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Online monitoring of exhaust emissions using mid-infrared spectroscopy

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Abstract. Existing automotive sensors do not quantify the levels of pollutants entering the atmosphere; instead they merely indicate that pollution is occurring. However to meet European legislation on emission control, it is necessary to quantify the levels of each type of pollutant leaving the exhaust of a vehicle. This paper discusses the development of an optical sensor suitable for the detection of gas emissions from a motor vehicle based on mid-infrared spectroscopy. Initial tests to detect carbon dioxide using low-cost mid-infrared components are described and a detection system, which could be fitted to an automobile, is outlined.

1. Introduction

Pollutants are substances that are perceived to have an adverse effect on the environment and either directly or indirectly on human health. Airborne pollutants can be gaseous or suspended particulate matter (liquids or solids ranging in diameter from 10nm to 100µm). Pollutants can be natural gaseous emissions such as carbon dioxide produced in animal and plant respiration, sulphur dioxide from geysers, or suspended matter such as salt spray or dust from volcanic eruptions. However in densely populated areas studies have shown that greater than 90 percent of the volumes of airborne pollutants are the result of human activities. Sources of pollution in these areas include combustion processes, solid waste disposal, construction and demolition. With an increasing number of vehicles on our roads annually the internal combustion process in a land transport vehicle is responsible for a significant amount of pollution in these densely populated areas [1]. The pollutant emissions from a vehicle include carbon monoxide (CO), oxides of nitrogen (nitric oxide, NO, and nitrogen dioxide, NO₂), hydrocarbons (HC), smoke particles (diameters of 0.05µm to 1µm) and also particulate matter. CO is produced when an engine does not completely burn fuel and is poisonous to humans at high concentrations (greater than 400 parts-per-million). NO is formed in an engine by the reaction of nitrogen present in fuel with oxygen (O₂) at very high temperatures (>1000°C). Although NO is not considered to be a health concern itself it further oxidises to NO₂ which is believed to be a pulmonary irritant. Carbon dioxide (CO₂) although not strictly speaking a pollutant, is also produced by exhaust gas emissions. The excess of CO₂ produced by exhaust emissions is considered to be responsible for the climate change known as the “Greenhouse Effect” [2].

In order to protect human health and limit damage to the environment, the European Commission has introduced a series of directives to automobile manufacturers to limit levels of exhaust emissions

entering the environment [3]. The first of these directives was implemented in 1992 and is referred to as *Euro I* while the latest, which will be implemented in 2008, is *Euro V*. Each successive directive has lowered the acceptable amounts of CO, NO_x, HC, particulate matter and smoke which may enter the atmosphere from land transport vehicles. The Euro I, for example, stated that the acceptable levels of CO leaving a heavy goods vehicle (HGV) as 4.5 grams per kilowatt hour (g/kWh). In contrast to this the Euro V states that a HGV may only have 1.5g/kWh of CO leaving its exhaust [4]. Figure 1 illustrates the decrease in acceptable emission levels.

