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A Low-Cost Instrument to Monitor Sulphur Dioxide Emissions Based on The DOAS Method

Nur Zen*[1,2], Haryono Setiyo Huboyo[1], Moch. Syarif Romadhon[3,4], Januar Arif Fatkhurrahman[2], Sidna Kosim Amrulah[2]

[1] Department of Environmental Engineering, Diponegoro University.
[2] Center for Standardization and Industrial Pollution Prevention Services.
[3] National Research and Innovation Agency.
[4] Atmospheric, Oceanic and Planetary Physics Department, University of Oxford.

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ABSTRACT

Various techniques to measure SO_2 concentration based on Differential Optical Absorption Spectroscopy (DOAS) have been widely developed and applied for various measurements. However, most of the applications are still relatively expensive. Some efforts have been made to reduce the cost by using Ultraviolet Light Emitting Diodes (LEDs) as light sources, showing promising results. Further reductions can be possibly made by providing an alternative to replace high spectral resolution spectrometers widely used in DOAS applications since those spectrometers are commercially expensive. This paper studies the feasibility of a DOAS instrument using a low-cost spectrometer and UV-LEDs as light sources. The resolution of the spectrometer is 0.7 nm. With this resolution, it is expected that the instrument hardly captures narrow band structures of SO_2 optical absorption in the spectral range between 280 nm and 320 nm when measuring SO_2 gas concentration lower than the limits of SO_2 emissions regulated by the Indonesian government. To compensate for this drawback, narrow and broad bands of optical absorption structures are considered in the data analysis to achieve a detection limit far below the regulated limits. To capture the broadband structures, four UV-LEDs are used to cover spectral absorption from 250 nm to 320 nm. The instrument was calibrated using eight different standard concentrations of SO_2. The correlation between the readings and the standard concentrations is high, indicated by the Pearson correlation coefficient of 0.9999. It was also found that the lowest concentration the instrument can distinguish from blank samples or the Limit of Detection is 16 ppm. However, the instrument can precisely measure concentrations higher than or equal to 25 ppm with a standard deviation of less than 10% of the mean concentration measured from five measurements. This is far below the required legal limits, below 229 ppm. After the calibration, the DOAS instrument was used to measure SO_2 sampled from the emission of burning coals. To compare, a commercial SO_2 sensor was used to measure the same gas. The results indicate that the difference in the readings between the two instruments is around 6% of the concentration.

1. INTRODUCTION

One of the major pollutants in the atmosphere is Sulfur Dioxide (SO_2). The sources of atmospheric SO_2 can be anthropogenic and natural activities such as fuel combustion (Akimoto & Narita, 1994) and volcanic activities (Bani et al., 2022). In general, the formation of SO_2 in the combustion process follows the following reaction:

$$S_{(s)} + O2_{(g)} \rightarrow SO2_{(g)} \qquad (1)$$

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*Correspondence author.
E-mail : nurzen.st@gmail.com (Nur Zen)

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Atmospheric SO_2 can have adverse effects on the environment and human health. For example, SO_2 can be oxidized to form sulfuric acid (Laaksonen et al., 2008) and sulfate aerosols that lead to environmental acidification (Rodhe, 1999). Meanwhile, exposure to high concentrations of SO_2 can cause irritation and malfunction of the human respiratory system (Kampa & Castanas, 2008). The presence of SO_2 in the atmosphere can cause acid rain with pH < 7 (Yunita & Kiswandono, 2017) because of the reaction below:

$$\frac{1}{2}O_{2\,(g)} + SO_{2\,(g)} + H_2O_{\,(l)} \rightarrow H_2SO_{4\,(g)} \qquad (2)$$

To tackle the negative impacts of atmospheric SO_2, some regulations were issued by the Indonesia Ministry of Environment. For example, legal limits for SO2 emitted from internal combustion engines were introduced in 2019 (MenLHK RI, 2019), and some of the limits are listed in Table 1. However, the measurement standard approved by the ministry is either not environmentally friendly since they produce chemical waste (Badan Standardisasi Nasional Indonesia, 2005, 2009) or expensive since they require periodic maintenance (EPA CTM-022, 1995). Furthermore, there is a need to measure SO_2 continuously at emission sources, as long-term measurements can provide a reliable assessment of the contribution of emission sources to the level of atmospheric SO_2 around the sources. None of the approved measurements are economically practical for continuous measurements. For example, based on USEPA CFR 40 part 75, continuous measurements can be done using chemical reagents such as sulphuric acid and hydrogen peroxide or an instrumental analyzer. The first method produces chemical wastes, and the second method is expensive since the corresponding instrument can cost between \$20,000-\$50,000 with periodic maintenance and calibration required.

