DOAS Calibration Technique for SO₂ Emission Measurement Based on H₂SO₄ and Na₂SO₃ Reaction

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ABSTRACT

The coal used as a primary fuel in an Indonesian power plant produces sulfur dioxide emission from its burning process. Several testing and monitoring methods developed, from laboratory analysis, CEMs based instrument, and absorption spectroscopy method developed for this purpose. Differential Optical Absorption Spectroscopy (DOAS) method based on Lambert-Beer law used as emission quantification. DOAS instrumentation developed in this research to measure sulfur dioxide as one of the emission parameters. Sulfur dioxide generated from the reaction between the sulfuric acid and dilute sodium sulfite. CCD spectrometer used to measure sulfur dioxide spectrum intensity at 260 to 350 nm absorption cross-section. There is a high correlation between sulfur dioxide gas produced by that reaction to spectrum intensity, with coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or coefficient correlation (r) 0.989, 0.991, 0.993, and 0.996 from lowest range concentration to highest range concentration. Precision analysis from gas calibration standard using Horwitz ratio indicates instrument setup precise enough with 0.504 Horwitz ratio, according to its acceptable range. The suspended particulate matter may interfere with UV penetration into CCD detector in emission simulation test using gasoline generator exhaust that causes 2.5 times deviation error between typical 800 ppm concentrated sulfur dioxide from chemical reaction and gasoline generator exhaust.

1. INTRODUCTION

Several power plants in Indonesia use coal as the primary fuel for power generation. As coal burned for generating steam, it releases a massive amount of emission into the atmosphere. Sulfur dioxide was a significant emission pollutant that releases as coal burned in the power plant industry (Lin et al., 2018). Different coal types contain different sulfur content. Low-sulfur coal contains less than 1% sulfur, and medium sulfur will have approximately 1% to 3% sulfur content. High-sulfur coal will have more than 3% sulfur content (Chou, 2012). By 2020, power plants in Indonesia will use more than 200 million tons of coal per year and increase continuously year by year progressively based on ministry of energy data on 2019. It will impact on sulfur dioxide emission escalation in

the atmosphere. Sulfur dioxide pollution can address the damaging effect on human health like respiratory problems and cardiovascular (Shepherd, Haynatzki, Rautiainen, & Achutan, 2015). It also develops acid rain in the environment (Sudalma, Purwanto, & Santoso, 2015; Wang, Xing, Zeng, Ding, & Chen, 2005). It increases the acidity of the soil lead to soil microbial activity degeneration (Mohajan, 2019). It also affects the dissolution of limestone in wall building lead to integrity losses of the wall.

Regulation of Ministry of Environment Number 21 of 2008 limits sulfur dioxide below 750 mg/Nm³ before safely released into the atmosphere. To fulfill this regulation, the coal power plant uses a testing laboratory to measure air quality releases into the atmosphere by using a stack sampling method. It is an accurate method based on chemical absorption reagent (US EPA, 2017). This data hardly to be evaluated as a continuous emission profile from the coal power plant. Another coal power plant might have a continuous emission monitoring system (CEMs) to monitor its emission based on electrochemiluminescence or non-dispersive infrared (NDIR) instrument. At the same time, it can be an expensive application as high as USD 90000 per unit installed (Clapsaddle, 2002).

In this research, we arrange an experimental design of sulfur dioxide emission measurement based on differential optical absorption spectroscopy (DOAS), produced sulfur dioxide from sulfuric acid, and sodium sulfite reaction used as calibration. Typically, DOAS is a method to determine concentrations of trace gases by measuring their specific narrow band absorption structures in the UV and visible spectral region (Platt & Perner, 1983). Generally DOAS instrument following Lambert-Beer Law in absorption spectroscopy, it states that the radiant intensity traversing a homogeneous medium decreases exponentially with the product of the extinction coefficient and the path length (Furukawa & Fukuda, 2012),(Mellqvist & Rosén, 1996), in the mathematic formula we can describe as below;

$$I(\lambda) = I_0 e^{\left(-\sum_{j=1}^{n} S^j(\lambda) C_j\right)} \qquad \ldots\ldots (1)$$

Where;

I_0 : spectrum intensity without air contaminant

I : measured spectrum intensity in existing air contaminant

S_j : absorption cross-section of the species j, with wavelength-dependent structures [cm2/molecules]

