

Advanced Chemistry – 2008

FTIR Spectroscopy Lab Experiment

Prepared by

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Determination of the amount of carbon monoxide in exhaust samples by FTIR spectroscopy

In this experiment we will use FTIR spectroscopy as a quantitative technique to determine the amounts of CO in exhaust samples. We will use automobile, lawn mower, and leaf blower exhaust (as well as any other gasoline powered equipment that you choose) samples.

Before conducting a quantitative experiment in FTIR spectroscopy, it is important to validate that the Beer's law holds true for the samples you are trying to test.

Determining the validity of Beer's law:

99.5% CP grade carbon monoxide, purchased from MG Scientific Gasses in a lecture bottle is provided for this purpose. The lecture bottle is fitted with the required regulator valve for ease of use.

Please note that carbon monoxide is a colorless, odorless, toxic gas. Proper handling is necessary to ensure your safety as well as that of others. Please follow the guidelines provided for safe handling at all times. Make sure that a CO detector is on during lab at all times.

Background Spectrum:

Place KBr windows on the 10 cm gas cell. Evacuate the cell using the gas handling manifold. Record a background spectrum of the cell at 4 cm^{-1} resolution and co-add 50 scans between 400 to 4800 cm^{-1} . Save this spectrum as your background spectrum.

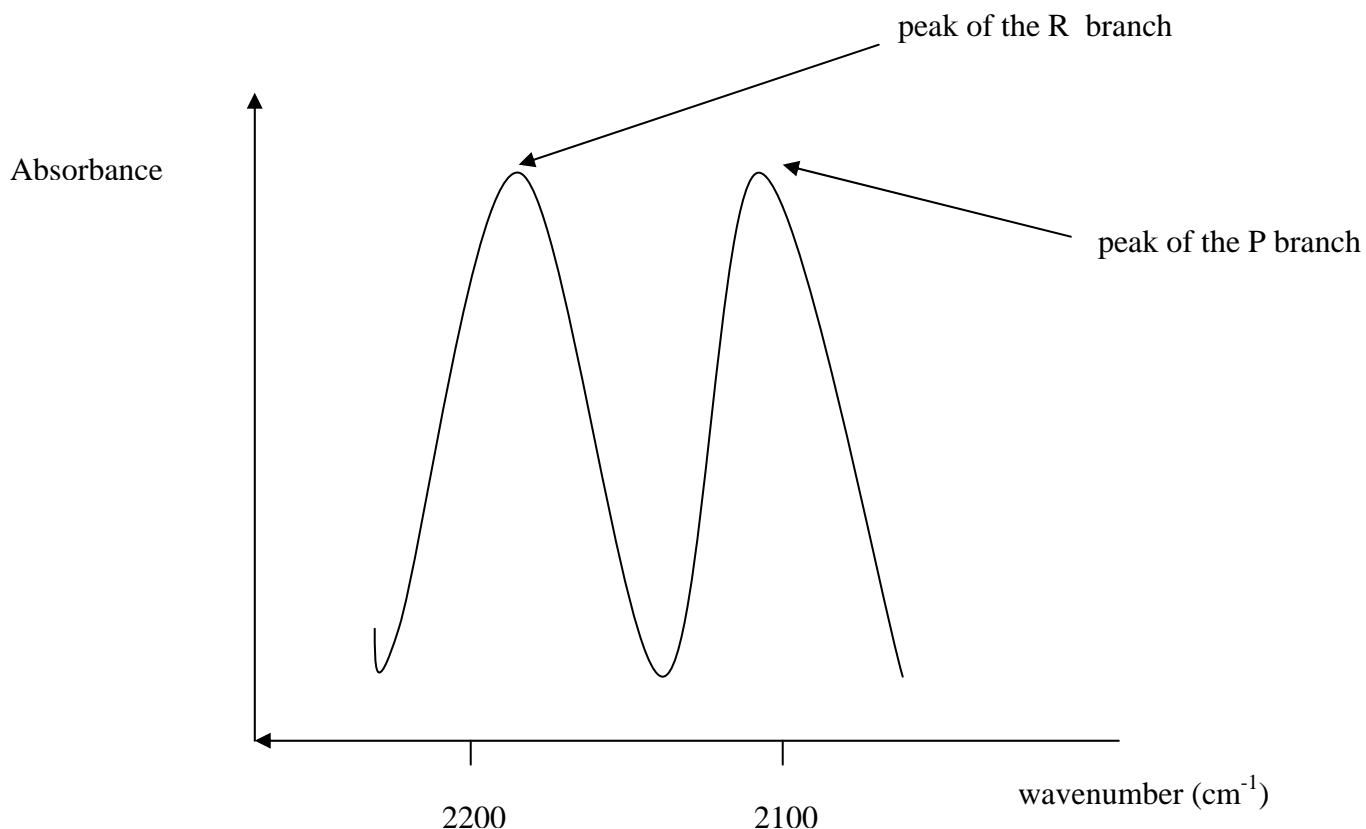
Fill the glass cell with CO at pressures ranging from 10-500 torr. A suitable list of pressures is given below. While you may use other pressures than those listed below, it is **very important to record the exact pressure of the CO gas each time you fill the cell.**

