Experiment 3: Gas Phase Analysis of Air Components and Air Pollutants Using FTIR
CH3420: Environmental Chemistry, Plymouth State University


Introduction:

The vibrational energies of molecules are in the range of energy carried by infrared light, according to the equation $E = h\nu$ (Planck’s constant $h = 6.626 \times 10^{-34}$ J·s; $\nu$ is "nu", the frequency in s$^{-1}$, which is Hertz). Infrared (IR) spectroscopy is a technique that measures the amount of infrared light absorbed by a molecule as a function of the frequency of the light. The result is a spectrum that reveals information about the vibrational modes of the molecule. This technique is useful not only because of the specific information it reveals about a molecule, but also because molecules have unique "signatures" in the IR spectrum as a result of their unique bonding structure. Thus, IR spectroscopy can be used to identify molecules. Fourier Transform InfraRed (FTIR) spectroscopy records the spectrum in the time domain and uses a computer to transform it into the frequency domain. As a result, FTIR is much faster than traditional IR, making it the most common IR technique in use today.

The simplicity and power of FTIR, combined with the ability to make small, portable spectrometers, has resulted in its wide use for remote sensing. As routine components of satellites, deep space probes, and earth-bound telescopes, FTIR spectrometers are used to determine the composition of stars, planets, and even our own atmosphere.

Every warm mass ($T > 0$K) emits a spectrum of light as a function of its temperature, in accordance with the "black body radiation" theory. The figure below shows the spectra of the sun and of Earth. Because the Earth is much cooler than the sun (288 K vs 6000 K), it emits light of much lower energy, primarily in the infrared region. As the light is emitted, it may be re-absorbed by molecules in the air and changed into heat energy. This "greenhouse effect" keeps the atmosphere and surface of the Earth warmer than it would be otherwise.

In this lab, you will use an FTIR to record the IR spectrum of several common air components and pollutants. The relative absorbances of these gases will be related to their ability to contribute to the greenhouse effect.

In many forms of spectroscopy, spectra are Absorbance vs Wavelength. However, IR spectra are Transmittance vs Wavenumber. Rather than the length of the wave of light, the "wavenumber" is frequency given as the number of waves in a distance reported in cm$^{-1}$. Wavenumber ($\omega$) relates to wavelength ($\lambda$) by $\omega = 1/\lambda$ and is both the frequency of the light as well as the molecular vibration.

![Emission Spectrum](http://ockhams-axe.com/yahoo_site_admin/assets/images/emissionspec.293103427_std.gif)
Safety Considerations:
Use extreme caution when handling syringe needles to prevent inadvertently sticking yourself.
NO$_x$ is a toxic gas that can cause lung irritation. Any steps involved in synthesizing, transferring, or disposing of NO$_x$ should be done in a hood.

Procedure:
[Note: your group will be assigned to prepare one of the following]

Part 1: Synthesis of atmospheric gases and air pollutants

CO$_2$

1. Prepare your 250 mL vacuum flask for gas collection:
   a) Make sure your vacuum flask is DRY, and you have a rubber stopper that snugly fits the opening of the flask.
   b) Stretch out a balloon, attach it to the side arm of the flask, and secure it with a rubber band.
2. Place enough CO$_2$(s) (a.k.a. dry ice) in the vacuum flask to cover the bottom of the flask.
3. Lightly place stopper on the flask so that gas can escape around the stopper without filling the balloon. Wait about 2 minutes for enough CO$_2$ to be formed that the initial air in the flask has been replaced by CO$_2$. It may help to submerge the bottom of the flask in warm water.
4. Once the air has been purged, firmly stopper the flask and hold the stopper in place to fill the balloon.
5. Fill the balloon.
6. Carefully remove the balloon from the side arm and tie a knot in the neck of the balloon.
7. Label the balloon with a marker as “Dry CO$_2$”.
8. Clean up: Pour the excess dry ice into the sink.

NO$_x$
NOTE: NO$_x$ attacks rubber and will likely cause the balloon to break within 3-5 minutes. To ensure you can use your collected gas, analyze this sample first.

