**Analysis of Ethanol in Gasoline by Gas Chromatography and Fourier-Transform Infrared Spectroscopy**

**Abstract**

The addition of ethanol into gasoline has long been a method to help the hydrocarbons of gasoline burn smoother in an internal combustion engine by adding oxygen into the fuel. Gas stations list ethanol content in gasoline can be up to 10% ethanol but no more than 10% ethanol. By using the methods of standard addition, using known concentrations and volumes of spikes of ethanol into the gasoline, we may extrapolate back the original concentration of ethanol in the mixture of gasoline. Quantifying these results with gas chromatography, we received 10 (±1) volume percent ethanol at the 95% confidence interval and looked for the 1.87-minute retention time. Similarly, we constructed the same samples under the same environments and ran them using Fourier-Transform Infrared Spectroscopy and looked for the peak near 1100 cm\(^{-1}\). Using infrared spectroscopy, it was determined that the ethanol content in gasoline was 13 (±2) volume percent ethanol. Both methods were examined at the 95% confidence interval and subsequent F\(_{\text{test}}\) and T\(_{\text{test}}\) confirm that these two methods of analysis for ethanol are statically different.

**Introduction**

Internal combustion engines, such as the ones in automobiles, intake air from the environment to burn a fuel to produce work. The fuel used would be gasoline but when gasoline is bought from the gas station, 100% pure gasoline is not being purchased\(^1\). The actual composition of the gasoline being purchased is near 90% where the rest of the 10% is from the added ethanol. Ethanol has been added to because it oxygenates the fuel for internal combustion engines to create more work. Since the fuel is already oxygenated with ethanol, the fuel will burn easier and cleaner compared to 100% gasoline. The structure of ethanol (fig. 1) confirms this theory by having a very small structure with an alcohol group attached. This alcohol will be the oxygen used to help the fuel burn when added in small amounts of up to 10% by weight. The oxygenated fuel will help the engine always contain some amount of oxygen to burn for the engine. Gasoline, in itself, is not a pure substance but a mixture of many different lengths of hydrocarbons ranging from 4 to 12 carbons\(^1\). The general reaction for the combustion of a hydrocarbon from gasoline is as follows in equation 1.

\[
2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O}
\]  

(1)

Knowing that gasoline is a mixture of hydrocarbons with added ethanol, it will be challenging to select the amount of ethanol due to the amount of compounds in the solution. Current techniques such as a calibration curve, UV-Vis spectrophotometry, and atomic adsorption spectroscopy are not the most optimal instruments to use to analyze the composition of ethanol in gasoline\(^2\). Techniques used in this experiment are designed to work around the obstacle of having multiple similar compounds in the mixture. Fourier Transform Infrared spectroscopy (FT-IR) and gas chromatography (GC) are the instruments better suited for this analysis. Using these techniques with standard addition will allow the determination of ethanol in a mixture of hydrocarbons.

Standard addition is similar to standard calibration in which a graphical analysis approach is taken. Standard addition employs adding known concentrations and quantities of standard into the analyte which may contain many unknown compounds in unknown concentrations. Measuring 5 different test tubes that all contain the same amount of analyte and increasing amounts of percent standard added, the initial concentration of a compound can be found\(^3\). In this experiment, known quantities of percent ethanol are

![Fig. 1 The Lewis structure and condensed structure of ethanol.](image)
added increasingly into each test tube to form a linear line on a graph. Once the graph is made, deducing where \( y = 0 \) will give the initial concentration of ethanol in gasoline. The standard addition approach uses the matrix effect where a change in signal is made only from adding the standard and not from anything in the analyte. Since all test tubes have the same amount of gasoline, which may contain many versions of hydrocarbons, they will give identical amounts of signal in each of the test tubes. The percent volume ethanol spike can be found by using equation 2.

\[
\frac{[X]}{[S_j][X_f]} = \frac{I_X}{I_{1+X}}
\]

Using this technique with Fourier transform infrared spectroscopy and gas chromatography, will allow the determination of the ethanol content in gasoline.

