PROJETO DE ESPECTRÔMETRO FOTOACÚSTICO DE EXTRACAVIDADE BASEADO EM DIODO LASER AZUL NA DETECÇÃO DE GÁS NO₂ (DIÓXIDO DE NITROGÊNIO)

DESIGN OF EXTRA CAVITY PHOTOACOUSTIC SPECTROMETER BASED ON BLUE DIODE LASER IN NO₂ (NITROGEN DIOXIDE) GAS DETECTION

RANCANG BANGUN SPEKTROMETER FOTOAKUSTIK EKSTRAKAVITAS BERSUMBERKAN LASER DIODA BIRU DALAM PENDETEKSIAN GAS NO₂ (NITROGEN DIOKSIDA)

HARJUM^{1*}; UTOMO, Agung Bambang Setio²; MITRAYANA³.

^{1,2,3} Universitas Gadjah Mada, Mathematics and Natural Science Faculty, Physic Department, Indonesia

* Corresponding author
e-mail: harjumfisika@gmail.com

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RESUMO

Introdução: A detecção de NO₂ é necessária porque o NO₂ é um poluente do ar que causa poluição fotoquímica e chuva ácida. Além disso, as doenças respiratórias são causadas por altos níveis de NO₂ no ar inspirado. **Objetivo.** O objetivo deste estudo foi detectar NO₂ usando PAS utilizando Arduino Uno, uma pesquisa fácil, simples e de baixo custo. **Métodos:** Foi realizada a detecção do gás Dióxido de Nitrogênio (NO₂) com um Espectrômetro Fotoacústico (PAS) usando um microcontrolador Arduino Uno. O sistema PAS usa um laser de diodo azul com comprimento de onda de 450 nm como fonte de radiação porque esse comprimento de onda é adequado para gás NO₂. A intensidade do feixe de laser é modulada usando um sistema de modulação com um esquema liga-desliga usando o Arduino Uno. A frequência de modulação foi variada para obter a frequência máxima de detecção. A célula fotoacústica usada foi uma única célula fotoacústica ressonadora com sensores de som tipo H. Sensor de som e fotodiodo foram usados nesta medição. A amplificação do sinal foi feita utilizando o amplificador Lock-in, e o tempo de amplificação também foi determinado para otimizar o PAS. O gás nitrogênio foi usado para detectar sinais de fundo. **Resultados e Discussão:** A partir da otimização do espectrômetro fotoacústico, os resultados obtidos foram uma frequência de diodo laser de 1.000 Hz com ciclo de trabalho de 50% e uma amplificação Lock-in de 10.000 vezes com tempo constante de 3,3 ms. A concentração máxima alcançada nesta medição foi de 6 ppm. O sinal de fundo obtido nesta medição foi 0,00002 V / W. O limite de detecção mais baixo alcançado nesta medição foi de 0,0064 ppm. **Conclusões:** Os recipientes de amostra de gás contendo NO₂ com tamanhos maiores tendem a ter uma concentração maior. Às vezes, a concentração de NO₂ do grande recipiente de amostra de gás foi ultrapassada pelo pequeno recipiente de amostra.

Palavras-chave: Espectrômetro fotoacústico de laser azul, dióxido de nitrogênio, células fotoacústicas, modulação, Arduino Uno.

ABSTRACT

Background: NO₂ detection is necessary because NO₂ is an air pollutant causing photochemical smog and acid rain. In addition, respiratory diseases are caused by high levels of NO₂ in the inhaled air. **Aim:** The purpose of this study was to detect NO₂ using PAS utilizing Arduino Uno, an easy, simple, and low-cost research. **Methods:** The detection of Nitrogen Dioxide (NO₂) gas with a Photoacoustic Spectrometer (PAS) using an Arduino Uno microcontroller has been carried out. The PAS system uses a blue diode laser with a wavelength of 450 nm as the radiation source because this wavelength is suitable for NO₂ gas. The intensity of the laser beam is modulated using a modulation system with an on-off scheme using the Arduino Uno. The modulation frequency has been varied to get the maximum detection frequency. The photoacoustic cell used was a single resonator photoacoustic cell with type H. Sound sensor and photodiode were used in this measurement. The amplification of the signal was done by utilizing the Lock-in amplifier, and the constant time of Lock-in amplifier was also determined to optimize the PAS. Nitrogen gas was used to detect background signal. **Results and Discussion:** From the photoacoustic spectrometer optimization, the results obtained were a laser diode frequency of 1,000 Hz with a duty cycle of 50% and a Lock-in amplifier amplification of 10,000 times with a constant time of 3.3 ms. The maximum concentration reached in this measurement was 6 ppm. The background signal achieved in this measurement was 0.00002 V/W. The lowest detection limit achieved in this measurement was 0.0064 ppm.

