excited electronic states. The increase in temperature increases the probability of the decay from excited electronic states into vibrational energy, which decreases the fluorescent signal.

• Within a diesel engine environment, for temperatures below 50 °C the fiber sensor is able to detect small changes in carbon dioxide concentration. Above this threshold temperature, a steady decrease in the fluorescence signal is observed. After 24 hours, the fiber sensor had been rendered inoperative by a change in composition of the sensing layer.

Chapter 6

Recommendations for future work

Based on the present study, further work can be recommended in order to further explore the capabilities of the present fiber optic carbon dioxide sensor.

For the composition of the sensing layer, the chemicals that were used were chosen to have the best chance of success given the literature which was reviewed. However, it was found in other works that the phase transfer agent, tetraoctylammonium hydroxide is the most sensitive in the region from 0 - 1%, while other phase transfer agents are more sensitive in different regions for sol-gel monoliths [C. von Bültzingslöwen et. al, 2002]. By introducing a new phase transfer agent which has higher sensitivity in the range typical of the carbon dioxide levels it may be possible to obtain a sensor with better resolution in the working area of the carbon dioxide levels of diesel engine exhaust gases.

Furthermore, in order to obtain more reproducible and accurate results, it would be beneficial to have a working motion controller in order to dip cast the fibers, instead of the method outlined above where they were hand dipped. This would yield uniformly thin layers, which would have more consistent effects across fibers. The equipment itself could be improved. Currently the spectrometer that was used was a small compact spectrometer obtained from Ocean Optics, which connected to a computer via USB, which is also how it was powered. As computer load increased during the data acquisition, it is likely that the power being supplied to the USB interface and the spectrometer was also affected, causing fluctuations and an increase in noise. Perhaps the use of a separate spectrometer or photodiode for intensity measurements with a more stable power supply would reduce the amount of noise being generated from the intensity measurements, enabling a better representation of what the true lowest detection limit would be. Using equipment with a higher spectral resolution would be beneficial for sensing the blue shifting effect, in order to determine if it might actually be feasible as a method of carbon dioxide detection. To have a greater certainty in the true lower detection limit of the fiber optic sensor a dedicated carbon dioxide sensor with better accuracy than 0.3% would be required.

An adjustment to the environmental chamber could also be made which would enable work to be done to determine response time of the sensor. Using a much smaller volume chamber with a more regular shape that could easily and quickly be purged with a new gas would be ideal, as a current gas changeover times from this study is on the order of a minute due to the irregular shape.

Given that it is still unknown whether the hydrocarbons do have an effect on the sensor, it would be beneficial to test the interference effects of hydrocarbons by performing the same type of tests as above at the 150 - 200 ppm level of propane, or by evaporation of a heavier hydrocarbon such as decane or even diesel. Also, it would be beneficial to test the effects of nitrogen dioxide at elevated temperatures, in order to determine which of these two effects, or potentially even an unknown third option, caused the decreasing signal during the diesel exhaust gas environment test and led to the destruction of the fiber sensor the following day.

In order to improve the performance of the fiber sensor in the diesel environment, it would be beneficial to place the sensor after the catalytic converters that are found in most diesel engines. The catalytic converters are downstream of the engine, after an air pump to allow for the conversion of carbon monoxide, hydrocarbons and nitrogen oxides into carbon dioxide, water, nitrogen and oxygen, and also decreases the temperature of the exhaust gases. Placing the sensor here would allow it to operate in an environment that would remove the damaging nitrogen dioxide, and also reduce the amount of hydrocarbons in the exhaust gas. A filter using a gas permeable membrane which could also be added as a second protective layer could also be used. In the literature review (Chapter 2) Teflon AF2400 was described as having very good selective properties for filtering out hydrocarbons, should there be an effect, and would also be effective in preventing soot build up upon the sensing tip. The filtering properties of this material on nitrogen dioxide could also be explored to see if it would be able to protect the sensor as well. Since the teflon is also able to be dip-coated, it could provide an ideal filter to be easily added upon the sol-gel material.

Lifetime testing would also be beneficial. It would be possible to recirculate gases within an enclosed chamber to simulate long term effects of specific gases, namely nitrogen dioxide, but if the flow rate was high enough particulate could be added and would become fluidized. This would more reasonably describe the scenario inside the diesel engine and any erosion effects or cumulative nitrogen dioxide effects could be explored, as well as hydrocarbons, to determine if there is any effect.

