Lab Documentation

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1. Instructor Notes

1-1. Photoacoustic (PA) experimental system for infrared absorption of gases

1-1-1 Overall configuration

The device configuration of the main portion of the non-dispersion photoacoustic experimental system is shown in Figure 1. The main portion is divided into two parts; Part I consists of an IR source, a sample cell and an electret condenser microphone and Part II consists of a chopper system (a DC motor and a five-bladed disk), a photosensor and a battery box. Each part is mounted on a brass plate. Being divided into two parts, this system has a flexibility about the relative position of the chopper to the light path of IR radiation. By inserting the chopper into the light path and pulling it out, students are able to confirm that the periodic modulation of IR radiation is essential for the photoacoustic effect.

The signal of the microphone (photoacoustic signal) is sent to the input terminal of the oscilloscope. The output of the photosensor is also sent to the oscilloscope and used as trigger signal. Figure 2 shows an example of the setting of the oscilloscope. Most conventional oscillators can be used for this experiment.

The PA signal can be measured as an AC voltage also by using a digital multimeter with a precision of 0.1 mV or better. The difference in the measured AC voltage between with and without the modulation of IR radiation corresponds to the PA signal intensity (an AC voltage of around 0.5 mV is observed even at zero-modulation frequency, which is probably due to high frequency noise of the microphone). Usually, a signal intensity of a few mV level is observed for most IR-absorbing gases. The parallel use of a digital multimeter will help the students who have some difficulty in operating an oscilloscope.
Figure 1. Schematic diagram and photograph of the main portion of the PA system.
Figure 2. Setting of the oscilloscope. The horizontal scale is 5 ms/div. The vertical scale is 1mV/div for the signal of the electlet microphone (CH2) and 5V/div for the reference trigger signal of the photosensor (CH1).

Upper: Only a trigger signal is input to the oscilloscope. The trigger signal appears as a rectangular wave.

Lower: Both a trigger and a microphone signal are input to the oscilloscope. The photoacoustic signal appears as a sine-like wave having the same frequency as the trigger signal.
1-1-2 Parts for the PA system

The key parts used for building the PA system are listed in Table 1. The followings are additional information for the production of the PA system.

Chopper: The chopper consists of a five-bladed disk, a DC motor connected to a DC power supply, a reflection-type microphotosensor driven by a battery of 9 V, output terminals, and a blade guard, as shown in Figure 3. The five-bladed disk (diameter: 100 mm, thickness: 0.5 mm) was made from a stainless plate and attached to the axis of the DC motor with an aluminum fixture. When the blade is in front of the photosensor, a signal of 9 V is output to the terminals connected to CH1 terminal of the oscilloscope. The modulation frequency is controlled by changing the voltage of the DC power supply.

Sample Cell: The gas sample cell is a tube with an inside diameter of 2 cm and a length of 10 cm and is equipped with a microphone, an inlet, an outlet and a pair of windows. All parts making up the cell are shown in Figure 4(1) and the cross section in Figure 4(2). The dimensions of each part are shown in Figure 4(2) and Table 2 together with some related information. Parts b and c were welded to the tube, Part a. The windows and the microphone were fixed with o-rings and screwed fastenings, which allows easy replacement of these parts.

Windows: Materials that are transparent in the region of 2.5-17 µm (4000-600 cm⁻¹), such as, KBr and NaCl can be used as windows. KBr that is transparent until 29 µm (340 cm⁻¹) is suitable for the comparison in the long-wavelength range. The window on the opposite side to the IR source can be substituted with a metal disk when carrying out qualitative characterization.

1-1-3 Simple substitute for the sample cell

The PA cell described above is convenient, but its production needs several kinds of machine tools, which are expected to be unavailable in many high schools. However, the PA experiments can be carried out with the following simple PA cell, which can be made quite easily with materials and tools available in a home center and an ordinary high-school laboratory.

