

The Modern Student Laboratory: Exploring the Environment

good results are obtained. Small deviations toward the low side are more common than high results. However, this method gives results that are very suitable for use in an undergraduate course. The entire analysis can be carried out during a one-afternoon laboratory provided that previously ignited samples are available. However, since we found no problem with sample storage, students can ignite samples during one laboratory period and analyze them during the next. There are no major safety problems. Performing this experiment always leads to discussion of why one does a sulfur analysis in the first place (3), as well as how one samples a coal pile 50 ft high by 500 ft long (4). Also, the "burning" of coal in the presence of basic metal oxides and carbonates demonstrates an alternative

method for the prevention of SO₂ emission into the atmosphere, which can also lead to further discussion (5).

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Atmospheric Smog Analysis in a Balloon using FTIR Spectroscopy

A Novel Experiment for the Introductory Laboratory

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One of the persistent complaints regarding general chemistry laboratory is that the experiments are boring and irrelevant (1, 2). This point manifests itself in the national trend of students leaving chemistry, frequently after only one year (3). In our department we believe that one way to reverse this trend is to incorporate modern instrumentation into the laboratory early and often. Unfortunately, many modern instruments are unsuited for massive hands-on use by freshman students. They are expensive, complicated, and vulnerable to breakdown in the middle of a lab session.

With the commercial development of reliable and sturdy Fourier transform instruments, however, we can now have entire classes of students make individual measurements in a single laboratory period (4). A Fourier transform infrared (FTIR) spectrophotometer is a natural instrument for integration into the general chemistry laboratory. Although the principles of interferometry and the Fourier transform are rather complex (5), the fundamentals of infrared spectroscopy are grasped easily (6). FTIR instruments are simple to operate. In many general chemistry courses, infrared spectroscopy can be introduced as early as the third week. At that time, the students are taught the relationship between vibrational frequency and bond order and that different bonds absorb at different regions in the infrared spectrum.

A Simple Experiment

At Occidental College we have developed a simple experiment that examines and identifies some of the components of Los Angeles air by FTIR spectroscopy using an inexpensive toy balloon as a sample gas cell. The balloon is filled to a constant, easily reproduced diameter that is determined by passing it through a laboratory iron ring supplied to each student. The balloon is then placed on a suitably sized cork ring that is centered and taped to the floor of the FTIR's sample compartment. This simple procedure provides the student with a sufficiently reproducible pathlength for the generation of qualitatively distinguishable difference spectra.

Students are led through inquiry and observation to discover (4, 7) the identity of each gas from its characteristic spectrum. First they fill the balloon with dry air or nitrogen from a cylinder source and measure the spectrum. Then they refill the balloon with a selection of other gases prepared in a variety of ways.

Experimental

Spectroscopic Equipment

Spectra were collected with a Beckman FT2100 FTIR spectrophotometer at 8 cm⁻¹ resolution averaged over 25 scans with triangular apodization. Data were transferred to an MS DOS-based computer and analyzed using Spectra-Cal software from Galactic Industries. Although a higher resolution could be chosen and more scans could be

performed, our selection provides adequate spectra while limiting total scan time to less than 30 s. Thus, a lab section of 40 students can obtain their first spectra in less than half an hour.

The Balloons

Uninflated rubber balloons of 2.5-in. diameter were expanded to fit through a 4-in.-i.d. lab-type iron ring; then they were tied shut and placed upright in a 3-in. diameter tapered cork ring. The latter was taped to the compartment floor so that the sample beam passed through the approximate center of the balloon. Since balloons seldom are symmetrical at this stage of inflation, several orientations (sideways, tilted, rotated, etc.) were tested for reproducibility. Little significant difference was detected.

We noticed that each balloon had a faint strip that encircled it from the opening to the other end and back up the other side where the rubber was slightly thicker than elsewhere. This strip ran from the opening to the opposite end and back up the other side. It is probably caused by the manufacturing process. The balloon should be oriented so that the beam will not pass through this strip because unacceptably high absorbances will be recorded.

The effect of differently colored balloons was also examined and found to be slight. This difference could probably be ignored when more than one color is used. However, it is a simple matter to record and store reference spectra of nitrogen or air in differently colored balloons and subtract the suitable one from the student's sample balloon.

It should be noted that some balloons are coated internally with talc that can be removed easily by slapping the balloon several times before filling. Although they are not necessary, convenient "balloon fillers" can be rented from most compressed-gas supply companies. These permit students to easily and safely fill their own balloons with nitrogen or air when you want them to run their own background spectra.

