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Blue-LED Calibration on DOAS System to Measure Nitrogen Dioxide Emission Compared with USEPA Method 7B Standard

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Abstract. Air polution level measurement sometime needs tricky instrumentation, costly, and use chemical reagent that could bad impact to environment, it also time consuming for analysis. In other hand, air polution level measurement, include nitrogen dioxide (NO2) needs accuracy, rapid and environment friendly for its analysis and measurement. Differential Optical Absorption Spectroscopy (DOAS) develop as spectrum measurements both UV and visible, transmitted by specific canal using absorption Lambert Beer's Law principal. On this basic method, NO2 measurement needs light source with 330 – 500 nm wavelength, it is possible to use cheap blue-LED for this measurement. This research intends to calibrate prototype instrumentation for measuring NO2 by DOAS based using Blue-LED (375 nm) passed in continual gas container. NO2 emission simulated in laboratory scale by reacting copper (Cu) with nitric acid (HNO3) result NO2 gas formation. Blue-LED spectrum analysed by compact CCD Spectrometer for its absorbance spectrum, then calibrated with NO2 measurement using USEPA Method 7B standard that is commonly used in testing laboratory as standard method for NO2 measurement. It has good corelation between spectrum absorbance in CCD Spectrometer to USEPA Method 7B with more than 95% linierity. As rapidity of this measurement and shown good accuracy, more development for this method could carry fast, accurate, cheap, also environmentally friendly method for NO2 measurement.

Keywords: DOAS, Blue-LED, USEPA Method 7B, CCD Spectrometer

1. Introduction

Nitrogen Dioxide commonly major pollutan in industrial emission gas that give several bad effect for environment, both for worker health aspect also for decreasing environmental quality, including childhood asthma (Naidoo 2019). In industry nitrogen dioxide released from utility process like boiler, heater and generator set, while others generated both from anthropogenic, biomass burning, and soil emissions (R. Zhang, Tie, and Bond 2003). For environmental conformity industry periodically inspect their NO2 emission using environmental testing laboratory. They used standard method like SNI, the Indonesia Standard, JIS, the japanese standard, or USEPA, the US Standard. This measurement method is accurate, but seems resulting bad effect for environment as this method using chemical reagent that need another waste treatment (L. Zhang et al. 2018)(Ivanković and Hrenović 2010), also industry could take long time to get this result from testing laboratory. Several alternative method developed to resolved this problem, industry could use electrochemical based sensor (Cross et al. 2017) and chemiluminescent based instrument (Maeda, Aoki, and Munemori 1980) for NO2 measurement so they can get the result in realtime. But this method seems unreliable for lower and middle scale industry, as they dont have enough extra cost for environmental testing. (Platt and Stutz n.d.) nowadays, differential optical absorption spectroscopy (DOAS) seems to be another breakthrough for gas measurement, DOAS widely used in investigating stratospheric and troposheric air quality (Otten et al. 1998). Concentration of the gases retrieved from their absorption characteristic in the UV-VIS spectral range, originally this method based on Lambert-Beer law (Stutz et al. 2017). As DOAS spectrum quantification needs to be calibrated to inform true quantitive value, calibration using comparative method with USEPA Method 7B Standard will be additional

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breakthrough for another step research in DOAS method (Zielcke et al. 2013). For this challenge, we evaluate in comparative method between DOAS and USEPA Method 7B for NO2 emission measurement, also formulation for future work for DOAS emission measurement system made in latest technology like Integration of IoT technology

2. Experimental Details

Main idea of this research is developing NO2 gas measurement system on DOAS based system. In this research, NO2 generated by reacting Copper metal with diluted Nitric Acid, this reaction generated NO2 gas follow this reaction path (Jörg Kleffmann, Thorsten Benter, and Wiesen 2004):

$$Cu(s) + 4HNO3(aq) \rightarrow Cu(NO3)2(aq) + 2NO2(g) + 2H2O(l)$$

We variate 0.01 g and 0.03 g copper metal reacted with fixed nitric acid molarity (3 M), also we use 0.01 g copper weight in nitric acid variation (2 M – 9 M). Generated NO2 gas flowed into the measuring path with 15 cm path length, made from acrylic tube. One of its end, we setup 415 nm single wavelength LED (lieteratur). Another end connected with optical fiber that directly pointed to CCD Spectrometer, we use Thorlabs CCS 100 Spectrometer in this research. CCD Spectrometer analyse intensity absorption varians for each generated NO2. This intensity varians analyzed with Excel. Typical blank intensity and NO2 concentration intensity observed like figure 1.