Gas chromatography can be used to separate and identify ethanol in a mixture of fuel by exploiting their differences in movement through a charged column using a carrier gas. A unique aspect about gas chromatography is that a liquid is injected and the instrument vaporizes it. The vapor then travels down the column with the use of a carrier gas. In this case, the carrier gas is the mobile phase and the charged column is the stationary phase. Since gasoline is a mixture, gases will be vaporized simultaneously but come out on the detector in different times. These differences in times will help determine which peak is the ethanol peak. The gas comes out at different times because each gas will interact with the stationary phase by different amounts. When an interaction occurs on the column, it inherently slows down its path to towards the detector at the end of the column. The mobile phase continues to push it so that it does not stay affixed to the column. In elution, the eluent will be the entry and injection of gasoline-ethanol mixture and the eluate is the gases at the detector. Once at the detector many peaks will form due to the various hydrocarbons. The retention time can be used to determine the identity of the gas. Some compounds will be longer and some will be shorter than ethanol but ethanol can be identified and quantified by measuring the retention time of each peak and measuring the peak area. Since ethanol has an alcohol group attached (fig. 1), it will want to interact with the charged column and result in a longer time to exit the column.

Using standard addition and the measurements from the peak area of the ethanol peak given by gas chromatography, a graph can be made to determine the starting ethanol concentration. This can be done by plotting the points which will make a linear line on the graph. Using the equation of the line, extrapolating the line back where \( y = 0 \) will give us the initial concentration of ethanol in the sample.

Fourier Transform infrared spectroscopy is another method utilized to determine the percentage of ethanol in a mixture of gasoline. Amongst the various lengths of hydrocarbons present in gasoline are ethanol molecules. These molecules differ greatly because ethanol has an alcohol group present (fig. 1). This distinguishing factor will be used to select ethanol absorption with the other hydrocarbons. In infrared spectroscopy, the distinguishing O-H group will absorb near 3500–3000 cm\(^{-1}\) so it is expected to see a peak there and will be used to determine the concentration of ethanol in gasoline. The other alkane C-H groups that are found in gasoline will be found 3000-2800 cm\(^{-1}\) in the infrared spectrum which will help aid the determination of percentage of ethanol in gasoline. The most important peak in which the analysis of ethanol in gasoline will be used in this experiment is the C-O bond that is found near 1100 cm\(^{-1}\) while all other alkane groups will be absorbed at 3000-2800 cm\(^{-1}\).

Similarly, standard addition can be used with the measurements from the peak area of the ethanol peak given by the Fourier Transform infrared spectroscopy to form a linear line on a graph with a known equation. This equation can be used to extrapolate back to \( y = 0 \) and yield the initial concentration of ethanol in sample.

**Experimental**

The procedures of the lab manual provided by California State University, Fullerton were followed precisely to determine the percent of ethanol in gasoline by using gas chromatography (GC) and Fourier-transform infrared spectroscopy (FT-IR). A standard addition curve was created for both instruments using 1.000 mL of gasoline in each of the 5 vials used. The standards were created by adding 0, 25, 50,
75, and 100 μL using a micropipette to make the 5 samples that will be used in each technique. Capping the vials and placing parafilm on the beaker used for ethanol is imperative as to not allow ethanol to evaporate into the environment. All gasoline samples were made in the fume hood. The same steps to make the 5 samples are used for both gas chromatography and Fourier-transform infrared spectroscopy.

The 5 samples were analyzed using gas chromatography (SCION 436-GC) which is an autosampling GC. Before placing the 5 vials of varying additions of ethanol, 3 measurements of the zero spike were taken for the limit of detection calculation.

The 5 samples were analyzed using Fourier-transform infrared spectroscopy (NICOLET-380 Fourier Transform Infrared Spectrophotometer). A salt plate was obtained and needed to be cleaned using 100% chloroform. The salt plate used did not have to be opened to be cleaned with chloroform. A syringe was used to withdraw the chloroform and place through the holes of the salt plate to clean. 6-10 rinses with the chloroform was necessary to ensure that new contaminants were trapped under the salt plates for the analysis of ethanol. A separate syringe was used to withdraw the ethanol from each sample to avoid contamination of the chloroform.

Results
Gas Chromatography

The expected volume percent for ethanol in gasoline is 10% but not to exceed 10% ethanol stated at the gas station in which the gasoline was obtained. We were able to determine the volume percent by utilizing both gas chromatography and standard addition. The 5 test tubes started with 1.000 mL of gasoline and was spiked with 0, 25, 50, 75, and 100 μL. The axis on the graph, though, cannot be in added mL ethanol but volume percent of ethanol spiked. The volume percent can be calculated by dividing the initial volume by the final volume and converting that number into a percent as shown in equation 3.

\[
\text{Volume percent} = \frac{\text{Initial volume}}{\text{Final volume}} \times 100\% = \frac{25}{1025} \times 100\% = 2.43902 = 2.4\% 
\]

Using this, the standard addition curve was made after sample measurements of each vial containing various amounts of ethanol. A sample plot for the addition of 75 μL is shown in figure 2. The ethanol retention time was found to be 1.87 minutes. At this time, the ethanol peak is first starting where the peak area units are measured in μV*min and the x axis in minutes.
Figure 2: Sample data from a 75 μL spike of ethanol in gasoline using gas chromatography. The spike of ethanol is equated to a 7.0% spike of ethanol. The retention time for ethanol was 1.87 minutes.

