

INFRARED SPECTROSCOPY

PURDUE UNIVERSITY INSTRUMENT VAN PROJECT

HOW DO YOU TELL ONE WRAPPER FROM ANOTHER? THE INFRARED SPECTRA OF FILMS

(Revised: 1-23-93)

INTRODUCTION

Everything these days seems to come in a wrapper. Most of these wrappers are some sort of a thin plastic film. These plastic films consist of giant molecules composed of long hydrocarbon chains, called polymers. In the recycling process it is important to know the identity of the polymer because different kinds of materials must be processed separately. One way to correctly identify a polymer is to require the manufacturer to stamp an identifying symbol on every product. In the laboratory materials can be identified by measuring their physical properties, such as density, solubility, hardness, or melting and boiling points. Another laboratory method of determining a material's identity is to record its infrared spectrum.

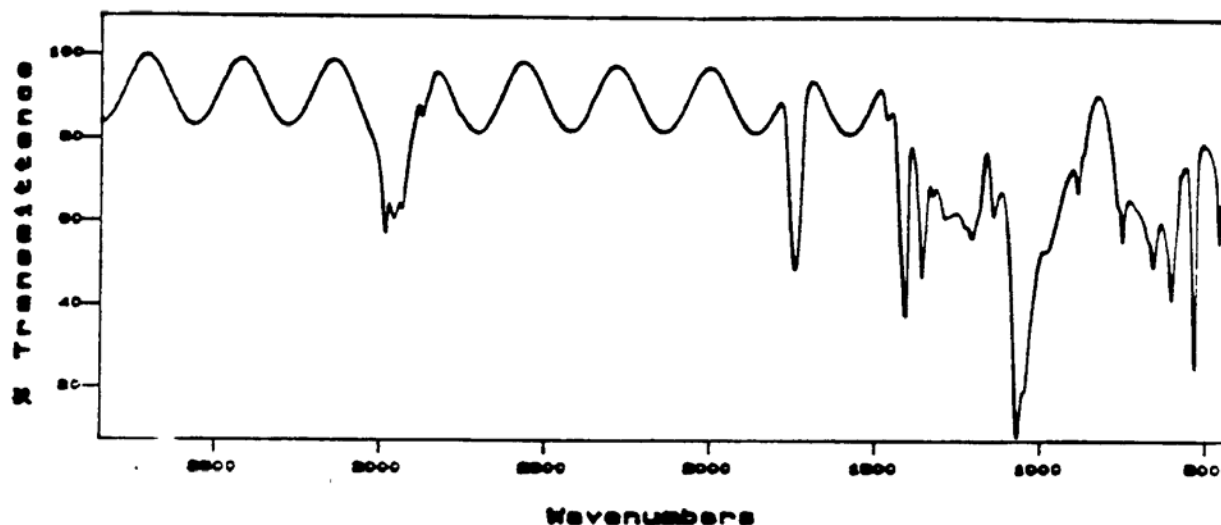
An infrared spectrum is really a graph. It is obtained by aiming a beam of infrared (IR) radiation at a sample and measuring the amount of radiation absorbed by the sample. The y- axis, labeled % transmittance, is the ratio of the intensity of the radiation transmitted through the sample compared to the intensity of the incoming beam. The x- axis is a scale of energies, labeled in units which are proportional to energy called wavenumbers. The graph therefore is the plot of the percent transmittance versus the energy of the radiation.

It is found that different parts of a molecule absorb different energies of radiation depending on the sequence of specific atoms in the molecule and how they are bonded together. The exact energy absorbed depends on the mass of the atoms and the strength of the bonds between them. When some of the radiation is absorbed, less of it is transmitted resulting in an absorption band in the spectrum. The specific arrangement of atoms which give rise to an absorption band is called a functional group.