Figure 4 is an example. The main body is an aluminum rectangular pipe (outside dimensions: 100x30x20 mm, thickness: 2 mm), to which two KBr windows, a condenser microphone, and two copper tubes (30 mm long, outer diameter: 1/4 inch) are attached with epoxy glue. A silicon rubber tube is attached to each copper tube. A loaded sample gas is kept in the cell by closing the rubber tubes with pinchcocks. This cell can be made by with a handsaw, a hand drill and a few kinds of files in a short time.

Although this simple cell has some drawbacks compared with the stainless cell, that is, it is sensitive to the outside noise and the windows cannot be replaced, its performance is sufficient for some simple PA experiments of greenhouse effect gases.
Table 1. Information about main components of the PA system.

| Item            | Manufacturer and part number | Comments                                                                                                                                 |
|-----------------|------------------------------|----------------------------------------------------------------------------------------------------------------------------------------|
| IR source       | IR System Co. (www.irsystem.com), IRS-001C | This IR source is a continuous type of 8W in which a coiled resistance wire operates at about 900 °C. Boston Electronics (www.boselec.com) supplies similar products (IR-12 or IR-12K with a parabolic reflector). |
| microphone      | SONY Corp. (www.sony.com), ECM-C115 | This microphone is designed to record business meetings, lectures, and interviews. It has an amplification circuit.                       |
| airtight valve  | Swagelok (www.swagelok.com), SS-4P4T |                                                                                                                                         |
| microphotosensor | SUNX Ltd. (www.sunx.com), PM2-LH10 with connector CN-13 | RS Components Ltd. (www.rs-components.com). supplies the sensor and connector with stock Nos. 352-7851 and 352-7902.                   |
| DC motor        | MFA/Como Drills (www.mfscomodrills.com), 719RE385 | RS Components Ltd. (www.rs-components.com). supplies this motor with stock No. 238-9738.                                               |

Figure 3. An overall photograph of chopper part (left) and a circuit for the microphotosensor (right). In the photograph, A: protective plate, B: five-bladed disk, C: DC motor, D: microphotosensor, E: battery, and F: output terminals.
Figure 4. (1) A photograph of all parts used for the PA cell, and (2) the cross section of the PA cell. The dimensions are given in millimeters.
Table 2  Information about the parts used for the PAS system

| Part | Dimension (mm) | Comments |
|------|----------------|----------|
| a    | *              | Thread cutting was carried out at both ends. |
| b    | *              | Basal portion of a microphone connector. |
| c    | *              | 1/4 inch tube |
| d    | φ(inner): 21.5, t:1.5 | O-ring (S-22) |
| e    | φ 25.0, t:2    | Window (KBr, NaCl, etc.) |
| f    | *              | Knurling was carried out on the side surface. |
| g    | φ(inner): 8.5, φ(outer):11.8, t:2.0 | |
| h    | φ(inner): 7.8, t:1.9 | O-ring (P-8) |
| i    | φ(inner): 8.5, φ(outer):11.8, t:5.0 |  |
| j    | φ(inner): 7.8, t:1.9 | O-ring (P-8) |
| k    | φ(inner): 8.5, φ(outer):11.8, t:4.0 |  |
| l    | *              | Knurling was carried out on the side surface. |
| m    | φ: 8.2         | Microphone |
| n    |                | Airtight valve |
| n    |                | 1/4 inch tube |

* The dimensions are shown in Figure 4(2).

Figure 5. Handmade PA cell.
1-2 Procedure

Preparation of the PA system: The following procedures are carried out to make ready for the experiment.

(1) Install KBr (or NaCl) windows to the sample cell (because they are deliquescent, KBr and NaCl windows should be kept in a desiccator).

(2) Connect a battery and a DC power supply to the photosensor and the DC motor of the chopper, respectively.

(3) Connect the output terminals of the photosensor and the microphone to CH1 and CH2 terminals of the oscilloscope, as shown in Figure 2.

(4) Turn on the switches of the oscilloscope and DC power supply.