By using equation 3 the volume percent of ethanol added could be determined for all other vials. The volume percent of the first spike with 25 μL was found to be 2.4% by using this equation. The subsequent percent volumes of ethanol that were used was 4.8, 7.0, and 9.1%. These volume percent of ethanol was used for all standard addition curves for the x axis. The plot for the standard addition curve contains the percent of ethanol added for the x axis and the signal for the y axis as seen below for gas chromatography in figure 3. The signal for GC would be in units of peak area under the curve.

Figure 3: The standard addition curve for the analysis of ethanol volume content in gasoline using GC. The calibration curve shows a fairly linear relationship with an $R^2$ value of 0.9736.

The standard addition curve for the GC was shown to have a fairly linear relationship with 0.9736. The $R^2$ value could have been higher and it seems to be lowered due to the 4th data point which was
responsible for the 7.0% volume ethanol added. This standard addition curve also lead to the derived x and confidence interval of the experiment through the LINEST function. The LINEST function calculated the confidence interval as shown in equation 4 where the student's t is multiplied by the standard deviation of the data set. The confidence interval was shown to be 5% volume ethanol for our use in the GC with a derived x of 10. According to our data, we are 95% confident that the volume percent of ethanol in gasoline as determined by GC is 10% (±1) and within 4.65% of the true value. This overlaps with the expected value of 10% volume percent ethanol in gasoline. Since the data from GC overlaps with the expected value, GC is a valid method to analyze such analytes in the future.

$$\text{Confidence Interval} = t\sigma_x = 3.182 \times 1.4832 = 5 \% \text{ volume ethanol} \quad (4)$$

The limit of detection was needed after the analysis of ethanol to determine if the instrument was legitimate to analyze the concentrations of ethanol in the experiment. Since we added known amounts of ethanol into the solution, the limit of detection would be thought to be started at 0.00% ethanol added. It must be known that since gasoline already contains up to 10% of ethanol, the limit of detection would be for the 10% of ethanol and not 0% of ethanol. Since this is known, we may interpret our limit of quantitation and limit of detection data accurately.

The limit of detection is the lowest concentration of analyte that the instrument can detect with accuracy. The limit of detection may be calculated using equation 5 which needs two variables, standard deviation and the slope of the calibration curve.

$$\text{LOD} = \frac{3 \hat{s}}{m} = \frac{3 (2.44)}{1.38 \times 10^3} = 0.5 \text{ vol } \% \text{ ethanol} \quad (5)$$

The limit of detection was determined to be 0.5 volume percent of ethanol. The limit of quantitation was needed as well which is the lowest concentration that the instrument cannot be a reliable method because of how low the concentration is. Quantitation below the limit of quantitation would lead to significant decrease in accuracy and precision. The limit of quantitation is similarly calculated as the limit of detection but uses the standard deviation and slope of the standard addition curve, 244 and 1.38 \times 10^3, and multiplying by 10 as seen in equation 6.

$$\text{LOQ} = 10 \frac{s}{m} = \frac{10 (244)}{1.38 \times 10^3} = 2 \text{ vol } \% \text{ ethanol} \quad (6)$$

It should be noted that the LOQ is a higher value than the LOD. This limit of quantitation should be used to understand where the limit of analysis for the ethanol for the GC. The limit of quantitation was determined to be 2 volume percent ethanol.

The sensitivity can be determined using the same variables but instead dividing the slope of the standard addition curve by the standard deviation as seen in equation 7.

$$\text{Sensitivity} = \frac{m}{s} = \frac{1.38 \times 10^3}{244} = 6 \text{ vol } \% \text{ ethanol}^{-1} \quad (7)$$

### Fourier Transform Infrared Spectroscopy

The same solutions were made for the sample analysis in Fourier Transform Infrared Spectroscopy (FT-IR). The volume percent of ethanol added was determined through equation 1 for each of the 5 samples. The 5 samples of percent ethanol were placed on the x axis and the signal would be plotted on the y axis. The standard addition curve was constructed using the values of from the FT-IR seen in figure 4.
Figure 4: The standard addition curve for the analysis of ethanol volume content in gasoline using FT-IR at 1100 cm\(^{-1}\). The calibration curve shows a fairly linear relationship with an \(R^2\) value of 0.9753.