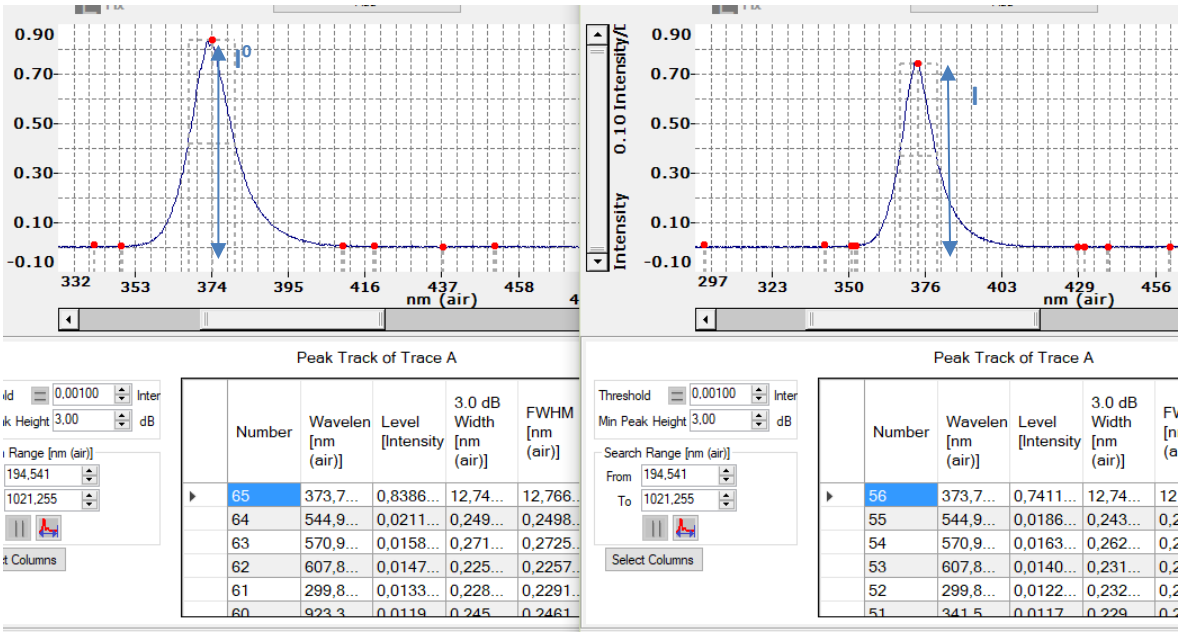

Figure 1. Typical Absorption Intensity on CCD Spectrometer; (left) blank intensity, (right) NO2 concentration intensity

NO2 gas outlet then connected to vacuum tube with USEPA Method 7B reagent, it will be analyzed by spectrophotometer to get NO2 concentration, later this method we used as quantification reference and linearity test. All of the experimental setup visualized as figure 2.

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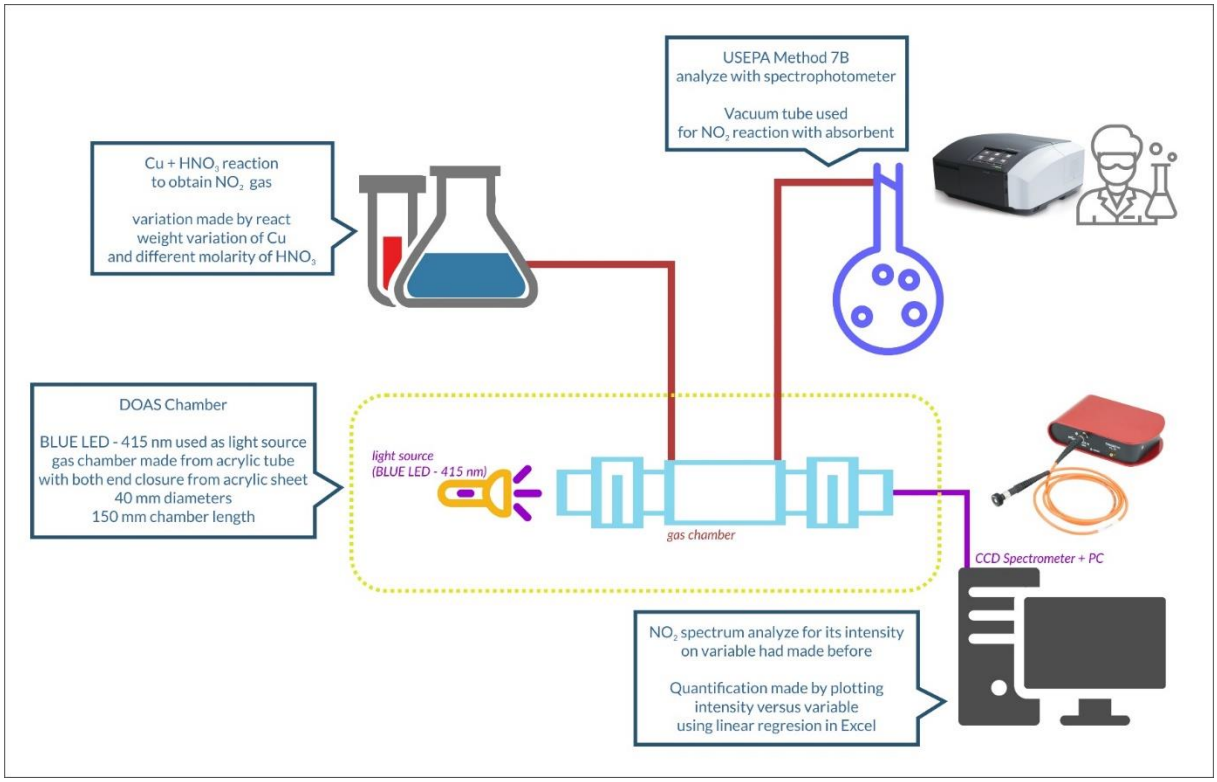

