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Detection of Methane Gas Using Absorption Spectroscopy Technique in Non-Dispersive Infrared (NDIR) Region

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Abstract: The number of manufacturing plants is growing every day, resulting in air pollution. Typically, haze is caused by air pollution. This work aims to design a methane gas sensor based on absorption spectroscopy in the non-dispersive infrared (NDIR) region. This starts by determining the range of methane absorption wavenumber at the NDIR region by using Spectralcalc.com® gas cell simulator. From the simulation results, the absorption cross-section of methane is 3.4677 x 10^{-19} cm^2/molecule at wavenumber 2949.8507 cm^{-1}. For validation purposes, a comparison between the previous experimental work and this simulation work shows small percentages of differences which is below 1% differences. Next, an analysis of the pressure effect on the methane absorption cross section was carried out by varying the pressure from 1000 mbar to 1200 mbar. The results indicate that at wavenumber 2940.3909 cm^{-1} the methane absorption cross section is less dependent on pressure changing. Furthermore, it continues with the analysis of the temperature effect on methane absorption cross sections. Here, the temperature varied from 273.15 K to 333.15 K. The results showed that temperature changes do not affect methane absorption cross sections at wavenumbers of 2940.3909 cm^{-1}. For both analyses, this work used three different wavenumbers and the results showed that the absorption cross section at wavenumber 2940.3909 cm^{-1} is less pressure and temperature dependent compared to other wavenumbers. To optimize the length of a gas cell for the hazardous level of methane concentration, both simulation and theoretical calculations were carried out by using Spectralcalc.com® gas cell simulator and theoretical formula, respectively. The results from both simulation and theoretical calculations gave almost similar results where the optimized length that needs to detect 50000 ppm of methane gas is 1.600 cm. In conclusion, this work successfully simulates and proposes a methane gas sensor based on the absorption spectroscopy technique in the NDIR region.

Keywords: NDIR, Methane, 50000 ppm, Absorption Cross Section

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1. Introduction

There are 60% of methane gas found around it comes from human actions and sources before humans began to dramatically affect the carbon cycle. Natural methane emissions come largely from moist sources that include wetlands that include swamps. Methane is a colorless and odorless gas that has a lower density than air. Because methane has a lower density than air, it climbs to the tops of stagnant confined structures and tightly sealed dirt storage holes. It is most easily formed during hot and humid weather. Without gas detection devices, methane is exceedingly difficult to detect. There are many technologies that can detect methane gas. The technologies are catalytic sensors [1], electrochemical sensors [2], infrared sensors [3], flame ionized detectors (FIDs) [4] ,and semiconductor sensors [5]. All of them have their respective advantages and disadvantages. Recently, infrared sensors have been widely used to analyze substances in the atmosphere due to its ability to detect variety of gases in infrared regions. Although, infrared gas sensors are more expensive compared to other types of gas sensors, their lifespan is longer. Therefore, this work aims to design a methane gas sensor based on absorption spectroscopy in non-dispersive infrared (NDIR) region.

1. Absorption Spectroscopy

In the late 1930s, non-dispersive infrared gas (NDIR) measurement was introduced as one of the applications of infrared spectroscopy in the United States [6]. One of the most extensively used optical gas detection techniques is NDIR gas sensing, and there are a variety of cell types available in commercial manufacture [7]. The NDIR gas measurement technology looks for wavelength absorption in the infrared spectrum to identify specific gases. The "molecular fingerprint" area is defined as the mid-infrared (mid-IR) spectra (wavelength 2 to 20 μm), which reveals exceptionally unique vibration bands and rotational transitions. In the intermediate infrared range, the absorption intensity of molecular transition is generally 10–1000 times larger than that of the visible or near-IR range [8]. From the sentences above, it shows that gas sensors equipped with mid-IR spectroscopy could be utilized to identify and detect the existence of chemicals with sensitive and selective.