Conclusion: The gas sample containers containing NO₂ with larger sizes tend to have a greater concentration. Sometimes, the NO₂ concentration of the large sample gas container was overtaken by the small sample container.

Keywords: *Blue Laser Photoacoustic Spectrometer, Nitrogen dioxide, Photoacoustic Cell, Modulation, Arduino Uno.*

ABSTRAK

Latar Belakang: Deteksi NO₂ diperlukan karena NO₂ sebagai polutan udara yang menyebabkan kabut asap fotokimia dan hujan asam. Selain itu penyakit pernapasan disebabkan oleh tingginya kadar NO₂ dalam udara yang dihirup. **Tujuan:** Tujuan dari penelitian ini adalah untuk mendeteksi NO₂ yang menggunakan SFA yang memanfaatkan Arduino Uno yang merupakan sebuah riset yang mudah, sederhana dan biaya murah. **Metode:** Pendeteksian gas Nitrogen Dioksida (NO₂) dengan Spektrometer Fotoakustik (SFA) yang menggunakan mikrokontroler Arduino Uno telah dilakukan. Sistem SFA menggunakan laser dioda biru dengan panjang gelombang 450 nm sebagai sumber radiasinya karena panjang gelombang tersebut sesuai untuk gas NO₂. Sinar laser dimodulasi intensitasnya dengan menggunakan sistem modulasi berskema *on-off* dengan menggunakan Arduino Uno. Frekuensi modulasi telah divariasi untuk mendapatkan frekuensi dengan deteksi maksimum. Sel fotoakustik yang digunakan adalah sel fotoakustik resonator tunggal dengan tipe H. Sensor bunyi dan Fotodioda digunakan dalam pengukuran ini. Penguatan sinyal dilakukan dengan memanfaatkan Lock-in amplifair dan waktu tetapan Lock-in amplifair juga ditentukan dalam rangka mengoptimasi SFA. Gas nitrogen digunakan untuk mendeteksi sinyal latar. **Hasil dan Diskusi:** Dari optimasi spektrometer fotoakustik, hasil-hasil yang diperoleh adalah frekuensi laser dioda 1.000 Hz dengan *duty cycle* 50%, dan penguatan Lock-in amplifair 10.000 kali dengan waktu tetapan 3,3 ms. Konsentrasi maksimum yang dicapai dalam pengukuran ini adalah 6 ppm. Sinyal latar yang dicapai dalam pengukuran ini adalah 0,00002 V/W. Batas deteksi terendah yang tercapai dalam pengukuran ini adalah 0,0064 ppm. **Kesimpulan:** Wadah sampel gas yang mengandung NO₂ dengan ukuran-ukuran yang lebih besar cenderung mempunyai konsentrasi yang lebih besar. Kadang-kadang konsentrasi NO₂ wadah sampel gas yang besar dikalahkan oleh wadah sampel yang kecil.

Kata kunci: *Spektrometer Fotoakustik Laser Biru, Nitrogen dioksida, Sel fotoakustik, Modulasi, Arduino Uno.*

1. INTRODUCTION:

1.1. Background

NO₂, as the most common air pollutant, can cause health problems for humans. NO₂ causes photochemical smog and acid rain. The primary sources of ambient NO₂ are anthropogenic combustion processes, such as the emissions from cars, power plants, and factories. There has been respectable interest in building a sound and cost-effective NO₂ sensor system (Yin *et al.*, 2017). NO₂ can become toxic if it has a high concentration and is inhaled (Dong *et al.*, 2020). NO₂ concentrations above 100 ppmV are chronic human exposure, so NO₂ is classified as a highly hazardous substance. It can cause pulmonary edema leading to death (Ruck *et al.*, 2017).

Greenhouse gases such as NO₂, CO₂, and CH₄, are also responsible for global warming (Yehya and Chaudhary, 2012). Electrochemical-based sensors are used to detect NO₂, but these sensors lack long-term stability and undergo cross-sensitivity to other gases (Breitgesser *et al.*, 2020). IR absorption photometers used to measure NO₂ are very large and costly (Kapp *et al.*, 2018). Accurate and easy measurement of

NO₂ at ppb levels is essential for monitoring environmental pollution and can be used to maintain a healthy living environment. NO₂ characterized by broadband absorption in the visible region of the spectrum has been a subject of frequent research. Gas detection using photoacoustic with blue diode laser sources is a perfect, well-established, and sensitive detection technique for NO₂ gas based on the generation of sound waves (Kalkman dan Kesteren, 2008).

The increasing use of photoacoustic techniques to control trace gases is mainly due to the constant growth of short, medium, and long-wavelength infrared semiconductor lasers (Ruck *et al.*, 2017). Photoacoustic Spectroscopy has characteristics like a fast response, high selectivity and sensitivity, and compact detection module, so it is widely used for detecting trace gas (Gong *et al.*, 2020).