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Appendix A

Brief Summary of Diesel Exhaust Treatment Project

Previous to starting work developing the optical carbon dioxide sensor, work was done to develop a method for in-situ treatment of diesel engine exhaust gases. As mentioned in this thesis (Chapter 3), diesel engine exhaust gas contains CO, NO and NO₂. NO₂ is a harmful gas known to cause acid rain, have harmful effects to humans via production of smog, and assist in ozone depletion. NO is easily oxidized in air to form NO₂. For these reasons, mitigation of the emission of these gases from diesel engines is of great concern. Currently, in most automotive applications, there is treatment of these gases by use of a catalytic converter which allows for decomposition of these compounds into N₂ and O₂. There are two catalytic converters within the exhaust stream, the first is an oxidizing converter used to convert any unburned hydrocarbons into water and carbon dioxide ; carbon monoxide to carbon dioxide and nitric oxide to nitrogen dioxide. The second catalytic convertor is a Selective Reduction Catalyst, it is used to reduce the nitrogen dioxide into nitrogen and oxygen, however it requires the use of a reduction gas to work. This would require the need of storage of a reduction gas to be transported with the vehicle in order for the catalyst to work, which is the case for large diesel-powered ships and for some industrial processes where high temperature combustion takes place. However, for consumer-level passenger diesel vehicles, this is less than desirable.

A potential solution to this problem lies in the use of non-thermal plasma treatment of the exhaust gases, combined with an electrohydrodynamic atomized mist of a dense hydrocarbon to act as a reducing gas.

This project followed three main steps. The first was the characterization of nonthermal plasma treatment system. The non-thermal plasma was generated using pulsed high voltage discharge, where a high voltage discharge was generated through use of an ignition coil which was charged using a 12 volt DC power supply. This is ideal because the ignition coil is a part which is already found in many automobiles, and the alternator generates 12 V DC from the diesel engine. Allowing air flow through hollow electrodes, and applying the high voltage, it is possible to generate a nonthermal plasma at much higher voltages, due to the flow stabilization of the discharge. The electrodes were arranged within a ring annulus, held within an insulator. The air flow prevents any ion buildup by pushing the gas, which prevents spark discharge, and maintains the discharge within the regime of corona discharge, or non-thermal plasma discharge. In order to characterize the discharge, current and voltage waveforms were observed as well as optical emission while the varying experimental parameters where the input charging voltage, the stabilizing air flow rate and the discharge frequency.

The purpose of the work was to obtain the maximum discharge power, while observing the optical emission to determine the optimal morphology of the discharge.
The full details of this work are presented in the paper entitled "Discharge Characteristics of Ring-Type Flow Stabilized Pulsed Corona Radical Shower Systems." which was accepted to IEEE Transactions on Industry Applications and is awaiting publication (January, 2010 acceptance date). This work was authored by V. Lakhian, F. Bocquet, D. Brocilo, G.D. Harvel, J.-S. Chang, D. Ewing, M. Watanabe, H. Matsubara, H. Hirata and S. Matsumoto, P. Fanson. It was also presented by myself at the IEJ-ESA-IEA-IEEE-IAS-SFE 2009 Electrostatics Joint Conference at Boston University on June 18, 2009, and the CAGE Club Student Conference on Electrostatics at University of Ontario Institute of Technology in August of 2008. The CAGE club presentation was co-authored by François Bocquet, but presented by myself. The work was done as a part of his requirement for the B. Tech program at L'Université Joseph Fourier, Grenoble, France.

The second stage of this work was to characterize the gaseous and liquid byproducts which would be created by injection of the dense hydrocarbon, decane ($C_{10}H_{22}$), through a Plasma ElectroHydroDynamic Atomization needle (PEHDA). It is called as such because by applying a pulsed high voltage to the needle, a plasma is generated at the needle tip and electrohydrodynamic atomization takes place, atomizing and spraying the decane in a fine mist. This mist then passed through the aforementioned Ring-type Corona Discharge Radical Shower (RCDRS), where the highly reactive plasma species interacted with the decane mist. This experiment showed that the PEHDA-RCDRS systems combined had fuel reforming capabilities.

The gaseous by-products were examined by FTIR and showed the production of methane, acetylene,ethylene, ethane and propene as well as various amines. The liquid by-products were analyzed using a Gas Chromatograph - Mass Spectrometer and showed formation of 9 carbon chain hydrocarbons, and the formation of cyclic bonds. The amounts of these byproducts were also found to increase with increasing discharge voltage on the PEHDA and RCDRS systems. This work is explained in detail the paper entitled "Fuel Reforming Characteristics of Electrohydrodynamic Atomization - Flow Stabilized Pulsed Corona Discharge Radical Shower Systems" by J.-S. Chang, V. Lakhian, D. Brocilo, G.D. Harvel, D. W. Ewing, M. Watanabe, H. Matsubara, H. Hirata, S. Matsumoto, and P. Fanson. This paper was accepted to the Ukranian Journal of Physics and was presented by Dr. Jen-Shih Chang at the Third Central European Symposium on Plasma Chemistry in August, 2009.