The infrared spectrum of a compound is analyzed by identifying absorption bands in the spectrum and matching the absorption bands to the functional groups responsible for the absorption. Every functional group has its own characteristic absorption band in an IR spectrum. The ability to identify functional groups from their absorption bands enables the spectroscopist to piece together the identity of unknown materials from their infrared spectra. A table, listing functional groups and the energies at which they absorb radiation is called a correlation chart.

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Occasionally, the spectrum of a polymer film will exhibit an area that contains a symmetrical repeating wave-like pattern, similar to that on either side of the large absorbance band in the spectrum below. This reflected radiation emerges from the film interfering constructively or destructively with the transmitted beam. This results in an interference pattern, called fringes, in the spectrum indicated by these wave-like patterns. When they occur, these interference fringes may be used to calculate the thickness of the film. (If you want to know more about interference of light waves, look in a physics textbook under fringes or interference of light waves.)

OBJECTIVE

The purpose of this lab is to introduce you to the infrared spectrophotometer as an analytical tool in the description and possible identification of thin polymer films. A correlation chart will be used to identify functional groups in an unknown plastic film.

PRE-LAB QUESTIONS

1. What is a correlation chart? How will a correlation chart be used in this lab?
2. What is a functional group? What knowledge can be gained from knowing the specific functional groups in a molecule?
3. What are two factors that determine the energy at which a functional group will absorb radiation?

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4. Percent transmittance is a ratio between what two quantities?

MATERIALS

An infrared spectrophotometer

Scissors

Correlation chart

Known standards or their spectra

A variety of thin transparent wrappings, such as:

envelope windows

sandwich bags

oven bags

food or product wrappers

Saran Wrap[®], Glad Wrap[®]

trash bags

inner package linings

transparent films

PROCEDURE

Bring in from home, the garage, your bedroom wastebasket, or your favorite source of trash, several samples of various types of thin plastic wrappers (films). The piece of film you use should be clean, dry, and not too thick. If your film is much thicker than a sandwich bag, it will absorb too much of the radiation and will not produce a good spectrum. Record the type of film (what it was used for) and the brand name or some identifying feature of each of the samples you bring in. Using the IR spectrophotometer record the IR spectrum of your polymer film as demonstrated by your teacher.

If time permits, you may want to do a second spectrum. If your film has regions of different color in it, try running spectra of each of these regions to determine if there is any effect from the coloring.

ANALYSIS

Determining the identity of a polymer by analysis of its IR spectrum is carried out by assigning functional groups to the prominent absorption bands. Divide the spectrum into two general regions. The region from 4000 cm^{-1} to 1500 cm^{-1} is called the functional group region. As the name suggests, every functional group has a characteristic absorption in this region, largely independent of the rest of the molecule. The region from 1500 cm^{-1} to 400 cm^{-1} is called the fingerprint region. Absorptions in this region are due to larger molecular groups or the molecule as a whole. Just like

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humans, every molecule has a different fingerprint.

Beginning at the left side of the spectrum, and working from left to right, write down the average wavenumber at which each of the major absorption bands appears. Estimate its intensity (size) as strong (s), medium (m) or weak (w). Most of the spectra you will examine will have five to ten absorption bands which will be of interest.

Once you have the wavenumbers for each band listed, refer to the correlation chart to try to identify some of the possible functional groups which you feel might be present in your sample. Locate the wavenumbers on the correlation chart and write down the functional group indicated.

Determining the functional groups in a polymer from its IR spectrum is not easy at first and takes practice. Even the spectra of simple molecules can contain many absorption bands and a lot of experience is required to make a positive identification of an unknown substance with certainty. Concentrate on the left side of the spectrum at first, from 4000 cm^{-1} to 1500 cm^{-1} . Check the correlation chart as you proceed. Exact wavenumber values will vary a little, but if a wavenumber you select is not close to one on the chart you will probably be justified in omitting it. Once you have identified the functional groups in your sample and have completed your data table, compare your spectrum with the spectra of known substances, if they are available, for a possible match.

