A simulation process of tunable open path diode laser spectrometer to detect a carbon monoxide gas in NIR region

Ruia Kahtan Mahmood¹, Samira Adnan Mehti²
¹,² Physics department, College of science, University of Babylon

¹ruaa.mazloom@student.uobabylon.edu.iq, ²sci.samira.adnan@uobabylon.edu.iq

Abstract: By modifying the wavelength of the open path tunable diode laser spectrometer (TDLS) in the near infrared region, theoretical research was implemented to improve the detection limit of carbon monoxide gas. To adjust the correct wavelength in the NIR area, MatLab code was created. Following that, frequency domain measurements were performed in order to extract the second harmonic as an indicator of gas presence. According to the results, the correct wave length in the NIR area is (1584.877 nm), and the lowest limit of CO gas concentration is (0.012 ppb).

Keywords: TDLS, carbon monoxide gas, wavelength tuning.

1. INTRODUCTION
The TDLS's principal function is to sweep a narrow-bandwidth laser beam over the absorption peak of a given gas. If the gas is discovered, the energy beam will be reduced. To monitor the gas absorption signal, frequency domain methods are generally used since the procedure needs computing a modest reduction in a massive background signal. Based on the gas measurement method, TDLS may be divided into many types. The following TDLS systems are available: -Multiple-Reflection Cell Spectrometer and Open-path Tunable Spectrometer. The most common diode, according to Fabry Perot, is the commercial diode. In this arrangement, mirrors are placed at either end of the diode facet to allow for standing wave production. The design generates a broad bandwidth. By changing the diode temperature and current flow, the particular wavelength may be changed. [1].
In weakly mixed atmospheres, the long open-path technique may consistently estimate gas concentrations across a broad region of space [2, 3]. It may also offer exact, simultaneous measurements of a variety of trace gas concentrations over extended open routes. Similarly, the long open-path device can trace the flow of gas emissions by detecting changes in gas concentration in real time over a long distance [4]. It
was also used to assess air quality and the quantity of pollution released by road vehicles [5-6]. In addition, it simply consists of a tunable diode laser, a photodetector, a hardware device to manipulate the absorption signal for a specific gas concentration, a retro-reflector and, occasionally, a telescope is needed to collect an absorption signal from a remote target [7]. The open-path spectrometer hardware is much simpler than that for long-path spectrometers, which include a multi-reflection cell, a diode laser photodetector, several laser light alignment mirrors through the spectrometer, a pumping system, and a hardware absorption signal handling system (lock amplifier, frequency generator, power supply, computer). The present technology is intended to detect gases on Mars. The TDLS is intended to be installed on a moving robot capable of measuring gas concentrations in the Martian atmosphere over distances ranging from 20 meters to two kilometres. As a result, unlike most high-precision spectrometers, which require reference gas cells and operate at high frequencies, the spectrometer should be durable, simple, light, and portable.

![Figure 1: An open-path spectrometer design, adapted from [8].](image)

First applications for TDLs have been identified for emission monitoring and combustion control in the power industry. A variety of opportunities were then identified in the iron and steel industry. Most recently, TDL analyzers have been introduced for various applications in the chemical industry. Application areas may be divided into combustion, environment, process and safety, and storage and transport. Because of CO's wide fundamental absorption band at 4.7 m, extremely sensitive species identification is achievable even across short distances (10 cm). However, until recently, cryogenic cooling systems were necessary for mid-infrared (> 3 m) laser technology, making the lasers unsuitable for most sensing applications outside of the laboratory. Because room-temperature diode lasers and optical hardware in the near-infrared wavelength domain (1–3 m) are widely available, most prior CO absorption-based sensors were developed to investigate the overtone vibrational bands at 1.55 m [9–12] and 2.3 m [13-15], which are more than four orders of magnitude and two orders of magnitude weaker than the fundamental band, respectively. Near-infrared CO sensors are inappropriate for most short path-
length combustion systems due to low absorption strength and spectrum interference from carbon dioxide and water.

J. Sebastian et al., [16] describe the use of a tunable diode laser-based sensor to detect carbon monoxide (CO) concentration under conditions comparable to those used in laboratory-scale studies to characterize the behavior of heavy crude oil during in situ burning (ISC).