The absorbance values were taken from the peak near 1100 cm\(^{-1}\) which is the peak for the C-O bond on the FT-IR. The standard addition was fairly linear with the \(R^2\) value of near 1 at 0.9753. Again, the \(R^2\) value was fairly close to 1 and we see a trend with the two middle data points are over the trend line. Comparing the two calibration curves, there seems to be an even bigger trend considering the position of the data points in relation to the trend line. The trend line shows that the first two data points are underneath or very close to the trend line with the 4\textsuperscript{th} data point wildly above the trend line. The last data point is seen to have a significant decrease with where the expected point would be in relation to the trend line.

The data points from above were taken from the FT-IR where the FT-IR will graph absorbance values vs wavelength in cm\(^{-1}\). A sample plot of the sample was done and zoomed in at around 1100 cm\(^{-1}\) where the sample standard addition was analyzed at seen in figure 5.

Figure 5: The sample was run against a small spike of 25% ethanol in a solution of gasoline using Fourier Transform Infrared Spectroscopy.
The confidence interval was calculated through the LINEST output where the student’s t was determined to be 3.18 and the standard deviation which is 1.648. Using these two numbers and multiplying, the confidence interval was determined to be 5.25 seen in equation 8.

\[
\text{Confidence Interval} = t_s x = 3.182 \times 1.648 = 5 \% \text{ volume ethanol}
\] (8)

According to our data, we are 95% confident that the volume percent of ethanol in gasoline as determined by FT-IR is 13\%(±2) and within 5.25% of the true value. This overlaps with the expected value of 10% volume percent ethanol in gasoline. Since the data from FT-IR overlaps with the expected value, FT-IR is a valid method to analyze such analytes in the future. The data of both methods of analysis, GC and FT-IR, were compiled to compare the experimental volumes, their uncertainties, and the expected volume of ethanol in gasoline in table 1.

<table>
<thead>
<tr>
<th>Method</th>
<th>Experimental Vol. %</th>
<th>Expected Vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>10 (±1) %</td>
<td>10%</td>
</tr>
<tr>
<td>FT-IR</td>
<td>13 (±2) %</td>
<td>10%</td>
</tr>
</tbody>
</table>

Table 1: The experimental volume was obtained and compared against the expected volume percent. The experimental volumes were very close to the expected value.

The limit of detection was also needed to be calculated to characterize the instrument and determine if the instrument was accurate enough to use for the measurement of ethanol in gasoline. The limit of detection was calculated by multiplying the standard deviation of the data set from FT-IR and using the slope of the standard addition curve which was determined to be 0.03 and 0.0787 respectively. These values would be multiplied by 3 and to be used for the calculations in the limit of detection and sensitivity. The calculations for limit of detection was found using equation 9.

\[
\text{LOD} = 3 \frac{s}{m} = 3 \left(\frac{0.03}{0.0787}\right) = 1 \text{ vol % ethanol}
\] (9)

The LOD was determined to be 1 volume percent ethanol which is under the lowest concentration of ethanol measured, 10%. This would make the FT-IR a legitimate method for the analysis of ethanol in gasoline through standard addition. The LOQ is similarly calculated using the same values with the standard deviation and the slope of the standard addition curve but multiplying by 10 instead of 3 as seen in equation 10.

\[
\text{LOQ} = 10 \frac{s}{m} = 10 \left(\frac{0.03}{0.0787}\right) = 3 \text{ vol % ethanol}
\] (10)

The limit of quantitation was determined to be 3 volume percent of ethanol that is the lowest concentration that can be used to accurately measure the ethanol in gasoline.

\[
\text{Sensitivity} = \frac{m}{s} = \frac{0.0787}{0.03} = 3 \text{ vol % ethanol}\^{-1}
\] (11)

The sensitivity was determined to be 3 volume percent ethanol\^{-1}. The LOD, LOQ, and sensitivity measurements can be seen compiled for both the GC and FT-IR in table 2.
Table 2: The limit of detection, limit of quantitation, and sensitive were compared between the two methods. Both methods show a lower LOD and LOQ for their lowest ethanol measurement.

<table>
<thead>
<tr>
<th>Method</th>
<th>LOD (vol%)</th>
<th>LOQ (vol%)</th>
<th>Sensitivity (vol%(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>0.5</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>FT-IR</td>
<td>1</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Comparison of Methods

After completing both sample analysis by gas chromatography and Fourier transform infrared spectroscopy, statistical analysis was performed to see if the two methods agree with each other. Comparison of the two methods can be seen in table 1 where both methods overlap in each of their measurements considering the confidence interval and uncertainty. To determine whether the two methods were statistically different, an F test and T test can be performed.