Pressure of CO (torr)	Absorbance at the peak of the P branch	Absorbance at the peak of the R branch
10.00		
20.00		
30.00		
40.00		
50.00		
75.00		
100.00		
125.00		
150.00		
175.00		
etc.		
500.00		

CO spectra for the calibration curve:

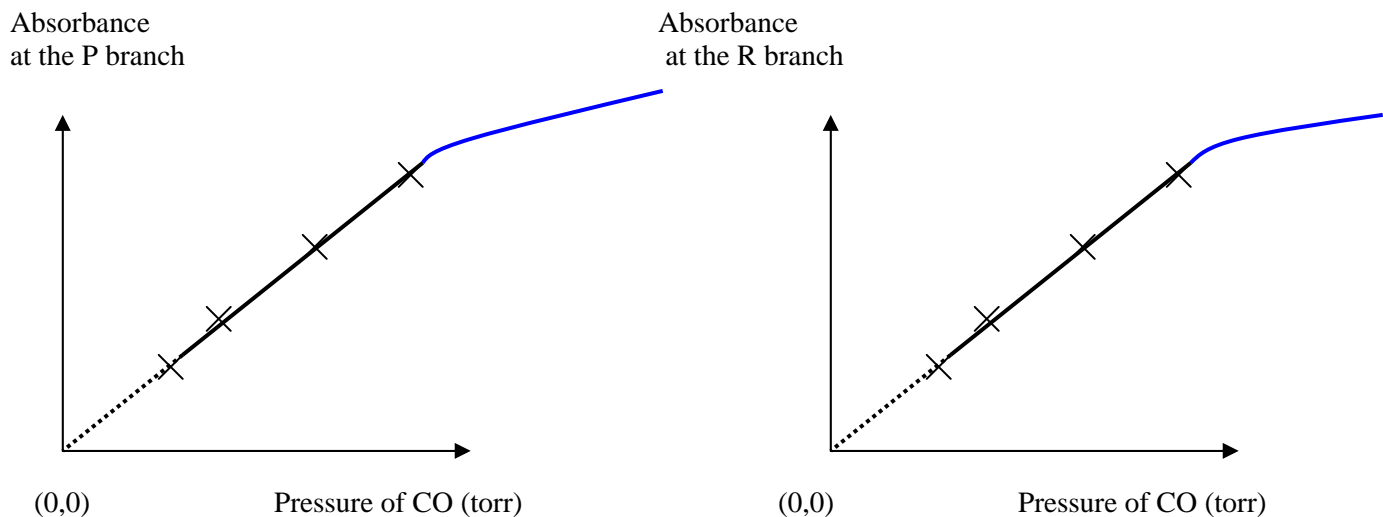
You need to divide your labor so that together as a class you produce a calibration spectrum (each student does not need to do this work on their own).