The disadvantage of lasers derived from lead-salt equipment is that they are cryogenically cooled. DFB lasers are high-priced lasers and work in only a few windows between 0.7 and 1.9 μm . The simple Fabry-Perot diode laser is more suitable for integrated, portable, and low-cost sensors (Gianfrani *et al.*, 1997). Extra cavity configuration was chosen because it made

instruments easier to combine with the lowest detection limit achieving the ppt order for ethylene gas (Mitrayana *et al.*, 2011). A different design for photoacoustic cells had been suggested, namely resonant cells with one resonator and two acoustic buffers. It aims to obtain efficient noise reduction, thereby increasing the signal-to-noise ratio results (Elia *et al.*, 2009).

The modulation method used in the green diode laser modulation was the amplitude-shift keying method (ASK) with the On-Off Keying modulation type (OOK). Calibration of the laser modulation system with a database technique is expected to improve accuracy with the recommended frequency of 500 Hz to 9,500 Hz with 500 Hz intervals (Rakhmadi *et al.*, 2018). The molecular concentration directly relates to obtained signal in on-off modulation, so it becomes the best practical modulation way. At atmospheric pressure, finding a wavenumber where no atmospheric molecule absorbs is quite impossible, but the absorption that can be low enough enables very weak error in using this detection method. (Grossel *et al.*, 2007). Laser intensity modulation for continuous wave laser can be applied at a fixed frequency or variable frequency with the laser light periodically turned on and off to form square wave fluctuations in photoacoustic imaging. The 532 nm diode laser modulation can affect photoacoustic image quality. Therefore, laser modulation must be applied in the optimum duty cycle to obtain the best quality from photoacoustic images (Widianingrum *et al.*, 2017).

Slezak carried out a simple experiment to detect NO₂ using visible laser photoacoustic with various wavelengths (Slezak, 2001). Elia *et al.* used a differential photoacoustic cell with two resonators for NO₂ gas with a concentration of 0.5 ppb for a continuous wave quantum cascade laser with $\lambda = 6.25 \mu\text{m}$ and 80 ppb for a pulsed quantum cascade laser with $\lambda = 6.2 \mu\text{m}$ (Elia *et al.*, 2009). Pushkarsky *et al.* reported detecting NO₂ levels of subparts per billion using photoacoustic spectroscopy based on a 350 nm tunable continuous-wave quantum cascade laser with minimum detection of 0.5 ppb (Pushkarsky *et al.*, 2006). Mitrayana *et al.* had successfully designed and built a PAS with a blue laser light source and used it to measure NO₂ gas with a detection limit of 10 ppbV (Mitrayana *et al.*, 2007). Zheng, H *et al.* used a sub ppb level QEPAS NO₂ nitrogen dioxide sensor built utilizing a cost-effective broad line diode laser emitting at 450 nm (Zheng *et al.*, 2015).

The H-type longitudinal resonant PA cell has easy processing, good matching with

axisymmetric laser beams, and good cooperating with axisymmetric PA fields. It has been utilized in recent years. Though researches on the structure optimization of an H-type PA cell are seldom. (Gong *et al.*, 2020).

1.2. Theory

1.2.1 Blue Laser

The layering of atomic orbitals in a semiconductor makes the electrons form a continuous band structure. The band structure consists of a conduction band and a valence band separated by an energy gap of typically 0.5-2.5eV. In undoped semiconductors, the electrons in the conduction band and holes in the valence band can move almost freely because the continuous band structure is approximately represented as an electron gas. Holes are the electrons lost in the valence band that can shift so that they flow current. Semiconductors are N-doped if group V atoms dope a semiconductor with the atom in group IV. Semiconductors are P-doped if a semiconductor with the atom in group IV is doped by group III atoms (Fuchs, 2006). A one-dimensional energy diagram for electrons and holes can be seen in Figure 1.

When an electric current is passed in a forward direction through a p-n semiconductor diode, the electrons and holes can rearrange in the p-n junction. They can emit recombinant energy in the form of electromagnetic radiation. The line width of the spontaneous emission is up to several cm^{-1} . The wavelength is determined by the energy difference between the energy levels of electrons and the holes, which is mainly determined by the bandgap (Demtroder, 2002).

Figure 1. One-dimensional energy diagram for electrons and holes. E_c is the energy of the conduction band, E_v is the energy of the valence band. Because of the combination of electrons with holes, photon energy can be emitted (Fuchs, 2006).

With the undoped layer of p-i-n heterostructure defined as a small area where the recombination

process is known to occur, the conditions for laser light amplification can also be met in this region.