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CALCULATIONS

If the recorded spectrum contains interference fringes, they may be used to calculate the thickness of the sample film. The thickness (d) may be calculated using the

$$d = \frac{m}{2n(\nu_1 - \nu_2)}$$

following formula:

where d is the thickness of the film in cm and m is the number of complete fringes. $(\nu_1 - \nu_2)$ is the region of wavenumbers which you select to make your measurements and n is the index of refraction of the polymer from which the film is made. Determine the number of complete fringes by counting from the crests (tops) of the waves. From the top of one wave to the top of the next wave is one complete wave.

When measuring fringes for your calculation choose an area free from absorption bands and use an interval that will give you a whole number of fringe waves. For example, using the spectrum of Saran shown in the introduction, an interval could be selected either above 3000 cm^{-1} or between 3000 cm^{-1} and 2000 cm^{-1} . Let's use the two fringes between about 2575 cm^{-1} and 2000 cm^{-1} . The index of refraction (n) for Saran is 1.58.

$$d = \frac{2}{2(1.58)(2575\text{ cm}^{-1} - 2000\text{ cm}^{-1})} = 1.10 \times 10^{-3}\text{ cm}$$

Your instructor will provide you with the values for the index of refraction of your film if needed.

POST-LAB QUESTIONS

1. Complete a data table for each spectrum you obtain, listing the wavenumbers and predicting the corresponding functional groups. Match your spectrum to spectra of known polymers if available and determine the identity of your film.
2. Look up the word spectrophotometer in the dictionary and write down the definition. If the word spectrophotometer is broken up into three parts: spectro-photo-meter, to what does each part refer?
3. If the IR spectrum is treated as a graph, what measurement is represented on the x-

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axis and the y-axis? What are the units of each?

4. A unit commonly used to indicate the thickness of a plastic film is mil, which is defined as thousandths of an inch. If the thickness of a plastic trash bag is calculated to be 2×10^{-3} cm, what is this thickness in mil?

5. Compare the spectrum of your sample to those of others in your class. Write down the names of three other wrappers. Make a list of the functional groups they have in common with your spectrum. List any functional groups that your contains that the others do not.

6. A student records the IR spectrum of a piece of video recording tape. The resulting spectrum fails to match that of any known plastic. What explanation would you offer for this observation?

7. Would you expect a colored region of a wrapper to exhibit an IR spectrum different from a region without color? Explain.

8. If the spectrum you made shows interference fringes, calculate the thickness of your film sample using the formula given under Calculations. If your spectrum did not exhibit any interference fringes, select a suitable range of fringes and calculate the thickness of the sample whose spectrum is shown below ($n = 1.50$)

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Correlation Chart of Molecular Vibrations

Arrangement of Atoms	Functional Group	Vibration	Frequency (cm^{-1})	Intensity
C-H	Alkane	(stretch)	3000 - 2850 and	s
		(rock)	900 - 600	
	-CH ₃	(bend)	1450 and 1375	m
	-CH ₂ -	(bend)	1465	m
	Alkene	(stretch)	3100 - 3000	m
		(bend)	1000 - 650	s
	Aromatic	(stretch)	3150 - 3050	s
	Alkyne	(stretch)	3300	s
	Aldehyde	(stretch)	2900 - 2800 and	w
			2800 - 2700	w
C=C	Alkene	(stretch)	1680 - 1600	m-w
	Aromatic		1600 and 1475	m-w
C≡C	Alkyne	(stretch)	2250 - 2100	m-w
C=O	Aldehyde	(stretch)	1740 - 1720	s
	Ketone	(stretch)	1725 - 1705	s
	Carboxylic Acid	(stretch)	1725 - 1700	s
	Ester	(stretch)	1750 - 1730	s
	Amide	(stretch)	1671 - 1640	s
C-O	Alcohol, ether, ester	(stretch)	1300 - 1000	s
	Carboxylic Acid, anhydride			
O-H	Alcohol, Phenol	(stretch)	3650 - 3200	m (broad)
		(bend)	1450 - 1200	m
	Carboxylic Acid		3400 - 2400	m (broad)
S-H	Mercaptan (Thiol)	(stretch)	2550	w
N-H	Amine	(stretch)	3500 - 3100	m (broad)
		(bend)	1640 - 1550	m-s
		(rock)	900 - 700	m
C-H	Amine		1350 - 1000	m-s
C≡N	Nitrile	(stretch)	2260 - 2240	m
N=O	Nitro (R-NO ₂)		1550 and 1350	s
C-X	Fluoride	(stretch)	1400 - 1000	s
	Chloride	(stretch)	800 - 600 and	s
			1500	m
	Bromide, Iodide	(stretch)	below 667	s