An alternative to measure SO_2 is using Differential Optical Absorption Spectroscopy (DOAS). Using this method, gases can be continuously measured with minimal maintenance and no chemical waste produced. The method is based on the optical absorption structure of SO_2 with no direct interaction between the sample and light sensors (Stutz & Platt, 1996). DOAS method works in a wide range of wavelengths, from UV to visible (Fatkhurrahman et al., 2020). Furthermore, this technique does not require complex sample preparation and can use Light Emitting Diodes (LEDs) as light sources. These characteristics make DOAS suitable for a low-cost and environmentally friendly continuous measurement system.

Further cost reductions in a DOAS instrument can be made by providing an alternative to replace high spectral resolution spectrometers widely used in DOAS applications since those spectrometers are commercially expensive. For example, a spectrometer with 0.02 nm resolution can cost more than \$30,000. This paper studies the feasibility of a compact DOAS instrument using a low-cost spectrometer designed to measure SO_2 from emission sources. The spectrometer used in the instrument has less than 2.0 nm of spectral resolution and costs around \$3,000. With this resolution, the spectrometer is unlikely to measure SO_2 concentration far below the legal limits when it is used in a compact instrument with a short light path for light absorption. Therefore, the combination of the narrow and broadband structures of SO_2 absorption is used to determine SO_2 concentration to achieve a detection limit far below that regulated by the Indonesian government listed in Table 1.

Table 1. Limits of SO_2 in Inner Combustion Engine based on the Regulation of Indonesia Ministry of Environment Number 15 of 2019

Capacity	Fuel	Limits	
		mg/Nm^3	Ppm
< 3000 KW	Refined Fuel Oil	1800	687
	Diesel Oil	800	305
> 3000 KW	Refined Fuel Oil	1200	458
	Diesel Oil	600	229

2. METHODS

The central idea of the DOAS method is to retrieve gas concentration based on the spectral structure of optical absorption by the gas. The optical absorption, denoted as A, can be determined experimentally using two light intensities: those emitted by a light source, denoted as I_o (λ), and those absorbed by the gas, denoted as I(λ). The absorbance can be expressed mathematically as

$$A_{exp} = \ln[I(\lambda)] - \ln[I_o(\lambda)] \qquad (3)$$

where A_{exp} is experimentally determined absorbance. Optical absorption can be modelled as the absorption of light by gas. In a simple system where the length of optical absorption is relatively short, and there is only one gas that absorbs the light with no particles interfering with the absorption, then the absorption can be formulated as

$$A_{mod} = s\sigma(\lambda) + P(\lambda) \qquad (4)$$

where A_{mod} is modelled absorbance; $\sigma(\lambda)$ is the absorption cross-section of the gas (cm^2); $P(\lambda)$ is a linear function of λ representing interferences by other processes; s is a coefficient calculated by

$$s = nL \qquad (5)$$

where n is the density of gas molecules (particles/cm^3); L is the length of optical absorption (cm). The density can be derived from gas concentration as follow:

$$n = \frac{xN}{10^6} \qquad (6)$$

where x is the gas concentration (ppm); N is the density of air molecules ($1/cm^3$). In normal conditions, N is equal to 2.68×10^{19} particles/cm^3.

There are two components of $\sigma(\lambda)$: narrow and broad band cross-section denoted as $\sigma^n(\lambda)$ and $\sigma^b(\lambda)$, respectively. Mathematically, $\sigma(\lambda)$ can be expressed as

$$\sigma(\lambda) = \sigma^n(\lambda) + \sigma^b(\lambda) \qquad (7)$$

Most DOAS applications separate $\sigma^n(\lambda)$ from $\sigma^b(\lambda)$ as $\sigma^b(\lambda)$ is susceptible to interferences from light scattering due to air molecules and particles. In a condition where the scattering is minimized, such as in a relatively short light path, separation can be avoided. This condition is an advantage for an instrument using a low-resolution spectrometer, as the spectrometer is unlikely to resolve the structure of $\sigma^n(\lambda)$ when measuring optical absorption by low-concentration gas.