The F test can be done by comparing the standard deviations from the two data sets from each method. The F test can be performed by taking the standard deviations and squaring them. Dividing the larger standard deviation by the smaller standard deviation will yield the \(F_{\text{calculated}}\) value as seen in equation 12.

\[
F_{\text{calculated}} = \frac{s_1^2}{s_2^2} = \frac{(1.65)^2}{(1.48)^2} = 1.24
\]  

(12)

The \(F_{\text{calculated}}\) value can be used and compared to an \(F_{\text{table}}\) value where the \(F_{\text{table}}\) value is 6.31\(^2\). The \(F_{\text{table}}\) value is obtained through using 4 degrees of freedom for \(s_1\) and 4 degrees of freedom for \(s_2\). Degrees of freedom is taking the \(n\) data points and subtracting one which results in 4 degrees of freedom from each data set.

The T test can be performed but instead of comparing the standard deviations, the data set means are compared. The T test can be performed by taking the means and calculating the \(s_{\text{pooled}}\) value.

\[
s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1-1)+s_2^2(n_2-1)}{n_1+n_2-2}} = \sqrt{\frac{1.65^2(4)+1.48^2(4)}{8}} = 1.57
\]  

(13)

This \(s_{\text{pooled}}\) value can be put into the \(t_{\text{calculated}}\) equation shown in equation 14.

\[
t_{\text{calculated}} = \frac{|x_1-x_2|}{s_{\text{pooled}} \sqrt{n_1+n_2}} = \frac{|0.4-13.6|}{1.57 \sqrt{10}} = 2.62
\]  

(14)

The \(t_{\text{calculated}}\) was determined to be 2.62 by comparing the means of each data set shown in the \(t_{\text{calculated}}\) as \(x\). Since the \(t_{\text{calculated}}\) value was determined to be 2.62, the \(t_{\text{table}}\) value was needed to be found. The \(t_{\text{table}}\) value was found by using the 95% confidence interval with 8 degrees of freedom. The 8 degrees of freedom was found by taking the 10 data points and subtracting 2, 1 for each data set. Using this, the \(t_{\text{table}}\) value was found to be 2.306. The values for all statistical analysis for the data sets can be seen in table 3.
Table 3: Statistical analysis was done on the two data sets for each instrument to find if the instruments were significantly different. Since $F_{\text{calculated}} < F_{\text{table}}$, the data is not significantly different but the T test does not confirm this. Since $T_{\text{calculated}} > T_{\text{table}}$, the two data sets are significantly different. In this case, the two methods are statistically different through their means but not their respective standard deviations.

Discussion

Gas Chromatography

Gas chromatography vaporizes a liquid into a gas while carrying it with a carrier gas such as helium or argon through a long column where the gas phase will interact with the column. In this case, the carrier gas is considered the mobile phase while the column that the gas interacts with is the stationary phase. The differences in which the gas will interact with the column will determine the time at which the analyte will come out, also known as the retention time. The analyte comes out from the column and reaches a detector where the detector records the concentrate of the analyte coming from the column. This is the basis of separation for ethanol from the hydrocarbons that are present in the gasoline. The column being used was an Agilent J&W GC Column HP-Innowax that has a polyethylene glycol polar stationary phase that would attract polar molecules and delay their exit through the column at the detector. Since the ethanol is the only polar molecule present due to the oxygen it possesses, it will interact with the polar stationary phase and slow its descent through the column. The hydrocarbons, which are notoriously non-polar will not interact with the column and be pushed through the column with the mobile phase, the carrier gas. Since gasoline is being used in addition to various small amounts of spikes of ethanol, we may find out the peak that changes by increasing peak area.

Using SCION 436-GC for use in gas chromatography, we did not have to load the liquid into the column ourselves. There is much error associated with loading the column by hand compared to an auto sampler like the SCION 436-GC has. Some error associated with loading the column by hand would be a variance in sample delivery or improper loading of the column which would vaporize the sample before even leaving the syringe. The auto sampler ensures that equal amounts of sample is loaded into the column and loaded in the same duration at the same velocity. By reducing the error associated with the injection, asymmetric band shapes can be avoided which is caused by overloading the column.

