REAL-WORLD PROJECTS:
CHALLENGES FROM THE POLYMER INDUSTRY
INTRODUCTION

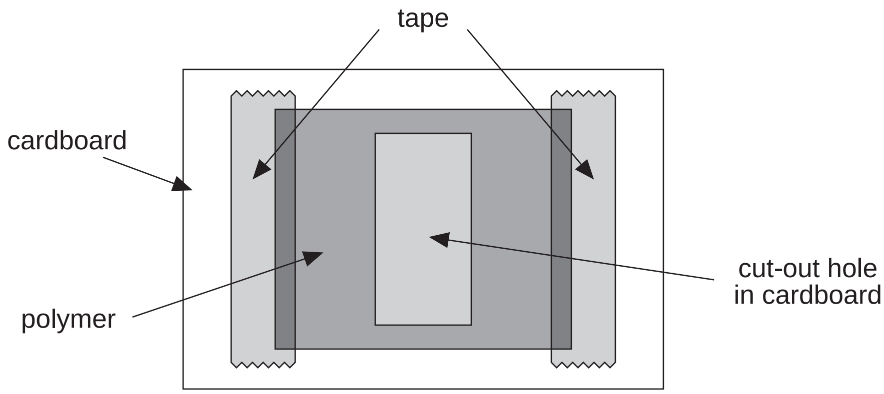
Description
This exploration involves two different scenarios that require the use of infrared spectroscopy: In "Wrapping It Up at the Submarine Sandwich Shop," students take an infrared spectrum of Reynold's brand plastic wrap and of an unknown plastic wrap. In "Lumpy High-Density Polyethylene Bottles," students use infrared spectroscopy to determine if the lumps in a polyethylene bottle are polyethylene or a contaminant. Detailed information on operating an infrared spectrometer is provided for the students.

Goals for This Experiment
The goals for this experiment are to have students:
1. apply knowledge gained in the Sorting Plastics for Recycling lab,
2. analyze and solve a type of problem often seen in the polymer industry,
3. be introduced to the basic theory of infrared spectroscopy, and
4. gain experience using an infrared spectrometer.

Recommended Placement in the Curriculum
These investigations are intended as a capstone experience at the end of second semester. You may choose to have students do one or both investigations, or let students choose which scenario to investigate.

Special Notes
Due to the open-ended nature of these investigations, detailed instructor notes are not provided. However, some special notes are provided here.

"Wrapping It Up at the Submarine Sandwich Shop"
- The following materials are needed:
  - ➢ IR spectrometer
  - ➢ Reynold's plastic wrap (one roll of clear and one roll of colored wrap)
  - ➢ Handi-wrap plastic wrap (one roll of clear and one roll of colored wrap, preferably the same color as the Reynold's brand)
  - ➢ piece of cardboard that will fit into the sample slot on the IR spectrometer—an index card cut to the correct size will work and is inexpensive. (Cut a small (1 inch x $^1/_2$ inch) rectangular hole out of the center of the cardboard. Tape a piece of the plastic wrap across this hole. The sample piece should be large enough to completely cover the hole. The tape should not be across the hole. See figure.)



- If all the bands in the IR spectrum go to the bottom of the spectrum and are flat instead of sharp (“bottomed out”), the sample is too thick. Try stretching the sample over the hole in the cardboard.
- Students will see a band at approximately 1735 cm^{-1} (an ester carbonyl band) in the Reynold’s brand plastic wrap due to the plasticizer. (Reynold’s brand plastic wrap is a polyvinyl chloride. Cheap plastic wraps are often polyethylenes.) The added plasticizer is one possible reason that Reynold’s brand sticks to itself better than cheaper brands do.
- In the infrared spectrum of blue Reynold’s wrap, a small sharp band is present at 1610 cm^{-1}. This band is most likely due to the dye present in the wrap that gives the wrap its blue color.
- Students can compare the infrared spectra of their different wraps with standard infrared spectra such as those found in the Coblentz Society Deskbook of Infrared Spectra (Clara Craver, ed.), Sadtler’s library of infrared spectra, or other reference books on polymers.
- The time it takes to complete this lab depends greatly on the type of infrared (IR) spectrometer your lab has access to. An old dispersive IR instrument will take longer to record a spectrum (on average about 10–15 minutes) than the new Fourier Transform (FT) type IR instrument (on average about 1–2 minutes). For this experiment, each student or group needs to take an IR spectrum of Reynold’s brand plastic wrap and an IR spectrum of the unknown plastic wrap. Students may also want to take IR spectra of other types of plastic wrap to see if they can identify the brand of the unknown sample. The students may also want to take spectra of different colors of plastic wrap to see if they can identify IR bands due to the dyes. However, in our experience, the dye is so dilute that the peaks due to the dye do not readily appear in the spectrum. This leads to the idea that the different dyes can be distinguished by students’ eyes (a type of visible light detector) but not by infrared light.
- If a dispersive IR spectrometer is used, each group will take about 30 minutes to acquire their data. If an FT-IR spectrometer is used, each group will take about 15–20 minutes to acquire their data. However, since a lab typically has access to only one IR spectrometer, the entire lab period is needed for all students to collect data. Also, in our class, students became very interested in the samples and wanted IR spectra of all samples that were available. We took spectra of four different types of Handi-Wrap (clear, cranberry, grape, and watermelon), three different types of Reynold’s wrap (crystal clear, crystal blue, and crystal rose), and Saran wrap.

