APPLICATION OF CO_2 LASER PHOTOACOUSTIC SPECTROSCOPY FOR ETHYLENE (C_2H_4) GAS DETECTION IN SOIL DURING THE RAINY SEASON

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Abstract

The photoacoustic spectrometer technique has become the standard in measuring trace samples with the advantages of high sensitivity (up to ppt order), on-line, real time detection and range of operations that are close to 10^8order. This article reports an experiment usingCO$_2$ laser photoacoustic spectroscopy for ethylene (C_2H_4) gas detection in the soil during the rainy season based on variations in depth and sampling location using a CO_2 laser extracted spectrometer. The lowest limit of detection value (LOD) was obtained at (416 ± 104) ppt. The concentration of ethylene gas in the soil during the rainy season based on the variations in soil depth were (0.18 ± 0.04) ppm for a depth of 0 cm (ground level), (0.17 ± 0.04) ppm for a depth of 15 cm from the ground, and (0.15 ± 0.03) ppm for the depth of 30 cm from the ground. Based on the variations of location of soil, the obtained values were (0.19 ± 0.04) ppm, (0.18 ± 0.04) ppm, and (0.15 ± 0.03) ppm respectively for locations in the North, Center and South were taken around the Biology forest of Gadjah Mada University, which is situated in the western part of the Faculty of Biology and northern section of the Faculty of Mathematics and Natural Sciences. It was concluded that the concentration of ethylene gas in the soil during the rainy season was not significantly affected by depth and location factors.

Keywords: *Photoacoustic spectrometer, ethylene, rainy season*

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I. INTRODUCTION

Soil is the most important factor for the growth of plants. Soil fertility is determined by the conditions of physics, chemistry and biology of the soil itself. The physics condition of the soil includes the effective depth, texture, structure, humidity and air conditioning. The chemistry condition of soil includes the soil reaction, base saturation, organic matter, large amounts of nutrients and the availability to plant growth. Meanwhile, the biology state of soil includes microbial activities of organic matter in the process of binding nitrogen in the air. During the rainy season, the roots of plants will have difficulties in penetrating dense soil structures, so that the roots will not develop properly. The activities of plants and soil organisms are among the main factors in the formation of soil aggregates. (1)

Soil is a mixture of inorganic and organic materials, air, water and microorganisms, with each interacting with the others. The reaction of the available solid materials affects the quality of the water and air, the water and air deteriorate the solids, and the microorganisms catalyze some reactions. Soil particles have very much different sizes. They are usually classified based on the size into sand, dust, and clay. Sand measures between 2 and 0.05 mm, dust measures between 0.05 and 0.002 mm, and clay measures smaller than 0.002 mm. The fine fraction consisting of dust and clay greatly determines groundwater retention capacity, soil aeration and nutrient supply. (2)

Soil formation is influenced by climate. There are two most important elements that influence soil formation, namely rainfall and temperature. The rainfall and temperature affect the speed of chemical and physics processes. The effect of having a large volume of rainfall and high temperature is an optimum condition in the soil. During the dry season, the sun rays directly get onto the soil so that chemical and biological reaction processes occur; one of which is the decomposition of soil organic matter (decomposition). During the rainy season, rainwater falls directly on the ground, resulting in the breakdown of soil aggregates, rising surface water until reaching the surface and simultaneously transporting soil particles and other materials including organic matters. The rainwater will affect the chemical composition of soil constituent minerals, depth, and soil physical properties.

The deterioration of the physical properties of the soil will cause soil erosion. The influence of rainfall on the chemical composition is the increasing Al_2O_3, SiO_2, K_2O, Na_2O and CaO which will result in the lowering level of the soil pH and soil fertility. Fertile plant growth is influenced by the hormones in plants, one of which is ethylene, ethylene is a hormone produced from the plant metabolism. Ethylene is also called ethane, an organic compound that is a hydrocarbon with the following formula: C_2H_4 or $H_2C = CH_2$. The main function of ethylene is on the fruit ripening process and stimulating the growth of roots and stems. (3)

