Fourier Transform Infrared Spectroscopy

FTIR DETERMINATION OF MTBE IN GASOLINE AND ETHANOL IN VODKA AND MOUTHWASH

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INTRODUCTION

As a part of the 1990 Clean Air Act Amendments, certain urban areas were required to add oxygenates to gasoline in order to meet attainment levels of carbon monoxide.[1] In California, since June 1996, virtually all gasoline sold has contained MTBE (methyl tert–butyl ether) as its primary oxygenate. However, there has been controversy over the use of MTBE as an oxygenate for making cleaner burning gasoline.[2-5] The additive has been found to contaminate ground water supplies by release from leaking gasoline storage tanks. MTBE has been classified as a possible human carcinogen and drinking water standards for this compound are being established. As a result, MTBE has been banned from being used in gasoline in California since 2003,[6] and other additives, primarily ethanol, are used as the oxygenate. However, small quantities of MTBE are typically found in gasoline, even where it is not the major oxygenate. The amount of MTBE in gasoline samples will be determined in Part I of this experiment.

Ethanol is a nervous system depressant with a broad variety of physiological effects based on the blood alcohol level. It is found in various amounts in different alcoholic beverages and other household items. Ethanol content is most commonly described in terms of proof, which is just the ethanol volume percentage multiplied by 2. The potency of an alcoholic beverage used to be tested by putting it on gunpowder and burning it for "proof" it was at least 50% ethanol by volume. The pervasiveness of alcohol consumption in the general populace, and with high school and college students in particular, is widespread. The effects of alcohol abuse on death rates, drug abuse, violence, health issues and economic costs are beyond the scope of this introduction. In Part II of this experiment, the amount of ethanol in vodka and mouthwash will be measured.

BACKGROUND

I: Qualitative Analysis

The technique of Infrared (IR) Spectroscopy takes advantage of the fact that many molecules strongly absorb IR radiation and that the degree of absorption is proportional to the molecular concentration. The wavelength range of the IR region extends from about 780 nm to 1,000 μm, with the relation between energy (E), wavelength (λ) and frequency (ν) shown in Equations I and II below:

$$E = h\nu = \frac{hc}{\lambda}$$ **Equation I**

$$c = \lambda\nu$$ **Equation II**

In Equations I and II, h is Planck's constant (6.626×10^{-34} J s), and c is the speed of light in a vacuum (taken to be 3.00×10^{8} m s^{-1}).

In IR techniques, the absorption or transmission of the IR radiation is commonly measured as a function of wavenumber. A wavenumber is the reciprocal of the wavelength and is

most commonly expressed in units of cm^{-1}. Thus the range of wavenumbers corresponding to the IR spectrum would be about 12,800 to 10 cm^{-1}. This is broken down into 3 main IR regions: near-IR (12,800 to 4000 cm^{-1}), mid-IR (4000 to 200 cm^{-1}), and far-IR (200 to 10 cm^{-1}). The most commonly scanned wavenumbers are from 4000 to 670 cm^{-1}, which encompass absorptions by the majority of common organic functional groups.

For a molecule to absorb IR radiation, it must change its dipole moment upon vibration, and the frequency of the radiation must exactly match the natural vibrational frequency of the molecule, resulting in a change in the amplitude of the vibration. Some simple molecules (O_2, N_2, etc.) have no fluctuating dipole moment, and so they do not absorb IR radiation. But many vibrations of MTBE and ethanol change the dipole moment; such vibrations are said to be IR active.

The two fundamental types of molecular vibrations are stretching and bending modes. The stretching mode consists of a change in the distance along the axis of a bond between two atoms. The bending mode results from a change in the angle between two bonds. There are four types of bending vibrations: rocking, twisting, wagging and scissoring. Organic functional groups have particular absorption peaks that can be used in qualitative analysis, varying only by the molecular environment. For example, the "ether band" of MTBE around 1092 cm^{-1} is easily distinguishable from absorptions by other components of gasoline and will be analyzed in Part I of this lab.

From quantum theory, the vibrational states are quantized and the allowed vibrational transitions are those in which the vibrational quantum number changes by unity. The more atoms there are in the molecule, the more complicated the IR spectrum becomes due to increased vibrational coupling and possible overtone peaks and combination bands. These effects create a unique IR absorption spectrum for each molecule that can be used as a “fingerprint” in qualitative experiments.