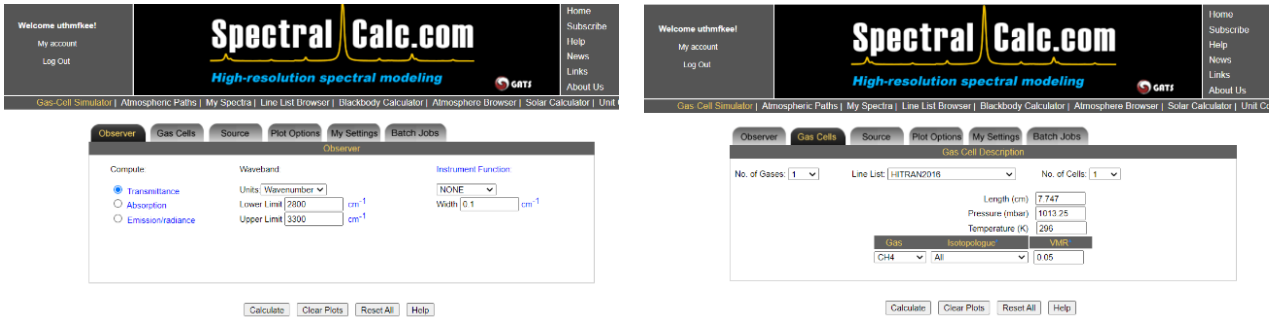
Analysis of Absorption is a technique for determining how much energy is absorbed. ABSORB substances emit light with varying wavelengths, which is used in spectroscopy. In the analysis, the sample is the amount of emitted light that is absorbed. Beer-law Lambert's may be used to quantify an absorption spectrum and its relationship to the amount of substance present [9]. By measuring the spectra of a calibration standard with a known quantity of the target, or by measuring the spectrum of a calibration standard with a known concentration of the target, the absorption coefficient for different substances may be estimated. By measuring the light intensity in and exit the sample, the Absorbance (or optical density) and Transmission (or Transmittance) of light through to the sample may be estimated [10]. The equations that make up the Beer-Lambert Law are as follows [10]:

$$Light\ Absorbance\ (A) = KCL \quad Eq\ 1$$

Where C is the concentration of analyte in a sample, K is a constant for a particle solution and wavelength and L is the length of the light path in glass sample cuvette.

2. Simulation Tool

Spectralcalc.com® is one of the cell gas simulators that will be used to simulate the wavenumber of methane absorption in the NDIR area. This simulation tool is based on Hitran Database that provide the researchers to obtain high-resolution molecule spectra and other spectroscopy data. Figure 1 (a) and (b) shows the important parameter setting as input in Spectralcalc.com® gas cell simulator at Observer Tab and Gas Cell Tab, respectively.



(a) (b)

Figure 1: Set the parameter input in Spectralcalc.com® gas cell simulator in the (a) Observer Tab (b) Gas Cell Tab

The output of Spectralcalc.com® is further used to calculate the methene gas concentration by using the following equation [11].

$$c_{ppm} = -\frac{1000000RT}{\sigma N_A PL}\ln(T) \quad Eq2$$

Where c_{ppm} is s concentration of gas in ppm (part per million), R is the ideal gas constant, 8.205746 x 10^{-5} (atm m^3 mol^{-1} K^{-1}), T is the absolute temperature (K), σ is the absorption cross section (m^2 $molecule^{-1}$), N_A is the Avogadro's constant, 6.0224199 x 10^{23} ($molecule^{-1}$), P is the pressure (atm), l is the optical path length (cm), $I(\lambda)$ is a transmitted intensity at certain concentration and $I_o(\lambda)$ is the incident intensity at zero concentration. Meanwhile, the transmittance can be calculated by

$$T = \left(\frac{I(\lambda)}{I(\lambda_0)}\right) \quad Eq3$$

3. Results and Discussion

The results and discussion section presents data and analysis of the study. This section can be organized based on the stated objectives and the scope of study in this research. It consists of four subtopics which are wavenumber simulation of methane absorption, analysis of temperature effect, analysis of pressure effect and wide range analysis by different path length and optimization of gas. The result shown below are based on simulation results and theoretical calculations for verification purposes.

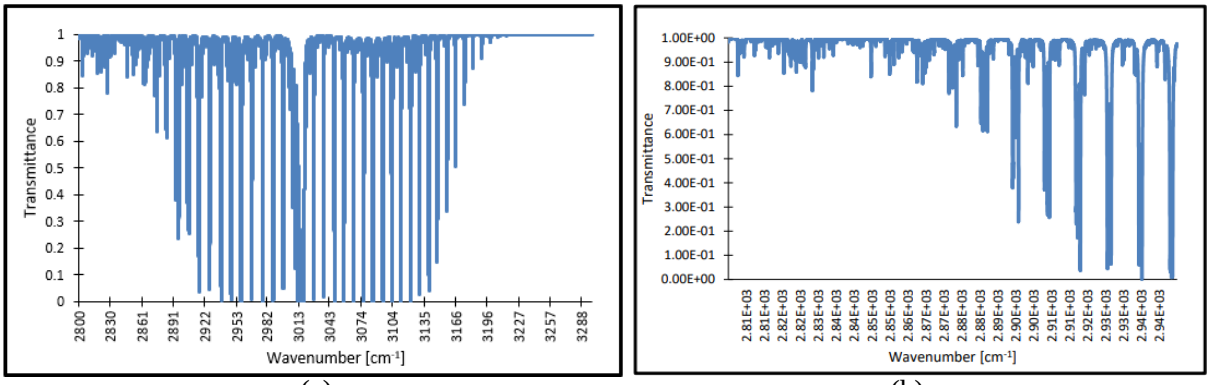
4.1 Simulation of Methane Absorption Wavenumber