Since the error was reduced using an auto sampler, we avoided a big portion of error associated with using the GC. The obtained experimental volume percent was determined to be 10 (±1) % as seen in table 1. This is consistent with the expected volume percent in gasoline at 10%. The derived $x$ is spot on and the uncertainty associated with the measurement is considerably low. The confidence interval was also considerably low with 5% ethanol meaning that we can be 95% confident that our derived answer is within 5 percent of the true value.

The limit of detection was also lower than the measured volume percent by a lot by having an LOD of 0.5 volume % ethanol added as seen in table 2. The lowest amount of ethanol that was added was the 0% spike ethanol which only measured the expected 10% ethanol in the gasoline. Since the 10% ethanol is greater than the LOD, we may safely say that the GC is a capable instrument to analyze the ethanol in the mixture of gasoline. The LOQ was also determined to be 2, which is also less than the 10% ethanol being analyzed in the gasoline. The LOQ is used to characterize the instrument and what is needed to safely analyze the gasoline ethanol content with true precision and accuracy. The sensitivity is another calculation that can be done to characterize the GC for the analysis of ethanol. The sensitivity for the GC was found to be 6 volume %$^{-1}$ meaning that the GC was the more sensitive instrument. One can see this in figure 2, the sample plot of a 7.0% spike of ethanol where the signal response values maximizes at 240,000 making it a very sensitive instrument to use.
Since this instrument is very sensitive, the results rely on the instrument being calibrated. The auto sampler function of this GC has reduced error but to further reduce error calibration is needed. The GC must be calibrated because as the column ages, the stationary phase's ability to interact with the mobile phase is decreased. Standard calibration must be done by measuring the retention factor of a standard. Without a periodic standard calibration, the stationary phase tends to bleed off and not work as well. The bleed also contributes having a higher background signal and affect the detector’s ability to distinguish between signal and noise. The signal to noise ratio is needed to be able to resolve peaks from the background noise. The bleeding from the column can also lead to contamination of the detector which would also skew results. The column used was a new column used for this experiment as shown by the instructor, Dr. John Haan, to ensure that results are acceptable. We were the second group to use the auto sampler GC for this experiment using this column so there should not be much bleeding expected but there was not a GC calibration curve provided after installment of the new column.

**Fourier Transform Infrared Spectroscopy**

The Fourier Transform Infrared Spectroscopy method using a NICOLET-380 Fourier Transform Infrared Spectrophotometer will selectively measure the C-O bond that is present in ethanol at 1100 cm\(^{-1}\). Since ethanol is unique to gasoline having the C-O bond, as seen in figure 1 in the introduction, we used this distinguishing factor to identify the peak of ethanol amongst the high concentrations of hydrocarbons present in gasoline. The distinguishing peaks to look at are the O-H peak and the C-O peak. The peak that we identified and quantified through standard addition was the C-O bond due to the smaller amount of absorbance readings compared with the O-H bond. The other peak that is available to use, the O-H peak, can be used but the absorbance will be too high for the measurement without introducing noise. The measurements are on a logarithmic scale and such as the absorbance values get larger, the introduction of more noise is present. This is due to the with each raise in 1 unit of absorbance, there is a tenth of light being detected by the detector. By the time the absorbance measurements reach 4 or 5, the light reaching the detector is almost 10,000\(^{-1}\) when compared to absorbance measurements near 1 which would only be 10\(^{-1}\). Thus, error can be avoided by using peaks with the lowest absorbance values but still show the characteristic of the standard addition of ethanol.

As with any electronic instrument, electronic noise will always be present. There is Johnson noise, drift, and line noise which may be from the environment and cannot be determined\(^2\). FT-IR has the ability to reduce the noise significantly by measuring the spectrum at the same time. By taking multiple measurements of spectrum, FT-IR can then use signal averaging through the root-mean-square and improving the signal-to-noise ratio\(^2\). In this way, FT-IR can reduce a lot of noise given off by the environment and reduce the amount of error associated with this type of noise. FT-IR also has an advantage at taking the spectra wavelengths all at once. The instrument does not scan all of the wavelengths individually. This is advantageous in mixtures that are highly volatile such as the mixture of ethanol in gasoline where ethanol can be slowly evaporating while measurement wavelength scans are taking place.

The limit of detection, as seen in table 2, gave acceptable numbers that were smaller than the lowest value of ethanol measured. The limit of detection was found to be 1 volume % ethanol and as stated above, the lowest amount of ethanol present was in the 0% spike which contained 10% volume ethanol in gasoline. The limit of quantitation also characterized the FT-IR for this experiment giving a value of 3 volume percent ethanol which was also lower than the 10 volume percent ethanol measured in our samples. The FT-IR sensitivity was 3 volume percent\(^1\) which was fairly sensitive. As stated above, having a overly sensitive instrument is not ideal, especially for FT-IR where high absorbance values are correlated with high errors due to the fractions of light entering the detector.