"Lumpy High-Density Polyethylene Bottles"

- The following materials are needed:
  - ➢ IR spectrometer
  - ➢ sample of the HDPE bottle (1-cm x 2.5 cm strip)
  - ➢ sample of the lump from the bottle (This could be polypropylene or HDPE—our sample was ironed and pulled to make it thin and "lumpy." This isn't as satisfactory as a "pressed" sample.)
- If students decide they want to measure the densities of the samples, they will need to prepare solutions of known density as in the "Sorting Plastics for Recycling" scenario lab.
- The time required for the actual laboratory experiment depends on the approach the students take. If they use infrared spectrometry, the time required will depend on the type of infrared instrument used. If a FT-IR spectrometer is used, an acceptable spectrum can be obtained in under two minutes. It may take up to 10–15 minutes to obtain a spectrum from a dispersive instrument.

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Based on your instructor's directions, use infrared spectroscopy to explore one or both of the following scenarios. (Detailed instructions on operating the infrared spectrometer are provided on a separate handout.)

Lumpy High-Density Polyethylene Bottles

A company that makes household chemicals such as detergents and other cleaning products also molds its own polyethylene bottles. It has just been reported that some bottles, a few in every hundred, have lumps in them. The lumps are not always in the same position on the bottles, which rules out a bottle production problem such as a dirty die, mold, or extruder. Contamination of the feed materials is suspected. Samples of the bottle and bottle lumps are available. Is contamination of the polyethylene feed material the problem? Why or why not? Be sure to include the use of infrared spectroscopy in your plan.

Wrapping It Up at the Submarine Sandwich Shop

A submarine sandwich shop that specializes in wrapping sandwiches in school colors has just expanded to three other college towns. One of the guarded secrets of the business is a special dressing containing olive oil and herbs. In order to prevent the dressing from leaking out of wrapped sandwiches, a special folding pattern was developed. With that folding pattern, the plastic wrap made by Reynolds was observed to seal tighter and minimize leaks. Even though it is more costly than the wrap made by Handi-wrap, the sandwich shop decided to use Reynold's Wrap. Now, one of the new locations is reporting problems with messy, leaky sandwiches. Is cheaper wrap being substituted for Reynold's Plastic Wrap? What makes the Reynold's Plastic Wrap stick tighter under these conditions?

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CHALLENGES FROM THE POLYMER INDUSTRY

INFRARED SPECTROSCOPY

Background Information
In a sense, spectroscopy is already a familiar tool in the chemistry laboratory. A solution of copper sulfate is recorded as a blue solution by almost all chemists. In addition, two solutions (of the same solute) can be discerned with the darker, more intense color belonging to the more concentrated solution. With appropriate instrumentation, light of wavelengths other than visible light ($3x10^{-3}$ cm) can also be used. Radio ($3x10^{3}$ cm) and sound waves are useful in some medical and industrial applications, while x-rays ($3x10^{-8}$ cm) are used in various medical, dental, and industrial applications.

If light of the infrared region of the electromagnetic spectrum is used, the infrared energy corresponds to the energy of various vibrations of atoms in molecules. Chemists have compiled extensive lists of such vibrations with specific energy absorptions associated with specific arrangements of atoms in molecules. Since some molecules can contain many atoms of many different elements and bonding schemes, some infrared spectra can be quite complex. However, if molecules are small or contain simple repeating units of atoms, the infrared spectra can be easily interpreted and instructive as well.

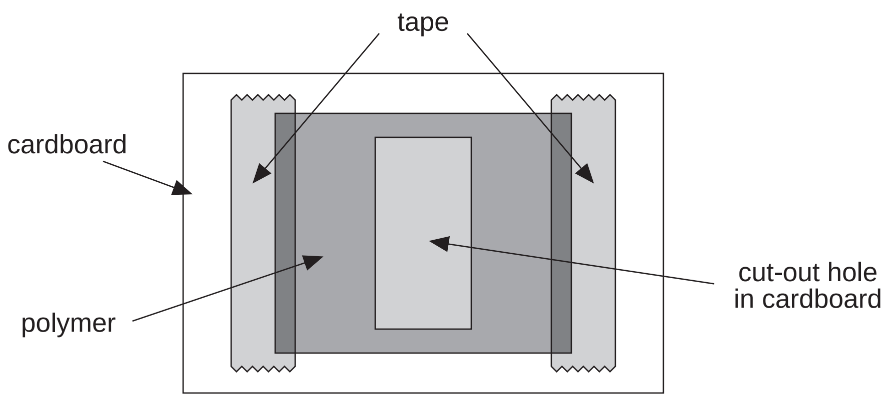
Polymers are very, very large molecules prepared from small repeating units of atoms. This means the molecular vibrations are limited to those of the repeating units of atoms. The infrared spectrum of a simple polymer film of polyethylene (HDPE or LDPE) is an example of an interpretable and instructive infrared spectrum.