Methane concentration needs to be determined early because methane concentration is also one of the required inputs. Equations (2) are used when calculating the initial methane concentration based on the previous work by [12] and also as stated in Table 1. Table 1 shows all of the inputs that will be used to calculate the methane absorption cross section.

Table 1: All inputs in the Observer tab and Gas Cell tab to model methane absorption cross section in the NDIR range.

Tab	Input Parameter		Value
Observer	i.	Compute	Transmittance
	ii.	Wavenumber	2800 cm^{-1} - 3300 cm^{-1}
Gas Cells	i.	No. of gases	1
	ii.	Line list	HITRAN 2016
	iii.	No. of cells	1
	iv.	Gas	Methane, CH_4
	v.	Concentration	50000 ppm
	vi.	Length (cm)	7.747cm
	vii.	Pressure (mbar)	760Torr (1013.25 mbar)
	iii.	Temperature (K)	296 K

Figure 2 depicts the output transmittance of the simulator as a result of 50000 ppm of methane. Figure 2 shows two graphs, one with wavenumbers ranging from 2800 cm^{-1} to 3300 cm^{-1} in Figure 2 (a), and the zoom in version wavenumbers ranging from 2800 cm^{-1} to 2950 cm^{-1} in Figure 2 (b). The goal of the zoomed-in graph in Figure 2 (b) is to highlight in greater detail that the major wavenumber that has to be confirmed is in the vicinity of that wavenumber. The absorption cross section of methane at 2949.8507 cm^{-1} is determined to be 3.4677 x 10^{-19} cm^2/molecule, equating to a transmittance value of 0.967. The simulation findings are compared with previous experimental work in order to validate the applicability of the Spectralcalc.com® gas cell simulator in determining methane absorption cross section. Comparison is done between this simulation work and previous experiment work by [12] as shown in Table 2. At wavenumber 2949.8507 cm^{-1}, absorption cross section of methane that obtained by this simulation work and previous experimental work are 3.4677 x 10^{-19} cm^2/molecule and 3.45 x 10^{-19} cm^2/molecule, respectively.



(a) (b)

Figure 2: The transmittance result for 50000 ppm of methane at wavenumber (a) 2800 cm^{-1} – 3300 cm^{-1} (b) 2800 cm^{-1} – 2950 cm^{-1} using the Spectralcalc.com® gas cell simulator

Table 2: Comparison of the methane absorption cross section (σ) between the previous experiment and current simulation (in units of 10^{-19} cm^2/molecule).

Wavenumber (cm^{-1})	This simulation work	Experimental Work [12]
2949.8507	3.4677	3.45

As illustrated in Table 3, a comparison is made by calculating a percentage of difference. The percentage of difference is calculated using the comparison in Table 3. At 2949.8507 cm^{-1}, for example, the difference between work by [12] and this simulation result is estimated by $\left(\frac{3.4677-3.45}{3.4677}\right) \times 100\%$

which provide a difference of 0.51%. The discrepancy between the past experimental work and this simulation work is only a small percentage, demonstrating the Spectralcalc.com® gas cell simulator's capacity to produce promising findings.

Table 3: The difference in methane absorption cross section between the prior experiment and this simulation work as a percentage (in a unit of percent)

Wavenumber (cm^{-1})	Percentage of difference
2949.8507	0.51 %

Percentage of difference: $\left(\frac{\sigma s-\sigma}{\sigma s}\right) \times 100$, where σs is the methane absorption cross section obtained in simulation work. In the following step, the effects of pressure and temperature on the methane absorption cross section is investigated using the Spectralcalc.com® gas cell simulator. It is critical to use an exact methane absorption cross section value for accurate methane concentration calculations.