**Comparison of Methods**

GC and FT-IR are used to determine the volume percent of ethanol in gasoline but by different means. Since gasoline is a mixture, gas chromatography will separate the components by exploiting their
boiling points and ability to interact with the column. At the end of the column is a detector which will graph the response from the different gasses as they arrive at different times and will be graphed digitally. The difference in times, also called the retention times, and concentrations are then used to determine the location of the ethanol peak and the concentration at each peak. The more selective method would be the FT-IR because of the ability to view the wavelengths at which you are adding increasing amounts of standard. The wavelengths are associated with the bonds at 1100 cm\(^{-1}\) which would correlate to the C-O bond present in ethanol.

By using a F test, we may determine if the two methods statically agree with each other by comparing their standard deviations. The standard deviations were found to be 1.48 for GC and 1.65 for FT-IR. Once both methods are squared and an F test was completed, the \(F_{\text{calculated}}\) value was 1.24. Comparing that \(F_{\text{calculated}}\) value to the \(F_{\text{table}}\) value using \(n\) data points of 5. 5 data points means that we have 4 degrees of freedom for each data set and we can determine that the \(F_{\text{table}}\) value is 6.39. Comparing our \(F_{\text{calculated}}\) to the \(F_{\text{table}}\), we see that the \(F_{\text{calculated}}\) value is smaller than the \(F_{\text{table}}\) value which means that the difference between the standard deviations not significant. To confirm this claim from the F test, we may use the T test. Instead of comparing the two standard deviations from the data sets, the T test compares the means from the data sets. The \(t_{\text{calculated}}\) was determined to be 2.62 using the t test equation. The degrees of freedom are obtained by adding the number of data points for data set 1, \(n_1\), and adding it to the number of data points from the other set, \(n_2\), and subtracting 2. This gives our degrees of freedom value to be 8 with a 95% confidence interval gives us a \(t_{\text{table}}\) value of 2.306. Comparing this \(t_{\text{table}}\) value to the \(t_{\text{calculated}}\) value, we see that \(t_{\text{calculated}}\) is smaller than the \(t_{\text{table}}\) value which illustrates that the differences in the means obtained through GC and FT-IR are statistically different from each other. In conclusion, since the \(F_{\text{calculated}}\) is less than the \(F_{\text{table}}\) value, the data set is not significantly different based on their respective standard deviations. In addition, since the \(t_{\text{calculated}}\) value was greater than the \(t_{\text{table}}\) value, the two data sets are considered to be significantly different.

Based on the confidence intervals, both methods are extremely accurate. The overlap is more prominent in GC because it has a derived \(x\) of 10% which is very accurate considering the expected value was 10%. The confidence interval shows that we are 95% confident that it falls within a smaller range of values compared to the IR which has a slightly greater confidence interval. The precision of the two instruments are about the same, both having only 5% ethanol uncertainties. It should be noted, however, that the 5% uncertainty can be large relative to the actual percent of ethanol in gasoline. The uncertainty is half the actual value and such creates a huge range for the values to lie in. Taking more replicate measures in the future would decrease this uncertainty range and provide more precision in the data.

The precision of the calibration curve shows a great deal about the precision of the experiment as well. Using the coefficient of determination, \(R^2\), we can determine how linear the relationship of our standards are. For GC, the \(R^2\) value is 0.9736 which is fairly linear. The most ideal \(R^2\) value is 1 so the GC standard addition curve is adequately high. For FT-IR a similar \(R^2\) value was obtained with 0.9753 which is slightly higher than the GC. The slightly higher \(R^2\) value illustrates the linear more linear relationship for standard additions which means that the standards were prepared more accurately. The derived \(x\), however, was not closer to the true value having 13%\((\pm1)\) percent ethanol and a larger confidence interval.