Figure 2. Instrument Setup for Measurement

3. Result and Discussion

From the experiment, we get NO2 spectrum absorbance for each variables. This NO2 spectrum absorbance plotted with NO2 concentration from spectrophotometer analysis based on USEPA method 7B like visualized on figure 3. These two variables may generate NO2 concentration from 20 mg/Nm3 to 1500 mg/Nm3. This experiment conduct by two variations of Copper weight, 0.01 g and 0.03 g with different nitric acid molarity.

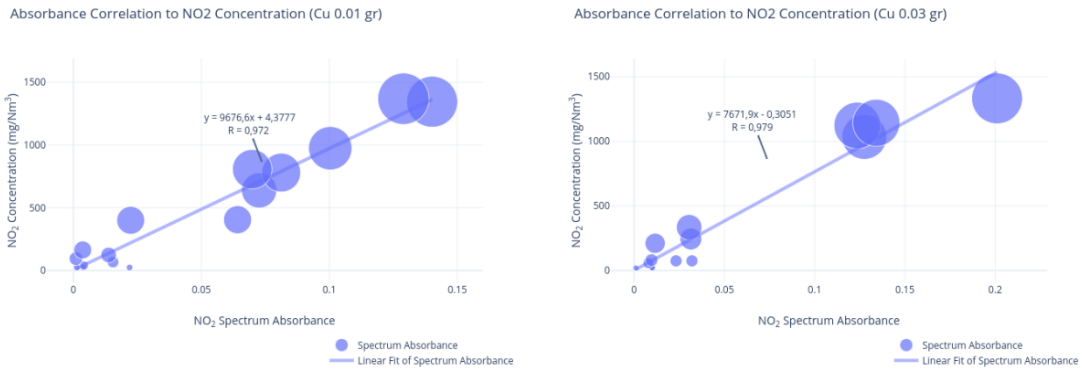

Figure 3. Absorbance Corelation (a) Cu 0.01 g and (b) Cu 0.03 g

Copper weight correlation to NO2 concentration for both variable reach more than 95%. Also resulting identical respond from two variables. This indicate positive correlation between NO2 spectrum absorbance to NO2 concentration quantified with USEPA Method 7B.

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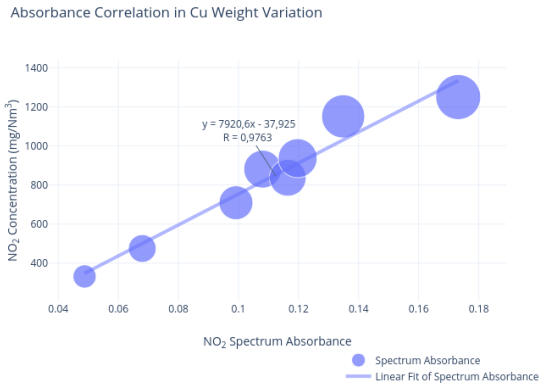

Figure 4. Absorbance Corelation in Copper Weight Variation

In other experiment, we made trial on Copper weight variation on fixed nitric acid molarity, this result more than 95% liniearity. Generated NO2 read by USEPA method 7B standard method using UV-Vis Spectrophotometer, while CCD Spectrometer read absorbance intensity. Absorbance intensity have linear correlation to copper weight and NO2 concentration.

In conclusion we have developed a new instrument setup for NO2 gas measurement using DOAS System correlated with USEPA Method 7 standard method. This measurement used Cu + HNO3 reaction to generate NO2 gas. Entire measurement on DOAS System seems to be positive result for alternative method in NO2 measurement. We are in the process of developing this method and measurement for NO2 gas in industrial emission, combine with IoT Technology.

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