C_j : column density of the species j [molecules/cm2]

The variation of the absorbed light intensity $I(\lambda)$ with wavelength can be though as the sum of two parts, one that varies fast and the other is slowly varying. The fast part is due to the fast varying absorption cross-section of gas molecules, while the slowly varying part is due to slow varying absorption cross-section of gas molecules. DOAS can extract the fast part from the overall spectrum, making it a compassionate technique to determine specific molecules (Platt, 2017). DOAS allows the quantitative determination of atmospheric trace gas concentrations by recording and evaluating the characteristic absorption structures (lines or bands) of the trace gas molecules along an absorption path of known length in the open atmosphere. The DOAS technique characterized by the following: (1) measuring the transmitted light intensity over a relatively (compared to the width of an absorption band) broad spectral interval; (2) high-pass filtering of the spectra to obtain a differential absorption signal and eliminating broad-band extinction processes such as Rayleigh and Mie scattering and (3) quantitative determination of trace column densities by matching the observed spectral signatures to prerecorded (reference) spectra by, for instance, least-squares methods (Platt, 2006).

DOAS method work in a wide range of wavelength from UV-wavelength area to visible-wavelength area. Based on (Hu, Wen, & Wang, 2016) NO_3 can be detected in 220-230 nm absorption cross-section in water species, chemical oxygen demand (COD) and total organic carbon (TOC) detected in 280-290 nm absorption cross-section, while watercolor, turbidity, and total suspended solids (TSS) measured in the visible-wavelength area. According to (Zhang, Fang, & Zhao, 2013) they develop a portable spectroscopy method to measure ammonia nitrogen, nitrite nitrogen, hexavalent chromium, and arsenide in water using a multiwavelength LED. (Theys et al., 2015) develop sulfur dioxide retrieval from ozone DOAS monitoring with Linear

Fit and Principal Component Analysis algorithms. These algorithms calculate sulfur dioxide concentration based on ozone concentration monitoring; this method reads the noise spectrum intensity of ozone in 270 nm to 500 nm wavelength based on (Levelt et al., 2006). (Theys et al., 2019) also, develop sulfur dioxide monitoring for volcano's sulfur dioxide emission using TROPOspheric Monitoring Instrument (TROPOMI). Many researchers develop DOAS monitoring based on existing and fabricated instruments. There is a possibility for emission monitoring using cheap and simple setup based on the DOAS method that this research work on. In this research, LED-UV with 285 nm wavelength used as a continuous light source specific for sulfur dioxide detection (Platt & Stutz, 2008). In this range, DOAS is very sulfur dioxide selective as there are no significant interferences due to the absorption from gases commonly existing in the air (Platt & Stutz, 2008). As the optical pathway, we use a clear acrylic tube, and for spectrum intensity detector, we use CCD spectrometer (Poole, 2015). Quantification of spectrum emission conducted by the least square analysis using gas standard calibration (Margelli & Giovanelli, 2002). Another calibration method could be conducted by on the fly correlation with a calibrated gas analyzer (Hasenfratz, Saukh, & Thiele, 2012; Rivera et al., 2009). (Al-Jalal, Al-Basheer, Gasmi, & Romadhon, 2019) set DOAS experiment for nitrogen dioxide measurement using chemical reaction preparation for its nitrogen dioxide calibration, by reacting copper wire with nitric acid. In this research, we adopt this method by reacting H_2SO_4 and Na_2SO_3 solution that would produce sulfur dioxide gases, sodium sulfate and amount of water, following this reaction (Abrash, 2020);

$$20\ Na_2SO_3 + 10\ H_2SO_4 \rightarrow 20\ Na_2SO_4 + H_2O$$
$$+ 10\ SO_2 \qquad .....(2)$$
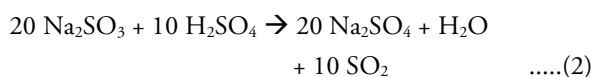
Produced sulfur dioxide then quantified using a gas analyzer, which correlated with sulfur dioxide spectrum intensity, which is the cheapest and straightforward DOAS calibration technique and will be analyzed by the least square method analysis.