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DATA TABLE

Description of film (brand name, type of product, use):

Energy of Absorption (Wavenumber)	Intensity (s, m, w)	Arrangement of Atoms (Functional Group)

Identity of
Polymer: _____

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DATA TABLE

Description of film (brand name, type of product, use):

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TEACHERS' GUIDE THE INFRARED SPECTRA OF FILMS

LEVEL

This lab is geared to the first year chemistry or physical science student as an initial exposure to IR spectroscopy. It works well with students in groups. Each person in the group can record the spectrum of a different film and the group can then compare them for similarities or differences. This will provide students with the opportunity for collaboration. Class results can be tabulated matching by brand names or applications to the type of polymer film.

The lab can be integrated into the curriculum with the introduction of physical properties, the study of electromagnetic radiation, in conjunction with an organic unit, the study of bonding or as a demonstration anywhere in your course. The NSTA book on polymers is a good reference and contains a computer program simulating several common types of polymer synthesis reactions.

PREPARATION

Prior to doing this lab, students should have a background in the electromagnetic spectrum, relative energies and frequencies, and a conceptual idea of how atoms make up molecules. A comparison of relative bond strengths would be helpful. A pre-lab discussion may include a demonstration of the ways in which atoms vibrate, rotate, bend and stretch with respect to one another in a molecule. Students should be familiar with spectroscopic terms such as absorption and transmission and what is meant by percent transmittance.

Students should each bring in a sample, with perhaps an incentive for creativity to avoid twenty-four samples of the same thing. The thinner the film the better the spectrum. Films the thickness of cellophane, for example, usually work well.

Spend a day or so prior to using the instrument to show the students the basics of identifying peaks from sample spectra. This works well on an overhead. Use spectra containing functional groups students are most likely to encounter and show them how to estimate the wavenumber and identify the corresponding functional group from the

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correlation chart. Showing how to estimate the intensity of the absorption band (s, m, w) would also be helpful.

TIME ALLOTMENT

Students can cut and prepare their film samples while others are running their spectra. Spectra can then be printed out as fast as the samples can be loaded and scanned. Each student in a class of 24 should have no problem running their own spectrum within two or three lab periods.

SAFETY / DISPOSAL

Garbage in, garbage out. Throw it away, or if you're a collector, save some of the more unique samples for next year. The leftovers could also be used to generate a bulletin board or display case, displaying spectra and applications of IR spectroscopy.

SAMPLE RESULTS

Some spectra may be rather simple such as that for polyethylene - essentially the C-H stretch just below 3000 cm^{-1} and the bands at 1470 and 720 cm^{-1} . Polyvinyl chloride exhibits a slightly more complex spectrum with the 720 cm^{-1} peak absent and an additional C=C band around 1650 cm^{-1} . The C-Cl stretch is observed at $700\text{-}600\text{ cm}^{-1}$. The C=O and C-O frequencies, at around 1720 cm^{-1} and 1100 cm^{-1} respectively, are easily recognizable features of spectra of polyesters.

Some of the films contain phthalate esters, added plasticisers, or colorings, but students can still do good qualitative determination of most functional groups. Representative spectra for some of the more common polymers can be consulted by the teacher (Sadtler is an excellent source), or as a student activity, for a more positive identification of unknowns. There are a couple of polymers that yield spectra which are really difficult to interpret. One example is ABS (acrylonitrile butadiene styrene) which is made up of three different monomers, all of which have different functional groups.