Three parameters are defined to characterize the performance of an instrument. The parameters are the Limit of Blank, Limit of Detection, and Limit of Quantification, denoted as LoB, LoD, and LoQ, respectively. The definition used in this study is as explained by Armbruster (Armbruster & Pry, 2008). The value of LoB and LoD can be determined as

$$LoB = \bar{c}_0 + 1.645\ \delta c_0 \qquad (8)$$

$$LoD = LoB + 1.645\ \delta c_{low} \qquad (9)$$

Where $\bar{c}_0$ is the mean of measured concentrations when the instrument measures blank samples; δc_0 and δc_{low} are the standard deviation of measured concentrations when the instrument measures blank samples and the lowest concentration distinguishable from blank samples, respectively. The value of LoQ can be defined as the lowest concentration the instrument can precisely measure. Two parameters can indicate the instrument's ability to precisely measure SO_2 of a particular concentration: the standard deviation of repetitive measurements and the Signal Noise Ratio (SNR) value. A minor standard deviation with Higher SNR can indicate the high ability of the instrument to precisely measure the concentration of interest. In the case of DOAS, the value of SNR can be calculated from the ratio between the sum of optical absorbance and the sum of residue signal. The residue signal is the difference between optical absorbance and A_{ext} and A_{mod}. There is no strict rule for the threshold of SNR. However, many consider the SNR of 1.0 is the threshold to indicate high-precision measurements.

3. INSTRUMENT DESIGN

The basic principle of the design is to measure $I_o(\lambda)$ and $I(\lambda)$ with minimum interference from other gases or particles. This requirement leads to a design with three major components: light sources, a cell, and a spectrometer. The design of the instrument is shown in Figure 1. As shown in the figure, SO_2 gas flows through the cell made of acrylic with a length of 30 cm. To capture $\sigma(\lambda)$ over a broad spectral range, four UV-LEDs with different spectral profiles are used to illuminate the gas. On the other side, a spectrometer is installed to measure transmitted light. The spectrometer used in the instrument is a CCS200 Spectrometer made by Thorlabs. The measurement range of the spectrometer is from 200 nm to 1000 nm with spectral accuracy lower than 2 nm. The spectrometer was calibrated using a mercury lamp, and it was concluded that its spectral accuracy is around 0.7 nm, evaluated at the spectral line of 365.0 nm. This spectral accuracy was used to convolve high-resolution SO_2 absorption cross-sections downloaded from the HITRAN database (Hermans, Vandaele, & Fally, 2009) ("HITRANonline - Absorption Cross Section Search," 2022). The high-resolution cross-section is shown as a blue line in Figure 2.a. The convolution was done for a range between 275 nm and 315 nm, and the results are shown as a red line in Figure 2.a. The UV-LED emission spectra were measured using the spectrometer, and the results are shown in Figure 2.b.

The depth of broad and narrow band structures is illustrated as dashed lines in Figure 2.a. As shown in the figure, the depth of the narrow structure significantly decreases when a low resolution of the spectrometer is used, while that of the broad structure only slightly changes. Therefore, the data analysis in this study uses both structures to ensure that the instrument has a significant sensitivity when measuring low concentrations of SO_2.

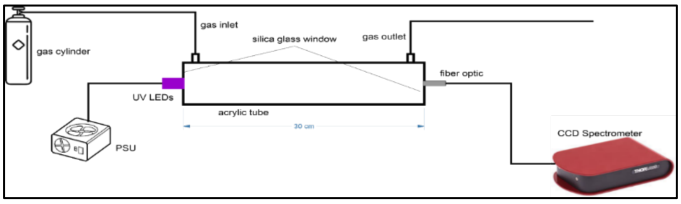

Figure 1. The DOAS instrument used in this study and its calibration setup.

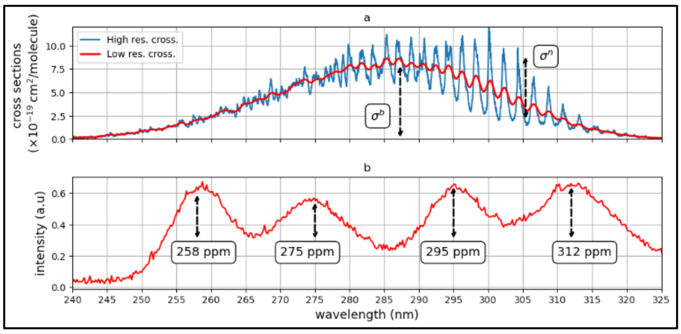

Figure 2. (a) The high and low resolution of SO_2 absorption cross-sections are shown as blue and red lines, respectively. As seen in the figure, there are broad and narrow band structures over a wide spectral range between 240 and 325 nm. One example of narrow band structures is indicated at absorption cross-sections around the wavelength of 305 nm. (b). The spectral intensity of the four UV-LEDs used in the DOAS instrument. It can be seen that the intensity covers the strong SO_2 spectral absorption between 250 nm and 320 nm.