The p-i-n structure acts as a waveguide using total internal reflection because the undoped layer has a higher refractive index than the surrounding cladding layer (Fuchs, 2006). Thus, in a simple bulk laser, the active region does not confine the optical radiation produced by stimulated recombination of electron-hole pairs, and absorption processes outside the active (or gain) medium surpass a significant fraction of the optical radiation (Nakamura *et al.*, 2000).

1.2.2 Photoacoustic Spectroscopy

Photoacoustic spectroscopy is based on the absorption of electromagnetic radiation by analyte molecules. Non-radiative relaxation processes (such as collisions with other molecules) induce local heating of the reference sample. Pressure fluctuations generated by thermal expansion can be detected in the form of acoustic or ultrasonic waves (Bageshwar *et al.*, 2010).

The acoustic signal is converted to an electric signal by equation 1.

$$S(\nu) = C_{cell} I_{po} S(T) g(\nu) N \quad (1)$$

(Jiang *et al.*, 2016).

The eigenfrequency is the same for an open-open or closed-closed cavity and is given by equation 2.

$$\omega_j = 2\pi f_j = \pi c_s \sqrt{\left(\frac{k}{L}\right)^2 + \left(\frac{\alpha_{mn}}{R_c}\right)^2}. \quad (2)$$

The eigenvalues represent the longitudinal, azimuthal and radial indices, respectively (Besson and Thevenaz, 2006). For both sides of the open or closed resonator tube, the maximum resonance amplification frequency f_{res} is related to the effective tube length L_{eff} through the speed of sound following equation 3.

$$f_{res} = n \frac{c}{2L_{eff}} \quad (3)$$

(Ruck *et al.*, 2017).

The acoustic pressure equation is obtained using equation 4

$$p_j(r, \omega) = \frac{\cos}{\sin}(m\Phi) [AJ_m(k_r r) + BY_m(k_r r)] [C \sin(k_z z) + D \cos(k_z z)] \quad (4)$$

with $m = 0, n = 0, n_z = 1$ so that $\alpha_{mn} = 0$ and $J(0) = 1$ result in equation 5 for the buffer space

$$\tilde{p}_b(z, \omega_l) = \frac{Q_{lb}}{\omega_l} \left[\frac{\beta \tilde{I}(\gamma - 1)}{V_{ob}} \right] \frac{1}{\sqrt{2}} \cos\left(\frac{\pi}{l} z\right), \quad (5)$$

and in the resonator space (equation 6)

$$\tilde{p}_b(z, \omega_l) = \frac{Q_{lr}}{\omega_l} \left[\frac{\beta \tilde{I}(\gamma - 1)}{V_{or}} \right] \frac{1}{\sqrt{2}} \cos\left(\frac{\pi}{l} z\right) \quad (6)$$

(Mitrayana *et al.*, 2014).

The electronic transition ${}^2B_1 \leftarrow X^2A_1$ and ${}^2B_1 \leftarrow X^2A_1$ are the suitable broad absorption spectrum of NO_2 (Ruck *et al.*, 2017).

In a range of 460-370 nm, absorption occurs from the ground state to the 2B_1 and 2B_2 levels, and above 600 nm, the transition occurs only to 2B_2 (Slezak., 2001). The wavelength that photochemical dissociation can occur is below 415 nm (Zheng *et al.*, 2015). Figure 2 shows energy exchange between and from low electronic levels of NO_2 in the presence of N_2 .

Figure 2. Energy exchange between and from low electronic levels of NO_2 in the presence of N_2 (Slezak, 2001).

1.2.3 Arduino UNO R3 and Amplitude Shift Keying (ASK) Methode

Arduino Uno R3 is a microcontroller development board based on the ATmega328P chip. Software used to develop microcontroller applications, starting from writing source programs, compiling, uploading compilation results, and testing them in a serial terminal, is IDE (Integrated Development Environment). Arduino Uno board can be seen in Figure 3.

Amplitude-Shift Keying (ASK) modulation modulates the amplitude of the carrier signal output to be changed by the modulation signal. Changes in the carrier signal amplitude will occur in this ASK method according to the logic of input signal bits. Bit 1 and bit 0 are used to symbolize

digital information signals.

The duty cycle can be used to adjust the number of high logic and low logic in a signal with the equation 7:

$$\text{Duty cycle} = \frac{T_{on}}{T_{on} + T_{off}} \times 100\%. \quad (7)$$

(Solihah, 2016).

1.2.4 Nitrogen dioxide

Nitrogen dioxide is a strong oxidant, is reddish-brown, and is soluble in water. Nitrogen dioxide is an important atmospheric trace gas. In addition to its health effects, it absorbs visible solar radiation. Thus, it contributes to the visibility of a damaged atmosphere. It is an absorber of visible radiation, potentially impacting global climate change if concentrations are high enough. Figure 4 illustrates nitrogen dioxide structural formula.