ANSWERS TO PRE-LAB QUESTIONS

1. A correlation chart is a listing of functional groups and the average wavenumbers at which they absorb IR radiation. One will be used here to identify functional groups,

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given the average wavenumber.

2. A functional group is a particular arrangement of atoms which impart certain characteristics to a molecule. Is a means by which molecules can be identified or classified. Knowing the functional groups in a molecule gives information as to how the molecule will behave physically or react chemically.
3. Two factors which determine the energy at which a functional group will absorb are the bond strengths between the atoms and the masses of the atoms.
4. Percent transmittance is a unitless ratio of the intensity of the radiation transmitted through a sample and the incident radiation.

ANSWERS TO POST-LAB QUESTIONS

2. spectro: continuous sequence or range
photo: light
meter: instrument or means for measuring
 3. The y-axis represents the intensity (size) of the absorbance peak. It is a ratio of incident intensity versus transmitted intensity and is unitless. The x-axis represents the energy at which an absorption occurs. The units are wavenumbers.
- $$2.0 \times 10^3 \text{ cm} \times \frac{1 \text{ in}}{2.54 \text{ cm}} \times \frac{1000 \text{ mil}}{1 \text{ in}} = 0.79 \text{ mil}$$
- 4.
 6. The film is not a pure specimen. The magnetic coating used to record the data is contributing its own spectrum to that of the plastic film.
 7. Additives like colorings or plasticisers will contribute their own absorbances to the spectrum of the material being analyzed.

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8. This spectrum has a wide range of uniform fringes. Anywhere in the region between 2200 cm^{-1} and 2000 cm^{-1} could be selected and answers would be comparable, within the limits of determining the exact wavenumbers. Selecting a range and using the formula given in the student handout, students should be able to obtain an answer reasonably close to the following:

$$\nu_1 = 2200\text{ cm}^{-1} \quad \nu_2 = 2135\text{ cm}^{-1} \quad \nu_1 - \nu_2 = 65\text{ cm}^{-1} \quad n = 3$$

Indices of refraction, for thickness calculations, are listed here for some of the common polymers. Others can be found in the Polymer Handbook.

cellulose	n=1.54
cellulose acetate	n=1.49
poly(ethylene), low density	n=1.52
poly(ethylene), high density	n=1.48
poly(methyl methacrylate)	n=1.49
poly(propylene)	n=1.47
poly(styrene)	n=1.59
poly(vinyl alcohol)	n=1.51
poly(vinyl acetate)	n=1.47
poly(vinyl chloride)	n=1.54

The interference fringe pattern results from interaction between waves of radiation reflected between the inner surfaces of the film and then transmitted. While most of the radiation is transmitted a small amount is reflected, depending on the difference in refractive index between the film and the surrounding air and then transmitted. This reflected radiation, when finally transmitted, will vary from in phase (reinforcing) to out of phase (interfering) with the incident radiation, producing the interference fringes.

VARIATIONS

The SPI (Society of Plastics Industry) has developed a coding system that identifies what kind of plastic many containers are made from. A listing of the codes is frequently obtainable from grocery stores or other retailers. Bottles and containers are identified with a triangular symbol stamped on the bottom of the product to help consumers

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identify and separate plastics for recycling. Students have fun sorting and classifying containers they bring in from home. Most of these types of product containers are too thick to obtain a good spectrum, but it is an interesting aside that relates the relevancy of recycling and the importance of knowing the identity of the material. Students can be divided into groups, each assigned one of the seven plastic types, to compile a list of the types of products found in each of the types of plastic. This could be discussed in terms of compatibility of product to container or the physical characteristics of the plastic which make it the most suitable for the purpose.

Research can also be done to identify markets for recycled plastic goods. A good source for polymer classification by physical and chemical tests is Vogler.

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