4. CALIBRATION OF INSTRUMENT

The instrument was calibrated using eight different concentrations of SO_2. The concentrations are 0, 25, 50, 75, 100, 300, 500, and 1000 ppm. For each concentration, five measurements were performed. Based on the measurements, A_{exp} and A_{mod} were determined. To illustrate, some of the measurements are shown in Figure 3. The standard and measured SO_2 concentrations are indicated in the figure denoted as c_{std} and c_{mea}, respectively. As can be seen from the figure, $\sigma^b(\lambda)$ is predominant in the measurements of a concentration lower than 50 ppm. In the measurements of those higher than or equal to 75 ppm, both of $\sigma^b(\lambda)$ and $\sigma^n(\lambda)$ can be identified.

Based on the measurements, a calibration curve can be determined. The curve can be seen as a dashed blue line in Figure 4 with the corresponding scale on the left. In the figure, the mean and the standard deviations of the concentrations measured by the DOAS instrument are also indicated. As seen from the figure, the slope of the curve is nearly one, and the intercept is -6.4 ppm. The Pearson correlation coefficient between standard and measured concentrations is 0.93. Also, the ratio between the standard deviations and the mean of measured concentrations is lower than 2% of the mean concentration when the instrument measures concentrations higher than or equal to 300 ppm. For example, the standard deviation is 3 ppm when the instrument measured 300 ppm of SO2 five times with the mean of measured concentration 293 ppm. This higher precision when measuring high concentration can be due to the strong absorption structures for both broad and narrow absorption structures.

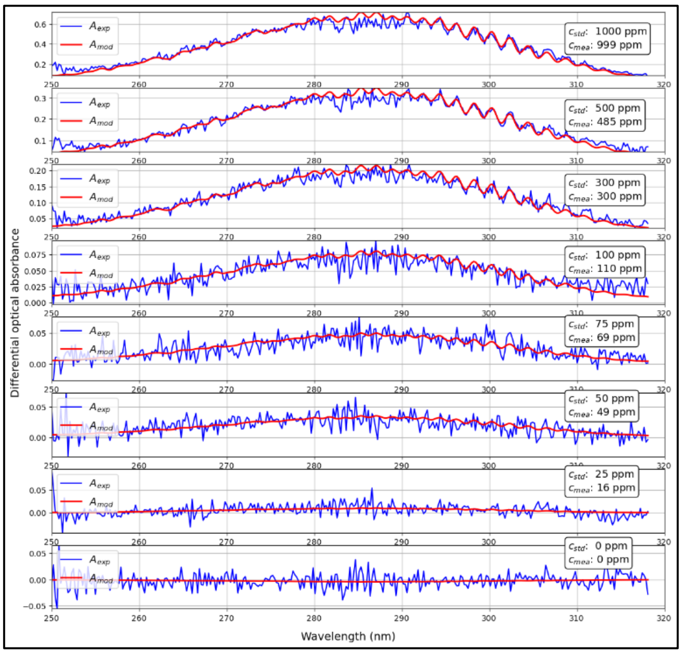

Figure 3. Some examples of optical absorption measurement for various SO_2 concentrations in the DOAS instrument calibration. The measured and modelled optical absorption are shown as blue and red lines, respectively. The concentrations were retrieved from the fitting between measured and modelled optical absorption. The results are indicated in the figure with c_{std} and c_{mea} denote the concentration of the gas standard and measured by the instrument, respectively.

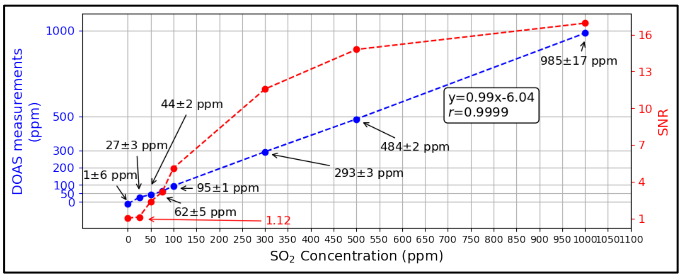

Figure 4. The calibration curve and the SNR of the measured optical depth.