2. METHODS

Figure 1 shows the schematic diagram of the employed experimental setup. The output light of UV LED taken from Tao Yuan 285 nm wavelength LED, this LED built-in lens, reflector, and protective window are removed. The circuitry used to enlighten LED from battery also removed, and the LED connected directly to 3 volts regulated DC power supply. UV light from LED emitted directly into the closed channel to eliminate possible light interference from the ambient light into a 30 cm acrylic tube, as an optical pathway with 40 mm od and 36 mm id. Each end of the acrylic tunnel windowed by 1.5 mm Azom thick fused silica glass, with 98% UV light transmittance. At the end of the optical pathway, Round-to-Linear Bundle, 7 x Ø105 µm optical fiber connected to Thorlabs CCS 200 CCD Spectrometer as spectrum intensity detector. The spectrum digitized by the line CCD camera is acquired to a personal computer using Thorlabs OSA software. The gas inlet of the optical pathway connected to the dilution chamber that produces sulfur dioxide, while its outlet line connected to a bacharach PCA 3 gas analyzer with 0.5 liters per minute flow as a quantitative measurement correlating instrument.

Sulfur dioxide gas prepared by reacting 5 mL, 0.5 M (171.5 mg/L) sulfuric acid with 5 mL sodium sulfite in different concentration, pipetting 3, 4, 5, and 10 mL from 1 gram sodium sulfite diluted to 100 mL as variable to produce different sulfur dioxide gas concentration. 50 ppm gas calibration standard used as a replicability analysis and instrumentation precision test. Prepared gasoline generator exhaust will be used as a stationary emission source to simulate measurement from the emission source. In the simulation test, inlet sulfur dioxide from the dilution chamber replaced by gasoline generator exhaust using stainless steel tube connected with gas hose. Sulfur dioxide produced from the chemical reaction, 50 ppm gas calibration standard, and gasoline generator emission compared with spectrum analysis using Thorlabs OSA software. Each test will take 5 minutes continuous spectrum reading data from CCD Spectrometer and gas analyzer directly saved as a CSV file format.
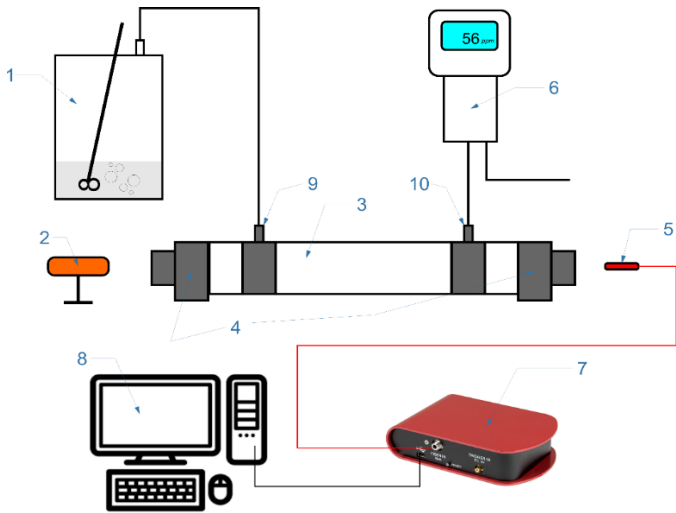
Figure 1. Instrument Setup for SO2 Spectrum Intensity Measurement (1. Dilution chamber, 2. LED-UV, 3. Optical Pathway, 4. Fused Silica Window, 5. Optical Fiber, 6. Gas Analyzer, 7. CCD Spectrometer, 8. PC, 9. Gas Inlet, 10. Gas Outlet)
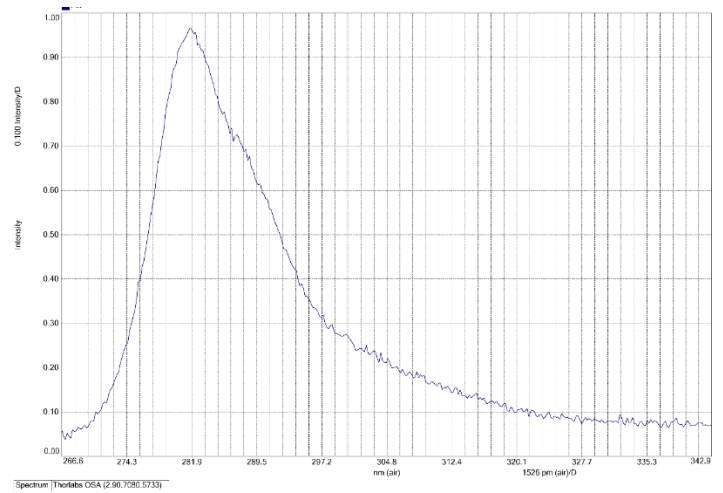