NO₂, together with NO, becomes the primary regulator of the oxidizing power of free troposphere by controlling the addition and destruction of radical types, including hydroxyl radicals and NO₂. Moreover, it plays a critical role in determining the concentration of ozone (O₃) in the troposphere. Whether in a polluted or unpolluted atmosphere, the photolysis of nitrogen dioxide is the only key initiator of the photochemical formation of ozone (WHO, 2000).

Figure 4. Nitrogen dioxide structural formula (Mills, B., 2007).

Therefore, this study aimed to make a simple, easy, and low-cost experiment in detecting NO₂ gas using PAS with a blue laser diode utilizing on-off modulation.

2. MATERIALS AND METHODS:

NO₂ detection was carried out using a photoacoustic spectrometer with a blue laser source with a wavelength of 450 nm. The photoacoustic cell used is a single resonator photoacoustic cell with type H. In most studies, a mechanical chopper is used to modulate the laser beam. In contrast, an Arduino Uno microcontroller can be used to modulate laser beam working on-off according to frequency input (Rakhmadi *et al.*, 2019). The blue diode laser intensity is modulated using an on-off scheme. The modulation period is

adjusted until the maximum photoacoustic signal value is found. Nitrogen gas is used to determine the background signal that plays a role in determining the concentration of NO₂.

The equipment and material of this study are the Blue Diode Laser with a wavelength (λ) of 450 nm, class IIIA position, 12 V DC voltage, and 2W power. Other instruments are the actuator system, which is a series consisting of a power supply, TTL laser, and Arduino Uno, whose system modulates laser current by adjusting the modulation frequency of the Arduino UNO microcontroller programming, resistors, lock-in amplifier, computer, a photodiode sensor, multi-size gas containers, Outcoupling window glass, an Arduino UNO sound sensor, BNC oscilloscope cables, male and female circuit cables. Figure 5 shows the series of tools. The material used was gases containing NO₂, such as motor vehicle exhaust gas and environmental air.

The photoacoustic cell consists of a single cylindrical channel as an acoustic resonator. The channel length is 90 mm, and the channel diameter is 8 mm. Photoacoustic cell can be seen in Figure 6.

An electric condenser microphone is placed against the wall in the middle of the channel to detect acoustic pressure. Two identic buffer volumes have 10 mm long and 30 mm diameter. The distance between the two windows is 110 mm.

Figure 6. Photoacoustic Cell.

The difference between this research and others is that in optimizing and characterizing the blue diode laser spectrometer and determining the resonance curve, we used a gas containing NO₂ instead of pure NO₂ gas. For the linearity curve, it refers to another reference to get a gradient variable. A Diagram of the research phase can be seen in Figure 7.

Determining the lock-in amplifier amplification was carried out by inserting 1.5 liters of gas containing NO₂ into the photoacoustic cell and irradiating it for 2 minutes, respectively, from 1 to 10,000. On turning the buttons, care was required to be taken so it was not to overload. The lock-in amplifier constant time was determined by inserting 1.5 liters of gas containing NO₂ into the

photoacoustic cell and irradiating it for 2 minutes, respectively, from 3.3 ms to 1s. On turning the buttons, attention should be given to avoid overloading.

The duty cycle laser was determined by inserting 5 liters of gas containing NO₂ into the photoacoustic cell and irradiating it for 2 minutes, respectively, from 16.67% to 83.33%. The photoacoustic signal appearing not associated with absorption in the medium under investigation is called the background signal. These signals are caused by the absorption of radiation in the walls and windows of the photoacoustic cells, by scattered radiation entering the acoustic detector, by the presence of impurities that are extraneous to the absorption bands in the spectrum range in the study, and others (Zharov dan Lethokov, 1986). Measurement of background signal was carried out by passing nitrogen to the photoacoustic cell.

Determination of the resonance curve and quality factor was done by modulating the diode with the on-off method to see the maximum signal frequency at the 2 L gas sample and determine the quality factor. The linearity curve is determined by referring to a selected reference. It was referred from an article by author Yi Hongming *et al.* in 2011 entitled "Application of a broadband blue laser diode to trace NO₂ detection using off-beam quartz-enhanced photoacoustic spectroscopy". The linearity curve graph is presented in Figure 8 with a gradient of 24.51 and a mean laser power of 7 mW.

Figure 8. NO₂ linearity curve (Yi *et al.*, 2011).

Measurement of noise and the lowest detection limit of PAS was done by injecting 250 ml of gas containing NO₂, turning off the blue laser, and recording the signal.

Testing NO₂ concentration from gases

containing NO₂ was carried out by injecting gas containing NO₂ from various motor vehicle exhaust gases and from environmental air in multi-size containers. Calculating the concentration of the signal can be done with equation 8:

$$\text{Concentration} = \frac{S_N - S_{\text{background}}}{\text{Gradient}} \quad (8)$$

(Mitrayana, 2008).