4.2 Analysis of Pressure Effect

Absorption cross section has been considered a significant factor in calculating methane concentration, as illustrated in Equation (2). In addition, absorption cross section is dependent on numerous parameters, including pressure, as shown by Equation (2). Pressure may differ in practice. As a result, the focus of this section is on the pressure effects on the methane absorption cross section. Although given various pressures from 100 mbar to 1200 mbar in Figure 3, pressures from 1000 mbar to 1200 mbar were used in the analysis. It is also visible at wavenumbers of 2800 cm^{-1} to 3000 cm^{-1}, where the pressure absorption cross section is less sensitive than at other wavenumbers. To explore the effects of pressure on the methane absorption cross section, the pressure was changed from 1000 mbar to 1200 mbar. Figure 4 depicts simulator output transmittance for pressures ranging from 1000 mbar 1200 mbar. Overall, increasing the pressure caused the output transmittance to drop, while the other parameters remained constant. Beer's Law in Equation (1) predicts this outcome. The transmittance decreases as the pressure rises. Using Equation (2), the methane absorption cross section is calculated.

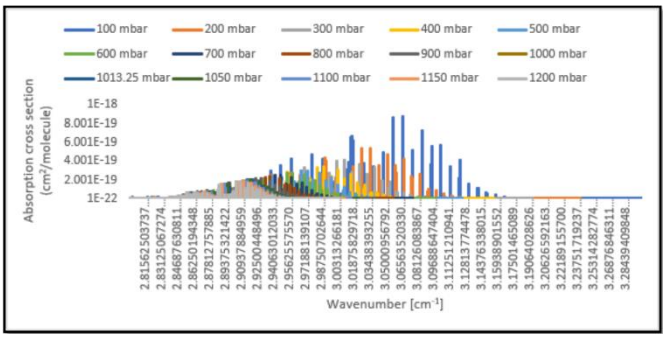


Figure 3: Output transmittance of the Spectralcalc.com® gas cell simulator at pressures ranging from 100 mbar to 1200 mbar and wavenumbers ranging from 2800 cm^{-1} to 3300 cm^{-1}.

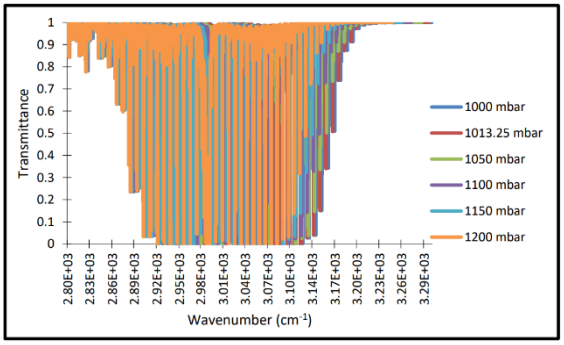


Figure 4: Spectralcalc.com® gas cell simulator output transmittance at various pressures according to 50000 ppm of methane.

Methane absorbs light in the NDIR zone at different transmittance for different pressure as seen in Figure 4. Therefore, the pressure effect on the methane absorption cross section is studied at wavenumber as shown in Table 2 with two other additional wavenumbers. The anticipated wavelengths are 2828.3264 cm^{-1}, 2940.3909 cm^{-1} and 2949.8507 cm^{-1}. To investigate the pressure effect, Figure 5 is plotted for graph of methane absorption cross section and transmittance vs. pressure for three wavenumbers.