Figure 2. Typical Measured Spectrum Intensity of UV LED in Sulfur Dioxide Absorption Cross Section
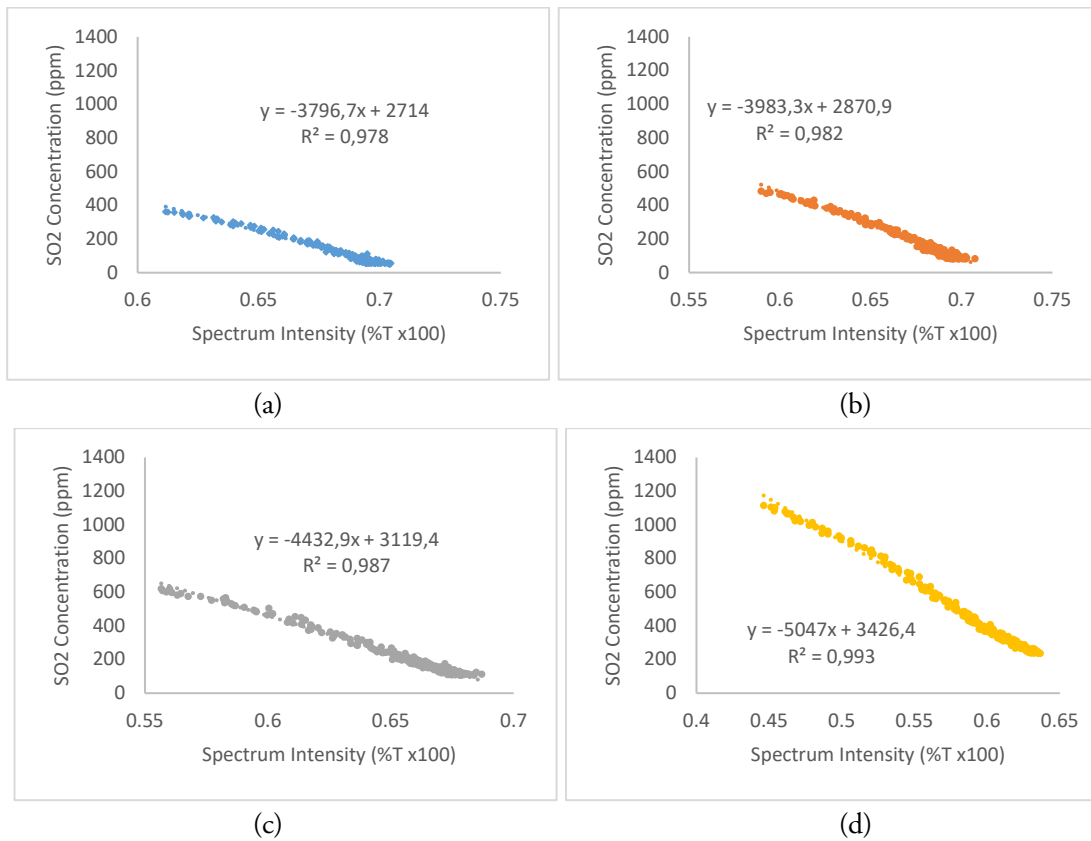

(a)

(b)

(c)

(d)

Figure 3. Spectrum Intensity Correlation to sulfur dioxide Concentration for variation of sodium sulfite (a) 3mL, (b) 4mL, (c) 5mL, and (d) 10mL

3. RESULT AND DISCUSSION

Figure 2 shows the measured intensity spectrum of the emitted light from UV LED and sulfur dioxide high-resolution absorption over the UV region from 255 to 345 nm. The LED intensity spectrum has a broad and smooth peak located around 280 nm. Based on (Platt & Stutz, 2008), sulfur dioxide has absorption cross-section around 260 to 350 nm.

Peak intensity of sulfur dioxide spectrum analyzed as peak value versus sulfur dioxide concentration read by bacharach PCA 3 gas analyzer. Both spectrum intensity and gas analyzer data reading saved every second for 5 minutes running time, CSV file contains raw data tabulated into an Excel spreadsheet for correlating between sulfur dioxide spectrum intensity and gas analyzer concentration reading. Each sodium sulfite volume variation then corresponds to sulfur dioxide spectrum intensity and gas analyzer concentration reading, list as follows.