As stated, both are precise and accurate instruments for the analysis of ethanol in gasoline. The limit of detection was also found to be lower than the lowest concentration analyzed shown in table 2. The lowest % volume of ethanol added was 2.4% for FT-IR so it is in the accepted range for detection using FT-IR. The limit of detection (LOD) was 1 which is smaller than the smallest volume of ethanol added. With GC, the lowest volume percent added was 2.4% ethanol. Since the LOD is 0.5 volume percent ethanol added, we may keep the data points that are above 2.4. Both the FT-IR and GC are utilized to look at the 0% ethanol added but it should be noted that this the amount of ethanol added. Therefore, this data point should still be utilized because the gasoline still contains 10% of ethanol. This means that FT-IR and GC both have legitimate points to use because the ethanol volume percent content will always be above their respective LOD. The LOQ was 2 and 3 for GC and FT-IR respectively which are also smaller than the lowest concentration detected for each instrument.
The more sensitive method is GC compared to the FT-IR with a sensitivity of 6 vol%\(^{-1}\) compared to 3 vol%\(^{-1}\). This can be seen just by looking at the response values where GC maximizes at 240,000 response values for a given measurement and FT-IR only goes up to 1.7. Therefore, GC must be more sensitive at measuring responses from the detector. The sensitivity, however, is not always a good thing. As values get larger on the FT-IR, the values get logarithmically larger and introduce exponential amounts of error. It is important to choose a peak on the FT-IR that extremely small and gets slightly larger after each standard addition as to not introduce error. The math can confirm that this error is apparent when the data gets near 4 and 5 on the response. Getting a response near 4, the detector would be trying to analyze fractions of light and introducing more error as less light travels to the detector. Staying near a response of 1 will allow the maximization of light to enter the detector with greater accuracy and ensure no information is lost.

In addition, errors are abundant in the technique used to transfer the various amounts of ethanol spikes into each sample of 1.000 mL of gasoline. In this experiment, we used two different pipets: the micropipette and the volumetric transfer pipets. Using two different techniques may throw off the results as well. In our experiment, I noted that the last data point could be different because we used a volumetric pipet for the first samples but the last sample we used the micropipette. I noted this in my lab notebook in case thinking that it might change our results of our calibration curve, making a smaller linear relationship. In the GC, there was a large outlier which was responsible for the error associated with the micropipette.

There are many errors due to the pipet itself depending on when the last calibration was done and the age of the pipet. As the pipet ages, the mechanical internal parts degrade and offer decreasing amounts of accuracy and precision so the age must be taken into account. The pipets in lab were of unknown age and contributes to the error. Also, additional measures to calibrate the pipet such as cleaning, seal replacement, and lubricant\(^2\) must be done at least every 2 months to stay within the confidence interval of 95\% of the pipet. There are obvious errors that can be associated with the pipets and some may even deliver up to 10\% more or less from the intended value. The pipet used in lab was a P200 which as a range of 20-200 µl but error can be associated with it as well. Since we only added 25 µl, 50 µl, 75 µl, and 100 µl, the pipet has varying degrees of error. As you get closer to the bottom limit of the pipet, there is more error than the top limit of pipet. The misconception is that the level of error form the pipet is linear with all values in its range but that is incorrect. The smallest volumes taken up by the pipet are the ones with the greatest error so the added ethanol in our experiment has varying of error. Micropipets are calibrated at sea level pressure which the laboratory is not. The lab is located at California State University, Fullerton where the elevation is around 150 feet above sea level\(^4\) which also may affect the calibration of the pipet if the pipet has not been calibrated since it was bought.

The transfer volumetric pipet also has some tolerances associated with the delivery of how much liquid it expels. For this experiment, we measured out 1.000 mL but the tolerance is \(\pm 0.006\) mL which would equate to 6 µL\(^2\). The 6 µL tolerance is small but still a factor to consider when pipetting amounts of gasoline to start with.

For future gasoline analysis studies, I would modify the methods by adding more percent volume ethanol added to each so to increase the n amount of data points. Getting a \(R^2\) value closer to 1 will also help with the accuracy of the experiment. Both methods are valid methods to determining the volume percent in ethanol and great methods for anyone to learn as an analytical chemist.

**Conclusion**

Gas chromatography and Fourier transform infrared spectroscopy are both exceptional methods to analyze and quantify the amount of ethanol in a mixture of gasoline. By using standard addition and spiking the samples with known concentration and volumes of ethanol, we may visually see the peak of ethanol rise. This allows the quantification of ethanol based only on the ethanol present. All other compounds in solution will be constant due having the same concentrations in all 5 samples. Therefore, the ethanol will selectively be identified solely from its peak height increases. The two methods both hit the expected value of 10\% having 10 (±1) \(\pm 5\) volume percent ethanol for GC and 13 (±2) \(\pm 5\) volume percent ethanol for FT-IR.
percent for IR. The confidence intervals of both 5% show that, at the 95% confidence interval, our measurement is within 5% of the true value. This is apparent and such both instruments are valid in use for the analysis of ethanol in gasoline.

References


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