Measurement of NO₂ gas was carried out by taking gas samples containing NO₂ in 4 types of vehicles and campus air on the same six gas containers. One type of vehicle was varied in the collection time, namely 1 minute and 2.5 minutes.

3. RESULTS AND DISCUSSION:

3.1. Results

From the experiment, the lock-in amplifier amplification achieved is 10,000 times. We can see the result of the experiment in Figure 9.

Figure 9. Lock-in amplifier amplification graph.

It was achieved 3.3 ms for lock-in amplifier constant time from the experiment like in Figure 10.

Figure 10. Lock-In Amplifier constant time graph.

The experiment result of lock-in amplifier

constant time can be seen in Table 1 and the experiment result of the lock-in amplifier amplification is in Table 2.

Table 1. Lock-in Amplifier constant time.

Lock-in Amplifier constant time (ms)	Sound sensor value (Bit)	Sound Voltage (V)
3.3	386	0.000189
10	118.5	0.000058
33	3.5	0.000002
333	34.3	0.000017
1,000	26.5	0.000013

The duty cycle achieved was 50%, as shown in Figure 11 and Table 3.

Figure 11. Duty cycle curve of blue diode laser modulation.

The background signal gotten was 0.00002 V/W. Figure 12 shows a graph of the background signal, and the experiment result can be seen in Table 4. The quality factor obtained is $Q = 6.67$.

Figure 12. Graph of the background signal.

According to the experimental results, the resonant frequency obtained was 1,000 Hz. Figure 13 shows resonance curve, and the experiment result can be seen in Table 5. The maximum laser output power received by the photodiode is 0.193353 Watt. The airflow rate to the photoacoustic cell is 24 liters/hour.

Figure 13. Resonance curve.

The lowest detection limit obtained at 250 mL volume was 0.00640 ppm or 6.40 ppb with a signal noise of 3.97 V/W or 0.011 V, and Table 6 shows the experiment result.

In detecting NO_2 gas from motor vehicle exhaust gases and campus air, Figures 14, 15, 16, 17, 18 and 19 show the experiment result of gas sample container from vehicle A for 1 minute take time, vehicle A for 2.5 minutes take time, vehicle B, vehicle C, vehicle D, and campus air respectively. The experiment result can be seen in Table 7.

Figure 14. NO_2 concentration curve for vehicle A ($t = 1$ minute).

Figure 15. NO_2 concentration curve for vehicle A ($t = 2.5$ minutes).

Figure 18. The curve of NO_2 concentration for vehicle D.

Figure 16. The curve of the NO_2 concentration of vehicle B.

Figure 19. The curve of air NO_2 concentration in the campus environment.

Figure 17. The curve of NO_2 concentration for vehicle C.

3.2 Discussion

In using a photoacoustic spectrometer, the resonance curve is first determined to know what the maximum modulation frequency measurement is. Likewise, the amplification and the constant time of lock-in amplifier, and the blue diode laser duty cycle are determined in advance to maximize the photoacoustic signal.

The extra cavity blue diode laser photoacoustic spectrometer designed was successfully tested by detecting NO_2 -containing gases from motor vehicle exhaust gases and the campus air. The extra cavity blue diode laser photoacoustic spectrometer utilizing Arduino Uno is used to measure the concentration of NO_2 gas in a gas sample whose performance can increase by increasing its sensitivity. The design and use of the right equipment can improve the accuracy of measurement. Optimization needs to be done to find the maximum measurement conditions.

The nitrogen dioxide concentration in each sample shows the number of NO₂ molecules accommodated in each sample. In taking campus environment air, the sample air was taken in the night to avoid the dissociation effect. From the calculations using achieved photoacoustic signals, larger volumes of gas show a tendency to increase in concentration even though some are decreasing.

From the analysis of the variables needed to determine the concentration, these variables have increased, and some have decreased, especially in the sound sensor voltage and photodiode power. The final concentration result is that it generally increases. The estimation is that NO₂ gas breaks out during sampling from the concentration decrease undergone in the measurement. The estimated cause is that the sampling process is still simple, so there is a possibility that NO₂ gas will come out when closing the container. Another factor is the possibility of frequent shifting of the equipment during sampling, which can change the laser and photodiode alignment position. The alignment that is less than the maximum can affect the measurement results. Another possibility is the number and the size of other exhaust gas types that dominate more than NO₂ occupying each container. The amount of NO₂ is surpassed by the number of other exhaust gases. PAS was arranged only to detect NO₂ gas.

From the six sample containers used, the 5-liter volume of the container often has the highest concentration calculation of the six types of sample sources. Likewise, the second-largest 2-liter container is always in second place even though it is in the first place with the most concentration. From these results, the greater container volume tends to have the greater concentration. In addition, the sample container that the time of the take from a vehicle is longer has NO₂ concentration higher.