Based on the calibration results, the value of the instrument's LoB, LoD, and LoQ can be determined. The mean concentration measured by the instrument was 1 ppm with a standard deviation of 6 ppm when the instrument measured blank samples. Using Eq. 8, the LoB of the instrument was calculated, and the result was around 11 ppm. The instrument also showed its ability to distinguish the concentration of 25 ppm from the blank, with a mean concentration of 27 ppm and a standard deviation of 3 ppm. So, LoD can be determined from the measurements of this concentration. Using Eq. 9, the value of LoD was calculated, and the result was around 16 ppm. The SNR of the measurements was calculated to analyze the LoQ of the instrument. The results are shown as a red line in Figure 4 with the corresponding scale on the right. Based on the figure, the SNR when the instrument measured a gas concentration of 25 ppm is slightly higher than 1. So, it can be safely assumed that the LoQ of the instrument is 25 ppm.

5. THE MEASUREMENTS OF SO_2 SAMPLED FROM INDUSTRY

The instrument was used to measure SO_2 gas sampled from coal-burning emissions. The gas was collected using a bag sampler. The measurements were done by transporting the gas into the cell of the DOAS instrument, and, as a comparison, a calibrated SO_2 commercial sensor was installed at the outlet of the instrument. To keep the air pressure inside the DOAS instrument at the ambient level, a T connector was installed at the outlet to split the flow into the commercial sensor and the ambient.

The commercial sensor used in this measurement was a PCA 3 Gas Analyzer made by Bacharach Inc. The gas analyzer has a measurement range of SO_2 between 0 ppm and 3000 ppm with a resolution of 1 ppm. It measures gas by drawing a small volume of the gas and passing it into an SO_2 sensor. The sensing mechanism of the sensor is based on an electrochemical reaction between SO_2 and SO_2-sensitive-material of the sensor generating electrical currents proportional to the concentration of SO_2.

The measurements can be divided into three stages. The first stage was the measurement of a blank sample. The blank sample was an ambient sample with a negligible concentration of SO_2. The second stage was the increasing concentration in the cell when the SO_2 sample started to flow into the cell. The third stage was the stable concentration when the SO_2 was well mixed inside the cell. The measurement results are shown in Figure 5. In the first stage, the reading of the DOAS instrument is around 25 ppm, indicated by a dashed line. This reading corresponds to the LoQ of the instrument. In the second stage, the reading of the DOAS instrument and the gas analyzer increased at a different rates. In the third stage, the reading of both instruments started to level off with a small amount of fluctuation. In the third stage, the average reading of the DOAS instrument and the gas analyzer were 211 ppm and 225 ppm, respectively. The difference is around 12 ppm or around 6% of the concentration.

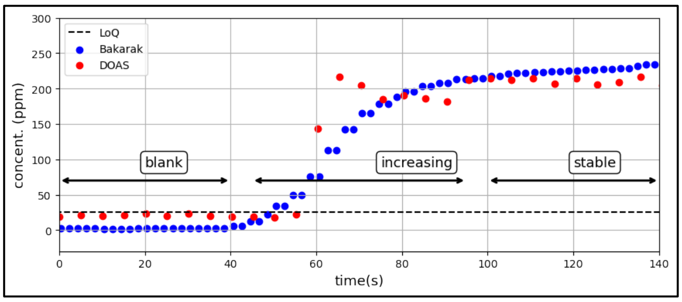

Figure 5. The measurement of SO2 sampled from the emission of coal burning.

6. CONCLUSION

The feasibility study of a low-cost instrument to measure SO_2 using a low-cost spectrometer and UV-LEDs as light sources were performed. The spectral range of the UV-LEDs is from 250 nm to 320 nm and can be used to measure a broad band structure of SO_2 absorption in this range. The low-cost spectrometer has a relatively low spectral resolution and is unlikely to resolve narrow band structures when measuring relatively low SO_2 concentration. Hence, in this study, broad band structures of SO_2 absorption were included in DOAS data analysis. The instrument's calibration shows the instrument's ability to measure concentrations higher than 25 ppm. Next, the instrument was used to measure SO_2 sampled from the emission of coal burning. As a comparison, a commercial SO_2 sensor was installed at the outlet of the DOAS instrument and measured the sampled gas when the gas left the cell. The results indicate that the DOAS instrument deviated from around 6% of that measured by the commercial sensor.

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