Generation of the Gases

Gases are generated by each student in a 250-mL vacuum flask fitted with a solid rubber stopper. A small plug of glass wool is inserted into the side arm to prevent any aerosol droplets from entering the balloon. The deflated balloon is then attached to the side arm with a rubber band. After generation of the gas commences, the stopper is inserted and held firmly in place while the balloon expands. When suitably filled, the balloon's neck is pinched and the stopper carefully removed. Then the balloon can be released from the side arm and tied shut.

CO₂ and H₂O in the Breath

Students begin by blowing up a balloon with their own breath. This quickly produces a sample that yields several peaks, but only two components (8).

"Dry" CO₂ from Marble Chips

Cover the bottom of the flask with marble chips and carefully, but quickly, add 2–3 droppersful of concentrated sulfuric acid from a disposable, approximately 7.5-mL, polyethylene transfer pipet. Stopper and collect.

"Wet" CO₂ from Alka-Seltzer Tablets

Cover the flask's bottom with about one half inch of hot water. Add two Alka-Seltzer tablets and stopper. This can be varied by having some students collect CO₂ from carbonated mineral water. When available, 33-mL plastic bottles outfitted with a one-hole stopper and a 2-in. piece of glass tubing also work well.

Water Vapor

Replace the solid stopper with a one-hole stopper that contains a piece of glass tubing that almost reaches the bottom of the flask. Fill it one-third full with very hot water. Then stopper it, and attach the glass tube to a source of compressed dry nitrogen or air. Cautiously bubble the gas until the balloon is filled.

Nitrogen Oxides (NO_x)

- Caution: NO_x is both *caustic* and *irritating* to skin, eyes, and the respiratory system.

In a fume hood place a pre-1982 one-cent piece in the flask and carefully but quickly add 2–3 droppersful of concentrated nitric acid with a disposable polyethylene transfer pipet. Quickly stopper and collect gas until the balloon is extended horizontally, but is not expanded (9). Rapidly, but carefully, remove the balloon and fill it to size with nitrogen or air. Because NO_x attacks natural rubber, the balloon will usually break some 3 min after filling. Thus, it is imperative that the spectrum (scan time: less than 30 s) be run immediately after filling.

Discussion

The Pollutant Species

We often start by running a spectrum of the ambient laboratory air in the unflushed sample compartment and analyzing it (10). Figure 1 shows a typical spectrum. The students observe two regions (centered around 2340–60 cm⁻¹ and 1600 cm⁻¹) of spectral activity, but are not told what they represent. After a brief discussion of possible air components and contaminants, the list of possibilities usually is reduced to N₂, O₂, CO₂, and H₂O.

Since class lectures have explained that IR activity is based on the existence of a bond dipole (11), N₂ and O₂ are quickly eliminated. By examining their "breath" balloon spectrum, and by discussing the major components of exhaled breath, each student can confirm the presence of water vapor and carbon dioxide. Next, by generating CO₂ in a variety of ways, with and without water vapor present, they can observe an enhancement of the 2350 cm⁻¹ doublet of carbon dioxide. The alert student may also observe changes in the sharp peak at 674 cm⁻¹ and correctly identify it with carbon dioxide (12).

By default the students may assign the remaining peaks to water. However, a balloon filled by nitrogen that is saturated with water vapor quickly convinces them that the prominent peaks at 3657 cm⁻¹ and 3756 cm⁻¹ and the broad band centered at 1595 cm⁻¹ are due to water vapor. Although it may be beyond the scope of this experiment, advanced classes might cover the concept of bulk effects and hydrogen bonding differences in liquid versus gaseous water with the appearance of the broad band in the liquid centered at 3440 cm⁻¹ (13).

(Continued on page A150)

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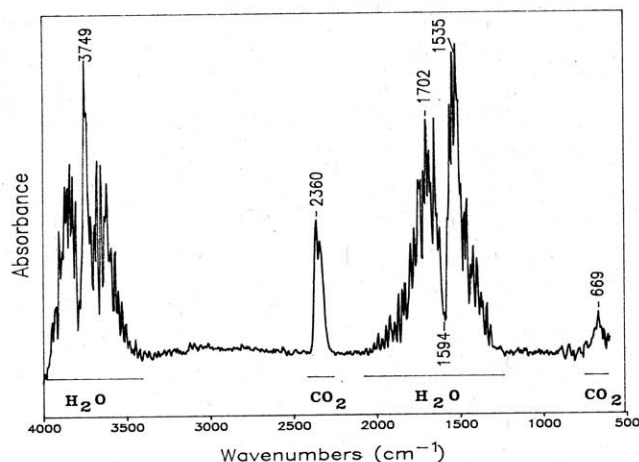


Figure 1. FTIR difference spectrum of atmospheric water and carbon dioxide (8 cm^{-1} resolution; triangular apodization; averaged over 25 scans) produced by subtracting the spectrum of a cell compartment that was flushed with dry nitrogen from a compartment that was filled with lab air.

