Experiment #4: Fourier Transform Infrared Spectrometry:

ANALYSIS OF LIQUIDS AND SOLIDS USING FTIR: METHYL t-BUTYL ETHER IN GASOLINE, ETHANOL IN VODKA, AND HYDROCARBONS IN SOIL

INTRODUCTION

Transmission FTIR Spectrometry - Although infrared spectrometry 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 and hence this technique can be used for quantitative analysis as well.

The base line method, depicted in Figure 1, involves selection of an absorption band of the substance that does not overlap bands due to the solvent or other components. The value of the incident radiant energy ($P_o$, or measured as $T_o$) is obtained by drawing a straight line tangent to the spectral absorption curve at the position of the sample's absorption band. The transmittance ($T_s$) is measured at the point of maximum absorption. Before the determination of MTBE in gasoline you will familiarize yourself with identifying a peak in this way.

$$A = \log_{10} \left( \frac{T_o}{T_s} \right) = \log_{10} \left( \frac{P_o}{P} \right)$$

Figure 1: Schematic diagram of a typical absorption band in the transmission mode and its relationship to absorbance.
In the first part of the experiment, you will quantify the amount of MTBE in gasoline from its absorption of the infrared radiation transmitted through the solution. The ether band of MTBE at 1092 cm\(^{-1}\) is easily distinguished from other absorptions by the hydrocarbon components of gasoline. A series of MTBE/hexane standards can be used to prepare a linear calibration plot of absorbance vs. concentration of MTBE. From this plot, the concentration of MTBE in a sample of gasoline can be derived.

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 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, the use of MTBE is being phased out as the major oxygenated additive and other compounds such as ethanol are being considered as alternatives. However, small quantities of MTBE are typically found in gasoline, even where it is not the major oxygenate.

**Attenuated Total Reflection Spectrometry** – In the second part of this experiment you will measure an organic compound in an aqueous solution using infrared attenuated total reflection spectrometry (ATR). 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 2, 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:

![Figure 2. Schematic diagram of single-bounce ATR accessory.](image)
At the point of internal reflection, an evanescent wave penetrates a small distance into the sample where infrared absorption by the surrounding sample can occur. This absorption of infrared can then be detected and measured.

Increased sensitivity can be obtained by using a multipass ATR accessory. Figure 3 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.

![Diagram of multiple reflections](image)

Figure 3. Schematic diagram of multiple reflections inside an multipass ATR accessory.

The number of reflections, N, can be obtained by taking the ratio of a peak absorbance measured using the multipass accessory to that obtained using the single bounce technique. This can be compared to the theoretical number of reflections given by

\[ N = \frac{l \cot \theta}{2t} \]

where \( l \) is the crystal length, \( \theta \) is the effective angle of incidence (determined by the optical configuration and provided by the manufacture of the ATR accessory) and \( t \) is the thickness of the crystal.

ATR is particularly useful for water solutions since the depth of penetration \( (d_p) \) into the sample on each reflection is small, depending on the wavelength \( (\lambda) \), the nature of the crystal material and the surrounding medium, and the angle of incidence, \( \theta \):

\[ d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2}} \]

where \( n_{21} = n_2/n_1 \) and \( n_2 \) is the index of refraction of the sample medium in contact with the crystal of refractive index \( n_1 \).

**Diffuse Reflectance Infrared Fourier Transform Spectrometry** - A common way of measuring contaminants in soil is to extract the soil with an organic solvent and use a chromatographic technique. While this can detect individual organics, it is time-consuming and the percentage recovery of organics is usually much less than 100%. When making IR measurements on solid samples, like soil, one is confronted with a challenge in sample preparation. One approach includes making a thin pellet and using transmission spectroscopy. However, it is not particularly easy to get a pellet that is thin enough to transmit infrared radiation, yet thick enough not to break during handling. Another way of examining solid
samples is to use a technique known as **Diffuse Reflectance Infrared Fourier Transform Spectrometry (DRIFTS)**. Figure 4 is a schematic of a typical DRIFTS apparatus.

![Schematic diagram of a typical DRIFTS apparatus](image)

Figure 4. Schematic diagram of a typical DRIFTS apparatus.