II: Quantitative Analysis

Although infrared spectroscopy is used extensively for qualitative analysis in organic chemistry, band intensities are related to the concentration and path length of the sample through the Beer–Lambert Law, shown in Equation III, and so this technique can be used for quantitative analysis as well.

$$A = \varepsilon l C \qquad \textbf{Equation III}$$

Where A is the Absorbance, ε is the molar absorptivity in L/(mol cm), l is the path length in cm and C is the concentration of analyte solution in moles/L.

If the absorbance of a series of known standard solutions are measured, a plot of Absorbance as a function of concentration can be made and least-square analyzed. Following the expected linear dependence format, $A = slope \times C + offset$, the slope of the linear plot would be equal to εl, allowing determination of the molar absorptivity if the path length of the cell, l is known (typically 1 cm). Also, an unknown solution’s concentration can be determined after its Absorbance is measured and applied to the linear least squares fit.

III: The Fourier Transform Technique (for Advanced Readers)

Most IR instruments used today are of the *Fourier Transform* type. There are three major advantages of using Fourier Transform techniques in IR spectroscopy.

1) Fourier transform instruments do not need slits to attenuate radiation and have fewer optical elements. The increased power reaching the detector gives a larger signal to noise ratio.

2) The high resolving power and wavelength reproducibility allow for more accurate analysis of collected spectra.

3) The multiplex advantage, or faster scanning. In Fourier techniques, all wavelengths are scanned simultaneously, allowing an entire spectrum to be scanned in 1 second or less. Since the signal to noise ratio $\left(S/N\right)$ increases as the number of scans, *k*, increases (as shown in Equation IV), then Fourier techniques allow many more scans in less time and much better signal to noise ratios.

$$\left(S/N\right)_{\text{k scans}} = \left(S/N\right)_{\text{one scan}} \times \sqrt{k} \qquad \textbf{Equation IV}$$

As you can see, the quality of the spectrum increases in proportion to the square root of the number of scans.

Fourier techniques basically differ from conventional techniques in that they measure radiant power as a function of time (time domain) whereas conventional spectroscopy measures power as a function of frequency (frequency domain). This time domain spectrum is then mathematically converted into a frequency domain spectrum using a Fourier transform. The process is so complex that it requires a high speed computer and will not be covered here.

Power variations at the very high frequencies of IR sources (10^{12} to 10^{14} Hz) cannot be measured directly with today's electronics (transducers measure averages instead of variations at these high frequencies). Therefore the high frequencies must be scaled down to much lower values in order to measure time domain signals. This is commonly accomplished using a *Michelson Interferometer*.

A Michelson Interferometer essentially splits the IR radiation beam from the source (high frequencies) into two beams using a beam splitter. One beam is directed to a fixed mirror and the other to a mirror moving at a constant speed, v_m. The two beams are then recombined and directed to the detector. The moveable mirror causes the radiation power at the detector to fluctuate in a predictable manner based on the constructive and destructive interference patterns of the recombined beams. These interference patterns are based on the difference in path length (or retardation, δ) for the two beams. The plot of output power from the detector vs. retardation is called an interferogram.

The *resolution* of the spectrometer, which is the difference in wavenumber between two peaks that can just be separated by the instrument, is equal to the inverse of the retardation. The relationship between the molecular emitter's frequency, *ν*, and the interferogram frequency, *f*, is based on the moveable mirror speed, v_m, according to Equation V below.

$$f = 2\frac{v_m}{c}\nu \qquad \textbf{Equation V}$$

Assuming a typical mirror velocity of 1.5 cm/sec and with the speed of light being 3.00 x 10^8 m/sec, then the interferometer reduces the frequency of the source radiation by a factor of 10^{-10} (i.e.: $f = 10^{-10}\,\nu$). This brings the frequency into the audio range and allows transducers to measure the power variations and thus record a time domain spectrum. The Fourier

Transform converts the time domain spectrum back to a frequency domain spectrum rapidly and with incredible resolution and signal to noise ratio.

Part I: Determination of MTBE in Gasoline

In the first part of the experiment, you will quantify the amount of MTBE in gasoline from its absorption of infrared radiation transmitted through the solution. The "ether band" of MTBE around 1092 cm^{-1} is easily distinguished from other absorptions due to the hydrocarbon components of gasoline. A series of MTBE/hexane standards can be used to prepare a linear calibration plot of absorbance at the ether band vs. concentration of MTBE. From this plot, the concentration of MTBE in a sample of gasoline can be derived.