When sulfuric acid begins to react with sodium sulfite, sulfur dioxide starts to produce, and it slowly lowers the % transmintance of spectrum intensity. It raises sulfur dioxide concentration read by the gas analyzer. Both spectrum intensity and concentration lapse through running time shown strong correlation, to convince this correlation a statistical analysis investigates the significance of the relationship, the study was done with SPSS software and Pearson Correlation as seen as table 1.

Table 1. Significance Test using Pearson Correlation

		Intensity	Concentration
Intensity	Pearson Correlation	1	-.981**
	Sig. (2-tailed)		0.000
	N	824	824
Concentration	Pearson Correlation	-.981**	1
	Sig. (2-tailed)	0.000	
	N	824	824

***. Correlation is significant at the 0.01 level (2-tailed).*

Table 1 from the statistical analysis shown significance level between spectrum intensity and sulfur dioxide concentration based on this hypothesis;

H_0 : There is no strong correlation between spectrum intensity and sulfur dioxide concentration

H_1 : There is a strong correlation between spectrum intensity and sulfur dioxide concentration

If Sig > 0.05, then H_0 accepted, else if Sig < 0.05 H_0 rejected, then from that analysis Sig < 0.05, so we should reject H_0, there is a strong correlation between spectrum intensity and sulfur dioxide concentration (Mukaka, 2012). Hence, we could use linear formula y = a + bx from Figure 3 as a calibration factor for sulfur dioxide measurement based on sulfur dioxide spectrum intensity. Each sodium sulfite variation generates variation sulfur dioxide concentration, for 3, 4, 5, and 10 mL variation approximately will generate maximum sulfur dioxide concentration of 350 ppm, 475 ppm, 650 ppm, and 1150 ppm. Linearity test from lowest concentration range to highest concentration range shows coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or correlation coefficient (r) 0.989, 0.991, 0.993, and 0.996. According to (Akoglu, 2018; Fatkhurrahman & Juliasari, 2016; Ratner, 2009) and another DOAS experiment (Chan et al., 2012; Romadhon, 2015) this indicates a strong correlation between sulfur dioxide spectrum intensity and measured concentration.

Measurement precision by replication analysis done by comparing spectrum intensity to sulfur dioxide generated by chemical reaction since there is unhomogenized concentration through time. 50 ppm gas calibration standard used as precision analysis, figure 4 shows measured sulfur dioxide concentration using linear formula between 2% calibration error requirement as stated in (US EPA, 1995, 2018)

Average sulfur dioxide concentration from data, as seen in Figure 4, is 49.992 ppm, then standard deviation (SD) 0.280, coefficient variance (RSD) can be calculated by equation 3.

$$RSD = \frac{SD}{Average} \times 100\% \qquad .....(3)$$

Based on equation (3), the RSD value is 0.560. Concerning among-laboratory precision, the acceptability of the methods calculated using Horwitz-ratio (Horrat) (Horwitz & Albert, 2006). While predicted RSD (PRSD) computed using equation (4).

$$PRSD = 2^{1-0.5logC} \qquad .....(4)$$

Acceptance limit evaluated by using Horrat equation below;