Soil organic matters consist of plant and animal remnants from all decomposition stages that occur due to the work of soil microorganisms. Sparling stated that a number of microbes play an important role in normal and healthy soils, and are indicators in determining soil quality. Ethylene is defined as an element contained in the soil atmosphere, both in aerobic and anaerobic conditions. Ethylene is produced from a microbial activity. Ishii and Kadoya suspect that ethylene is freed by both microbial and non-microbial activities, although non-microbial release is still debated. K.A. Smith and Restall suspect that any anaerobic microorganisms can almost certainly produce ethylene in the soil. Ethylene production occurs in both aerobic and anaerobic conditions. (4)

Ethylene is at the top layer of soil. Its existence is very influential for the fertile growth of soil. However, during the rainy season, there will be water inundation above the ground so that the aggregates become saturated with water. The air inside the soil pores is pushed out by the moving water so that small air bursts occur and cause larger aggregates or lumps to break into smaller clumps. (5)

Spectroscopy is the study of the interactions of electromagnetic waves with matter. One of the principles of spectroscopy is photoacoustic spectroscopy. Photoacoustic spectroscopy is generally used for the detection of samples with very low concentrations so that the application can be in various subject disciplines, namely agriculture, biology, medical, animal husbandry and environmental study. The use of the photoacoustic spectroscopy (PAS) technique in detection of trace samples is based on the occurrence of energy resonance between the radiation source and particle excitation energy of the sample. Then, the excited particles are conditioned to decay thermally and converted into an acoustic signal that characterizes a sample concentration. This opens up the possibility of detecting any particle provided as long as the energy of its existence corresponds to the energy of the radiation source and the decay mechanism is more thermally dominant. The detected sample can be in the phase of gas, liquid or solid. (6)

In the measurement of ethylene gas (C_2H_4), the gas chromatography (GC = Gas Chromatography) can also be used by combining it with a flame ionization detector (FID = Flame Ionization Detector). However, this method has a weakness, namely the sensitivity value is very low; while the spectroscopic method can provide high sensitivity values. (7)

The PAS technique has become the standard in measuring trace samples with the advantages of high sensitivity (up to ppt, or parts per trillion, order), on-line & real time detection, simple setting, having no accumulation of samples and wide range of operations close to 10^8 order. (8)

Biological footage (samples) will be detected by the CO_2 photoacoustic lasers if they have absorption characteristics in the CO_2 laser wavelength region. The principle used is to apply the CO_2 laser energy spectrum to the trailer gas and measure the absorption of energy by gas.

Furthermore, in this study the photoacoustic spectrometer detection method of ethylene gas (C_2H_4) will be used on the soil in the rainy season based on variations in the depth and variety of sampling locations.

II. EXPERIMENTAL METHOD

Photoacoustic spectroscopy (PAS) can work well first by using optical alignment and laser optimization. Optical alignment aims to obtain optimal laser action. The configuration used in this experiment is the extraction configuration shown in Figure 2.1. The extraction configuration is a configuration that places photoacoustic cells outside the CO_2 laser. Chopper is placed between the photoacoustic cell tube and the mirror of the intra cavity.

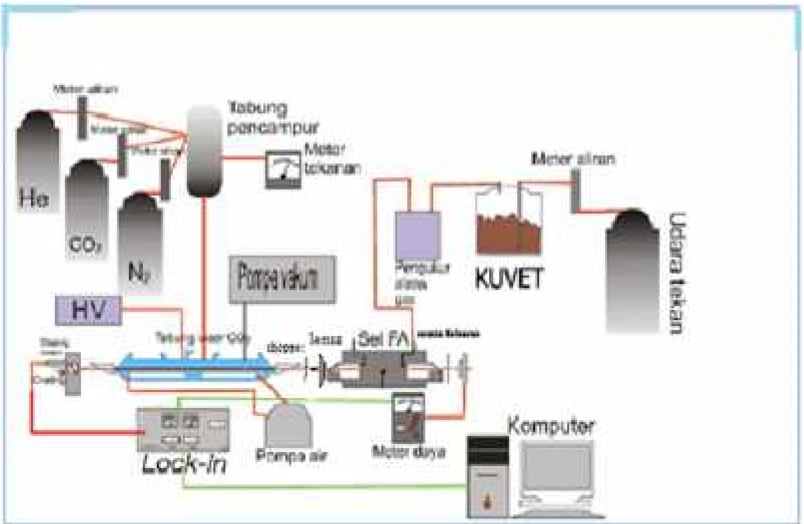

Figure 2.1 Laser CO2 photoelectric spectroscopy kit

The steps taken in this study were to determine the noise value, background signal value, limit of detection limit (LOD) and the concentration of each sample.