Each time you fill the cell **read the exact pressure, record it in your lab notebook**, take the cell off the gas manifold, place in the sample cell of the FTIR spectrometer and record a spectrum at 4 cm^{-1} resolution, co-adding 50 scans between 400 to 4800 cm^{-1} . Save the spectrum with a suitable name. Continue in this manner, collecting spectra of CO samples at various pressures between 10 and 525 torr. Note that in these spectra, there is a strong absorption band between 2000-2400 cm^{-1} . This band is due to the IR absorption of CO. The band will look like a double hump as shown below.



The lower energy hump is the peak of the P branch and the higher energy hump is the peak of the R branch. **We will record absorbance at the peak of the P branch and the R branch. This information is vital to the success of the experiment. Be sure to carefully select the peak of each branch and record the values of the absorbencies to the highest degree of accuracy.**

The intensity of the two humps will increase as the pressure of CO in the cell increases. The absorbencies at the peaks of the humps will be proportional to the pressure of CO in the sample cell for lower concentrations of CO (i.e. Beer's law will be followed). As the pressure of CO is increased, at some point, Beer's law will no longer be valid. (i.e. absorbance is not proportional to pressure of CO). Once you reach this point, take 3-4 more data points and stop. This means that you may not have to go all the way to 500 torr pressure of CO.



The region drawn in blue is the area where the Beer's law is no longer valid since absorbance is no longer proportional to the pressure of CO.

Once the class has collected all the calibration data, use the data to plot graphs similar to the above using your data and the Microsoft Excel program. Each student should do their own calibration graphs.

For each calibration curve, determine the molar absorption coefficient (ϵ) using Beer's law.

$$A = \epsilon l P_{\text{CO}}$$

where:

A is the absorbance at the peak (P or R branch)

ϵ is the molar absorption coefficient

l is path length of the cell in centimeters (measure the length of the cell accurately)

P_{CO} is the pressure of CO in the cell, read accurately from the pressure gauge prior to removing from the vacuum manifold

Note that P_{CO} is proportional to concentration since temperature and volume are held constant.

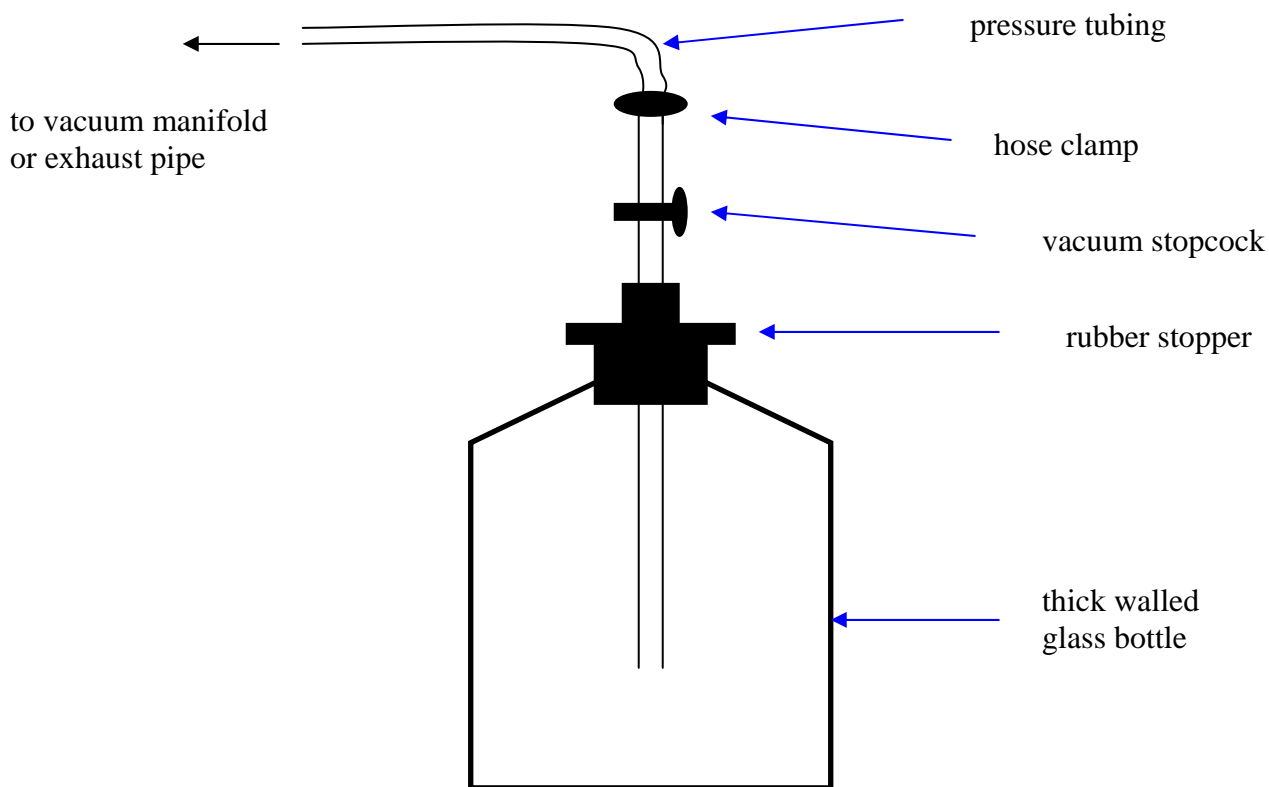
Collecting exhaust samples:

Determine the automobiles, lawn mowers and leaf blowers you wish to use. You will need to borrow these from people and they need to be contacted and informed about what you are planning to do. For reliability, select people from around campus (faculty, staff and students will work best). You can also contact Evergreen Shops and find all you need in one place. It would be great to select a

variety of old cars, old vans, new cars, new vans, manual lawn mowers, rider mowers, and leaf blowers (get a collection of old and new models in all cases). For comparison, it will be nice to have at least two of the automobiles in reference 1. You can also choose to use some of the “green cars” now available.

Before you collect exhaust samples, work with other students to determine which vehicles you are planning to use (as a class). Each student should collect exhaust samples from at least 2 vehicles.

Use the exhaust collection apparatus provided in the lab. This should look like the following.



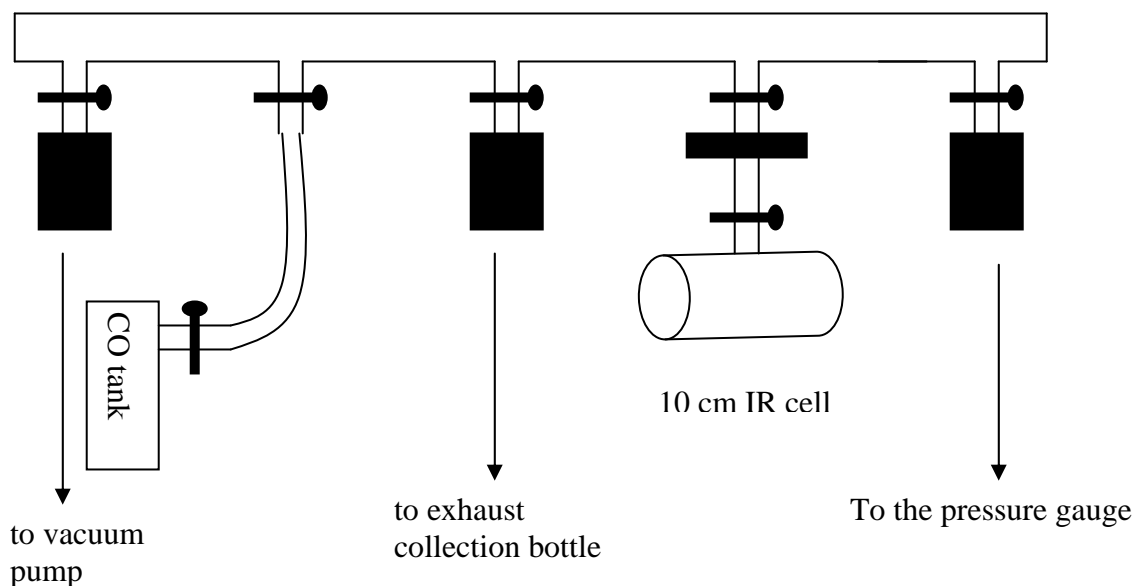
The exhaust collection apparatus

1. Evacuate the exhaust collection apparatus using the gas manifold. When this is completed, the vacuum stopcock should be closed.
2. Take the exhaust collection apparatus to the collection center (car, van, mower, etc.). Start the engine. Hold the engine at a fast idle (about 2000 rpm) for 30 seconds, then return to free idle. Wait for 30 seconds on free idle. While the engine is still running, insert the pressure tubing of the exhaust collection apparatus into the exhaust pipe (about 20 cm in), open the vacuum

stopcock for 30 seconds to collect the exhaust sample and shut off the vacuum stopcock. Shut off the engine.

- Bring the exhaust collection apparatus into the lab and connect it to the vacuum manifold. **While keeping the vacuum stopcock shut**, evacuate the pressure tubing. Connect the 10 cm IR cell to the vacuum apparatus and evacuate the IR cell.

The vacuum manifold



- Turn off the valve to the vacuum pump. Make sure that the system is still under vacuum (i.e. when you turn off the pump, the pressure should not go up). Slowly open the valve to the exhaust collection bottle so that its contents leak into the 10 cm IR cell. Measure and record the pressure of the system (this will be the pressure in the IR cell), close the valves to the IR cell and remove the cell from the vacuum manifold. Do not evacuate the exhaust until the IR spectrum of this sample