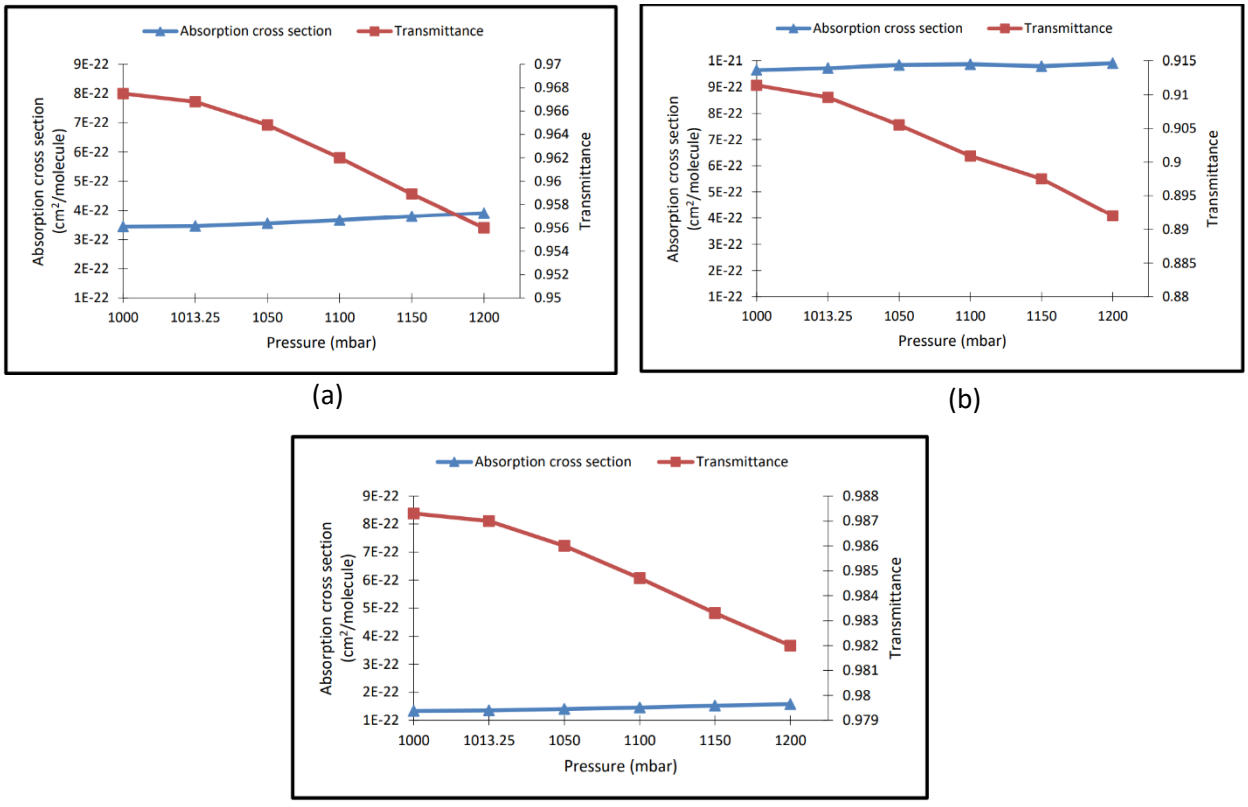


Figure 5: Analysis of pressure effect on methane absorption cross section at (a) 2949.8507 cm^{-1} (b) 2828.3264 cm^{-1} and (c) 2940.3909 cm^{-1} with output transmittance from the Spectralcalc.com® gas cell simulator.

At a methane absorption cross section of 3.67 x 10^{-22} cm^2/molecule, the wavelength of 2949.8507 cm^{-1} in Figure 5 (a) demonstrates a rise in pressure starting at 1100 mbar. Therefore, the methane absorption cross section in Figure 5 (a) is completely pressure dependent. Although there exist data on absorption coefficients based on temperature and pressure, Klingbeil, (2007) [13] found that some of these measurements are highly unclear, with data from multiple sources being inconsistent. Figure 5 (b) and (c) show simulation result for wavenumber 2828.3264 cm^{-1} and 2940.3909 cm^{-1} respectively. Meanwhile, as the pressure is raised, Figure 5 demonstrates a reduction in transmittance. As indicated in Equation (1), the result is consistent with Beer's Law. The lower the transmittance, the greater the pressure. The pressure shift from 1000 mbar to 1200 mbar had an effect on the methane absorption cross-sections at wavelengths 2828.3264 cm^{-1}, 2940.3909 cm^{-1} and 2949.8507 cm^{-1}. To minimize cross-sectional changes of methane absorption and reliable measurement of methane concentration in the NDIR zone, it is strongly advised to consider pressures between 1000 mbar and 1200 mbar in research activities by using the less pressure dependent wavenumber which is 2940.3909 cm^{-1}.

4.3 Analysis of Temperature Effect

The effects of temperature on the methane absorption cross section are being investigated further. Set the input to the simulator as shown in Table 1 to begin the analysis. For the purpose examining the temperature impact, the temperature is adjusted from 273.15 K to 333.15 K. A cross-sectional graph of the absorption cross-section of temperature versus wavelength has been provided in Figure 6. simulation result, it is observed that absorption cross section is less sensitive toward temperature changing at wavenumber from 2800 cm^{-1} to 2960 cm^{-1} compared to other wavenumbers.