(5) Set the horizontal scale of the oscilloscope at 5 ms/div, and the vertical scale at 5 V/div for CH1 and at 1-5mV/div for CH2.

(6) Select "Internal mode" of the trigger and set the trigger source to CH1.

(7) Select "CHOP mode" of the display so that both CH1 and CH2 signals can be seen on the display.

Sample loading: The PA system is intended to use at atmospheric pressure. The inside pressure of the sample cell that is higher or lower than atmospheric pressure should be avoided. Concerning a pressured gas cylinder, the pressure should be adjusted under 0.5 kgf/cm² by using a regulator. A sample gas can be introduced also by using a gasbag, as shown in Figure 6. When the sample gas is flammable, the IR light source should be turned off during the loading.

Sample loading is carried out in the following way.

(1) Turn off the switches of the microphone, DC power supply and IR source, and set the chopper away from the sample cell.

(2) Open both the inlet and outlet valves of the sample cell.

(3) Load the sample gas though the inlet valve.

(4) Close the inlet valve first and then the outlet valve second.

Measurements:

(1) Set the chopper blade between IR source and sample cell.

(2) Turn on the switches of the microphone, DC power supply and IR source.
(3) Choose a suitable modulation frequency for PA measurements by adjusting DC power supply. The modulation frequency is mostly set in the range of 40-100Hz.

(4) Adjust the trigger level to stabilize the display.

(5) Choose a vertical scale suitable for the PA signal (usually 1-5 mV/div).

(6) Read the amplitude of CH2 signal.

Note: Because KBr and NaCl windows are deliquescent, they sometimes become cloudy. The cloudiness can be removed by polishing them with a piece of soft cloth stretched on a flat plate. As for a heavily clouded window, polishing with a cloth partly wetted with a small amount of methanol is effective.

1-3 Examples of experiments using the PA system

1-3-1 Practical work for understanding the principles of the PA system

After a short lecture about the photoacoustic effect, students carry out the following procedures, which are useful for understanding the principle of the photoacoustic effect and the characteristics of the PA experimental system.

(1) Survey of the PA system

Students examine the location of each part such as sample cell, chopper, microphone and IR light source, and review their roles. By removing the windows from the sample cell, it can be confirmed that the sample cell is only a hollow tube with a microphone.

(2) Checking on the operation of the microphone

Students examine the operation of the microphone by making a voice in front of the sample cell with opened inlet and outlet valves and watching electric signals produced by the voice on the monitor screen of the oscilloscope with a vertical scale of 1 mV/div and 5 msec/div. The sound collected by the microphone is observed as an oscillating voltage, as shown in Figure 7(a). However, when both the valves are closed, students' voices do not cause oscillating signals within the sensitivity of this system, as shown in Figure 7(b). It follows that when both the inlet and outlet valves are closed an oscillating voltage appearing on the monitor screen corresponds to the sound produced by the enclosed gas.
(3) Checking of the characteristics of the IR light source

Students learn the characteristics of the IR light source by comparing it with a visible fluorescent lamp. By holding a hand palm in front of the IR light source, it can be confirmed that the IR light source emits heat (IR) rays.

(4) Checking on the operation of the PA system

Students operate the PA system and learn the photoacoustic effect. At first, a suitable amount of IR absorbing gas such as CO₂ is charged into the sample cell. By inserting and removing the rotating chopper disk between the light source and the sample cell, it can be confirmed that the modulation of the incident light intensity is necessary for the detection of light absorption with this system. By changing the chopper frequency, it can be shown that the PA signal is inversely proportional to the modulation frequency. If the IR light source is replaced with a fluorescent lamp or a LED lamp, the signal disappears, from which students can learn that the gas in the cell is transparent to the visible light but it absorbs IR radiation.

1-3-2 Experiments for the absorptivity of the gases contained in the atmosphere

Through the PA experiments using the following two groups of gases, students can learn that the minor components of the atmosphere determine IR absorptivity of the atmosphere. Except H₂O, these gases are introduced into the PA cell without dilution. As for H₂O, a water laden nitrogen gas, which has been passed through water, is introduced.