Noise is disturbance that comes from outside the photoacoustic cell which can create a signal. Noise needs to be measured in order to identify whether the recorded signal is an absorption signal or only noise so that errors in determining the absorption signal can be avoided. Meanwhile, the background signal is determined during the normal PAS setup, except that the photoacoustic cells are streamed with nitrogen gas or other non-absorbing gases on the CO_2 laser line. The signal that appears is clearly not from the sample of absorption but from heating the walls and windows of the cell. This background signal has a frequency similar to the frequency of sample absorption signals, so it cannot directly be separated and needs to be taken into account; especially if the ratio of the absorption signal to the background signal is not too large. LOD states that the minimum concentration that can still be detected by a machine does not always have to be properly quantified. For LOD gas applications, it is usually expressed in units of ppm, ppb or ppt.

The signal that appears as a result of heating the modulated footage is detected by a microphone. The microphone is placed in the middle of the photoacoustic cell, then the signal that appears is amplified by using a lock-in amplifier. The lock-in is able to amplify signals that have the same frequency as the reference frequency, namely the frequency of the chopper. The laser output power in the sample is not the same, and then the signal is normalized to power. It can be done by recording the acoustic signal output of the lock-in together with the laser power which is optimized using a computerized spectroscopic system.

The test material used is soil taken from the biological forest area located in the western part of the Faculty of Biology building and Faculty of Science building in the northern part of UGM. Then, the sample is placed in a cuvette as shown in Figure 2.1. After the sample is placed inside the cuvette, then pressurized air with a steady rate of 1 liter/hour is flowed to push the ethylene gas present in the soil into the photoacoustic cell. Ethylene gas has the highest frequency with the highest level of absorption, namely in the 10P14 laser line and the data is then stored in the computer automatically.

In detecting the concentration of ethylene gas on the soil during the rainy season, it is based on variations in depth and variation in sampling. For detection based on depth variations, 3 different depth levels were used, namely 0 cm (at the ground surface level), 15 cm deep from the ground surface level and 30 cm deep from the ground surface level. For detection based on variations, sampling was taken from three areas, in the south, middle and north.

III. RESULTS AND DISCUSSION

To get the optimal photoacoustic spectrometer performance, optical alignment was needed to aim for optimal laser action. The parts included in the optical alignment were the grating, laser tube and output mirror which all must be put in a straight line. Straightening was done with the help of a diode laser. Next, adjusting the composition of the active medium mixture, this was done to find the highest power with the right ratio of CO_2: N_2: H_e. In this study, the ratio used was 80:60:40.

3.1 Noise

Noise comes from outside the photoacoustic cell can cause a signal. Noise needs to be measured in order to identify whether the recorded signal is an absorption signal or only noise so that errors in determining the absorption signal can be avoided. Measurement of system noise was carried out in the following way.

a. The laser radiation source was turned off, while the modulator was remained turned on and set at resonance frequency.
b. The value of noise could be identified from the signal that appeared (obviously not from the radiation absorption) detected by the lock-in amplifier by installing it on NOISE mode. The sensitivity of the lock-

in amplifier was selected as small as possible but the amplifier must not show OVLD (overload).