The maximum measurement achieved by the blue diode laser PAS tool in this experiment is up to 6 ppm. This measurement has the lowest detection limit of 6.4 ppb. However, it is not so far from Ruck *et al.*, in 2017, having a detection limit of 2.0 ppbV NO₂. The resonance frequency based on theory is 1,559 Hz, but the practical resonance frequency in this measurement was 1,000 Hz.

4. CONCLUSIONS:

It can be concluded that large gas sample storage containers tend to contain more significant NO₂. The concentration number tends to increase

from small sample volumes to large sample volumes, although some have decreased. The decrease undergone is based on the estimation that some gases were wasted when the exhaust gas was entered into the container, and other exhaust gases surpassed NO₂. The maximum concentration obtained is six ppm. Paying attention to the take time of the sample is required in determining NO₂ concentration from a vehicle.

Arduino Uno can be used to modulate the beam of diode laser in replacing mechanic chopper. Optimization is needed by choosing the appropriate duty cycle and maximum frequency to achieve maximum measurement. The proper amplification and the proper constant time of lock-in amplifier must be chosen to get the maximum measurement.

This photoacoustic spectrometer with blue diode laser utilizing Arduino Uno can achieve low ppb levels for the measurement result. It is sensitive enough to detect gas. The experiment having been done can be more straightforward, more effortless, and low-cost. Modulation of the laser beam with Arduino Uno can be applied to detect other gases with different wavelengths and colors of laser using the photoacoustic spectrometer.

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Figure 3. Arduino Uno (Wicaksono, 2017).

Figure 5. Series of Tools.

Figure 7. Diagram of the research phase.

Table 2. Lock-In Amplifier Amplification.

No	Lock-In Amplification (Time)	Sound Sensor Value (Bit)	Photodiode Sensor Value (Bit)	Photodiode Power (W)	Sound Sensor Voltage (V)	Photoacoustic Signal (V/W)
1.	1	150.3	970	0.1896	0.00007346	0.00038745
2.	10	40.5	970	0.1896	0.00001979	0.00010440
3.	50	138.25	970	0.1896	0.00000921	0.00004857
4.	100	55	971	0.1896	0.00002688	0.00014178
5.	200	89	970	0.1896	0.00004350	0.00022943
6.	1,000	169.67	970	0.1896	0.00008293	0.00043738
7.	10,000	319	970	0.1896	0.00015591	0.00082233

Table 3. Blue Diode Laser Modulation Duty Cycle Curve.

No	Duty Cycle	Photodiode Sensor Value (Bit)	Sound Sensor Value (Bit)	Sound Sensor Voltage (Volt)
1.	16.67%	43.44444444	7.333333333	0.00000358
2.	20%	15.17647059	9.090909091	0.00000444
3.	25%	28	13.25	0.00000648
5.	33.33%	32.46666667	2.833333333	0.00000138
6.	37.50%	18.28571429	3	0.00000147
7.	44.44%	221.3658537	53.78333333	0.00002629
8.	50%	570	75.92941176	0.00003711
9.	55.56%	365.6842105	16.35416667	0.00000799
10.	62.50%	316.4285714	1.666666667	0.00000081
11.	66.67%	404.6666667	3.5	0.00000171
12.	71.42%	760.7826087	3	0.00000147
13.	75%	503.7241379	3.727272727	0.00000182
14.	80%	502.4310345	3.419354839	0.00000167
15.	83.33%	445.8	4.142857143	0.00000202

Table 4. Background Signal

Time (minute)	Sound Sensor Value (Bit)	Sound Voltage (Volt)	Photodiode Power (W)	Photodiode Sensor Value (Bit)
1	2	0.01	0.147	754.5
2	4	0.02	0.133	685
3	4	0.02	0.124	637
4	7	0.03	0.157	807
5	8	0.04	0.112	573
6	9	0.04	0.114	586
7	6	0.03	0.142	727
8	5	0.02	0.151	772
9	9	0.04	0.144	740
10	8	0.04	0.105	559

Background Signal = $(0.029/0.1329)/10,000 = 0.21/10,000 \text{ V/W} = 0.00002 \text{ V/W}$

Table 5. Resonance Curve.

