

THE DETERMINATION OF CARBON MONOXIDE IN AUTOMOBILE EXHAUST BY INFRARED ABSORPTION SPECTROPHOTOMETRY

INTRODUCTION:

While used extensively for structural characterization of organic compounds, infrared spectrophotometry also has several uses in quantitative analysis. Infrared spectrophotometry has been used extensively to monitor the exhaust emissions of combustion activities occurring in power plants, factories, and other facilities. Many airborne pollutants such as sulfur and nitrogen oxides and greenhouse gases like carbon dioxide and methane exhibit strong infrared absorbance. In this experiment we will apply the infrared technique to determine the CO concentration in automobile exhaust. This exercise will also provide experience in sampling and handling gas-phase samples, and will help illustrate differences between spectra from gas-phase and condensed-phase analytes.

In infrared spectroscopy of condensed-phase materials, the sample solution, liquid, or suspension is often deposited as a thin film onto an infrared-transparent plate (typically NaCl). A second plate is typically placed on top of the film, forming a “sandwich” where the pathlength for the optical measurement is determined by the thickness of the film of sample (typically $< 1\text{ mm}$). Such narrow paths are required because of the relatively large concentration of IR-absorbing molecules in the film. Because the concentration of absorbing molecules is much smaller, gas-phase spectra require much larger pathlengths (typically several cm). The cell used in this experiment (shown below) provides a 10 cm optical pathlength and consists of a Pyrex cell body enclosed by NaCl plates. Filling of the cell is typically accomplished by either purging the cell with the sample, or by first evacuating the cell, then filling with the sample.

Infrared Transmission Gas Cell used in this experiment.

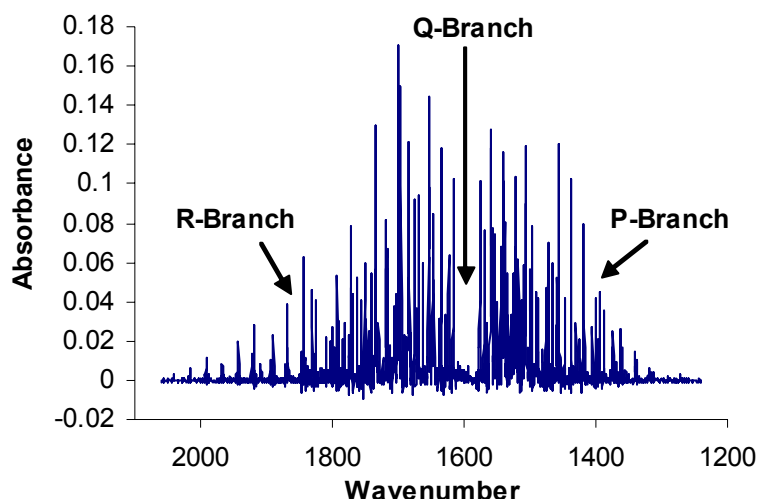
NOTE: NaCl windows are fragile and water soluble!



Spectra of gas-phase analytes exhibit several features not observed in the condensed phase. Because of the relatively large distance between molecules in the gas phase, it is possible to observe the quantized rotational and vibrational transitions for the analyte molecule. In the condensed phase, interactions between molecules and intermolecular collisions cause a broadening of these bands and produce broad bandshapes. In the gas-phase, these transitions are manifest as a grouping of three sets of peaks, termed the P, Q, and R bands, as shown in the water vapor spectrum below. The number and spacing of these peaks depends on the several parameters, including bond strength and the identity of species on opposite ends of the

bond. Typically, diatomic molecules exhibit the simplest gas-phase spectra and often do not produce Q-branches.