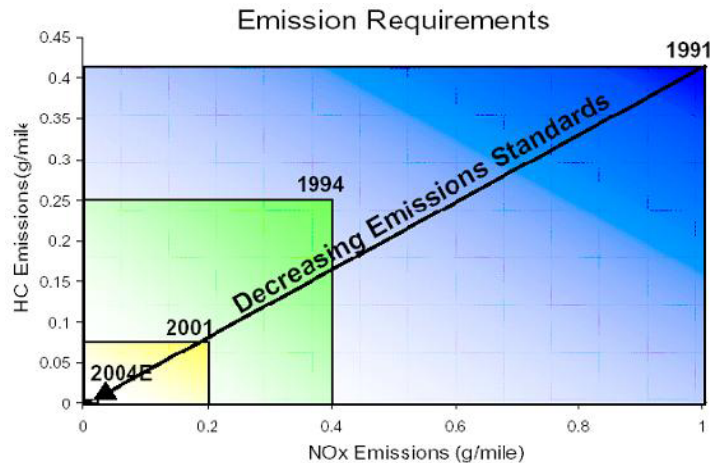


Figure 1. The decrease in acceptable emission levels in recent years

2. The requirement for improved automotive sensors

2.1. *The Lambda Sensor.* The sensor that is primarily used in automobiles to detect if pollution is occurring is the Lambda sensor. The Lambda sensor compares the ratio of ambient air to the amount of oxygen in the exhaust of the vehicle and signals to the engine if the ratio is correct. If oxygen is present in the exhaust of an engine it indicates that the engine is burning fuel, however if there is an absence of oxygen, pollution can be assumed to be taking place, as the engine is not burning fuel correctly. If the ratio of fuel to air is correct then the output voltage of the sensor will be low [5]. On the other hand if the vehicle is not burning fuel correctly and pollution is occurring then the output voltage will be high. The Lambda sensor may fail prematurely if it becomes clogged with carbon, or is contaminated by silicone from an antifreeze leak. In addition to this as the sensor deteriorates with age, its response to changing fuel ratios becomes slower. The malfunctioning of the sensor due to contamination or ageing leads to an increase in the fuel mixture resulting in higher levels of pollution or it can lead to the engine misfiring. If the fuel mixture is excessively high for a long period of time, the catalytic converter that cleans the exhaust emissions will become damaged [6].

It should also be noted that the Lambda sensor does not satisfy European emission control laws as it merely indicates if pollution is occurring or not. As was noted in the preceding section, the specified levels of a particular pollutant are quite exact and in order to prove that the standards for each substance are being met it is necessary to develop a new type of sensor.

2.2. *The NO_x Sensor.* The NO_x sensor was designed to detect the presence of nitric oxide (NO) and nitrogen dioxide (NO₂) in exhaust emissions at temperatures of greater than 600°C [7]. It can measure the gases down to parts-per million (ppm) levels and is therefore suitable for the quantifying the levels of each gas leaving the exhaust as required by the aforementioned emission control laws. However in a similar manner to the Lambda sensor the NO_x sensor becomes poisoned by the harmful gases it monitors which reduces its effectiveness and eventually prevents it working altogether. The NO_x sensor also has cross-sensitivity to other gases such as oxygen in the 20-80% range and is unable to

discriminate between NO and NO₂. It is also clear that it only addresses two out of several gaseous pollutants that are required to be monitored.

3. The detection of gases based on optical absorption spectroscopy

3.1 *Absorption spectroscopy and its applicability to exhaust emission detection.* The majority of compounds containing covalent bonds, whether organic or inorganic, absorb electromagnetic (e.m.) radiation. This occurs based on different mechanisms whose effects are manifested throughout the e.m. spectrum. For example absorption in the ultraviolet region of the spectrum occurs due to the excitation of electrons in molecules while absorption in the microwave region is due to a change in rotation of the bonds in a molecule. However it is the infrared region that is of interest in this study, as the majority of pollutant gases have absorption lines in this region. Absorption in the infrared region occurs due to the vibration of the bonds of a molecule [8]. The absorption spectrum of each species is unique and can be used to identify and quantify the presence of that species. The fundamental absorption lines of pollutant gases such as carbon monoxide, nitric oxide and nitrogen dioxide are all located in the mid-infrared region of the spectrum (above 2 μ m). Carbon dioxide also has high absorption in the mid-infrared region of the spectrum at 4.23 μ m [9].

In order to calculate the attenuation due to absorption of an infrared beam passing through a sample of gas, the Beer-Lambert Law is used. The Beer-Lambert law states that the transmittance of radiation, T, through a sample of concentration c is:

$$T = I/I_0 = 10^{-cd}$$

where I₀ is the incident radiation, I_t is the modulated output radiation, ϵ is the molar absorption coefficient and l is the path length of the sample [10].

In addition to being capable of identifying each gaseous pollutant simply by analysing its signature absorption spectrum a further advantage of absorption spectroscopy is that the components used do not have direct interaction with the measurand. The emitter and detector can be located behind infrared transparent windows. The beam from the emitter can be launched through the window into the gas sample where it undergoes absorption and can return through a second window to the detector. This should allow any absorption based automotive sensor developed to have a longer lifetime than the existing state of the art.

3.2 *Mid-infrared detection reported to date.* Mid-infrared spectroscopy for the detection of gases has been widely reported in the literature. The detection of nitrogen dioxide down to ppm levels using a mid-infrared LED has been reported by Wang et al [11]. However the mercury cadmium detector used requires cryogenic cooling which would make this scheme unsuitable for use in a vehicle. Smith et al reports the use of a mid-infrared filament lamp to detect the presence of carbon dioxide gas with a dual element thermopile as the detector [12]. The thermopile detector responds to steady-state radiation and while it is suitable for use in gas analysis when positioned close to a steady-state emitter with background radiation of much lower relative intensity, it would not be suitable for use in the exhaust environment where there is high steady state background radiation as it would not be capable of distinguishing the infrared signal from the ambient heat.

3.3 *The pyroelectric detector.* Clearly a detector is required which does not need to be cooled and is insensitive to background radiation. The pyroelectric detector only responds to a pulsed signal and is insensitive to steady state ambient radiation making it quite suitable for detecting output of a pulsed infrared source in a hot environment such as an exhaust manifold. A pyroelectric detector consists of a sensor crystal and two electrodes. When the sensor crystal is heated the charge is transferred to the electrodes and a current flows. If infrared radiation due to steady state heat is incident on the sensor no additional current is generated, therefore the pyroelectric detector only responds to a varying infrared

source. Typically the sensor element constructed from lithium tantalite and the tiny current it generates is converted to a voltage using a field effect transistor (FET). A narrow band optical filter fitted over the sensor element can provide selectivity to the wavelength range of interest.

4. Experimental work carried out to date

4.1 *Experimental set-up.* The emitter that has been used to date in our experimental work is a CalSensors SVF360-8M (3) broadband filament emitter. It was chosen due to its relatively high optical power, when compared with mid-infrared LEDs in particular, and also as it can be used to address a number of absorption lines in the mid-infrared region. Its spectral output of 0.13 to 10 μm means that it can be used to detect the absorption lines of CO (4.6 μm), CO₂ (4.3 μm), NO (5.2 μm) and NO₂ (6.2 μm). It has an emissivity of 88%, consumes 2W of electrical power and emits a blackbody spectrum. It is fitted with a calcium fluoride filter (CaF₂) to limit its spectral output from 0.13 to 10 μm .

It was decided to carry out the initial tests using CO₂ from a cylinder as it has the highest absorption in the mid-infrared region of the gases mentioned in the preceding paragraph.

The first pyroelectric detector used in our experimental work was a Perkin-Elmer Lhi807TC, it is a single channel detector consisting of a capacitive element and a JFET amplifier and it has an unfiltered responsivity of 320 V/W. It was fitted with a narrow band filter centred on the CO₂ absorption line at 4.23 μm to make it selective to the gas of interest.

Figure 2 shows the experimental set-up. A specially designed gas cell, 110mm in length by 75mm in diameter is used to hold the sample of CO₂ gas. Magnesium fluoride windows with a spectral range of 0.11 μm to 7.5 μm are sealed into each end of the seal. The pulsed infrared beam from the SVF360-8M emitter passes through the cell where it undergoes absorption by the CO₂ present. An increase in the voltage at the detector is noted as the concentration of the CO₂ in the cell decreases. The concentration is monitored using a Kane-May Quintox gas analyzer.

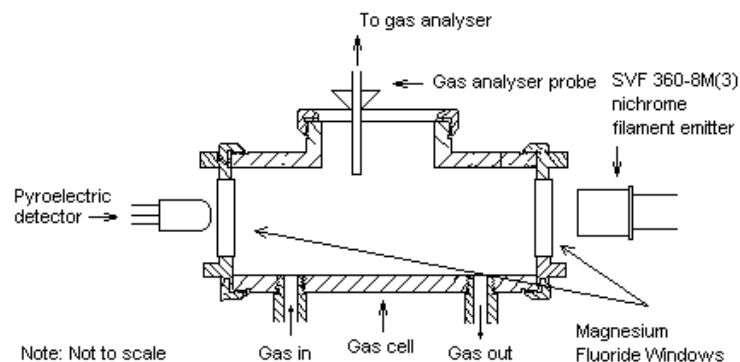


Figure 2 Detection of carbon dioxide using mid-infrared spectroscopy

4.2. *Results.* Figure 3 shows the results obtained when the concentration of CO₂ in the cell was decreased from 50% to 0 and the output voltage of the Perkinelmer LHi 807 pyroelectric detector was monitored.

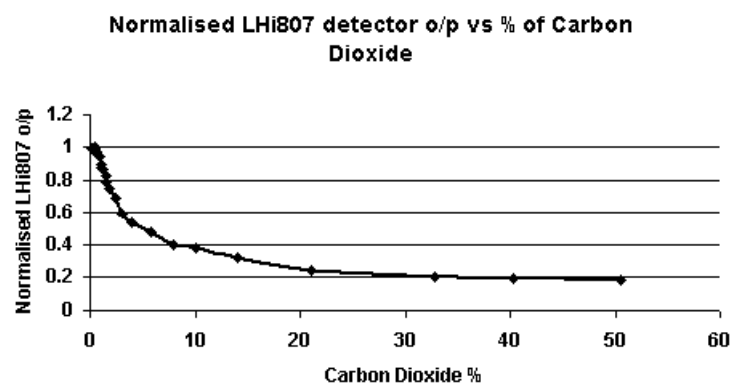


Figure 3. Variation of Lhi807 pyroelectric output with increasing percentage of carbon dioxide

The drop in output voltage of the pyroelectric detector with increasing concentration is similar to that of a decaying exponential as would be expected if absorption of infrared is occurring and the Beer-Lambert Law is being obeyed.

5. A possible application of the mid-infrared gas sensor

This sensing system is particularly suited to the specific application in which microwave plasma is used to clean harmful emissions from petrol and diesel engines [13]. This system has been developed for use in automobiles in place of the conventional three-way catalyst which, in a similar manner to the Lambda sensor, is prone to fouling by the substances present in the exhaust manifold. The new system can reduce the amount of back pressure exerted by the conventional catalyst leading to a significant fuel saving (up to 10%) and also greatly reduces the quantities of pollutants leaving the exhaust system. It should be possible to mount the mid-infrared optical gas sensor on the side of the exhaust manifold as shown in the Figure 4.

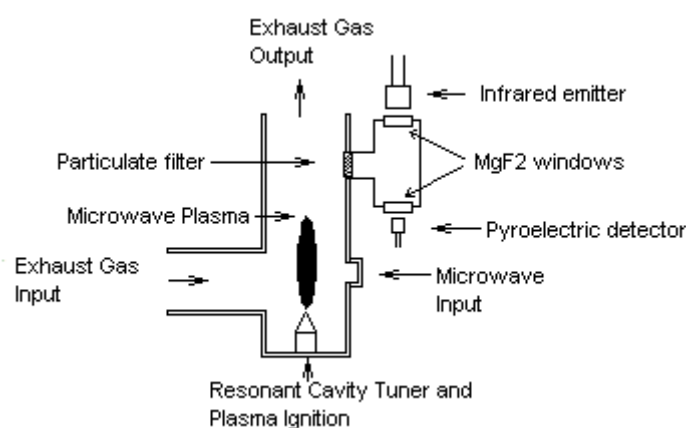


Figure 4. The mid-infrared gas sensor applied to a microwave catalytic converter

6. Conclusions and Future Work

A case was put forward in this paper for the requirement of a sensor that can quantify the levels of gaseous exhaust pollutants entering the atmosphere. The suitability of mid-infrared absorption

spectroscopy for this task was also discussed and a system to conduct detection in this wavelength range was described. The initial results from the experimental set-up using carbon dioxide from a cylinder indicate that this method may be feasible for use with other gases. The next phase of the investigation is to test the sensing system using other gases such as nitrogen dioxide that also have high absorption in the mid-infrared region of the spectrum.

Following this it will be necessary to test the sensing system using emissions from an engine. If these trials prove successful it may be possible to apply the detection scheme in conjunction with the microwave catalytic converter described in the previous section.

7. Acknowledgments

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