Experimental Procedure

Note: Detailed instructions on the start up, use, and shut down of the Jasco FT/IR–615 instrument are provided in the four page handout near the machine in the lab, please read them carefully before beginning.

1) In the fume hood, prepare a stock solution of 5% (volume/volume) MTBE by carefully adding hexane to 2500 μL of MTBE until you obtain a total volume of 50.0 mL in a volumetric flask. There are pipettes available for adding 250 μL of the MTBE. Be sure to condition the flasks and pipettes first.
2) From this stock solution, make five standard solutions:

Volume of 5% Stock Solution	Add Hexane to Total Volume	Final Concentration
1.0 mL	10.0 mL	0.5 % (v/v)
3.0	10.0	1.5 %
4.0	10.0	2 %
6.0	10.0	3 %
8.0	10.0	4 %

Be sure to condition each flask and label with tape. Close the flasks after preparation to avoid evaporation.

3) Dilute the “old” gasoline sample with hexane to make a 25% (volume/volume) solution by adding hexane to 2500 μL of the gasoline to a total volume of 10.0 mL of solution. Label the flask and close it. Make a similar solution with “new” gasoline.
4) Set the spectrometer resolution to 1 cm^{-1} and the number of scans to 16 by clicking on “Measure” and then “Parameters”.
5) Using a plastic pipette, flush the transmission IR salt crystal cell with the hexane solvent four times, then fill with hexane. After that, load this cell into the spectrometer compartment.
6) Take a background spectrum of the hexane solvent and save this spectrum for later use. To do a single beam spectrum, click on “Measure” then “Parameters + Background” and under vertical axis choose “single” for the background and “abs” for the sample. Click “OK” to run the background. (or click on the “B” icon with a box in it as a shortcut). The spectral analysis software will then automatically ratio the sample spectra with that of the most recent background spectrum. When the run is complete, the colors of the top tabs will return.

7) Now take the cell out and flush it four times with the standard solution you are going to use next. After that fill it with the standard solution and place it back into the spectrometer. Take a spectrum for your first standard by clicking on the "S" tab with no box in it (for run Sample) and save it.
8) Scale the spectra to focus on the ether peak around 1092 cm^{-1}. Do this by clicking on "View" then "Scale" and type in the desired x and y axis ranges (~ 1150 to 1050 cm^{-1} and 0 to 2, respectively). Use "Peak Find" to locate all peaks (click on "Processing ----> "Peak Process" ----> "Peak Find" ----> "Execute") and choose the appropriate peak from the Table listed.
9) Repeat steps 7-8 for your remaining MTBE standard solutions.
10) Now, record the spectrum of the 25% gasoline samples (old and new). Make sure the absorbance of the ether band falls on the calibration curve. Determine the absorbance of the sample from the same ether peak used in the standards as you did in step 8.

Data Analysis

1) Make a Table of MTBE % concentration vs. Peak Absorbance measured at the top of the ether band around 1092 cm^{-1} for the standard solutions.

Sample	Absorbance

2) Develop a Beer-Lambert Law plot for the MTBE in hexane standards and perform a least squares analysis of the linear best fit line on a computer or by hand on graph paper if a computer is not available (Microsoft Excel instructions for graphing are in the Appendix if needed). This will give you a dependence in the form:

$$Absorbance = slope \times C + offset \qquad (y = mx + b)$$

3) Using the *slope* and *offset* parameters determined from your fit, calculate the % MTBE in the diluted gasoline sample.
4) Calculate the volume percent of MTBE in the original undiluted gasoline samples. Make sure you take into account the various dilutions.
5) Assign the vibration responsible for the peak at 1092 cm^{-1} in the MTBE absorbance spectrum.

PART II: Determination of Ethanol in Vodka and Mouthwash

This part of the experiment will show that infrared spectroscopy can be carried out in water solutions using appropriate infrared-transmitting, but water-insoluble, crystals (of ZnSe in this case) using the technique of attenuated total reflectance (ATR) FTIR. You will use this technique to determine the ethanol concentration in vodka and mouthwash.