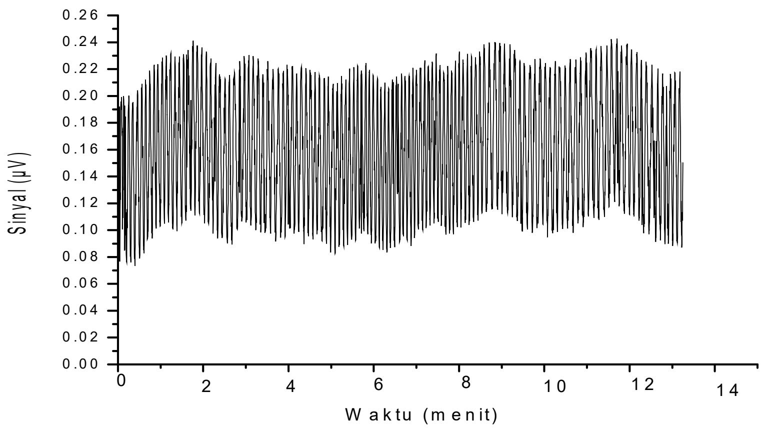

Figure 3.1 CO_2 laser noise

The noise value was measured from the maximum and minimum peak difference. The noise obtained in this experiment was (0.16 ± 0.04) µV / /$\sqrt{H}$ with 100 µV lock-in sensitivity.

3.2 Background Signal

The background signal was obtained from the heating of the cell windows and walls, having the same phase and frequency value. By passing CO_2 laser radiation into an FA cell that did not contain any gas trace then the background signal will be read at the same time as the sample absorbed photoacoustic signal on the lock-in. This signal occurs due to radiation uptake by the walls and windows of FA cells and the radiation that enters the acoustic detector. The background signal has the same frequency as the acoustic signal due to radiation uptake by gas trace. To get the actual photoacoustic signal, the signal that is read must be reduced by the background signal. The background signal is shown in Figure 3.2 with a lock-in sensitivity of 100 µV. In this experiment, the normalized background signal value obtained was (1.14 ± 0.04) µV / W.

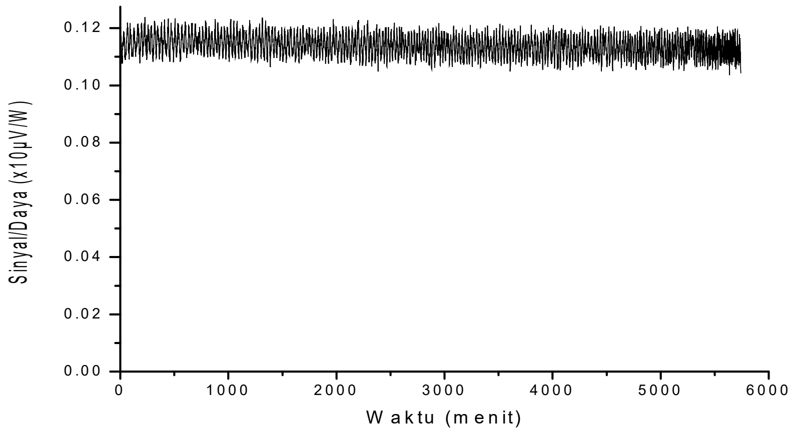

Figure 3.2 CO_2 laser background signal.

3.3 Determination of the Limit of Detection (LOD)

LOD states that the minimum concentration that can still be detected by a machine does not always have to be properly quantified. For LOD gas applications, it is usually expressed in units of ppm, ppb or ppt. The steps to determine LOD are as follows.

a. The standard ethylene gas is transferred into the photoacoustic cell continuously at a rate of 1 liter / hour.

b. Photoacoustic signals are recorded and normalized with the laser power.

c. LOD is determined using the following equation.

$$\text{LOD} = \frac{C}{S_n/N}$$

With C as the standard gas concentrations, S_n as the normalized photoacoustic signals and N as the system noise.

In this experiment, the value of LOD was obtained by looking for the maximum and minimum height difference based on Figure 3.2. The maximum and minimum difference value obtained was at 0.00020 mV and then converted into ppt units to 416 ppt. The value of ΔBDT was 0.00005mV or equivalent to 104 ppt. Then, LOD = (416 ± 104) ppt.

3.4 Determination of Ethylene Concentration in Soil in the Rainy Season

In this study, the first thing to do was detect ethylene gas in the soil, where soil samples were taken around the UGM Biology forest, which was in the western part of the Biology Faculty and northern of Faculty of Mathematics and Science, and the soil samples were taken from several different points. The soil sampling was divided into three areas, namely north, middle and south. Each area has three depth variations, namely surface (0 cm), 15 cm and 30 cm.

The detection process for ± 10 minutes of photoacoustic cells was fed with gas trace for each sample. The recorded acoustic signal value will be used in determining the concentration of ethylene gas from each sample.