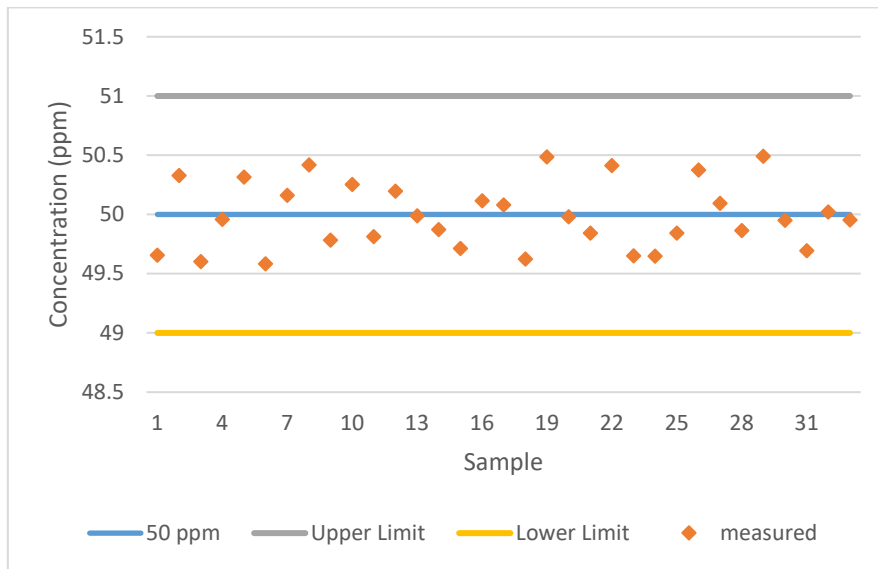$$Horrat = \frac{RSD}{PRSD} .....(5)$$

Figure 4. Measured sulfur dioxide between USEPA calibration error requirement
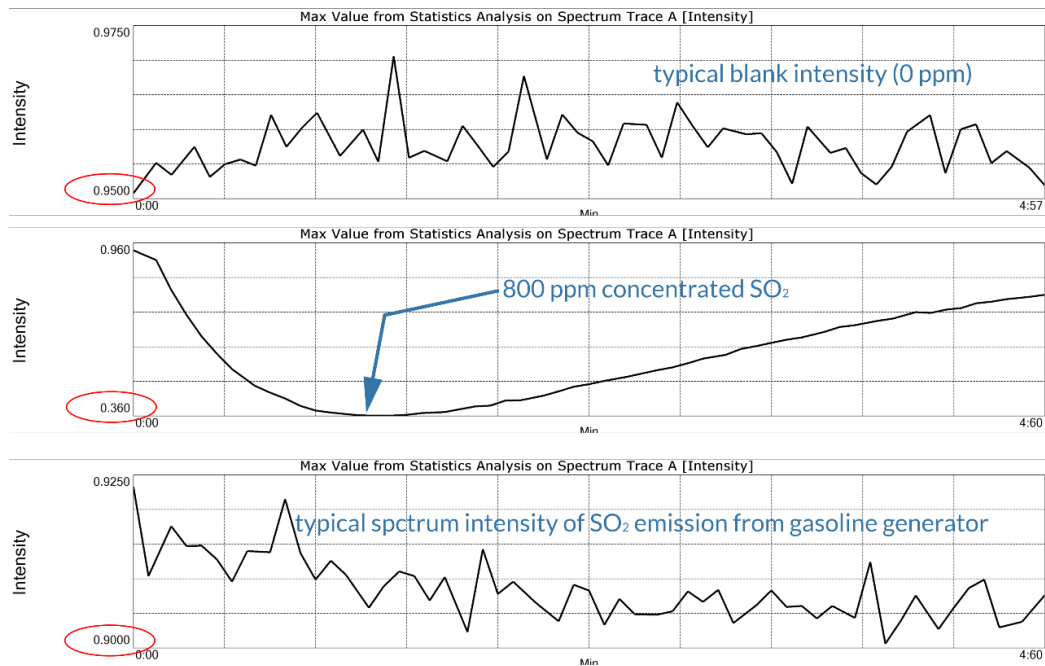

Figure 5. Spectrum intensity of sulfur dioxide from 0 ppm Concentration (up), 800 ppm Maximum Concentration of generated sulfur dioxide from H$_2$SO$_4$ and Na$_2$SO$_3$ reaction (middle), sulfur dioxide from gasoline generator emission (bottom)
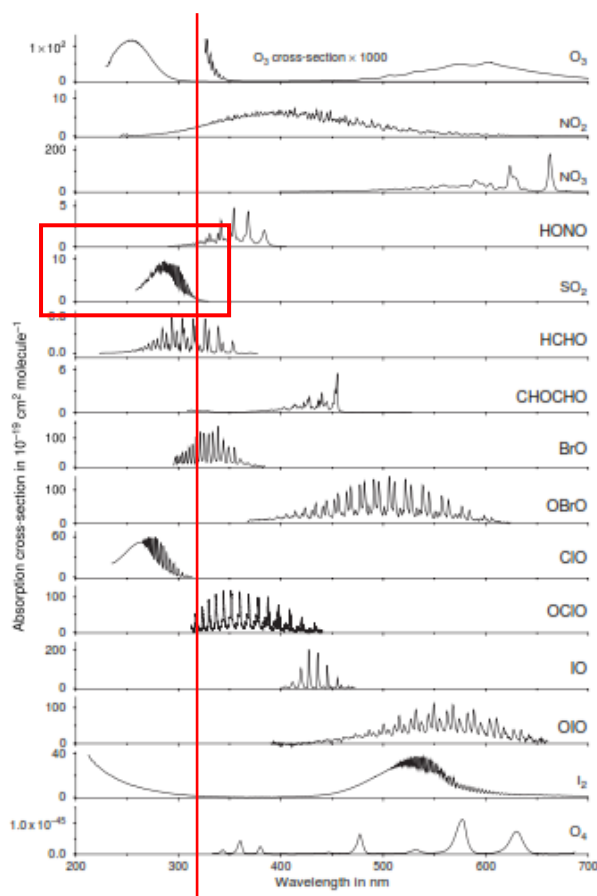
Figure 6. Absorption cross-section features of several species as a function of wavelength (in nm); picture from (Platt & Stutz, 2008)