(1) Greenhouse effect gases

H₂O, CO₂, CH₄, HFC-152a (1,1,1-trifluoro-1,2,2-trichloroethane: it was obtained from a can of air duster) etc. These gases exhibit a strong PA signal.

(2) Major components of the atmosphere.

N₂(content in the atmosphere: 78%), O₂(21%), and Ar(1%). These gases exhibit no pronounced signal.

Residual H₂O desorbed from the inside of the sample cell sometime gives a very weak signal during the measurement on the second group of gases. However, the difference in signal intensity between the first and second group of gases is quite large and obvious. Students are easily able to understand the difference in IR absorptivity between greenhouse effect gases and other gases.

1-3-3 Experiments for the absorptivity of air samples obtained from different places

The water vapor of ambient air gives a PA signal detectable by this PA system. Students are able to compare the signal intensity of air samples obtained from different places, such as, class room, shower room, kitchen, garden, and so on. The airbag shown in Figure 6 is convenient for this
purpose. The comparison of exhaled air with room air shows a clear difference in signal intensity; the exhaled air that contains 4% CO₂ and 5% H₂O exhibits a much stronger PA signal.

Figure 6. Sample gas loading by using a gasbag.

Figure 7. Signals produced by a voice with opened valves (a) and with closed valves (b).
1-3-4 Advanced Experiments

The followings are advanced experiments for the students who want to learn the IR absorption of gases more deeply.

(1) Relationship between signal intensity and sample gas concentration

Students examine how PA intensity depends on the concentration of a sample gas by diluting a sample gas (CO₂, H₂O, and so forth) with a large amount of N₂. Through this experiment students are able to learn that the absorption of infrared radiation by a gas shows almost linear increases with its concentration in the low concentration range.

Information for experimental procedure: As for CO₂ and CH₄, the use of a gas mixer consisting of two gas flow monitors shown in Figure 8 is a simple method to control the concentration. The concentration is simply determined by the flow rates between sample gas and diluent N₂. The error is estimated to be within 2%.

As for H₂O, a water laden N₂ gas that has been passed through water is mixed with a dry N₂ gas, and the humidity and temperature of the mixed N₂ gas are measured with a digital thermohygrometer. The water content can be estimated within 0.1 percent from the obtained humidity and the saturated vapor pressure at that temperature.

Figure 8. A gas mixer consisting of two gas flow monitors. The concentration of sample gas is adjusted by changing the flow rates of sample gas and N₂ gas.

Figure 9. H₂O concentration dependence of signal intensity: (a) 0.2 %, (b) 0.6 % and (c) 1.2 %.
(2) Wavelength range of major absorption

Students examine the signal intensity change caused by inserting a filter having a strong absorption band in front of the incident window or by changing the material of the window. Depending on what wavelength range the filter (or window) absorbs, the PA intensity changes. The gas in the cell is not irradiated with IR light of the absorption range. IR absorptivity of the gas in this absorption range does not contribute to the PA signal. Therefore, a large signal intensity change when inserting a filter means that major IR absorption is located in the absorption range of the filter. In this way, the wavelength range of major absorption can be roughly examined by using this PA system.

The following is an example that demonstrates this effect of absorption filters. IR transmission spectra of KBr, CaF$_2$, and Al$_2$O$_3$ (sapphire) are shown in Figure 10. KBr used as windows in this PA system is transparent in the range of 4000-400 cm$^{-1}$ (wavelength: 2.5-25 µm), while transmittance decreases rapidly below 1000 cm$^{-1}$ (10.0 µm) for CaF$_2$ and below 1800 cm$^{-1}$ (5.6 µm) for Al$_2$O$_3$. CaF$_2$ and Al$_2$O$_3$ plate can be used as filters that remove IR radiation in these low-frequency ranges by inserting them between the IR source and the incident window of the sample cell. In the absorption range of a filter, IR radiation does not reach the gas molecules in the cell and the IR absorptivity of the molecules does not contribute to the PA signal. Therefore, the intensity decrease by a filter for gases with strong absorption bands in the absorption range is more noticeable than that for gases without strong absorption bands. As shown in Figure 10, HFC-152a has many more strong bands in the absorption range of CaF$_2$ and Al$_2$O$_3$ filters than CO$_2$, exhibiting a larger intensity decrease by these filters, as shown in Table 3.