The sensor employs a DFB diode laser that works in the spectrum area of the first overtone's rotational transition R (11) where simulations of CO, CO2, and H2O spectral absorption bands revealed little spectral interference. At temperatures ranging from 150°C to 800°C, pressures ranging from 1 to 5 atm, and critical species concentrations typical of ISC characterization tests, the absorption spectra were estimated using the HITRAN 2008 database.

To test the CO sensor design under controlled laboratory conditions, CO concentration measurements were performed in a static borosilicate glass cell with a route length of 3.81 cm at ambient temperature and pressure. The calibration curve for CO was constructed by measuring the optical density at the line center of R (11) across a molar concentration range of 0.7 percent to 3.4 percent (coefficient of determination of 0.9986).

To test the CO sensor design under controlled laboratory conditions, CO concentration measurements were performed in a static borosilicate glass cell with a route length of 3.81 cm at ambient temperature and pressure. The calibration curve for CO was constructed by measuring the optical density at the line center of R (11) across a molar concentration range of 0.7 percent to 3.4 percent (coefficient of determination of 0.9986).

Barras et al. (2004) attempt to remote sense car emissions using a near-infrared diode laser-based spectrometer. They detect carbon monoxide and carbon dioxide absorptions at 1580 nm and can offer the CO/CO2 ratio for vehicle exhaust research. The device is battery-powered and is intended to be placed inconspicuously by the side of the road. The system's optics and electronics are detailed, and preliminary field trial results are reported. The spectrometer's sensitivity is increased by detecting the more powerful initial overtone of carbon monoxide at 2320 nm, as well as additional work on other species of interest [21].

Andrew et al. (2007) created a three-channel tunable diode laser absorption spectrometer to detect oxygen, carbon monoxide, and water vapor in real-time in fire situations to help in the assessment of water-based fire suppression systems. The spectrometer was tested in a 1350 L test enclosure with a tiny propane flame and a piezoelectrically created water mist of sub-10 m droplets. They were able to detect and quantify oxygen from transmission levels of 100 percent down to 0.01 percent with uncertainties of 0.1 and 0.4 vol percent, respectively. They discovered that carbon monoxide levels produced in the test enclosure were less than the 250-ppm detection limit determined by noise level analysis.
2. Theory

Beer-Lambert Law is used to simulate light absorption of carbon monoxide gas: [18]

\[ I = I_o e^{-\beta \eta N L} \] \hspace{1cm} (1)

Where I is the intensity of IR laser light, \( I_o \) is the incoming fundamental IR laser light intensity obtained by the photodiode in the absence of atmosphere, \( N \) is the gas concentration, is the absorption factor, and \( L \) is the distance between the laser diode and the retroreflector.

A sinusoidal waveform was used to vary the intensity of the incidence, as described in Eq. 2.

\[ I_o = \left[ (i_{\text{offset}} - i_{\text{ih}}) + a \sin(2\pi f_o t) \right] \frac{\delta}{\text{area}} \] \hspace{1cm} (2)

Where \( i \) (offset)\( = 99 \) mA denotes the alternating current offset, \( i_{\text{ih}} \approx 20 \) mA denotes the maximum current, and \( a = 42 \) The amplitude of a sine wave is measured in milliamperes (mA). The modulation frequency is \( f_o = 1000 \) Hz: The differential efficiency (the direct relationship constant used to convert laser current to laser power) is \( = 0.2055 \) mW/mA, \( t \) is the time. The active area of the photodiode is 3.1 mm\(^2\). A laser light beam with a narrow bandwidth was created and swept through the absorption peak of these gases. A mean pressure of about 730 Pa = 7.3 millibar [18]. Doppler dominates broadening, and the line-shape of the absorption cross-section becomes Gaussian, as shown in Eq. 3 [19].

\[ \sigma = C e^{\frac{(\omega_o + a y \sin(2\pi f_o t) - \omega_p)^2}{2\sigma^2}} \] \hspace{1cm} (3)

If we substitute Eq. (2) and Eq (3) in Eq. (1) we get

\[ I = \left[ (i_{\text{offset}} - i_{\text{ih}}) + a \sin(2\pi f_o t) \right] \frac{\delta}{\text{area}} e^{-\beta \eta N L} \left[ C e^{\frac{\omega_o + a y \sin(2\pi f_o t) - \omega_p)^2}{2\sigma^2}} \right] \] \hspace{1cm} (4)

