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CO_2 Laser Photoacoustic for Measuring NH_3 Gas Concentration on Exhaled Breath of Scavengers on Landfill

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Abstract: A CO_2 laser photoacoustic spectrometer intracavity configuration has been built and tested. The application was for determining the NH_3 gas concentration on exhaled breath of scavengers on the Landfill. The off-line experiment was conducted through non-invasive sample method using exhaled breath. Exhaled breath sample was taken by three daily variations of the morning, mid-day and post-day. The data was analized by multicompound gas method using the software of excel, origin and scilab. The result from the photoacoustic spectrometer intracavity configuration with the strongest frequency resonance(1650±5) Hz at biomarker gas occured on absorption lines 10R14, 10P14 and 10P16. The lowest detection boundary from ammonia is (23.3±0.5) ppbV. The highest ammonia concentration from scavengers was (2904±1) ppbV occured in the early morning and the lowest concentration was (1089±1) ppbV in the post-day. Meanwhile, on healthy volunteers, the highest ammonia concentration was (1676±1) ppbV in the morning and the lowest ammonia concentration was 377±1) ppbV in the mid-day. It shows the contamination of air ambien caused the increasing concentration of biomarker gas in the human body.

Key words: Spectro meter, scavengers, photoacoustic, occured, concentration

INTRODUCTION

In developing countries such as Indonesia, trash is generally transported and dumped into landfill. The most landfill still uses open dumping method (Meidiana, 2012). These trace components may arise from volatilisation of materials in the waste or can be formed through biochemical reactions associatied with the degradation processes (Anonymous, 2010).

Laser photoacoustic spectroscopy method in analyzing the gas tracking by exploiting its potential to investigate the composition of the air on mouth breathing provides important information about the various processes that occur in the human body (Miekisch and Schubert, 2006; Mitrayana *et al*., 2014; Bayrakli and Akman, 2015). The presence of specific compounds in a human breath can indicate a recent exposure to pollutants or a disease state of the individual (Hibbard and Killard, 2011). The principle of the science of breath analysis is based on cell biology. Pathophysiological processes produce inside the human body endogenous VOCs which are transported through the bloodstream diffuse from the blood into the breath via permeation across the alveolar membrane and are exhaled through the lungs as breath volatiles.

The photoacoustic method becomes significanly more intersting when its sensitivity exceeds. Inserting a photoacoustic cell in the laser cavity in a photoacoustic detection which becomes evens more sensitive due to high intracavity laser power. The combining of a high sensitivity with a small length is necessery for intracavity operation (Rosencwaig, 1980). In this study, we present such a performance photoacoustics sell place inside CO_2 Laser as called intracavity configuration. The application was to detect NH_3 gas on the breath of scavengers.

MATERIALS AND METHODS

Materials which had been used are CO_2, N_2 and he with concentration gas of 99% as CO_2 laser active medium. C_2H_4 as linearitas calibrator gas. Acetone 99% dan ammonia 25% solution, their resulting gas was taken for a calibrator. KOH and $CaCl_2$ scrubber to absorpt H_2O and CO_2 from breath which can interfere the performance of biomarkers absorption (Mitrayana *et al*., 2014; Rosencwaig, 1980). Aquades was used to cooling the CO_2 laser tube and alcohol 95% was used to cleaning the lens of the laser.

CO_2 laser photoacoustic spectrometer with intracavity configuration components are laser power

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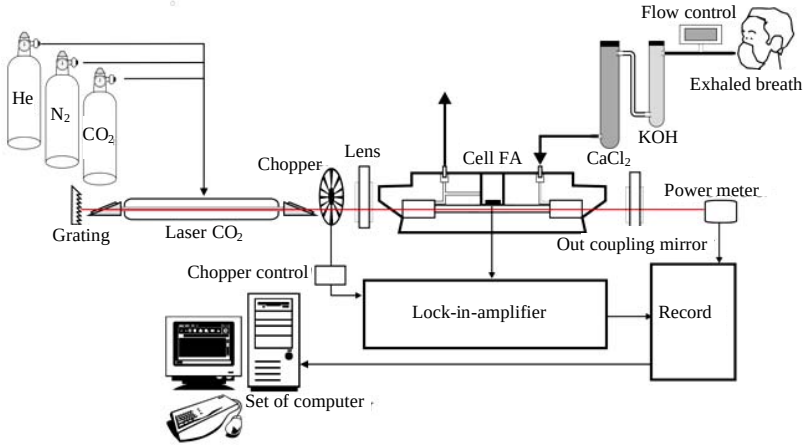