A variety of materials can be used as filters. For example, a cover glass for microscope, which is made of borosilicate glass, can be used as a filter that cuts IR radiation below 1500 cm$^{-1}$ (6.7 µm). By changing the combination between sample gases and filters, students are able to understand that the wavelength range of major absorption varies depending on the chemical structure of gases.

Here, we would like to stress that intensity changes of the PA signal by filters provides only a qualitative measure, because several factors relate to the extent of intensity changes. For example, the energy density of IR radiation is not constant but depends on wavenumber, as shown in Figure 11(a). The energy density is at maximum around 2300 cm$^{-1}$ and decreases with separation from this point. The concentration of gases also has a significant influence on the relative intensities of absorption bands. Figure 11 shows IR transmission spectra of CO$_2$ and HFC-152a at a concentration of 1%. It can be seen from the comparison between Figures 10 and 11 that weak absorption bands are enhanced at high concentrations. It follows that the contribution of weak absorption bands to the PA signal becomes large with gas concentration. IR transmissivities of windows and filters depend also on their refractive indexes. The greater the refractive index, the lower the transmissivity of a plate. As shown in Figure 10(a), the base line of CaF$_2$ with refractive index of 1.39 is higher than
those of Al$_2$O$_3$ and KBr with refractive indexes of 1.62 and 1.49, respectively.

![Figure 10](image1.png)

Figure 10. Transmission IR spectra. (a) KBr, CaF$_2$ and Al$_2$O$_3$ plates (2 mm thick), (b) CO$_2$ (1 atm, 10 cm path), and (c) HFC-152a (1 atm, 10 cm path).

|                  | CO$_2$ | HFC-152a |
|------------------|--------|----------|
| KBr window       | 1.00   | 1.00     |
| KBr window & CaF$_2$ filter | 0.95   | 0.89     |
| KBr window & Al$_2$O$_3$ | 0.75   | 0.54     |

Table 3. Effect of filters on PA signal intensity

The PA intensities were normalized by setting its value at 1.0 for each measurement without a filter.
Figure 11. (a) Calculated energy density of IR source operating at 900°C, and (b) and (c) transmission spectra of CO$_2$ and HFC-152a at 1 vol% (1 atm, 10 cm path).

1-3-5 Feed of the microphone output to a personal computer

It is possible to record the output signal of the microphone by feeding it into the audio input port of a personal computer and using a software for recording and editing sounds, such as Audacity (http://audacity.sourceforge.net/). Figure 12 shows an example of the recorded output signal. The use of the personal computer helps us store and display the output signal. However, it should be kept in mind that a wide frequency range of electric signals other than the PA signal, which are asynchronous with the chopper, would be contained in the output signal of the microphone. Careful attention is required for handling the recorded data for quantitative analyses. It seems better to use the signal appearing on the monitor screen of the oscilloscope, which is synchronized with the chopper,
for this purpose.

Figure 12. The microphone output recorded by using a PC and Audacity.
2  Student directions
The following is an example of student directions for an extracurricular class for high-school students.

IMPORTANT:
As for the operation of the oscilloscope and the photoacoustic system, follow the instruction of your teacher and teaching assistants. If you have some difficulties or questions, ask their assistance. Erroneous operation can be dangerous or can give significant damage on the system. Wear safety goggles when you use a pressured gas cylinder.

(1) The followings are the parts used for the photoacoustic system. Examine where each part is located and review its role.
   a. sample cell,  b. microphone, c. IR light source, d. KBr (or NaCl) windows, e. chopper blade,
   f. photosensor

(2) Remove one of the KBr windows of the cell, and look inside. Confirm that the cell represents an empty chamber with IR transparent windows and a microphone.