DRIFTS spectra are commonly described by the Kubelka-Munk function $f(R_\infty)$:

$$f(R_\infty) = \frac{(1 - R_\infty)}{2R_\infty} = \frac{k}{s}$$

$R_\infty$ is the ratio of the diffuse reflectance signal from the sample to that from a non-absorbing reference, $k$ is an absorption coefficient that is proportional to the analyte concentration and $s$ is a scattering coefficient. If specular reflection is small and the scattering coefficient is constant, the Kubelka Munk function should vary linearly with concentration. In practice, the analog of “absorbance”, i.e. log of the ratio of the signal from the reference to that from the sample, is often found to vary linearly with concentration, and can be used for quantitative analysis. Diffuse reflectance measurements can be carried out using a reference that does absorb infrared radiation, but the sensitivity is reduced.

Uptake of organics by soils can occur in a number of ways, for example by mixing with natural biogenic material (e.g., leaves, insects, etc.), by absorption of organics from air, and by spillage of hazardous organics such as those in motor oil. Contamination of soils with hydrocarbons such as benzene, toluene, ethyl benzene and the xylenes (often referred to as "BTEX") is a widespread problem around gas stations due to leaking storage tanks. Due to the fact that there are very characteristic IR sensitive -C-H stretching vibrations in the 2900 cm$^{-1}$ region for such organics, one can measure the hydrocarbon content based on their absorbance in this region.
PART A: TRANSMISSION FTIR SPECTROMETRY

I. 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. Test this by carrying out the following steps:

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

II. Resolution: Recall that it is the total displacement of the moving mirror which determines the resolution in FTIR.

1. Set the resolution to 0.25 cm\(^{-1}\) and the number of scans to 16. Scan both a background and sample without anything in the sample compartment. As it is scanning, look through the top compartment of the instrument, and use a ruler to estimate the total travel length of the moving mirror.

2. Repeat step one with the resolution set to 8 cm\(^{-1}\).

Data Analysis: Take the ratio of the mirror travel length for the two resolutions. Is this what you expect?
III. **Determination of MTBE in Gasoline:** In this part, you will prepare a set of calibration solutions and measure the absorbance of the MTBE peak to generate a calibration curve. You will then measure the absorbance of the peak in the gasoline sample to obtain the concentration of MTBE in the gasoline.

1. Prepare standard solutions of MTBE in hexane by first making a stock solution of 2% (v:v) MTBE by adding hexane to 1.0 mL of MTBE until you obtain a total volume of 50.0 mL. From this stock solution, make five solutions corresponding to 0.2%, 0.6%, 0.8%, 1.0%, and 1.6% by taking 1.0, 3.0, 4.0, 5.0, and 8.0 mL respectively of the stock solution and adding hexane to a total volume of 10.0 mL in each case.

2. Dilute the gasoline sample with hexane to make a 10% (v:v) solution by adding hexane to 1.0 mL of the gasoline to a total volume of 10.0 mL of solution.

3. Set the resolution to 1 cm$^{-1}$ and the number of scans to 16. Take a background spectrum of hexane and save this spectrum for later use. You will ratio all of your subsequent spectra for this part of the lab to this background in order to obtain your absorbance spectra of your standards and unknown.

4. You will use the baseline method for your first MTBE standard solution by recording it as a single beam spectrum. Convert this to a transmittance spectrum with the hexane background spectrum. Determine the values of $T_o$ and $T_s$ as shown in Figure 1 for the feature at $\sim$ 2851 cm$^{-1}$. Calculate the absorbance for this feature for comparison with the spectrum obtained in the next step.

5. Repeat your measurement for your first standard as an absorbance spectrum and then record all the rest of your spectra as absorbance spectra.

6. Record the spectrum of a gasoline sample and make any necessary dilutions so the absorbance of the ether band falls on the calibration curve.

**Data Analysis:**

1. Assign the principal bands in the spectra of MTBE and hexane to the functional groups responsible for these absorptions.

2. Develop a Beer-Lambert Law plot for MTBE in hexane and use it to determine the % MTBE in gasoline. Make sure you take into account the various dilutions.