In figure 3.3 is the result of detection for samples of the southern area with a depth of 0 cm (ground level). Based on the pattern of data obtained, it can be interpreted that ethylene gas was only found in about the first 2 minutes and after that ethylene gas cannot be detected by photoacoustic cells. This decreased the level of ethylene in the soil because there was little ethylene content in the soil. The data used in determining the ethylene concentration was data during the detection of the first 2 minutes or when the spectrum forms a peak and before experiencing a decrease in value in the photoacoustic signal recording. Likewise, was done for each sample in determining the ethylene concentration that the data used before experiencing a decrease in the value of the acoustic signal.

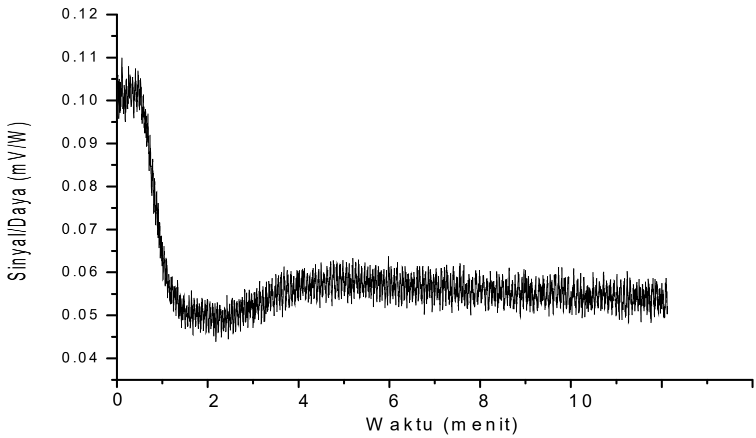

Figure 3.3 Acoustic signals for samples of land south of 30 cm.

The following is the table of detection results obtained from several samples:

Table 3.1 Ethylene concentration due to the influence of rainwater in UGM Biological forest soil

Soil Sampling Collection Location	**Ethylene Concentration (*ppm*)**
South; 0 cm from the ground surface	0,19 ± 0,04
South; 15 cm from the ground surface	0,19± 0,04
South; 30 cm from the ground surface	0,16 ± 0,03
Middle; 0 cm from the ground surface	0,18 ± 0,04
Middle; 15 cm from the ground surface	0,17± 0,04

Soil Sampling Collection Location	**Ethylene Concentration (*ppm*)**
Middle; 30 cm from the ground surface	0,17 ± 0,04
North; 0 cm from the ground surface	0,16 ± 0,03
North; 15 cm from the ground surface	0,15 ± 0,03
North; 30 cm from the ground surface	0,14± 0,03

Based on the research, the average value for the concentration of ethylene gas for each soil depth was as follows: (0.18 ± 0.04) ppm for a depth of 0 cm (ground level), (0.17 ± 0.04) ppm for 15 cm depth from the ground and (0.15 ± 0.03) ppm to a depth of 30 cm from the ground. Based on the variations in the location of land acquisition, the obtained value was (0.19 ± 0.04) ppm, (0.18 ± 0.04) ppm, and (0.15 ± 0.03) ppm respectively for locations north, center and south of the UGM Biology forest.

The concentration of ethylene gas in soil based on depth variations did not have a significant difference and based on variations in sampling locations did not have a significant difference. Therefore, based on research the concentration of ethylene gas in the soil during the rainy season is not significantly affected by depth and location factors.

IV. CONCLUSION

Based on research conducted with CO2 laser photoacoustic spectrometer obtained:

1. The value of LOD obtained in this experiment is (416 ± 104) ppt.
2. The average value for the ethylene gas concentration in the soil for each soil depth is as follows
   - (0.18 ± 0.04) ppm for a depth of 0 cm (ground level),

• (0.17 ± 0.04) ppm for a depth of 15 cm from (ground level)

• (0.15 ± 0.03) ppm for a depth of 30 cm from (ground level)

Based on variations in the location of land acquisition, the obtained value was:

(0.19 ± 0.04) ppm north

(0.18 ± 0.04) ppm in the middle

(0.15 ± 0.03) ppm in the south

Thus, it was concluded that based on this research study that the depth and location factors it do not significantly influence the concentration of ethylene gas in the soil during the rainy season.

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