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Photoacoustic Effect of Ethene: Sound Generation due to Plant Hormone Gases

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ABSTRACT. Ethene (C_2H_4), which is produced in plants as they mature, was used to study its photoacoustic properties using photoacoustic spectroscopy. Detection of trace amounts, with N_2 gas, of C_2H_4 gas was also applied. The gas was tested in various conditions-temperature, concentration of the gas, gas cell length, and power of the laser- to determine their effect on the photoacoustic signal, the ideal conditions to detect trace gas amounts, and concentration of C_2H_4 produced by an avocado and a banana. A detection limit of 10 ppm was determined for pure C_2H_4. A detection of 5% and 13% (by volume) concentration of C_2H_4 was produced for a ripening avocado and banana, respectively, in closed space.

Key words: Photoacoustic, Ethene, Trace detect, CO_2 Laser, Resonance frequency

INTRODUCTION

The Photoacoustic (PA) effect, discovered by Alexander Graham Bell in 1880, was first implemented in the use of his invention, the photophone. Later, the PA effect was employed in PA spectroscopy in research by L.B. Kreuzer in 1971 with trace gas detection.[1] The PA effect is created when a sample goes through the process of cyclic heating and cooling of a gas, solid, or liquid substance.[1] This cyclic heating and cooling is produced by the modulation of light of a particular wavelength, depending on the sample used, which causes pressure oscillations within the sample, produced by exposure to a light source.[2] Similar to other spectroscopy methods, the strength of the acoustic signal produced by the sample is proportional to the light absorbed.[3] However, since PA spectroscopy utilizes the production of acoustic waves, light scattering is not an aspect that needs to be taken into account in this system and has no influence on the results.[2,3] For detection of PA signal throughout the entire electromagnetic spectrum, a single microphone can be used.[3]

Ethene (C_2H_4) is used in many free radical reactions. The main free radical reaction that C_2H_4 is involved in, is the making of polyethylene, the most widely used plastic in the world. C_2H_4 is the byproduct of the aging process in plants, as well. This ripening process is called the methionine cycle and also produces CO_2, HCN, and H_2O. Also, C_2H_4 has aesthetic properties. The main problem with C_2H_4 is that when the gas is produced and released into the atmosphere it becomes flammable at 2.7 vol %. If humans are shipping any sort of plants, imported or domestically, the risk of fires or explosions increases greatly as fruits or vegetables start to ripen.[4] Negative effects of ethene often include reduced storage life, increased oxidative browning, and quickened senescence. More specific adverse effects of ethene include the formation of bitter-tasting chemicals in carrots, russet spotting on lettuce, and inhibited blooming of carnations.[5] Due to its large absorption coefficient, C_2H_4 is a strongly absorbing gas. Subsequently, PA spectroscopy is the ideal method for detection. One of the largest absorbance peaks of C_2H_4 is found near 10.6 μm; therefore in order to detect C_2H_4, the laser has to have the wavelength in the same range. A CO_2 laser was used in the experiment because it satisfies these requirements.[6] It has recently been shown that a PA laser spectrometer with CO_2 emission in the infrared range could detect C_2H_4. An acoustic signal is produced at the resonance frequency of about 2,400 Hz of 67 mm long and 18 mm of diameter resonant cell.[7]

Here, we investigate the detection of C_2H_4 from fruits. Temperature of C_2H_4 in the cell, concentration of C_2H_4 in the cell, length of the gas cell, and power of the CO_2 laser, are the parameters of the experimental setup that were varied to determine the effect on the PA signal produced from C_2H_4, detection limit using trace concentrations of C_2H_4 in an inert gas, N_2, and finally, detection of concentration of C_2H_4 from an avocado and banana in the process of ripening.[8]

EXPERIMENTAL

The simplified diagram of the experimental setup is pictured in *Fig.* 1. The light emitted from the CO_2 laser (Access Laser Company Model L3) was aligned through