NO_x Pollution

The generation of NO_x is both impressive and instructive. Most classes will have at least one student who has experienced "a smoggy day" somewhere and can identify the appearance, if not also the smell, of the generated gases. The reactive nature of NO_x necessitates a prompt spectral scan. You might want to institute "panic cuts to the front of the line" for those who get this far. The balloon bursting is dramatic evidence of the effect of smog on the environment.

Although there is little chance of damage to the spectrophotometer, KBr disks may be fitted across the openings to the laser source and the detector if desired. (This can be done easily by attaching the disks to a smaller hole in a 3-in. \times 5-in. card and positioning it in the opening until the beam can be observed through the disk.) The small but detailed bands centered near 2350, 2220, and 1615 cm^{-1} are characteristic of NO_x . (See Fig. 2.)

Hydrocarbon Pollution

Hydrocarbons are significant components in auto exhaust gases. Hydrocarbon pollution, which contributes to the greenhouse effect, can be simulated by collecting a sample from the laboratory's natural gas supply. Characteristically strong hydrocarbon absorption bands (14) appear prominently around 2860–3180 cm^{-1} .

Pollution from Aerosol Cans

An impressive example of the potential contribution of aerosol spray cans to environmental pollution can be shown by analyzing the propellant gases. Remove the spray button from an antiperspirant or deodorant aerosol can. Insert a small plug of glass wool into a short length of 3/32-in.-i.d. rubber tubing to filter out any aerosols. Then attach this to the spray tip. While holding the can in a vertical position, secure the balloon in place around the tube and push down on its tip to release contents. When the

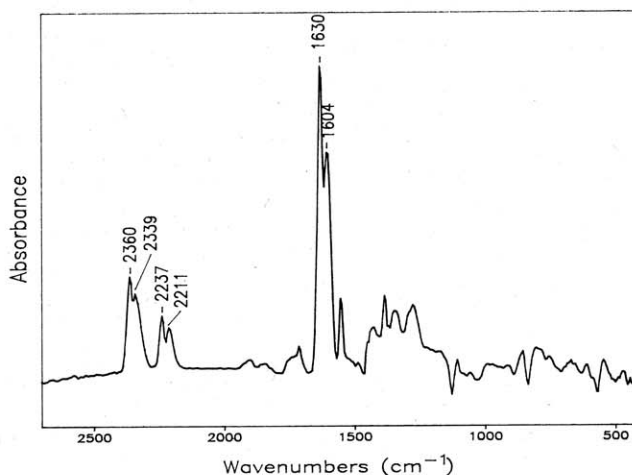


Figure 2. FTIR difference spectrum of NO_x produced by subtracting the spectrum of a balloon filled with dry nitrogen from a balloon filled with an NO_x sample. Other conditions are the same as in Figure 1.

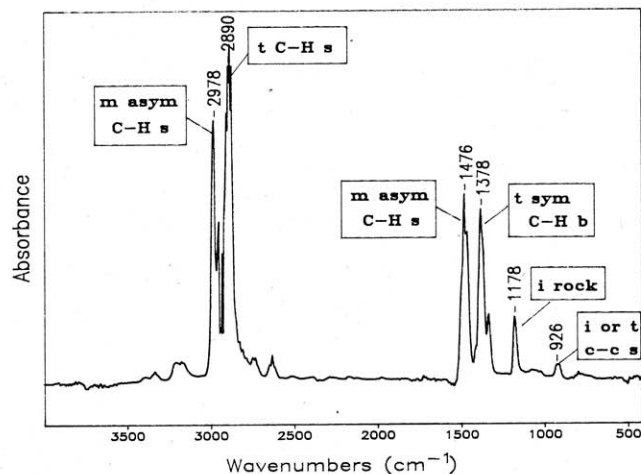


Figure 3. FTIR difference spectrum of hydrocarbon components of spray deodorant containing isobutane and traces of propane and *n*-butane. The following symbols are used in the figure: i = *iso*-butyl, t = *tert*-butyl, p = propyl, m = methyl, s = stretch, b = bend, sym = symmetrical, asym = asymmetrical. Conditions are the same as in Figure 2.

balloon is extended, remove and fill the remainder with nitrogen. The resulting difference spectrum (see Fig. 3) clearly shows the spectrum of isobutane, the major component in many aerosol cans. It also shows lesser amounts of *n*-butane and propane.

Although the experimental conditions are too crude to detect the trace components in a normal air sample, this experiment sets the stage for more exacting measurements of environmental pollution investigated in any advanced course.

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