is recorded and you are happy with the results. Record the infrared spectrum of the exhaust sample (at 4 cm⁻¹ resolution, co-adding 50 scans between 400 to 4800 cm⁻¹) and save it with an appropriate file name. If you are not happy with the spectrum connect the IR cell back up to the vacuum manifold and get another sample from the exhaust collection bottle and record the spectrum again. The goal is to get a decent spectrum so that you can get the absorbance at the peaks of the P and R branches.
- It is best if more than one determination (at least 2) per sample could be done, so that an average can be taken.
- Repeat this procedure for all the vehicles you selected for the experiment.

7. In each spectrum, locate the peaks of the P and R branches. Obtain the absorbance values at these peaks using your spectra. Use these absorbencies and the calibration curve you plotted above to determine the amount of CO (partial pressure of CO = P_{CO}) in the samples.

The CO content of the exhaust is expressed as a percentage based on pressure:

$$\%CO = \frac{P_{CO}}{P_{total}} \times 100$$

where

P_{total} is the total exhaust pressure in the IR gas cell (which you recorded)

P_{CO} is the partial pressure of CO

6. Using the above equation determine the % CO in all of the samples collected by the entire class. Consult with each other to get the information you need.
7. In order to detect if there is a dependence of % CO on P_{total} , take a single exhaust sample and collect absorbance data at various values of P_{total} . (see Table 2 in reference 1). Prepare a table to show the results of this experiment (similar to Table 2 in reference 1).
8. Prepare a table to compare your results with those published in reference 1. Discuss reasons for any discrepancies.
9. Read the information provided in reference 2 and suggest improvements to your experimental method so it can better represent the method suggested by the EPA (in reference 2).
10. Compare the %CO in automobiles with those of lawn mowers and leaf blowers (if you used these items). Use this information to discuss whether there is a reason for concern of air pollution when using these household items.
- 11. Look for any nitrogen oxides in the spectrum. If you can find these, you get a treat!**

References:

1. Seasholtz, M. B.; Pence, L. E.; Moe Jr., O. A.; *J. Chem. Educ.* **1988**, *65*, 820-823.
2. Environmental Protection Agency. *Fed. Register*, **1984**, *49*, 24320-24327