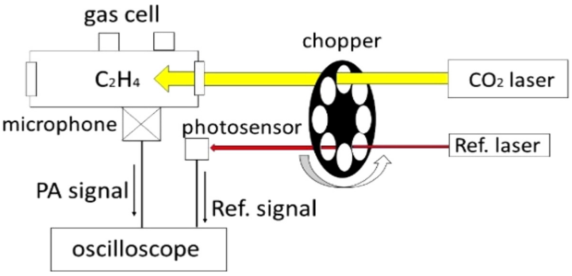

***Figure* 1.** Diagram of experimental set up used in experimentation.

an optical chopper (Thorlabs, Inc.) to chop the continuous laser irradiation, and directed to a gas cell (RJ Spectroscopy Company). Maximum laser power (200 mW) was used in experimentation, unless the power had to be varied. Germanium broadband precision windows (Thorlabs, Inc.) were used on the gas cell. A sensitive microphone (PCB Piezotronics, Inc. Model 130E20) was connected to the outside of the cell at a connection point on the edge of the gas cell. A diode laser (635 nm, Thorlabs, Inc. CPS182) was used as a reference laser and was detected using a Si photo detector (Thorlabs, Inc. DET36A). The microphone and Si photo detector were connected to a digital oscilloscope (Tektronix TBS 1202B). Each data point represented the average of 128 samples. To heat the cell during the experiments that involved temperature, a heating pad connected to a temperature controller (Thorlabs TC200) was placed inside the gas cell. All other experimentation was done at room temperature. During C_2H_4 detection in the fruit, an avocado and banana were left to ripen, separately, in one gallon airtight Ziploc bags for three days. These bags were then connected to the gas cell through a rubber tube and voltages were tested at certain data points over 128 samples using the oscilloscope.

RESULTS AND DISCUSSION

Fig. 2 displays the PA signal from the reference laser and sample as seen on oscilloscope.

The results of experimentation with cell length were used to compare the relationships with resonance frequency using Eq. 1:[8]

$$f_{res} = C_s\frac{1}{2L} \propto \sqrt{\frac{T}{M}\frac{1}{2L}} \qquad (1)$$

where f_{res} is the resonance frequency (Hz), C_s the sound velocity (cm s^{-1}), L is the length of the gas cell (cm), T is the temperature (K), and the M is the molar mass (g mol^{-1}).

In experiments with varying the lengths of the gas cell,

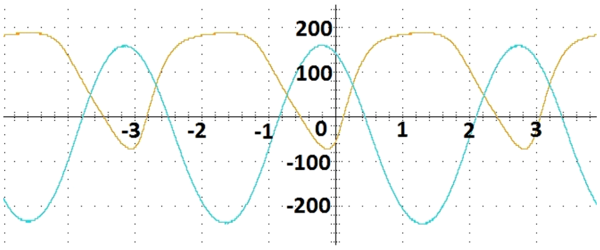

***Figure* 2.** Typical waveform of PA signal and the waveform of the reference signal. The y-axis is voltage (mV) and the x-axis is time (ms).

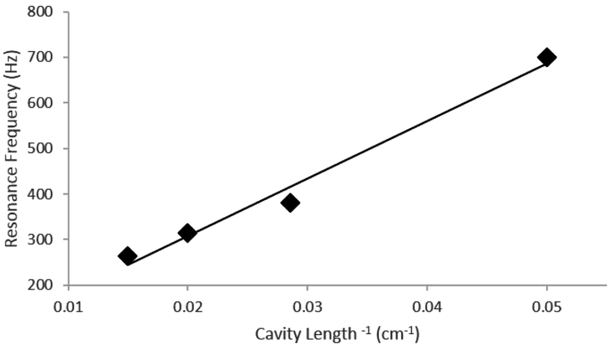

***Figure* 3.** First resonance frequency at varying cavity lengths with each cavity containing 100% C_2H_4. Data represents the average of 128 replicates.

lengths of 20, 35, 50, and 65 cm were used. After finding the resonance frequency for 100% C_2H_4 in each of these gas cells, a calibration curve was created, shown in *Fig*. 3. The linearity of the calibration curve show the relationship between the resonance frequency of C_2H_4 and the corresponding gas cell length.[8] The plot of resonance frequency versus cavity length gives the sound velocity. The experimental and theoretical values Cs of C_2H_4 are 327 m/s and 262 m/s. The percent error between these two values is 20%.[9]

The results from experimentation with laser power and temperature were used to compare the relationships with PA signal using Eq. (2).[10]

The amplitude of the PA signal for an optically thin gas is given by Eq. (2):

$$p_o \propto \alpha \mathrm{P} \qquad (2)$$

where p_o is the acoustic pressure amplitude (N m^{-2}), P is the power of the laser (mW), and α is the optical absorption coefficient (m^{-1}). From Eq. 2, it can be observed that the amplitude is proportional to the power of the laser. *Fig*. 4 displays the linear dependence between PA intensity and power of the laser as given by Eq. 2.

C_2H_4 was also tested varying the temperature against

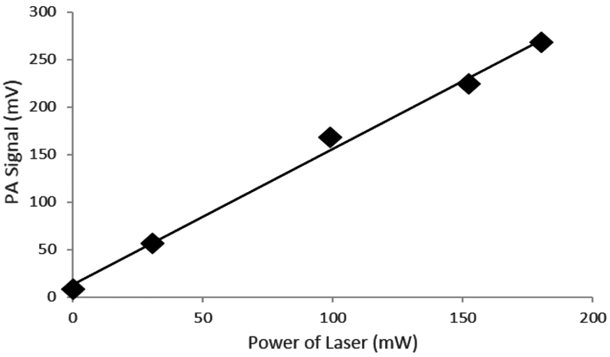

***Figure* 4.** Photoacoustic signal amplitude at varying laser power using a 50 cm gas cell filled with 100% C_2H_4 at 200 Hz.

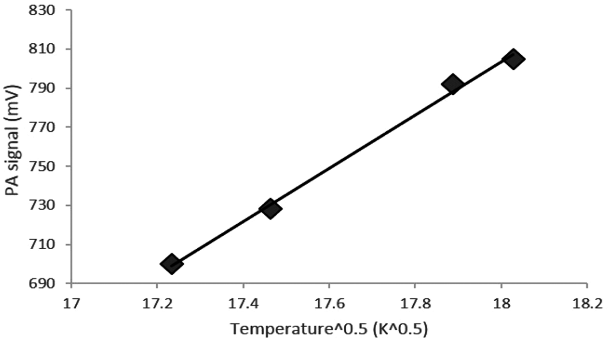

***Figure* 5.** Highest PA signal at varying temperatures with 100% C_2H_4 in a 50 cm gas cell. Data represents the average of 128 replicates.

the PA signal. Using amplitude at four different temperatures (22, 30, 45, 50 °C), the PA signal in the 50 cm cell containing 100% C_2H_4 was recorded. Since PA signal is proportional to the square root of the temperature of the system, the temperatures at which C_2H_4 was tested were plotted in a calibration curve against the corresponding PA signal.[8] *Fig.* 5 displays this relationship between the square root of the temperature and the PA signal, resulting in a linear dependence.

Detection of trace amounts of C_2H_4 was one of the main goals of this experimentation. A 10 mL syringe was used in the dilutions of the C_2H_4 gas. The syringe was filled with 1 mL of C_2H_4 and 9 mL of N_2, an inert gas. Out of 10 mL of gas mixture, 9 mL was released, and the syringe was filled again with 9 mL N_2, resulting in a 0.1 mL volume of C_2H_4. This dilution process was repeated and tested for a signal until a signal was no longer distinguishable from the noise. Each point was plotted and a calibration curve was constructed against the PA signal. This experiment was conducted at room temperature, using a gas cell length of 50 cm and laser power setting of about 100 mW (recorded temperatures from 89 to 130 mW). The detection limit obtained from this experiment on C_2H_4 was 10 ppm. *Fig.* 6 displays the calibration curve constructed from the trace concentration amounts of C_2H_4 and the corresponding PA signal.