(3) Connect the output of the microphone to CH2 terminal of the oscilloscope. Turn on the microphone and the oscilloscope. Set the vertical scales of CH1 and CH2 at 5V/div and 1-5 mV/div, respectively, and the horizontal scale at 5 msec/div. Open the inlet and outlet valves of the cell and see the electric signal on the screen. The sounds surround the cell are collected by the microphone to give electric signals on the screen. Produce a sound with your voice noting the changes in electric signals.
   Close both valves of the cell. What do you see on the screen when you vocalize? What is the difference?

(4) Remove the cell from the stage and turn on IR light source. Compare it with a visible fluorescent lamp in the following points.
(Warning! Do not touch the filament and its surroundings. The temperature of the filament is around 900 °C, and also the filament is mechanically fragile.)
   a. Which lamp emits more visible light?
   b. With which lamp do you feel warmer when you hold your palm in front of them?

(5) Load a provided IR absorbing gas into the cell. Prepare for the operation of the chopper, as described below. Connect a battery to the photosensor and confirm that its red LED is on only when
a metal blade is in front of it. Connect DC power supply to the DC motor, and connect the output of the photosensor to CH1 of the oscilloscope. Turn on the DC power supply, and increase the voltage watching the rectangular wave of CH1 on the screen, which is produced by the movement of the chopper disk. Adjust the trigger level. At a certain point, read the cycle length of the rectangular wave to obtain the modulation frequency of IR radiation by using the following relation: 

\[
\text{frequency (Hz)} = \frac{1000}{\text{cycle length (msec)}}.
\]

Insert the rotating chopper blade between IR source and the cell. Confirm that a sine-like wave of CH2 appears on the screen. What changes are observed in CH2 signal by the following changes?

a. Increasing and decreasing the modulation frequency of IR source.

b. Inserting and removing the chopper.

c. Replacing IR source with a fluorescent lamp.

What do you think is necessary for the appearance of the electric signal from the microphone on the basis of these observations?

(6) Observe CH2 signals of the following gases and classify them into IR absorbing and non-absorbing gases.

- N₂, CO₂, O₂, CH₄, Ar, He, H₂O, HFC-152a(1,1-CF₂HCH₃), and so on.

(7) Obtain air samples with gasbag at different places or different conditions, such as class room before and after a class, ground, kitchen, shower room, exhaled air and so on. Observe CH2 signals of these air samples and compare the signal intensities. How do you explain the outcome?

For Advanced Students

(8) Measure CH2 signal intensity of CO₂, H₂O or other gases at different concentrations. Plot measured signal intensities against concentration.

(9) Examine the changes in CH2 signal intensity of CO₂ and HFC-152a when a filter is inserted between IR source and the cell as indicated in the figure below. Use CaF₂ and Al₂O₃ plates as filters. Note the percentage change in signal intensity with each filter? List the results in a table. Using the provided information about the characteristics of the filters, interpret the results based on the idea that the absorptivity of gas depends on the frequency of IR radiation. Which gas has a larger absorptivity in the low frequency region?
3 CAS registry number

N₂:  7727-37-9  
O₂:  11062-77-4  
Ar:  7440-37-1  
H₂O: 857494-70-3  
CO₂: 124-38-9  
CF₂HCH₃: 75-37-6  

3 Safety and Hazards

In case the sample gas is supplied from a pressured gas cylinder, the experiment should be carried out with support of assistants who are accustomed with handling of pressured gas cylinders. Ventilation of the classroom is required. Some of the greenhouse effect gases, e.g., methane, are flammable. Attention should be paid to oxygen deficiency as well as flammability and explosibility of gases. A protective plate should be placed around the disk blade of the chopper. The chopping frequency should not be increased beyond necessity. It is recommended that an assistant should be assigned to each group of students to assist their experiments.