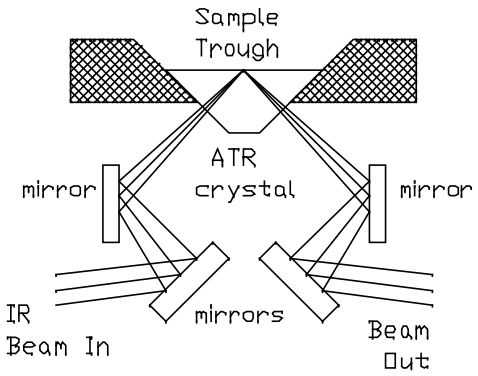

Figure 1. Schematic diagram of single-bounce ATR accessory.

This technique allows you to quantitatively measure the absorbance of ethanol in water, even though water is a very strong absorber of infrared radiation itself. As seen in Figure 1, in the ATR technique the sample is placed on an internal reflection element and the IR beam is directed into the element. It strikes the internal crystal-air interface at an angle greater than the critical angle, and as a result undergoes internal reflection inside the crystal. Most radiation is reflected at the point of internal reflection, but a small fraction is absorbed by molecules present at the surface of the ATR crystal. This absorption of infrared radiation can then be detected and measured.

Increased sensitivity can be obtained by using a multipass ATR accessory. Figure 2 shows a schematic of the light path in such a device; the increased number of internal reflections leads to a proportional increase in the absorbance and hence in the sensitivity.

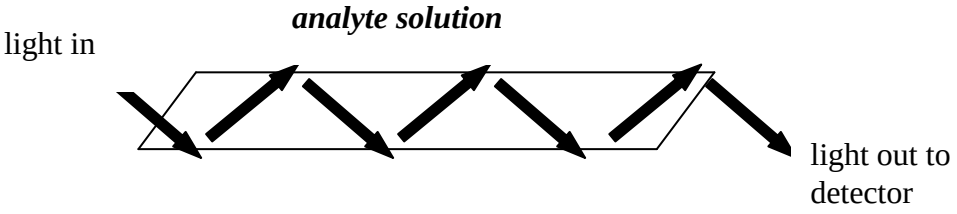

Figure 2. Schematic diagram of multiple reflections inside a multipass ATR accessory.

Experimental Procedure

1) Prepare a 10 % (by volume) 95% ethanol in water solution by adding nanopure water to 5.0 mL of ethanol to a total volume of 50.0 mL in a volumetric flask.
2) Now place the liquid multi-pass ATR accessory in the sampling compartment. Be sure not to turn any of the screws on the accessory as they have been tuned to make sure the infrared beam passes into the crystal and back out to the detector properly. When properly aligned, you should be able to see red dots where the HeNe laser is reflecting at the crystal surface along the center of the crystal. Try to count the number of reflections you can see in the crystal. You may want to do this in the dark, since it makes the spots easier to see.
3) Carefully fill the top of the crystal with nanopure water using a pipette (DO NOT SPILL WATER IN THE SAMPLE COMPARTMENT). Take a background absorbance spectrum using 16 scans and 1 cm^{-1} resolution (hit the "B" icon with a box in it). Remove the water carefully with a plastic pipette and then dab the trough with clean, lint-free tissue. Do not exert any pressure on the glass surface during this procedure.
4) Now condition, then fill the ATR accessory with the 10% ethanol sample. Take a spectrum of this sample and then take another scan immediately afterwards for reproducibility. Scale the spectra around the alcohol peak near 1044 cm^{-1}. Find the absorbance at that peak and record it in your lab book.
5) Prepare a set of standard solutions by diluting the 10% Ethanol solution with Nanopure H_2O.

Volume of 10% Stock Solution	Add Nanopure H_2O to Total Volume	Final Concentration
1.0 mL	10.0 mL	1.0% (v:v)
3.0	10.0	3.0%
5.0	10.0	5.0%

Label each flask with tape. Close the flasks after preparation to avoid evaporation. Find the absorbance of each solution as you did for the 10 % sample in step 4. Record the values in the Table below.