3. Report the volume percent of MTBE in the original undiluted gasoline sample.

**PART B: ATTENUATED TOTAL REFLECTANCE SPECTROMETRY**
I. Determination of Ethanol in an Aqueous Solution: This part of the experiment will show that infrared spectroscopy can be carried out on water solutions using appropriate infrared-transmitting, but water-insoluble, crystals using the technique of attenuated total reflectance (ATR) FTIR. You will use this technique to determine the ethanol concentration in vodka.

1. Prepare a 10% (by volume) ethanol in water solution by adding water to 1.0 mL of ethanol to a total volume of 10.0 mL solution.

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.

3. Carefully fill the trough above 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. Remove the water.

4. Now fill the ATR accessory with this sample. Take a spectrum of this sample and then take another scan immediately afterwards for reproducibility.

5. Prepare a set of standard solutions of between 1%-5% using the 10% ethanol stock solution and take spectra of all of them using the multi-path cell.

6. Prepare a 10% dilution of vodka with water. Record the spectrum of the diluted vodka sample and make any necessary dilutions so the absorbance falls on the calibration curve.

Data Analysis:

2. Compute the theoretical number of reflections given by $N = l \cot \theta / 2t$, where $l$ is the crystal length, $\theta$ is the angle of incidence (determined by the optical configuration and provided by the manufacture of the ATR accessory) and $t$ is the thickness of the crystal.

3. Develop a Beer-Lambert plot for ethanol in water and use it to determine the % ethanol in vodka. Make sure you take into the account the various dilutions.

4. Report the volume percent of ethanol in the original undiluted vodka sample.

PART THREE: DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROMETRY

I. Determination of Organics in Soil: In this part of the experiment you will construct a calibration plot of total hydrocarbon concentration vs. absorbance of a solid sample using a
DRIFTS accessory. The total hydrocarbon concentration will be modeled using motor oil as a surrogate.

1. Grind about 30 g of sand into a fine powder with a clean mortar and pestle and store in a dry beaker.

2. Drop 20 drops of motor oil into a clean beaker and record the weight before and after adding the oil. From this, calculate the mass of one drop of oil.

3. Weigh out about 10 g of the ground sand on a piece of weighing paper. Pour the sand into a separate mortar, add 1 small drop of oil on top of the sand, and mix very thoroughly with a separate pestle. This is your stock calibration mixture and will be diluted with clean, ground sand to provide a series of calibration standards. The mortar and pestle for mixing should not be used later to grind clean sand without a thorough cleaning.

4. Dilute the oil-sand mixture prepared in step 3 with the clean ground sand in the following manner:

<table>
<thead>
<tr>
<th>Grams of Oil-Sand Mixture</th>
<th>Grams of Clean Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>0.5</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2</td>
<td>5.0</td>
</tr>
</tbody>
</table>

5. Carefully fill the DRIFTS sampling cup with each of the diluted calibration mixtures. In the reference cup, use the clean ground sand you used to make these mixtures. Take the background spectrum using the clean ground sand, and the sample spectrum using the oil-sand mixtures. This will give you the data for a calibration plot using the -C-H stretches at 2925 and 2858 cm\(^{-1}\).

6. Collect a dry soil sample; if necessary, run it through a sieve to remove rocks and debris. Grind this soil into a fine powder in a separate mortar and pestle.

7. Carefully fill one of the DRIFTS sampling cups with your unknown soil sample. Note the absorptions at 2925 and 2858 cm\(^{-1}\) indicative of C-H stretching modes.

**Data Analysis:**
1. Calculate for each diluted oil-sand mixture the concentration of motor oil in parts-per-million by weight (ppm w/w):

   \[
   \text{ppm hydrocarbon (w/w)} = 10^6 \times \frac{\text{mass of oil}}{\text{total mass of oil + sand}}
   \]
2. Develop a calibration curve for total hydrocarbon content using both the –C-H stretches at 2925 and 2858 cm⁻¹. Is there a linear relationship between the absorbance of the peaks around 2900 cm⁻¹ and the concentration of oil over this entire range?

3. Use the calibration curve to determine the total hydrocarbon content in a soil sample. Express the concentration of organics in your unknown in parts per million by weight (ppm w/w).

4. Discuss possible methods to distinguish between the organics present in the soil from natural processes (biogenic and geogenic) vs. organics from man-made sources (anthropogenic) such as motor oil.

REFERENCES:


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:
