Dual Channel Double Wavelength Method in Optical Fiber-Based Gas Sensor for Carbon Dioxide Detection

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Abstract—**A novel double wavelength strategy in optical fiber-based sensor for detection of carbon dioxide (CO_2) gas is presented. The detection strategy works based on an open-path direct absorption spectroscopy in the mid-infrared (mid-IR) wavelength range. The sensor system comprises of a broadband filament emitter acting as the Infrared (IR) light source, Chalcogenide Infrared (CIR) Optical Fibers, two Pyroelectric detectors which been fitted built- in with a limited bandpass CO_2 channel and a reference channel. The sensor additionally uses calcium fluoride ($CaF2$) limit bandpass (NBP) channel for recognition of CO_2 gas without cross-sensitivity to different gasses exist in the surrounding environment. The correlation amongst test and computed sensor yields are additionally exhibited.**

Index Terms—**Beer-Lambert Law; Carbon Dioxide Gas; Environmental Monitoring; Fiber-Based Gas Sensing; Mid-Infrared Spectroscopy.**

I. INTRODUCTION

Environmental concerns have prompted the requirement for harmful gas discharges from different sources, for example, industry and engine vehicles, to be precisely observed and controlled [1]. Carbon dioxide gas emissions from the inner burning of motor vehicles are known to be a prime contributor to the present increment in worldwide ozone-depleting substance. Ordinary car contamination sensors neglect to meet checking prerequisites as indicated by the European Commission for various reasons, for example, not having the capacity to distinguish and evaluate singular toxins from the fumes gas stream. Consequently, much work has been done in the field of optical fiber-based gas detection because of many points of interest it offered compared to other conventional techniques [2]. For instance, using optical fiber will enable the sensor's emitter and detector hardware to be set at safe distance from a very corrosive and challenging condition where the measurement is conducted [3]. The optical fiber-based gas sensor system is appropriate for use of gas measurement and monitoring due to their robust nature and low susceptibility to chemical and electromagnetic interference. Also, sensor system based on optical fibers have been appeared to withstand extraordinary harsh conditions which exist in an exhaust system of vehicles [4].

II. PRINCIPLES

The developed optical fiber gas sensor system works based on detection of dual wavelength technique. The operation of the sensor depends on two wavelength channels at the detector. The first wavelength channel is the active channel where it monitors the changes of the intensity due to the changes of the concentration of the gas under study. The second channel is for the reference. The measured concentration of the gas in the gas cell is derived from the equation which related to the proportion between the Active signal and the Reference signal.

Figure 1 demonstrates the relationship of the Active channel, Reference channel and the Signal Ratio of the yields of the created gas detecting framework. The yield power of the reference is measured at the wavelength of $3.95\mu m$ where there is no critical absorption of any gas here. At the point when there is an outside interference, for example, a vibration, or small movement of the optical fiber, the output signal measured at both Active channel and Reference channel is influenced.

However, the Signal Ratio output will not change because of the outer interference. Accordingly, it is conceivable to eliminate the interference signal from the outside environment by utilizing this technique [4,5].
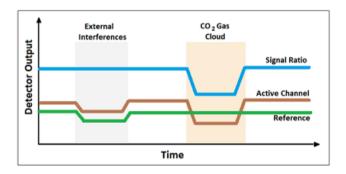

Figure 1: The relationship of the Active channel, Reference channel and the Signal Ratio of the outputs.

III. SYSTEM DESCRIPTION

The schematic diagram of the implementation of the absorption spectroscopic of the developed optical fiber-based gas sensing system is as shown in Figure 2 as follows.

The chosen method of gas absorption spectroscopy for analysis in this study involves the use of a broadband infrared light source transmitted through a 1-meter length of low-loss chalcogenide infrared fiber before interacting with the gas under study in the single pass gas detection cell.
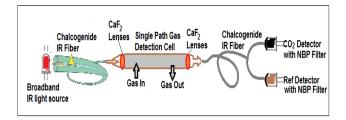
Figure 2: The implementation of the optical fiber-based gas sensor system

In the setup, the Calcium Fluoride (CaF_2) lenses are used to collimate the light beam across the cell and then focus into the detector in order to improve the process of transmission and coupling of the infrared signal between the gas detection cell and the low-loss chalcogenide infrared fiber (CIR), and vice versa. The end of the second CIR receiver fiber was placed at the effective focal length of the second Calcium Fluoride lenses so that the light signal from the gas chamber will transmit efficiently into the low-loss chalcogenide infrared (CIR) receiver optical fiber.

After the infrared signal has interacted with the gas of interest in the detection chamber, it is then directed to the infrared signal detector through another set of Calcium Fluoride collimating lenses and a 1-meter length of 1 X 4 chalcogenide fiber bundle. One of the fiber bundle output is connected to the pyroelectric detector fitted with carbon dioxide narrow band-pass (NBP) optical filter with a bandwidth of 4.0µm and 4.5µm, while the other output is connected to the reference NBP filter.

In the experimental test conducted, various concentrations of the gas under study were input into the single path gas cell. The flow and concentration mixture of the gas under study was controlled using a pair of Mass Flow Controller (MFC). The signal at the CO_2 detector and Ref detector were measured in terms of electrical voltage using NI DAQ card attached to a computer.

The Narrow Band Pass filter attached to the CO_2 detector was different to the one attached to the Ref filter in terms of the spectral wavelength region of the filter. The NBP filter at the CO_2 detector has a central wavelength at around 4.24µm that matches the absorption characteristic wavelength of the gas under study. On the other hand, the NBP filter of the Ref detector has a central wavelength at around 3.95µm, where there is no absorption characteristic of any other gas present in the environment of intended gas detection. The NBP filter at the Ref detector serves as a control and comparison at the output signal so that only changes of output voltages due to the changes of the concentration of the gas under study are considered. The usage of the NBP filter in the setup has made possible the exclusion of changes of the output voltage which due to other factors such as vibration or misalignment [6].

The detected output voltage at the CO_2 detector corresponds to the intensity of the detected infrared light signal within the spectral region of the absorption line intensities of the gas under study. In this analysis, the relationship between the received output voltage and the concentration of the target gas present in the gas cell is simulated. The simulation results are then related to the Beer-Lambert law [7].

IV. LIMITATION AND DEVIATION CASE OF THE LAW

The Beer-Lambert law is the principal law in the field of analytical spectrometry. In general, the Beer-Lambert law provides a direct nonlinear relationship between the Absorbance (A) of a molecule to the concentration (c) and the path length (l) propagated by the light signal in the sample [8]. This relationship is true for most of the cases, but if we limit the Beer-Lambert law to very small changes of absorbance (A), such as a very small concentration, then the law can be approximated to have a linear relationship. However, in certain cases, the Beer-Lambert relationship has some limitations and deviates from the ideal [9]. These deviations from the Beer-Lambert law can be classified into three main categories; namely, real limitations to Beer-Lamberts law, instrumental deviations and chemical deviations [10].

The Beer-Lambert law should only be applied to a dilute solution of less than 10mM. When applied to high concentration solution of more than 10mM, there is a high probability that the molecules of the solution can affect the charge distributions on the neighboring species in the solution, thus affecting the absorbance process of the light beam. It is also possible that the molecules will create a screen for other molecules and prevent them from the incident light [11], while causes scattering to increase. Those factors contribute to the limitation of the Beer-Lambert law.

Chemical deviations happen when chemical phenomenon involving the analyte molecules occur due to interaction with the solvent to form compounds that have different light absorption characteristics. An example of this behavior is the ionization reactions of acidic or basic indicators in a solution. The increase of the indicator concentrations can affect the pH of the solution, thus changes the molar absorptivity of the solutions [12].

Instrumental deviations happen because of the way in which the Absorbance (A) measurements are conducted. Basically, there are two main types of instrumental deviations, one is due to the polychromatic light source and another one is due to the effect of the stray light. The Beer-Lambert law is only valid for measurement of the Absorbance with monochromatic radiation [11]. However, in practice, it is common that a polychromatic light source is used together with a grating or an optical filter in order to produce a purer monochromatic beam from this source.

Figure 3 shows the comparison between the absorbance when measuring at a maximum wavelength of Absorbance (Band A) compared to the Absorbance when values are not at maximum absorbance (Band B). It can be seen that measurement at peak of the Absorbance provide very minimal change in Absorbance per unit change in wavelength, thus minimizing the difference in the value of the Molar Absorptivity, therefore resulting in the relationship in the Beer-Lambert law to obtain a straight line (Figure 3(b) – Band A) [12].
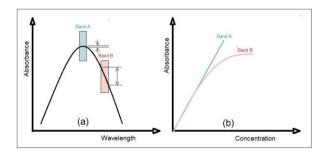

Figure 3: (a) The comparison between a monochromatic (Band A) and a polychromatic radiation of light source (Band B) and (b) the deviation in Beer-Lambert law due to polychromatic light radiations.

When measuring the Absorbance at wavelength other than the lambda max, it can be seen that there is a large change in Absorbance per unit change in wavelength, thus the difference in Molar Absorptivity is maximum, therefore resulting in the deviation from the law (Figure 3(b) – Band B) [11].

Stray radiation or scattered radiation, on the other hand, originates from within the instrument that is outside the nominal wavelength band of interest. Usually, the stray radiation is totally different from the operating wavelength band where Absorbance is measured. It is not uncommon that the radiation used in Absorbance measurement is usually corrupted with minute quantities of scattered or stray light. Usually, this radiation originates from the reflection and scattering from the surfaces of mirrors, lenses, gratings, windows and filters. Stray radiation is totally different with the principal radiation in terms of wavelength and may not have propagated through the measured molecules. If the molecules absorbed at the wavelength of the stray light, a deviation of Beer-Lambert law will occur similar to the deviation that is due to the effect of polychromatic radiation [12].

V. CARBON DIOXIDE CROSS SECTIONS

Carbon dioxide gas has shown a strong characteristic line intensity in the mid-infrared wavelength range due to its molecular vibration. It has two major absorption peaks; one is in the near-infrared region at around 2.6µm, while the other is in the mid-infrared region at around 4.26µm wavelength. The absorption cross section line intensities data of carbon dioxide gas is shown in Figure 4 for (a) near-infrared wavelength region at around 2.6µm and (b) mid-infrared wavelength region at around 4.26µm. The data is derived from the HITRAN2008 database [13].
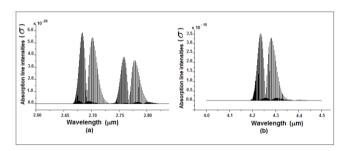

Figure 4: (a) near-infrared wavelength region at around 2.7 *µ*m (b) mid-infrared wavelength region at around 4.26 *µ*m from the HITRAN2008 database.

It is evident from these figures that carbon dioxide gas has a double- peak characteristic cross-section line intensities at around 4.3µm. The highest peak is at 4.23 µm with 3.52×10^{-18} line intensities while the second highest peak is at 4.28µm with 3.31×10^{-18} line intensities.

VI. SIMULATION OUTPUTS

From the resultant transmittance spectra shown in Figure 4, the expected optical sensor output which related to the Beer-Lambert law can be calculated. The same detected output signals can also be presented in terms of the optical Absorption which can be calculated according to the Beer-Lambert Equation [14].

Consequently, the output of the theoretical analysis plotted against the concentrations of the gas is shown in Figure 5. Using computer program software, the theoretical analysis output is fitted to the simulated detected outputs of the gas sensing system. The fitted graph and the related equation are as shown in the following Figure 5.
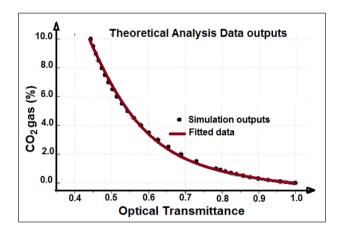

Figure 5: Theoretical analysis of optical transmittance data outputs from the developed sensor system.

Figure 6 shows the comparison between the theoretically calculated normalized sensor outputs for the carbon dioxide gas concentrations in the range between 0.0% and 15.0% compared to the experimental outputs of the developed gas sensor system in this study. From the figure, it is noted that the experimental and the theoretically calculated values are in good agreement throughout most of the selected wavelength range with a slight difference in readings was calculated to be about 5.0%.

It is believed that the main reason for the differences in the readings between the theoretical and measured Normalized Absorbance value is most probably due to the effects of non-absorptive infrared radiation such as the stray light present in the detection cell, which is not absorbed by the gas under study but is detected by the detector, as well as other reasons as previously discussed regarding the limitations and deviations from the ideal case of the Beer-Lambert law [15].
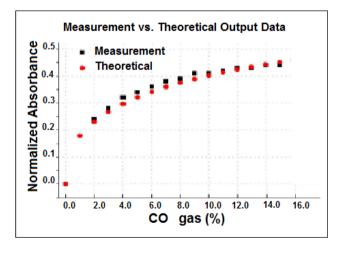

Figure 6: The comparison between experimental and theoretically calculated outputs

VII. CONCLUSION

To conclude, the theoretical analysis and simulation of the mid-infrared absorption spectroscopy method of the developed optical fiber-based CO_2 gas sensing system have been successfully demonstrated and presented. The Beer-Lambert law which plays a vital part in this analysis has been explained. The deviation and limitation case of the Beer-Lambert law has also been discussed where the strict conditions under which the law have not been fulfilled.

In this study, the theoretical analysis has been demonstrated in two different cases: firstly, using a simplified approximation of the optical transmittance spectrum of the gas, and secondly using the real optical absorption cross section line intensities data derived from the HITRAN2008 database. The outputs from the theoretical analysis and simulation have been fitted into an equation where this equation is later been used to calculate the gas sensor output in the measurement process in the laboratory setting.

A good agreement has been shown between the outputs obtained from using the simplified approximation and that from using real absorption data of the theoretical analysis with the laboratory measurement outputs data especially in terms of the logarithmic relationship between the optical absorption output and the concentrations of the gas. At the end of this paper, it has been successfully shown that the detected sensor outputs from the theoretical calculation have a good agreement with the data obtained from the measurement using the developed gas sensor in the laboratory setting.

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REFERENCES

[1] EEA. (2005). Greenhouse gas emission trends and projections 2005. *Greenhouse Gas Emission Trends And Projections* 2005 (p. EEA Report No 8/2005).

[2] Fang, Z., Chin, K. K., Qu, R., & Cai, H. (2012). Fundamentals of Optical Fiber Sensors. *Fundamentals of Optical Fiber Sensors*. https://doi.org/10.1002/9781118381717

[3] Yamini, K., Renganathan, B., Ganesan, A. R., & Prakash, T. (2017). Clad modified optical fiber gas sensors based on nanocrystalline nickel oxide embedded coatings. *Optical Fiber Technology*, 36, 139–143.

[4] Mulrooney, J., Clifford, J., Fitzpatrick, C., Chambers, P., & Lewis, E. (2008). A mid-infrared optical fibre sensor for the detection of carbon monoxide exhaust emissions. *Sensors and Actuators*, A: Physical, 144(1), 13–17.

[5] Mulrooney, J., Clifford, J., Fitzpatrick, C., Chambers, P., & Lewis, E. (2007). Monitoring of carbon dioxide exhaust emissions using mid-infrared spectroscopy. *Journal of Optics* A: Pure and Applied Optics, 9(6).

[6] Zhu, S. Z. S., Chen, Y. C. Y., Zhang, G. Z. G., & Sa, J. S. J. (2010). An optical fiber sensor based on absorption spectroscopy for carbon monoxide detection. *Computer Design and Applications (ICCDA), 2010 International Conference On*, 2(ICCDA), 0–3.

[7] Yarai, A., & Nakanishi, T. (2004). Optical fiber gas sensor based on thermal lens spectroscopy instrument composed of spherical lensed fibers. *Proceedings of IEEE Sensors*, 2004.

[8] Swinehart, D. F. (1962). The Beer-Lambert Law. Journal of Chemical Education, 39(7), 333.

[9] Allen, H. C., Brauers, T., & Finlayson-Pitts, B. J. (1997). Illustration of Deviations in the Beer-Lambert Law in an Instrumental Analysis Laboratory: Measuring Atmospheric Pollutants by Differential Optical Absorption Spectrometry. *Journal of Chemical Education*, 74(12), 1459.

[10] Mayerhöfer, T. G., Mutschke, H., & Popp, J. (2016, July 4). Employing Theories Far beyond Their Limits—The Case of the (Boguer-) Beer-Lambert Law. *ChemPhysChem. Wiley-VCH Verlag*. Mellqvist, J., & Rosén, A. (1996). DOAS for flue gas monitoring - II. Deviations from the Beer-Lambert law for the U.V./visible absorption spectra of NO, NO2, SO2 and NH3. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 56(2), 209–224.

[11] Zhang, Y., Xu, G., Li, A., Li, Y., Gu, Y., Liu, S., & Wei, L. (2006). Mid-Infrared Tunable Diode Laser Absorption Spectroscopy for Gas Sensing. In *2006 Joint 31st International Conference on Infrared Millimeter Waves and 14th International Conference on Terahertz Electronics* (pp. 181–181). IEEE.

[12] Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., … Vander Auwera, J. (2009). The HITRAN 2008 molecular spectroscopic database. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110(9–10), 533–572.

[13] Zhang, Y., Xu, G., Li, A., Li, Y., Gu, Y., Liu, S., & Wei, L. (2006). Mid-Infrared Tunable Diode Laser Absorption Spectroscopy for Gas Sensing. In *2006 Joint 31st International Conference on Infrared Millimeter Waves and 14th International Conference on Terahertz Electronics*, pp. 181–181

[14] Mellqvist, J., & Rosén, A. (1996). DOAS for flue gas monitoring - II. Deviations from the Beer-Lambert law for the U.V./visible absorption spectra of NO, NO2, SO2 and NH3. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 56(2), 209–224.