The incident and transmitted light strengths are \( I_o \) and \( I \) (W/mm\(^2\)), respectively; is a factor for converting the unit from ppm to cm\(^{-3}\) as follows. For the gas carbon monoxide:

\[ \beta = 1 \text{ ppm} = \frac{1 \text{ mg}}{L} = \frac{10^{-3} g}{10^3 M \text{ cm}^3} \] \hspace{1cm} (5)

where \( M \) Carbon monoxide gas has a molecular weight of, so:

\[ c = \frac{10^{-6} g}{\text{mol cm}^3} = 0.0357 \times \frac{10^{-6} \text{ mol cm}^3}{\text{cm}^3} \times N_A \] \hspace{1cm} (6)

\( N_A \) is the Avogadro number (cm\(^3\)/ppm), As a result:

\[ \beta = 0.0357 \times \frac{10^{-3} \text{ mol cm}^3}{\text{cm}^3} \times 6.022 \times 10^{20} \frac{1 \text{ mol}}{\text{cm}^3} = 0.214 \times \frac{10^{-3} \text{ cm}^3}{\text{cm}^2} \times 10^{20} = 0.214E17 \] \hspace{1cm} (7)

The gas concentration is \( N \) (parts per million), and the light path length through the gas is \( L=100 \) m. In Equation (4), \( C = 1E-21 \) cm\(^2\) denotes the cross-section area of the carbon monoxide gas maximum...
absorption and its variation. \( \epsilon = 0.1 \text{ nm} \) over the wavelength range mentioned in the phrase \( \omega_0 + ay \sin (2\pi f_0 t) - \omega_p \).

\( \omega_0 = 1584 \text{ nm} \) is the initial value of the diode laser's monitoring spectrum.; \( a \sin (2 f_0 t) \) is the alternating current waveform used to modify the spectrum of the laser's generated light., with \( a=3.5 \text{ mA} \) being the amplitude of the sine wave and \( a=0.01 \text{ nm/mA} \) being a modulation factor; The modulated frequency is 500 Hz, the duration in seconds is \( t \), the amplitude of the carbon monoxide gas absorption spectrum is 1584.6 [20] nm, and the full width half maximum (FWHM) is 0.37 [20].

3. Results and discussion

Figure 2 shows the absorption signal of the carbon monoxide gas at tuning current of laser diode 78.95 mA and the wavelength 1584.877 nm. The dip of the absorption peak locates exactly at the middle of the sine wave, and it is a slightly deep and sharp dip. That means there was a good sense of carbon monoxide gas for that specific wavelength 1584.877 nm, and the frequency of the laser light has been matching vibrational frequencies of the carbon monoxide gas at this wavelength. Note that the simulation measurements have been demonstrated at a constant concentration value 0.5 ppb and the length of the open path spectrometer at 100 m. To complete the picture of the CO gas sense, the time domain data when the wavelength of the laser diode little further away from its desired value for gas absorption has been shown in Figure 3.

**Figure 2:** Carbon monoxide absorption peak in near infrared region at tuning current of laser diode (78.95 mA) and the wavelength (1584.877 nm).
Figure 3: Absence of carbon monoxide absorption peak in near infrared region at tuning current of laser diode 81.31 mA and wave length 1584.901 nm.

A Fast Fourier transformation (FFT) have been adopted as in the gases studied above, that was done by written a MATLAB code to calculate the value of second harmonic as an indicator for the gas presence. Figure 4 shows the absorption spectrum in frequency domain, where the fundamental frequency located at 500 Hz and the second harmonic has been indeed in the 1000 Hz. Also, the value of the second harmonic seems to be significant 0.23 mW/m² that mean the energy of light has been mostly absorb by the CO gas. As compare as the absorption spectrum in frequency domain with another Figure 5 exhibits the fundamental frequency and the value of second harmonic. It seems that the second harmonic has been diminished (there is no absorption peak).