Calculation from equation 5, Horrat from this precision analysis is 0.504, The precision is better than expected if the ratio is less than 1, and poorer if greater than 1, while the acceptable empirical range is 0.5 to 2.0.

Prepared gasoline generator then tested for emission simulation test through DOAS instrument with the same procedure as spectrum intensity measurement in sulfur dioxide from chemical reaction and gas calibration standard method. As shown in Figure 5, there is a large deviation error comparing typical 800 ppm concentrated sulfur dioxide with 0.360 (36%) transmittance intensity than 0.900 (90%) transmittance intensity when conducted simulation test using gasoline generator exhaust. It indicated 2.5 times deviation error that needs identifications.

According to (Emmerich, Wang, & Persily, 2017), (Souza et al., 2016), (Peterka, Pexa, Čedík, Mader, &

Kotek, 2017) gasoline generator will emit SO_2, NO_x, CO, CO_2, hydrocarbon, and several suspended particulates (Emmerich et al., 2017), (Souza et al., 2016), (Peterka et al., 2017). Based on Figure 2, the only change is sulfur dioxide from the dilution chamber replaced with gasoline generator exhaust inlet using stainless steel pipe for emission stream into DOAS acrylic chamber as an optical pathway. Sulfur dioxide spectrum intensity from gasoline generator emission reveals some anomalies compare with spectrum intensity from H_2SO_4 reaction with Na_2SO_3. According to (Platt & Stutz, 2008), typically, sulfur dioxide absorption cross-section did not have substantial interference with any other gases in 250 to 300 nm UV range, shown in Figure 6.

There is sulfur dioxide, ClO, O_3, and a small section of NO_2 in the 250 to 300 nm absorption cross-section. Still, there is no possibility that species exist in gasoline generator exhaust according to (Elliott, Nebel, & Rounds, 1955). There is the only possibility of suspended particulate matter from gasoline generator emission that could obstruct UV light penetration from 285 nm LED-UV into CCD Spectrometer detector. Hence we could not analyze the spectrum intensity of sulfur dioxide from gasoline generator emission (Caro, Mateo-Martí, & Martínez-Frías, 2006; Christensen & Linden, 2003). This suspended particulate matter interference needs to be eliminated before it gets through the optical pathway, a dust filter will be a good point for this instrument development, and it needs another study of filtering effect on the DOAS instrument.

4.   CONCLUSION

We develop DOAS calibration technique for sulfur dioxide using a reaction between H_2SO_4 and Na_2SO_3 that produce several sulfur dioxide gases. There is a high correlation between sulfur dioxide gas produced by that reaction to spectrum intensity, with coefficient determination (r^2) 0.978, 0.982, 0.987, 0.993 or correlation coefficient (r) 0.989, 0.991, 0.993, and 0.996 from lowest range concentration to highest range concentration, also compared with another DOAS experiment. Precision analysis from gas calibration standard using Horwitz ratio

indicates instrument setup precise enough with 0.504 Horwitz ratio, according to its acceptable range. 2.5 times huge deviation error in emission simulation test using gasoline generator exhaust exist between typical 800 ppm concentrated sulfur dioxide from a chemical reaction and gasoline generator exhaust. Since there is no possibility ClO, O_3, and NO_2 exist in gasoline generator exhaust, the suspended particulate matter may interfere UV penetration into CCD detector that needs to be eliminated before emission gas stream flowed into the acrylic chamber as an optical pathway.

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