1. Prepare your 250 mL vacuum flask for gas collection:
   a) Make sure your vacuum flask is clean, and you have a rubber stopper that snugly fits the opening of the flask.
   b) Stretch out a balloon, attach it to the side arm of the flask, and secure it with a rubber band.
   c) Place a small amount of glass wool in the side arm of the vacuum flask to prevent aerosol droplets from entering into your balloon.
2. Place a piece of copper wire in the bottom of the vacuum flask
3. (Note: work inside a fume hood for the next steps) Add 2-3 mL of concentrated nitric acid to the flask. Loosely stopper the flask and swirl the contents. Wait 30-60 seconds to allow the generated gas to purge out the original air in the flask.
4. Secure the stopper and fill the balloon as much as possible. You will likely not generate enough pressure to expand the balloon very much.
5. Keep the balloon in the hood until you are ready to analyze the sample. As soon as your sample is ready, immediately inform your instructor and analyze it.
Part 3: Analysis of gases using FTIR

1. In addition to the two gas samples prepared by the class, you will also analyze water and methane (CH₄). Your instructor will prepare the sample of methane, and use it according to the steps below as an example for how to use the FTIR and analyze the spectra.

2. Obtain an Analysis balloon filled with N₂ from your instructor. Place it in the FTIR in the beam path with the knot facing upward and take a background sample. Leave the balloon in this position for the rest of the analysis. Save the background scan as EnvironChem-SAMPLE-Back, where SAMPLE is your sample (CH₄, CO₂, NOₓ, H₂O).

3. Using a 60 mL syringe fitted with a luer lock valve and a needle, withdraw 50 mL of your sample gas from your Sample Balloon in the following manner: (1) Insert the needle through the knot in the balloon; (2) open the valve; (3) pull the plunger to the 50 mL mark; (4) close the valve; and (5) withdraw the needle from the balloon.

4. Insert your needle into the knot of your Analysis balloon. Open the syringe valve and inject 10 mL of sample into the balloon. Close the valve. Leave the needle in the balloon.

5. Hit the "Scan" button. When prompted, save the file as EnvironChem-SAMPLE-X, where SAMPLE is your sample (CO₂dry, CO₂wet, NOₓ, H₂O) and X is the scan number (e.g. "1").

6. Inject another 10 mL of sample into your Analysis balloon and take a scan. Repeat this for a total of 5 scans, using all 50 mL of your sample.

7. The final sample to be done by the class is water. Get another Analysis balloon full of N₂ and take the background spectrum as in Step one. Then inject 10 mL of water into the balloon (Step 4), shake it to vaporize as much water as possible, and take the scan (Step 5).

Analysis
The following should be done in your notebook. You may choose to do this after the lab, but your lab will not be signed off, and your duplicate pages will not be accepted, until it is completed. This analysis should also appear in your formal lab report.

1. Analyze your spectra
   a) All of the 5 scans you made should appear together in one window. If the background spectrum also appears, highlight the filename in the list at the bottom of the spectrum and hit "Delete"
   b) Click the "VCursr" button and use your mouse to grab and move the vertical blue bar to the peaks of the spectrum. Use the "Text" button to enter the wavenumbers of the peaks directly on the spectrum.
   c) Use the Text button to enter the name of your sample somewhere convenient on the spectrum
   d) Print the spectra to a file using File -> Print -> Setup -> Print to PS -> Current Window -> SAMPLE-AllScans.ps where SAMPLE is your sample (CH₄, CO₂, NOₓ, H₂O).
   e) Decide which scan was the first one to saturate the detector. If none of them saturated the detector, choose the 50 mL injected scan. Open this spectrum in a new window.
   f) Use the Text button to label the scan, including the sample name and the volume of gas injected.
   g) Print this spectrum to a file as above with the filename SAMPLE-Saturated.ps
2. Make a table of the peaks for each compound.
3. Your instructor will supply you with a spectrum of a sample containing two of the compounds (CO₂, NOₓ, H₂O, CH₄). Use your table of peaks to identify the two compounds.

Conclusions

Answers to these questions must be included as part of your Conclusions in your written lab report. Include them in your Conclusions narrative, not as numbered list of questions and answers.

1. Compare the spectra and discuss the relative abilities of the compounds to contribute to the greenhouse effect.

Lab Report Notes

Your instructor will make available to you electronic copies of all the spectra. Include all the spectra in your report. You may shrink them to fit all on the same page.