Fig. 1: Scheme of ammonia concentration measurement with CO_2 laser photoacoustic

supply with model of DC current HCN 35020.000 (this maximum potential and current are 20 kV and 15 mA), rotary vacum pump, water pumping is used to circulated laser tube cooling water, grating, stepper motor, sample bag 3L SKC label, modulator and frequency range 200 Hz-2, 3 kHz CO_2 axial flowing laser tube, intracavity ZnSe lens lined by AR/AR @ 10.6 μm photoacoustic cell, outcopling mirror which has transmission <5%, power meter, lock-in amplifier two phase EG&G Model 5210 with sensitivity from 100 nvolt-3 volt, one unit of computer with LabVIEW 8.6 Programme and flow meter model Brooks 5860.

Figure 1 shows the schematic of photoacoustic spectrometer equipment that has been used in this study. The first step of characteristic photoacoustic spectrometer performance was optical alignment. Grating, laser tube, photoacoustic cell and lens were placed in one straight line with the aid of dioda laser. The next step was optimation of the power. Scanning and laser absorption line spectrum was made based on examined biomarker gas. Biomarker gas curve resonance was searched. Noise and backround signal was measured. Determining the limit detection from instrument and linearity curve with variated the concentration value from biomarkers gas sample standart normalized signal (signal/power) was recorded subsequently. Linearity curve was found for calibration factor which obtained from curve gradien m and it was used to find the multicompound. After we had determined the performance of CO_2 laser photoacoustic, then we analyzed the concentration level of biomarkers gas on th exhaled breath of the scavengers (22 sample) which located in Piyungan landfill and healthy volunteers as a control (22 sample) which located in pogung lor (45±0.5) km. Measurements were taken offline by volunteers aged between 20-40 years old. Sampling was conducted 3 times: early morning (08:00-09:00) mid-day (12:00-13:00) and post-day (16:00-17:00). The volunteer exhaled into sample bag through KOH and $CaCl_2$ scrubber. The sample bag was brought to the laboratory and the analysis was conducted at laboratory of nuclear physics UGM. The sample bag was connected by the device to flow the gas into the photoacoustic cell. Flowmeter and flow control were added to keep the constant and scalable flow. The flow rate of exhaled breath was (3.994±0.0005) L/h up to (4.017±0.0005) L/h. Then scanning was done based on biomarkers gas line absorption. The absorbed acoustic signal from biomarkers gas would be interpreted by labview Software with the power of laser radiation.

CO_2 laser radiation with wavelengths ranging between 9-11 μm as the excitation laser was modulated by mechanical modulator SR540. The light energy used for absorption was then converted into the heat. Pressure from this changing temperature was detected by the microphone chamber during the de-excitation process (Mitrayana *et al*., 2014). The photoacoustic signal S provided a magnitude in arbitrary units displayed as:

$$S = S_m PC\alpha \quad (1)$$

Where:

S_m = The sensitivity of the microphone (in units volts per pascal)
P = The power of incident laser radiation (in units of watt)
C = Constant for the cell-geometry, measurement conditions and modulation frequency (in units of pascal centimetres per watt)
α = The absorption cross-section of the transition being interrogated (in units of inverse centimetres) (Hibbard and Killard, 2011)

It was necessary to use a lock-in amplifier SR 530 due to the very small captured microphone signal. The other necessary lock-in signal was a reference signal derived from the modulator signal to trigger the photoacoustic signal. Thus an only acoustic signal which has the same frequency with reference signal would be amplified with lock-in. The ouput power from the laser was not constant so the signal had to normalize to the power. The output signal lock-in was recorded by electronic recording simultaneously with output power in the detection laser power meter. The normalized signal was processed using excel, origin 8.0 and scilab to facilitate the calculation of multicompound.