About the Machine
The infrared spectrometer in the lab is a smart, sophisticated piece of laboratory equipment. It contains a microprocessor—a computer or brain of sorts—and is attached to a recorder for output, in this case, a hard copy on special paper. However, the spectrometer is not directly interfaced with its various operators, so it is necessary for the operator to learn how it works.

The parts inside the infrared spectrometer include an infrared radiation source, a grating or prism to separate infrared radiation into light of specific wavelengths, and a detector to detect how much light is transmitted or absorbed after passing through a sample. Since infrared spectroscopy is commonly used qualitatively (rather than quantitatively), the output is presented as a plot of percent transmittance versus wave number or wavelength. (The operator doesn't need to know what wavelength a sample will absorb; all infrared wavelengths are swept in a scan.) Recall that with visible spectroscopy and the Spec 20, a specific wavelength was chosen for the analysis. Further recall that Beer's Law, a quantitative application of spectroscopy, used absorbance rather than percent transmittance.

Sample preparation for infrared spectroscopy is complicated by the fact that glass or plastic containers cannot be used since the container contains molecules that display vibrations. Likewise, water cannot be the solvent because it also vibrates in the infrared. The normal sample container is a cell made of a polished salt crystal. (Only nonaqueous samples can be used since water would dissolve the salt crystal. Cells cannot be cleaned with water either.) However, in this polymer laboratory experiment, our samples will be transparent plastic polymer films that only need to be cut to the appropriate size and placed on the sample holder in the light path.

The sample polymer film on the sample holder will look like this:



Look at the instrument control panel. Look for the following: “ABS TRAN,” “SCAN RESET,” “SCAN,” “WN,” “WN,” “SCAN TYPE,” “SCAN TIME,” “GAIN,” “GAIN,” and “PEN RESPONSE,” where “WN” means wave number, “ABS” means absorbance, and “TRAN” means percent transmittance.

Now look at the operating window, to the left of the control panel. Look for the following: “WAVENUMBER,” “TRANSMITTANCE ABSORBANCE,” “SCAN TYPE,” “TIME,” “GAIN,” and “RESP,” where “RESP” means response.

Preparing for and Doing a Reference Scan

1. To begin, turn on the instrument using the toggle switch on the upper-right back of the instrument. Let the instrument warm up for 15 minutes. The recorder (which is already attached) should go on at the same time as the spectrometer. (The power toggle switch on the recorder may also need to be turned on.)

   The first step in recording an infra red spectrum is to run a reference scan to cancel out any background water vapor in the air. Before running the reference scan, the scan time and gain need to be adjusted.

2. To set the scan time at 3 minutes, push the scan time button until 3 appears above TIME on the operating window. (Three minutes is the shortest scan time. Longer scan times may give

better resolution; however, a three-minute scan gives an adequate spectrum and allows more spectra to be run during limited class time.)

3. The gain and pen response are adjusted next. (Both gain and pen response may need adjustment.) A gain setting of about 0.65 (visible in the operating window above GAIN) has been observed to give better spectra of plastic films than 1.0-1.2. The gain can be adjusted up or down using the GAIN or GAIN button on the control panel. The actual pen position on the paper should be set at 85% transmittance after the gain is set. Moving the pen position on the paper is done by turning the knob on the top of the chart recorder.

(The knob moves the position of the pen on the paper. The pen should be at about 85% transmittance.)

4. Check that the operating window reads TRANS (or % T or TRANSMITTANCE below the TRANSMITTANCE/ABSORBANCE indicator on the window. If it does not, push the ABS/TRAN button on the control panel until TRAN appears in the operating window. Check that 400 appears below WAVENUMBER in the operating window.

5. Lastly, since a reference scan is to be run first, it should say REFERENCE above SCAN TYPE in the operating window. If it does not, push the scan type button on the control panel until it does read REFER or REFERENCE.

The instrument is now prepared to run the reference scan and store it for subtraction from future sample spectra. You could push the scan button at this time and record the reference scan. If a hard copy of the reference scan isn't wanted, simply turn off the power on the recorder—this disengages the recorder.

6. Push the SCAN button on the control panel to start the reference scan.

Turn the recorder's power back on when the scan is done. (Watch the operating window for completion of the scan.) The reference scan is recorded inside the spectrometer computer and will be subtracted from spectra run afterward as long as the instrument is not turned off.

Analyzing Plastic Film Samples

The instrument is now ready to run any number of plastic film samples.

1. Place the plastic film or polymer to be analyzed in the V-shaped sample holder.

2. Push the SCAN TYPE button on the control panel until RATIO appears above SCAN TYPE in the operating window.

3. Insert the pen in the pen holder if it is not there already.

4. Push SCAN to record the infrared spectrum of the polymer film.

5. Consult your instructor about interpreting the infrared spectrum obtained.