Infrared Spectrum of Water in the O-H Bending Region



EXPERIMENTAL PROCEDURE:

1. The instructor will provide an introduction to the vacuum line and instructions for filling the cell. Be extremely careful with the cell and the vacuum line as both are fairly expensive!
2. Evacuate the cell and collect a blank. Obtain the IR spectrum for CO at five pressures ranging from 5-150 torr. Be sure to record the CO pressure for each spectrum. It is especially important to obtain the absorbances in the range of 2000 cm^{-1} to 2300 cm^{-1} .
 - **Software:** Our Nicolet [Avatar](#) FT-IR is controlled using [OMNIC software](#). It is highly recommended that you take a few minutes to examine the OMNIC tutorial to get a better understanding of the software. The tutorial can be started by double clicking on the "OMNIC E.S.P Tutorial" icon on the Windows desktop. To start the data collection software click on the "EZ OMNIC E.S.P. 5.1" icon on the Windows desktop. Select "Instrumental Analysis – Gas Cell" from the dropdown menu that appears in the opening window.
 - Instrument and experiment parameters can be viewed by selecting **Collect** → **Experiment Setup** from the menu bar. Record the following settings:
 - From the **Collect** tab, record the number of scans, mirror velocity, and resolution
 - From the **Bench** tab, record the detector type, beamsplitter type, and the maximum and minimum voltage for the interferogram.

NOTE: Be sure to save your background and sample spectra. The directory *D:\Instrumental* exists for this purpose. Feel free to create a subdirectory for your group in this directory.

 - Collect a background spectrum using the evacuated cell as a blank and the default set of instrument parameters.

- Collect spectra for each of the 5 pressures of CO using the default set of instrument parameters. Label each spectrum with the CO pressure.
 - Before collecting the exhaust sample, plot Absorbance as a function of CO pressure to verify your calibration data. Collect additional standards if necessary.
3. Fill the cell with the automobile exhaust sample. Be sure to record the pressure inside the cell. Collect three spectra.
 - Do not collect the exhaust sample until you are ready to make your measurement.
 - Attach the collection bottle to the vacuum line and evacuate the bottle, be sure to close the stopcock before removing the bottle from the vacuum line.
 - Insert the pressure tubing ~20 cm into the automobile exhaust pipe. With the engine running, open the stopcock and allow the bottle to fill (~30 seconds).
 - Reattach the bottle to the vacuum line and evacuate the pressure tubing. Do not open the stopcock on the bottle! Attach the IR cell to the vacuum line and evacuate the cell also. Once both the pressure tubing and cell are evacuated, close the stopcock to the vacuum and open to the stopcock to the exhaust sample. After pressure has stabilized and the IR cell has filled, record the pressure in the system, remove the IR cell and collect three spectra of the sample.
 4. Plot the absorbance of CO as a function of pressure of CO in the cell. Choose the wavenumber that corresponds to the maximum CO absorbance for one of the standards. Using this relationship and the spectra of your exhaust sample, calculate the percent CO in the automobile exhaust, along with its standard deviation. Also calculate the detection limit for this method. Assuming that Beer's Law holds, calculate the average absorptivity for CO.
 5. Explore the impact of varying the wavenumber resolution for your measurement. This can be done by using either your exhaust sample, or by filling the cell with a fairly low pressure of CO (~30 torr). Whichever sample you choose, collect background and sample spectra at resolutions of 1 cm^{-1} , 2 cm^{-1} , 4 cm^{-1} and 8 cm^{-1} . You can change resolution through the **Collect → Experiment Setup** menu.

CAUTIONS AND PROCEDURAL HINTS:

- *Carbon Monoxide is a potentially hazardous compound! It is critical that you handle it with care! The IR cell should not be vented in the room, but rather under the fume hood. If you notice yourself or any of your lab partners complaining about headache or nausea, close the valve on the CO tank, place the IR cell*
- The cell windows are sodium chloride. Never touch the windows with your fingers. Also, do not contact the windows with any aqueous solution.
- To avoid contamination or loss of sample, be sure that the IR Cell is well sealed prior to removing it from the vacuum system.

QUESTIONS:

1. In the St. Louis area, cars made in 1980 or later may emit no more than 3.0% CO. Will the vehicle you tested pass this test?
2. Your exhaust sample spectrum is probably more complex than that for the CO samples. What other components may be present in this sample? What implications may this have on your method?
3. Several difficulties are often encountered when performing quantitative infrared analysis (mid—ir). Describe the factors that contribute to these problems.
4. What sources of Beer's law nonlinearities can be encountered in infrared spectrophotometry? Comment on any variability (or lack of) in the absorptivity of CO as a function of pressure. What implications does this variability (or lack of) have on your measurements?
5. Changing resolution has a large impact on both the time required to collect the spectrum, and in the quality of the resulting data. Discuss the causes for each of these observations.