RESULTS AND DISCUSSION

CO_2 laser photoacoustic intracavity configuration was designed to obtain the maximum detection limit. In this research, CO_2 laser worked optimal with the medium active gas composition of $He:N_2:CO_2$ at the pressure of 35, 60 and 50 mbar respectively while the current was 12.29-12.72 mA and the potential was 8.40-9.10 kV. Figure 2 represents the output power spectrum of CO_2 consisted of 15 absorption lines. The highest intracavity power value obtained at 10P20 is 34.12 W. The lines absorption used for biomarker analysis were 10R14 used for ammonia detection (the attenuation was 26.2 atm^{-1} cm^{-1}), 10P14 used for ethylen detection (the attenuation was 30.4 atm^{-1} cm^{-1}) and 10P20 used for acetone detection (the attenuation was 10.8 atm^{-1} cm^{-1}).

The method to determine measurement accuracy and sensitivity of photoacoustic spectrometer was by looked at the laser power stability. The stability of the laser power which was measured for 1 h shows the good results about 0.08 watts of power fluctuations without optimization grating. Table 1 shows the result from optimization of CO_2 laser photoacoustic.

The value of frequency from the three biomarkers gas was (1650±5) Hz. Based on the obtained data, the quality factor by experimental for ammonia result was (12.7±0.7). Theoritically, Mitrayana, dkk counted the resonance frequency value and quality factor and the result was $f_{resonance}$ = 1637 Hz and Q = 23.1 (Mitrayana *et al*., 2014). Based on the experimental, the losses was not only calculated from viscous and thermal but also from microfon, so the quality factor by experimental would always small.

Every resonance gas was absorpted by one or several spectrum lines. Absorption could be known by observing the absorption spectrum from standart gas which its concentration had been known. The value of

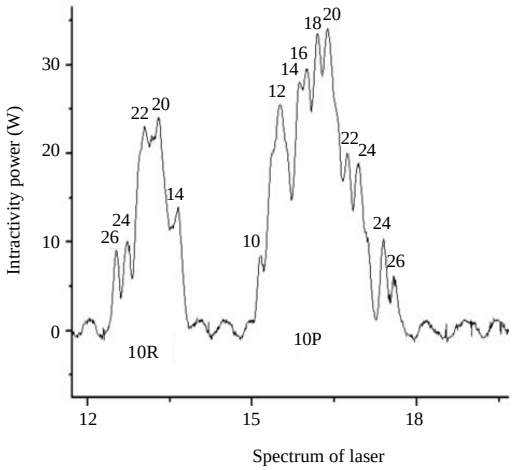

Fig. 2: Output power spectrum of CO_2 laser

normalized signal could be known from the standart gas absorption which was used to calculate the sensitivity factor from the system (the lowest detection limit). Besides there were several interfering signal which impacts on the sensitivity of the system. That interfering signal was acoustic noise which occured from the loud acoustic and vibe on the system due to elctronic devices and electromagnet modulator. The concentration from ammonia, ethylen and acetone standart which were used to obtain the value of the normalized signal, background signal, noise system and the lowest limit detection were 11, 8 and 3 ppm, respectively.

Multicompound analysis sistem was obtained by calibration. The sample was analized by several different compound gas (>1 type of gas). Some components of the gas were ammonia, ethylene and acetone. The analysis could be done by measuring the photoacoustic signal at each wavelength which was selected based on the absorption spectra of the individual gas components (Rosencwaig, 1980). Multicomponent matrix value was obtained from the gradient (m) curve linearity of each gas standard biomarker. The bellow equation was a matrix calculation of concentration for determining the concentration of multicomponent gas emissions from human respiratory bellows:

$$\begin{bmatrix} \left(\frac{S}{P}\right)_1 \\ \left(\frac{S}{P}\right)_2 \\ \left(\frac{S}{P}\right)_3 \end{bmatrix} = \begin{bmatrix} 0.0295 & 0.0011 & 0.0011 \\ 0.019 & 0.014 & 0.0121 \\ 0.0005 & 0.0002 & 0.00247 \end{bmatrix} \begin{bmatrix} C_1 \\ C_2 \\ C_3 \end{bmatrix} \quad (2)$$

where, C_1 is ethylene C_2 is acetone and C_3 is ammonia.