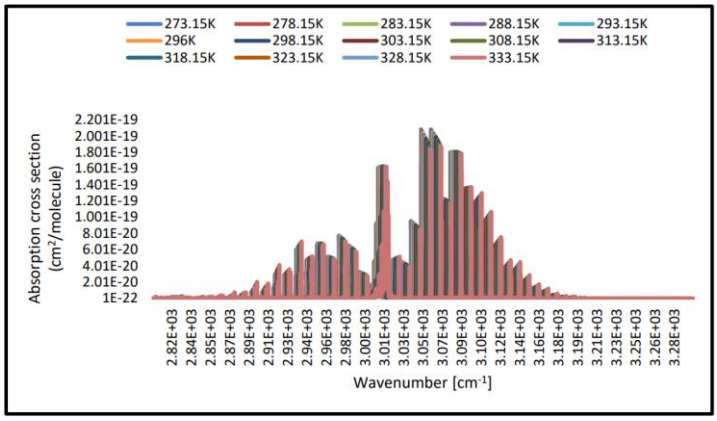
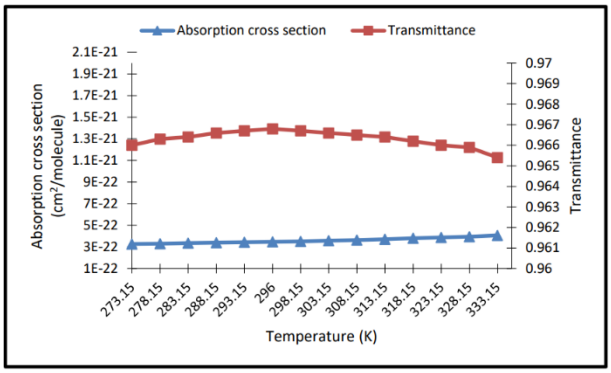
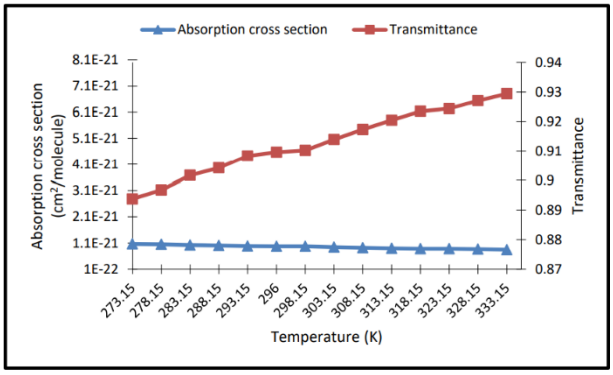


Figure 6: Output transmittance of the Spectralcalc.com® gas cell simulator at pressures ranging from 273.15 K to 333.15 K and wavenumbers ranging from 2800 cm^{-1} to 3300 cm^{-1}

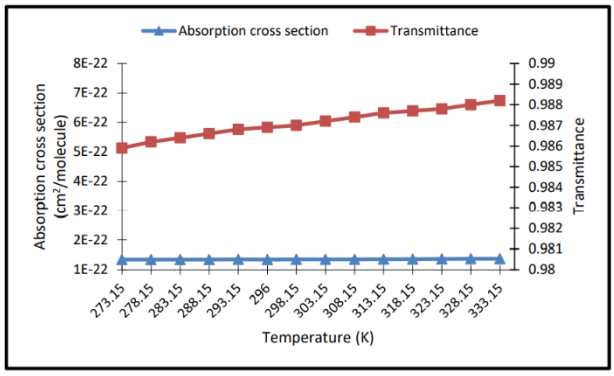
Figure 7 shows a graph of methane absorption cross section and transmittance vs temperature that is used to investigate the temperature effect. The analysis of temperature effect is studied at three different wavenumbers which are 2828.3264 cm^{-1}, 2940.3909 cm^{-1} and 2949.8507 cm^{-1}.



(a)



(b)



(c)

Figure 7: Analysis of temperature effects on methane absorption cross section at a) 2949.85 cm^{-1}, b) 2828.3264 cm^{-1}, and c) 2940.3909 cm^{-1} with output transmittance from the Spectralcalc.com® gas cell simulator

As the temperature is adjusted from 273.15 K to 333.15 K, the methane uptake cross section increased at 3.64 x 10^{-22} cm^2/molecule at a wavelength of 2949.85 cm^{-1} in Figure 7 (a). When inspected closely, transmittance rises from 273.15 K to 296 K, then drops at 298.15 K. The result follows Beer's Law as given in Equation (1). The transmittance decreases as the temperature rises. As a result, the absorption cross section was discovered to be totally temperature dependent. When the temperature rises, the apex's cross section drops, but when a higher rotation line develops, the wings' band expands [12]. The simulation results for wavelengths of 2828.3264 cm^{-1} and 2940.3909 cm^{-1} are shown in

Figures 7 (b) and (c), respectively. As a consequence, temperature changes from 273.15 K to 333.15 K have no effect on methane absorption cross sections at wavelengths of 2940.3909 cm^{-1}, but temperature changes from 273.15 K to 333.15 K have an effect on methane absorption cross sections at wavelengths of 2828.3264 cm^{-1}. To eliminate cross-variation of the methane absorption section for reliable measurement of methane concentration in the NDIR area, it is advised that operating temperatures between 273.15 K and 333.15 K be considered in concentration measurement by using the less temperature dependent wavenumber which is 2940.3909 cm^{-1}.

4.4 Wide Range Analysis by Different Path Length and Optimization of Gas Cell

One of the aims of this research is to expand the range of methane concentration measurements in the NDIR. Equation (2) depicts the link between gas cell concentration and path length. Due to the inversely proportional connection between concentration and path length of gas cell, it is projected that a short path length of gas cell may achieve a broad range of methane concentration. As a result, the focus of this section is on the effect of path length on the range of methane concentration. The wavelength 2940.3909 cm^{-1} is used in this study to calculate methane concentration, and the value of the methane absorption cross section was already determined to be 1.3518 x 10^{-22} cm^2 /molecule. Until then, the pressure and temperature are set as shown in Table 1. This investigation looks at three different gas cell path lengths which are 1.600 cm, 4.000 cm, and 7.747 cm. The effect of varied path lengths of gas cells on the range of methane concentration is seen by calculating methane concentration at transmittance values between 0.05 and 0.95 for 1.600 cm, 4.000 cm, and 7.747 cm gas cells.

Figure 8 depicts methane concentrations computed for gas cells with lengths of 1.600 cm, 4.000 cm, and 7.747 cm. It has been discovered that the 1.600 cm gas cell has the broadest range of methane concentrations, ranging from 900 ppm to 57000 ppm. As a result, it can be seen that a gas cell with a short path length can handle a wide variety of methane concentrations. Beer's Law in Equation (1) is supported by these facts. The length of the gas cell route is inversely proportional to concentration. Figure 9 displays the simulator's output transmittance for a 1.600 cm gas cell at various concentrations. Methane absorption caused a reduction in output transmittance as the quantity of methane increased. In Equation (2), this is Beer's Law. Low transmittance due to excessive concentration. This is true as long as the gas cell's pressure, temperature, and path length remain unchanged.

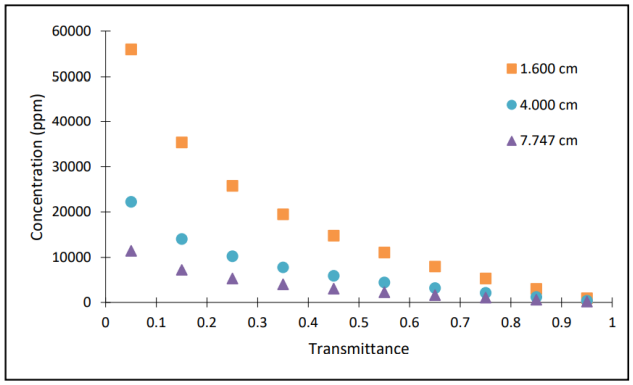


Figure 8: Methane concentrations calculated for 1.600 cm, 4.000 cm, and 7.747 cm gas cells.

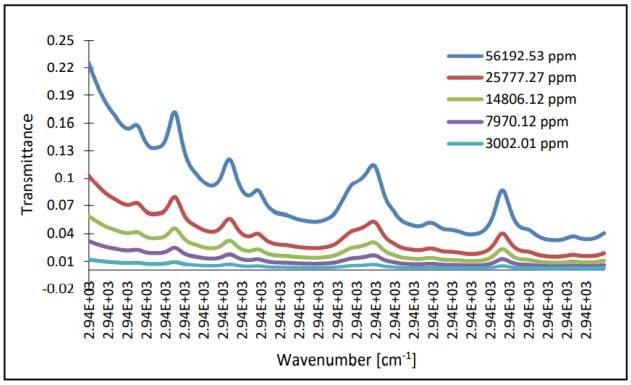


Figure 9: Spectralcalc.com® result of transmittance using a 1.600 cm gas cell at various methane concentrations.