No	Frequency (Hz)	Photodiode Sensor Value (Bit)	Sound Sensor Value (Bit)	Photodiode Power (Watt)	Sound Voltage (V)	Photoacoustic Signal (V/W)
1.	200	65.822	5.359	0.01287	0.026192446	0.00020354
2.	250	64.226	6.941	0.01256	0.033925594	0.00027019
3.	333.33	364.9	9.949	0.07134	0.04862521	0.00006816
4.	500	468.45	11.932	0.09158	0.058319665	0.00006368
5.	600	21.909	7.273	0.00428	0.035546077	0.00082988
6.	700	21.333	8.75	0.00417	0.042766373	0.00102539
7.	800	20.667	22.385	0.00404	0.109406722	0.00270782
8.	900	14.476	20.2632	0.00283	0.099037917	0.00349939
9.	1000	551.455	357.667	0.10781	1.748126426	0.01585014
10.	1100	20.929	5.167	0.00410	0.025252525	0.00603303
11.	1200	14.333	12.2	0.00280	0.059628543	0.00212791
12.	1250	31.7436	17.684	0.00621	0.086433092	0.00139274
13.	1666.67	68.833	25.364	0.01346	0.123966942	0.00092120
14.	2000	17.84	7	0.00349	0.034213099	0.00098094
15.	2500	229.75	21.4	0.04595	0.10459433	0.00022763
16.	3000	6.615	2.556	0.00129	0.012490496	0.00096576
17.	4000	9.385	3	0.00183	0.014662757	0.00079918
18.	5000	77.5	18.364	0.01515	0.089753843	0.00059238

Table 6. Noise Signal and Lowest Detection limit

No	Photodiode Sensor Value (Bit)	Sound Sensor Value (Bit)	Photodiode Volatge (V)	Photodiode Power (W)	Sound Voltage (V)	Photoacoustic Signal (V/W)
1.	88.2167	3.0976	0.4312	0.0172	0.01514	0.8778
2.	14.1765	2.25	0.0693	0.0028	0.011	3.9678

Table 7. Concentration Calculation of measurement samples

Type	Sample (L)	PD Sensor Value (Bit)	Sound Sensor Value (Bit)	PD Power (W)	Sound Voltage (V)	PA Signal (V/W)	Concentration (ppm)
Vega (A) t=60 s	0.25	557.100	11.333	0.1089	0.000006	0.000051	0.0088
	0.6	757.025	15.706	0.1480	0.000008	0.000052	0.0091
	1	531.630	15.630	0.1039	0.000008	0.000074	0.0153
	1.5	584.630	18.841	0.1143	0.000009	0.000081	0.0173
	2	563.060	74.300	0.1101	0.000036	0.000330	0.0885
	5	15.000	12.592	0.0029	0.000006	0.002099	0.5937

Vega (A) t=150 s	0.25	3.172	2.357	0.0006	0.000001	0.001858	0.5248
	0.6	4.261	5.091	0.0008	0.000002	0.002987	0.8474
	1	5.631	2.920	0.0011	0.000001	0.001296	0.3646
	1.5	6.828	3.308	0.0013	0.000002	0.001211	0.3402
	2	6.427	4.191	0.0013	0.000002	0.001630	0.4599
	5	5.825	10.091	0.0011	0.000005	0.004331	1.2313
Versa (B)	0.25	23.533	5.283	0.0046	0.000003	0.000561	0.1546
	0.6	21.567	9.519	0.0042	0.000005	0.001103	0.3094
	1	24.200	10.345	0.0047	0.000005	0.001069	0.2995
	1.5	14.638	8.096	0.0029	0.000004	0.001383	0.3892
	2	15.689	7.942	0.0031	0.000004	0.001266	0.3557
	5	14.673	6.590	0.0029	0.000003	0.001123	0.3149
Tiger (C)	0.25	10.672	3.847	0.0021	0.000002	0.000901	0.2517
	0.6	8.098	2.909	0.0016	0.000001	0.000898	0.2508
	1	7.551	6.077	0.0015	0.000003	0.002012	0.5689
	1.5	11.400	4.143	0.0022	0.000002	0.000909	0.2538
	2	4.828	17.429	0.0009	0.000009	0.009025	2.5717
	5	7.333	6.333	0.0014	0.000005	0.003245	0.9210
Force (D)	0.25	6.500	7.322	0.0013	0.000004	0.002816	0.7986
	0.6	4.475	7.155	0.0009	0.000003	0.003998	1.1360
	1	4.885	10.016	0.0010	0.000005	0.005126	1.4582
	1.5	4.250	5.383	0.0008	0.000003	0.003167	0.8987
	2	5.571	5.397	0.0011	0.000003	0.002422	0.6859
	5	5.587	7.419	0.0011	0.000004	0.003320	0.9424
Campus Environment Air	0.25	11.492	3.000	0.0022	0.000001	0.000653	0.1807
	0.6	4.567	4.212	0.0009	0.000002	0.002306	0.6528
	1	5.689	10.607	0.0011	0.000005	0.004661	1.3256
	1.5	13.741	115.667	0.0027	0.000057	0.021043	6.0043
	2	11.032	68.111	0.0022	0.000033	0.015435	4.4026
	5	5.016	5.862	0.0010	0.000003	0.002922	0.8287