Table 1: Performance of CO_2 laser photoacoustic spectrometer configuartion intracavity

Standart gas	Normalized signal (mV/W)	Normalized background signal (mV/W)	System noise ($mV/\sqrt{Hz}$)	Tle lowest detection limit (ppbV)	Stability power (W)	Resonance frequency (Hz)	Quality factor (Q)	Laser absorption line
Ammonia	$(32\pm5)\times10^{-3}$	$(1.8\pm0.4)\times10^{-3}$	$(0.56\pm0,1)\times10^{-3}$	23.3±0.5	17±1	1650±5	12.7±0.7	10 R14
thylene	$(24\pm5)\times10^{-3}$	$(1.3\pm0.2)\times10^{-3}$	$(0.56\pm0,1)\times10^{-3}$	18.5±0.3	20±1	1650±5	14.5±0.6	10 P14
Acetone	$(47\pm5)\times10^{-3}$	$(1.2\pm0.2)\times10^{-3}$	$(0.56\pm0,1)\times10^{-3}$	35.6±0.1	28±1	1650±5	14.6±0.6	10 P20

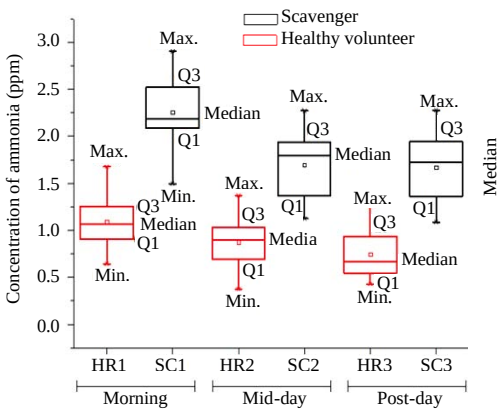

Fig. 3: Comparation of daily variation hour in ammonia concentration level for healthy volunteer and scavenger

Based on previous research no correlation between gender, age or BMI were established (Hibbard and Killard, 2011). Quistioner was conducted to ensure there is no disease, i.e., diabetes, kidney disease, bronchitis, etc. The analysis was conducted by comparing the gas concentrations of biomarkers using boxplot. Where the data was divided into 4 parts. Thus from this analysis, we got the maximum value minimum upper Quartile (Q1), the median or middle quartile and bottom quartile. Ammonia in the body resulted from protein breakdown.

In ammonia case, Fig. 3 shows that the ammonia concentration of scavengers on landfill was higher than the ammonia concentration from healthy volunteers.The highest ammonia consentration on scavenger was (2905±1) in the early morning and the lowest ammonia concentration on scavenger was (1089±1) ppbV in the post-day. Whereas for healthy volunteers, the highest ammonia concentration was (1676±1) ppbV in the early morning and the lowest was (376±1) ppbV in mid day. Median values of ammonia concentration on scavengers were (2189±2) ppbV in the early morning (1823±2) ppbV in mid-day and (1725±2) ppbV in post-day. That values approached upper quartil value: (2508±2) ppbV in early morning (1934±2) ppbV in mid-day and (1938±2) ppbV in post-day. Whereas the median value of ammonia concentration on healthy volunteers was (927±2) ppbV in the early morning (905±2) ppbV in mid-day and (703±2) ppbV in post-day. The value of healthy volunteers median were more variated, in the early morning the median value was in upper Quartil (Q3) of (1250±2) ppbV and lower Quartil (Q1) of (908±2) ppbV while in the mid-day approached to upper Quartil (Q3) of (1020±2) ppbV and in the post-day closed to lower quartil of (547±2) ppbV.

Based on the average of ammonia concentration, the consentration ammonia level on scavengers and healthy volunteers were decreasing. Concentration of scavenger level in the early morning, mid-day and post-day were (2257±1), (1695±1) and (1674±1) ppbV but concentration of healthy volunteer in the early morning mid-day and post-day were (1088±1), (877±1) and (744±1) ppbV. The previous literature stated that this decrease in ammonia might be a result of ingestion of food since the liver has a tendency to increase portal blood flow when eating (Hibbard and Killard, 2011; Smith *et al*., 1999). Ammonia concentration in normal human breath was in the range of 0.25-2.9 ppm (Wang and Sahay, 2009; Harren *et al*., 1990).

CONCLUSION

The CO_2 laser photoacoustic spectrometer configuration intracavity has a potential to be the viable tool for the concentrations analysis of ammonia in human breath. The highest power was obtained at 13.24 W with the lowest limit detection was 23.3 ppbV. The breath ammonia concentrations on 22 scavengers were found to range from 1089-2905 ppbV. Breath ammonia levels on daily routines decreased until mid-day and post day. The similiar result on healthy volunteers shows ammonia concentration decreased until mid-day and post-day.

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