Figure 4: Carbon monoxide gas has a fundamental frequency in the near infrared range of 500 Hz and an absorption peak at 1000 Hz.
Figure 5: Carbon monoxide gas has a fundamental frequency in the near infrared range of 500 Hz, and the quantity of the second harmonic reaches nearly zero around 1000 Hz. MATLAB code has been written to evaluate the amount at the operation current of laser diode (LD) that can be give a max second harmonic value and it was found that the relation has max. peak and min. valley at current values 78.95 mA, 81.31 mA respectively as appear in figure 6.

Figure 6: Variation of the second harmonic with carbon monoxide gas tuning current in the near infrared region.

Then the spectrum wavelength has been tuned around 1nm in 0.02 nm steps to increase the sensitivity of the tunable diode spectrometer (TDLS). And it was the main goal of this work. as illustrate in figure 7
and it was found the relation has maximum peak and minimum valley at was wavelength values 1584.877 nm, 1584.901 nm, respectively in near infrared that was done by MATLAB code.

Figure 7: The wavelength spectrum of carbon monoxide gas in near infrared region has a one peak at (1584.877 nm).

Figure 8 depicts the relationship between the gas concentration and second harmonic and at the required value of the laser diodes driven current and at the precise wavelength of 1584.877 nm. The relationship seems to be linear, and the minimum value of the gas constrainer was 0.05 ppb.

Figure 8: Relation between second harmonic and gas concentration of carbon monoxide gas in near infrared region.

In the near infrared area, carbon monoxide gas has the best wavelength and second harmonic at 1584.877nm and 0.23 mW/m2, respectively.
Gilbert & Swann (2002), found the value of the peak of monoxide (CO) in near infrared is 1584.2 $\omega_p$ (nm) [20]. While Teichert et al., (2003) clearly can measure best CO concentration at 1560 nm as a best peak value in near infrared region [23]. Another found by Zho et al., (2019) that diode laser at 1579 nm was chosen as the best laser source in near infrared region for CO measurements that emit from exhausts [24].

4. Conclusions
In this paper the simulation process of TDLS has been implemented to enhance the sensitivity of the spectrometer using a tuning wavelength of the DFB tunable laser diode by change the drive current of laser. The tuning limits reach about 0.001 nm. Also, the second harmonic has been extracted for each CO gas concentration using FFT technique, which has been done by a Matlab code. The tuning limits of the wavelength in the NIR region is about 0.001nm. And the sensitivity of the TDLS has been enhanced to reach about (0.011ppb).

References
[1] Adam, M. (2010). US EPA Contaminated Site Cleanup Information (CLU-IN). Journal of Environmental Monitoring, 12(5), 1100-1109.
[2] S.M. Anderson, and M.S. Zahniser "Open-Path Tunable Diode Laser Absorption for Eddy Correlation Flux Measurements of Atmospheric Trace Gases", Proceedings of SPIE Laser Spectroscopy Symposium, Measurement of Atmospheric Gases, SPIEVol. 1433, 167-178 (1991).
[3] M. Taslakov, V. Simeonov, M. Froidevaux, and H. van den Bergh, “Open-path ozone detection by quantum-cascade laser,” Appl. Phys. B 82, 501 (2006).
[4] D.D. Nelson, M.S. Zahniser, J.B. McManus, C. E. Kolb, J.L. Jimenez, “A tunable diode laser system for the remote sensing of on-road vehicle emissions,” Appl. Phys. B 67, 433–441, (1998).
[5] S.P. Beaton, G.A. Bishop, Y. Zhang, L.L. Ashbaugh, D.R. Lawson, D.H. Stedman, “ On-Road Vehicle Emissions: Regulations, Costs, and Benefits,” Science 268, 991, (1995).
[6] Hui Xia, Wenqing Liu, Yujun Zhang, Ruifeng Kan, Min Wang, Ying He, Yiben Cui, Jun Ruan, and Hui Geng, “An approach of open-path gas sensor based on tunable diode laser absorption spectroscopy”, Chines Optics Letters, Vol. 6, No. 6, June 10, (2008).
[7] Xin, F., Guo, J., Sun, J., Li, J., Zhao, C., & Liu, Z. (2017). Research on atmospheric CO 2 remote sensing with open-path tunable diode laser absorption spectroscopy and comparison methods. Optical Engineering, 56(6), 066113.
[8] Upschulte, B. L., Sonnenfroh, D. M., & Allen, M. G. (1999). Measurements of CO, CO2, OH, and H2O in room-temperature and combustion gases by use of a broadly current-tuned multisection InGaAsP diode laser. Applied Optics, 38(9), 1506-1512.
[9] Nguyen, Q. V., Edgar, B. L., Dibble, R. W., & Gulati, A. (1995). Experimental and numerical comparison of extractive and in situ laser measurements of non-equilibrium carbon monoxide in lean-premixed natural gas combustion. Combustion and Flame, 100(3), 395-406.