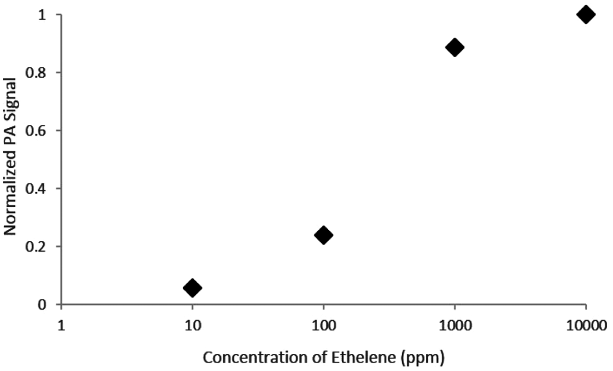

***Figure* 6.** PA signal for varying C_2H_4 concentration in a 50 cm gas cell with a frequency of 155-160 Hz. Data represents an average of 128 replicates.

After detecting trace amounts of gas concentration, the next question was how much C_2H_4 by volume a banana and avocado emit. During ripening, fruits produce CO_2, HCN, H_2O and C_2H_4, however only C_2H_4 has absorption peaks around 10.6 μm and generates the PA effect.[11] When there is no spectral overlap from other buffer gases, they will not contribute to the PA signal; the light passes the detection cell unattenuated. Thus, a single component could be detected out of gas mixtures. The experimentation started with 100% N_2 gas in the cell. After calculating the volume of the gas cell, various amounts, in mL (% of cell) of C_2H_4 were added to the cell and plotted against the PA signal to create a calibration curve for concentration of C_2H_4. After letting the avocado and banana ripen separately in bags for 3 days each, the bags were then connected via an attachment hose to the gas cell and squeezed. These signals were

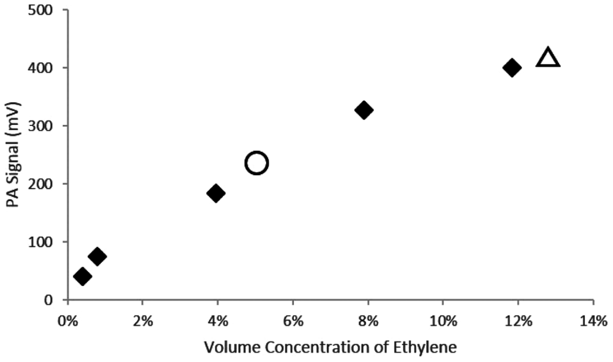

***Figure* 7.** PA signal for varying C_2H_4 concentration in a 50 cm gas cell with a frequency of 175-185 Hz compared against fruit (diamond=calibration, circle=avocado, triangle=banana).

tested and recorded against the concentration curve. The avocado and banana produced a 5% and 13% concentration of gas in the bag, respectively. *Fig*. 7 shows the calibration curve plotted with volume fraction against PA signal.

The danger about C_2H_4 is that this gas is flammable when its concentration in the air is above 2.7 vol%. At these levels, it is impossible for humans to detect C_2H_4 without special equipment. This is important because the economy has fruit food supply lines that can be in danger of possible fires and explosions. There are multiple documented fires at warehouses that store these fruits. If businesses implemented C_2H_4 trace gas detectors in workplaces, it would keep workers safe, whether it be on ships, trucks, warehouses, or all three. This application to the real world could save people's lives. PA spectroscopy is the most sensitive for C_2H_4 trace gas detection. Although the instruments used in this application are not yet cost-effective for the business world, getting those costs down would keep people safer and ultimately make the world safer.[4]

CONCLUSION

In this experiment, C_2H_4 gas was irradiated using a CO_2 laser, which resulted in thermal expansion and release of heat. This thermal expansion of the sample results in the generation of pressure waves that can be detected with microphone. The amplitude of the PA signal is linearly proportional to the power of the excitation laser light. This linearity has been investigated and the measurements done on C_2H_4 gas have given consistent results. The experimental results have demonstrated that the resonance frequency of PA is related to the cavity length. The experimental results have also demonstrated that PA signal is related to laser power and temperature. The C_2H_4 concentrations can be detected at levels as low as 10 ppm using this experimental setup. It is possible to improve the detection limit by using more powerful and stable CO_2 laser with less power fluctuations. The experimental setup also detects natural C_2H_4 from fruits, which could be improved with the use of a more airtight seal to stop leakage of the gas. This detection measured 5% and 13% by volume of air, of the avocado and banana, respectively.

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