To compute methane concentration, output transmittance at wavelength 2940.3909 cm^{-1} is utilized, which is comparable to the previous theoretical calculation. Figure 10 shows the predicted methane concentration based on output transmittance from simulation results. For broad range analysis, graph concentration vs transmittance for 1.600 cm, 4.000 cm, and 7.747 cm gas cells are displayed simultaneously. The higher the concentration, the shorter the gas cell. Meanwhile, in Figure 10 also presented the previously obtained findings based on theoretical calculations. From observation, both

calculation and simulation show almost same result for 1.600 cm, 4.000 cm and 7.747 cm gas cell. The transmittance value in Figure 11 is used to compare theoretical calculations and simulation results for verification purposes. For all methane concentration levels, the difference in transmittance between theoretical calculation and simulation is calculated to be less than 0.011% for 1.600 cm, 4.000 cm, and 7.747 cm gas cells. As a result, the simulator's capacity to perform a wide range of analyses using varied gas cell path lengths has been confirmed.

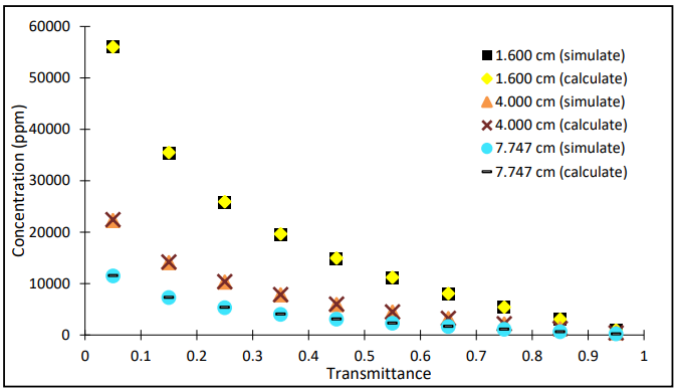


Figure 10: Calculated and simulated methane concentrations for gas cells with length of 1.600 cm, 4.000 cm, and 7.747 cm.

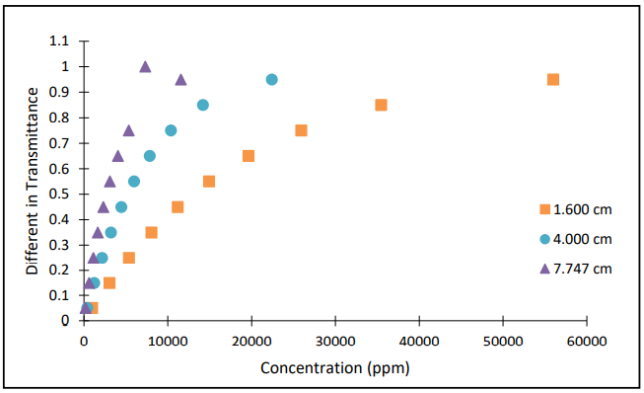


Figure 11: A difference in transmittance between theoretical calculation and simulation for 1.600 cm, 4.000 cm, and 7.747cm gas cells.

As a result, similar which is based on a repeated simulation method procedure to find out the optimal level the length of the gas cell path to be employed in this research given the presence of a methane monitor. The final simulation results demonstrate that a 1.600 cm long gas cell can offer methane rate readings up to more than 50000 ppm. A 1.600 cm gas cell may also produce methane concentration measurements up to 50000 ppm, as shown in Figure 11. As a result, a 1.600 cm gas cell was chosen for the actual experimental testing. Table 4 summarize all the parameter for methane gas sensor.

Table 4: Summary of optimization parameter for methane gas sensor

No	Parameter	Value
1	Operation wavenumber	2940.3909 cm^{-1}
2	Range of operation pressure	1000 mbar to 1200 mbar
3	Range of operation temperature	273.15 K to 333.15 K
4	Range of concentration measurement	50000 ppm
5	Length of the gas cell	1.600 cm

4. Conclusion

Spectralcalc.com® gas cell simulator has been effectively verified for determining the wavenumber of methane absorption in the NDIR range at 2949.8507 cm^{-1}. Meanwhile, the simulation findings reveal that pressure and temperature impacts on the absorption of methane cross sections at the examined wavelengths of 2828.3264 cm^{-1}, 2940.3909 cm^{-1} and 2949.8507 cm^{-1} are minimal from 1000 mbar to 1200 mbar and 273.15 K to 333.15 K. A 1.600 cm gas cell is chosen to provide methane concentration measurement up to 50000 ppm. And at the end of this thesis can be concluded that the objectives stated in chapter 1 have been achieved where the wavelength range used is 2800 cm^{-1} - 3300 cm^{-1} and uses 50000 ppm as the concentration. The idea for future work on this subject is to carry out this experimental set up for testing of methane sensor. This is because this thesis contains all of the necessary computations, including theoretical and simulation calculations.

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