Sample	**Absorbance**

6) Prepare a diluted vodka solution by adding nanopure H_2O to 1.0 mL of the original vodka solution in a 10.0 mL volumetric flask. Record the spectrum of the diluted vodka sample as before and make any necessary dilutions so the absorbance falls on the calibration curve. Record the value in the previous Table.
7) Prepare a diluted mouthwash solution by adding nanopure H_2O to 2.0 mL of the original mouthwash solution in a 10.0 mL volumetric flask. Record the spectrum of the resulting sample as before and make any necessary dilutions so the absorbance falls on the calibration curve. Record the value in the previous Table.
8) Record the dimensions of the crystal as well as its angle of incidence from the label in the ATR cabinet.
9) If there is extra time there are 2 possible solutions to test. First, if a non-alcoholic mouthwash is available, prepare a diluted solution as in Step 7 and scan it. Second, if a sample of newer (supposedly MTBE free) gasoline is available, make a diluted solution as in Step 3 in Part I and scan it. See if the MTBE peaks disappear and if the ethanol peaks appear.

Data Analysis

1) Calculate the theoretical number of reflections, *N*, along the crystal given the formula

$$N = \frac{l \cot \theta}{2\,t}$$

where l is the crystal length, θ is the angle of incidence (determined by the optical configuration and provided by the manufacturer of the ATR accessory) and t is the thickness of the crystal.
2) Develop a Beer-Lambert plot for the ethanol in water standards. Use the least squares fit to determine the % ethanol in the diluted vodka sample, as well as for the Listerine. Follow the same instructions as the plot made in Part I.
3) Calculate the volume percent of ethanol in the original undiluted vodka and mouthwash samples. Make sure you take into the account the various dilutions. You can show your work calculations below.
4) Determine the proof of the original vodka sample.

IF THERE IS STILL TIME LEFT, DO THE FOLLOWING EXTRA SECTION:

PART III: Instrumental Noise

A standard method for improving signal-to-noise (S/N) is to increase the number of scans. The S/N should improve by the square root of the number of scans as described in the background section.

Experimental Procedure

1. Set the spectrometer to capture an interferogram. Set the number of scans to be 1 and the resolution at 1 cm^{-1}. Make sure there is no accessory inside the sample compartment of the spectrometer.
2. Take a background spectrum with no cell in the sample compartment. Convert the interferogram into a single beam spectrum.
3. Now take another spectrum with no cell in the sample compartment. Convert the interferogram into a single beam spectrum and ratio this spectrum to your background spectrum. The resulting spectrum will be a transmittance spectrum of the noise of the instrument. Convert this transmittance spectrum to absorbance.
4. View the spectrum of noise from 2100 to 2000 cm^{-1} to find the lowest valley and the highest peak in this region. The difference gives you the peak-to-peak noise. Mark the valley and peak on the spectrum and print out.
5. Now set the number of scans to be 4 (leave the resolution at 1 cm^{-1}). Repeat step one through four to find the peak-to-peak noise with 4 scans.
6. Now set the number of scans to be 64 (leave the resolution at 1 cm^{-1}). Repeat step one through four to find the peak-to-peak noise with 64 scans.

Data Analysis

1) Make a table showing the number of scans and the peak-to-peak noise for each.
2) Quantitatively compare the change in the noise with the number of scans and compare to theoretical expectations.

REFERENCES

1. J. G. Calvert, J. B. Heywood, R. F. Sawyer and J. H. Seinfeld, "Achieving Acceptable Air Quality: Some Reflections on Controlling Vehicle Emissions", *Science*, **1993**, 261, 37.
2. "Air Toxics Program Summary: Adding Oxygenates to Fuel", Health Effects Institute, 1997.
3. http://tsrtp.ucdavis.edu/mtberpt/homepage.html
4. Reuter, J. E.; Allen, B. C.; Richards, R. C.; Pankow, J.; Goldman, C. R.; Scholl, R. L.; Seyfried, J. S. *Environ. Sci. Technol.* **1998**, *32*, 3666.
5. Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. *Environ. Sci. Technol.* **2000**, *34*, 210A.
6. http://www.calepa.ca.gov/programs/mtbe/eotasks.htm
7. Griffiths, P. R.; Fuller, M. P. In *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H., Hester, R. E., Eds.; Heydon and Sons: London, 1982; Vol. 9, Ch. 2, pp. 63-129.

Additional References:

1. D. A. Skoog, F. J. Holler and T. A. Nieman, *Principles of Instrumental Analysis*, 5th Ed., Harcourt Brace, Philadelphia, 1998, pp. 380-401, 404-421.
2. P. Griffiths and J. DeHaseth, *Fourier Transform Infrared Spectrometry*, Wiley, 1986.