The final stage of this project was to employ both of these two systems within the diesel exhaust environment in conjunction with the NO_x Storage and Reduction Catalyst (NSRC). The NSRC is a Selective Reduction Catalyst composed of Barium Carbonate and platinum upon an alumina substrate. Nitrogen dioxide replaces the carbonate and builds a barium nitrate layer surrounding the catalyst. The platinum and the presence of the injected ionized air from the RCDRS both act to oxidize the nitric oxide to nitrogen dioxide, and also has the beneficial side effect of oxidizing a portion of the unburnt hydrocarbons and carbon monoxide as well. The barium nitrate layer builds upon the catalyst until saturation is achieved. At this point, liquid decane is atomized through the PEHDA and interacts with the non-thermal plasma being generated by the RCDRS to create high temperature combustion, as well as a reducing gas. The combination of high heat and reduction capabilities of the gas result in the barium nitrate layer releasing a portion of the nitrogen dioxide, however a majority of it is reduced to form nitrogen and oxygen, and the byproducts of the reducing gas form water and carbon dioxide. This leaves the catalyst in a regenerated Figure A.1: Experimental Apparatus for PEHDA-RCDRS-NSRC Experiment [Presented at CAGE Club Conference, 2009]



Engine Load: 2.8 kW Engine Mass Flow Rate: 47 kg/Hour Tg A = 295 °C, Tg B and TgC = 225 °C form where it is once again barium carbonate, and the process can be repeated.

A schematic of the apparatus for this experiment is shown in Figure A.1. Two combustion gas analyzers were used to determine the concentration of O_2 , CO, NO, NO_x , NO_2 upstream and downstream of the PEHDA-RCDRS-NSRC system. Electrical heating tape was applied as shown in the figure to increase the temperature to approximately $225 - 295^{\circ}$ C, depending on the location due to the injection of cold air by the RCDRS. The mass flow rate was measured using Venturi flow meters and the engine was operated at an electrical load of 2.8 kW with a mass flow rate of 47 kg/hour. When in use, the PEHDA-RDCRS system were operated under the optimal conditions found in "Fuel Reforming Characteristics of Electrohydrodynamic Atomization - Flow Stabilized Pulsed Corona Discharge Radical Shower Systems" by J.-S. Chang, V. Lakhian, D. Brocilo, G.D. Harvel, D. W. Ewing, M. Watanabe, H. Matsubara, H. Hirata, S. Matsumoto, and P. Fanson.

The data from the upstream and downstream combustion analyzers are given in Figure A.2 and Figure A.3, respectively. The transients of O_2 , CO, NO, NO_x , NO_2 and hydrocarbons versus time are shown. Labelling is done to show the the order in which the equipment was turned on. Initially, the diesel engine is started and allowed to rise to its steady state temperature, after 16 minutes, with the NSRC and all equipment in place, with air flow constantly on from the RCDRS system though no electrical discharge was taking place.

Upstream of the treatment system, the results show a fairly constant level of NO_x of 550 ppm, and a steadily increasing CO content. Downstream of the treatment system, the NSRC has been able to reduce this concentration by 70 ppm to 480, and a steady CO level of 420 ppm, higher than the initial levels of CO upstream of

Upstream of PEHDA-RCDRS-NSRC System:



Figure A.2: Transients of Diesel Exhaust Gases upstream of the PEHDA-RCDRS-NSRC system [Presented at CAGE Club Conference, 2009]

Downstream of PEHDA-RCDRS-NSRC System



Figure A.3: Transients of Diesel Exhaust Gases Downstream of PEHDA-RCDRS-NSRC system [Presented at CAGE Club Conference, 2009] the treatment system. However, after the 16 minutes warm up period for the diesel engine, the RCDRS system was turned on and a drop in the amounts of NO, NO_x and CO of 20% was recorded. The RCDRS was turned off, and the levels of these gases began to rise again. The RCDRS system was again turned on, and the 20% reduction in these harmful gases was once again observed. Meanwhile, the amount of NO₂ was gradually decreasing until it reached a steady state value at t = 52 min, due to the saturation of the NSRC catalyst. At this time, the regeneration gas was produced by injecting atomized decane, through the PEHDA, which was able to regenerate the storage capabilities of the NSRC again, as is noticed by brief spike in the amount of NO_x at the time of injection, and its ability to decrease the subsequent NO_x levels after this regeneration by a further 20 ppm.

The results of this experiment showed that the RCDRS system alone was able to reduce the amount of NO_x and CO in the diesel exhaust gas stream by approximately 20%. The NSRC was able to store and reduce a small amount of the NO_x within the system, but compared to the effects of the RCDRS this was minimal.

This work was also presented at the CAGE Club Student Conference on Electrostatics at McMaster University in August 2009.