[10] Upschulte, B. L., Sonnenfroh, D. M., & Allen, M. G. (1999). Measurements of CO, CO2, OH, and H2 O in room-temperature and combustion gases by use of a broadly current-tuned multisection InGaAsP diode laser. Applied Optics, 38(9), 1506-1512.

[11] Duffin, K., McGettrick, A., Johnstone, W., & Stewart, G. (2007, July). Tunable diode laser spectroscopy for industrial process applications. In Third European Workshop on Optical Fibre Sensors (Vol. 6619, p. 661927). International Society for Optics and Photonics.

[12] Chao, X., Jeffries, J. B., & Hanson, R. K. (2013). Real-time, in situ, continuous monitoring of CO in a pulverized-coal-fired power plant with a 2.3 μm laser absorption sensor. Applied Physics B, 110(3), 359-365.

[13] Sur, R., Sun, K., Jeffries, J. B., Hanson, R. K., Pummill, R. J., Waind, T., ... & Whitty, K. J. (2014). TDLAS-based sensors for in situ measurement of syngas composition in a pressurized, oxygen-blown, entrained flow coal gasifier. Applied Physics B, 116(1), 33-42.

[14] Wang, J., Maiorov, M., Baer, D. S., Garbuzov, D. Z., Connolly, J. C., & Hanson, R. K. (2000). In situ combustion measurements of CO with diode-laser absorption near 2.3 μm. Applied Optics, 39(30), 5579-5589.

[15] Zhang, T., Kang, J., Meng, D., Wang, H., Mu, Z., Zhou, M., ... & Chen, C. (2018). Mathematical methods and algorithms for improving near-infrared tunable diode-laser absorption spectroscopy. Sensors, 18(12), 4295.

[16] Li, B., Zhang, S. C., & Chi, Y. D. (2018). Development and integration of a CO detection system based on wavelength modulation spectroscopy using near-infrared DFB laser. Journal of Spectroscopy, 2018.

[17] J. T. Houghton, The physics of atmospheres (2nd ed., Cambridge University Press, 1986), Cambridge, page 271.

[18] Mahdi, S. A. (2013). An investigation of electro-optical 1/f noise reduction in an open-path tunable diode laser spectrometer (Doctoral dissertation, University of Arkansas at Little Rock).

[19] Wen-Qing, W., Lei, Z., & Wei-hua, Z. (2013). Analysis of optical fiber methane gas detection system. Procedia Engineering, 52, 401-407.

[20] Gilbert, S. L., & Swann, W. C. (2002). Carbon Monoxide Absorption References for 1560 nm to 1630 nm Wavelength Calibration–SRM 2514 (12 C 16 O) and SRM 2515 (13 C 16 O). NIST special publication, 260, 146.
[21] Barrass, S., Gérard, Y., Holdsworth, R. J., & Martin, P. A. (2004). Near-infrared tunable diode laser spectrometer for the remote sensing of vehicle emissions. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 60(14), 3353-3360.

[22] Awtry, A. R., Fisher, B. T., Moffatt, R. A., Ebert, V., & Fleming, J. W. (2007). Simultaneous diode laser based in situ quantification of oxygen, carbon monoxide, water vapor, and liquid water in a dense water mist environment. Proceedings of the Combustion Institute, 31(1), 799-806.

[23] Teichert, H., Fernholz, T., & Ebert, V. (2003). Simultaneous in situ measurement of CO, H2O, and gas temperatures in a full-sized coal-fired power plant by near-infrared diode lasers. Applied optics, 42(12), 2043-2051.

[24] Zhu, X., Yao, S., Ren, W., Lu, Z., & Li, Z. (2019). TDLAS monitoring of carbon dioxide with temperature compensation in power plant exhausts. Applied Sciences, 9(3), 442.