From Corn Cobs to Gas Tanks

Determining the amount of alcohol in gasoline

Octane ratings and gasoline

In most gasoline engines, the air-fuel mixture is triggered to burn rapidly by a spark plug. If that mixture is compressed too much, it may self-ignite. When self-ignition occurs, it creates a higher pressure than the engine components are designed to withstand. The result is a "knocking" or "pinging" sound coming from the engine. In severe cases, knocking can cause major engine damage.

Most car engines today have a knock sensor that monitors whether a fuel is causing knock in the engine. If knocking is detected, the sensor will automatically adjust the ignition timing to reduce the knock.

One of the typical components of gasoline are octanes, a family of hydrocarbons containing eight carbons. They are colorless liquids that boil around 125°C (260°F). One member of the octane family is 2,2,4-trimethlypentane (isooctane).

Octane ratings (octane numbers) were developed using the isooctane molecule as a standard benchmark for the tendency of gasoline mixtures fuels to resist self-ignition or knocking. An octane rating of 100 is assigned to pure isooctane (100% isooctane, low knock). A second molecule also present in gasoline and used in octane testing is heptane, which has seven carbons, and has an octane rating of 0 (0% isooctane, high knock).

A test engine is used to determine the octane rating of a gasoline sample. The tested fuel sample results are then compared to a reference fuel containing isoctane and heptane that has the same anti-knocking capacity. The percentage of isooctane in that reference mixture is the octane number of the tested fuel sample. For example, gasoline with the same knocking characteristics as a mixture of 90% isooctane and 10% heptane would have an octane rating of 90.

An octane rating does not mean that the gasoline contains only isooctane and heptane. Gasoline sold for common use never consists solely of isooctane and heptane. Today's gasoline mixtures contain many hydrocarbons and often other additives. In fact, some current fuel mixtures are more knock-resistant than pure isooctane, which means that it is possible for a gas mixture to have an octane rating greater than 100.

Ethanol in gasoline mixtures

Fuel components that boost octane ratings are generally more expensive to produce. An exception is ethanol (ethyl alcohol, EtOH). This alcohol, often produced from corn, has an octane rating of 109. With a large increase in ethanol production since 2000, refiners have been adding ethanol to the gasoline mixture to improve octane ratings. Most gasoline in the U.S. contains up to 10% ethanol.

With such a high octane rating, consumers may question why a greater percentage of ethanol is not added to U.S. gas mixtures. The octane rating is not the only thing to consider when developing a fuel mixture—it is merely a measure of a fuel's blend and its tendency to burn in a controlled manner. Octane ratings are **not** indicators of the energy content of fuels. Fuels blended with ethanol to raise the octane number have less energy content per volume. This means that as the ethanol content increases, fuel economy decreases (miles per gallon goes down). Most premium gas blends contain no ethanol.

Alcohol and small engines

The difference in combustion characteristics between ethanol and gasoline may cause even bigger issues with two-cycle engines (e.g., lawn mowers, garden equipment, marine engines, and ATVs). Most two-cycle engines do not have the sensors that automobiles have to prevent knocking.

Because ethanol is a strong solvent, it can break down sludge and other deposits in the fuel system. When released into the fuel system, these deposits can clog ports and jets in the engine and reduce performance. Ethanol may also dissolve or otherwise damage plastic, rubber (gaskets), and other hose materials found throughout a two-cycle engine, especially in older equipment. Many engines today are built with plastics able to withstand ethanol, but there is no universal manufacturing date that identifies when these ethanol-resistant properties were incorporated into small engines.

Finally, ethanol mixtures in gasoline increase the risk of water absorption into the fuel tank, which is especially true when the fuel mixture sits in the tank for long periods of time. Water and ethanol are both polar molecules. The more ethanol in the gas mixture, the greater affinity the mixture will have for absorbing water in humid or marine conditions.

Removing alcohol from gasoline

Ethanol can easily be separated from a gasoline mixture based on the "like dissolves like" solubility principle. The majority of components in gasoline (octanes, heptanes) all tend to be nonpolar (covalent) in nature. Ethanol and water, on the other hand, are small polar molecules. Based on "like dissolves like", if water is added to a gasoline mixture, the ethanol will dissolve in water and will be removed from the nonpolar gasoline.

Purpose

To experimentally determine the percentage of alcohol in gasoline mixtures with different octane ratings.

Procedure

Part A: Removing the alcohol from gasoline

1. Carefully add 10–15 mL of distilled water to a burette.
2. Record the initial burette reading (water level).
3. Carefully add 35–40 mL of a gasoline mixture.
4. Record the brand of gasoline and its octane rating.
5. Record the final burette reading.
6. Gently stopper the top of the burette with a **cork** stopper (do **not** use a rubber stopper).
7. With a thumb over the stopper, carefully invert the burette 2 or 3 times.
8. With the burette inverted, open the stopcock to relieve any buildup of vapor pressure in the burette. ***Caution: Gently cover the tip of the burette with a paper towel to prevent the spray of small amounts of liquid from the burette.***
9. Close the stopcock and repeat steps 7–8.
10. Place the burette in the clamp and allow the contents to settle for several minutes (3–5). Two layers should become visible.
11. Measure and record the "new" volume of the water layer (bottom layer).
12. Using the stopcock, carefully separate the water layer from the gasoline layer.
13. Store the separate layers in labelled glass containers. Use cork stoppers.

Lab Data Part A

Octane rating	________	
Brand of gas	________	
Initial burette reading (water, Step 2)	________	mL
Final burette reading (water + gas, Step 5)	________	mL
Water layer reading (after mixing, Step 11)	________	mL
Gasoline volume (Steps 2–5)	________	mL
Alcohol volume in gas (Steps 2–11)	________	mL

Calculate ethanol in your gasoline sample as the percent by volume:

$$\% \text{ volume} = \frac{\text{alcohol volume}}{\text{gasoline volume}} \times 100 = \frac{\quad}{\quad} \times 100 = \_\_\_\_ \ \%$$

NMR spectroscopy

Spectroscopy is a scientific measurement technique. It measures electromagnetic radiation that is emitted, absorbed, or scattered by materials and can be used to study, identify, and quantify those materials.

Nuclear magnetic resonance (NMR) spectroscopy is one of the main methods of analysis for organic compounds. In many cases, NMR provides a way to determine an entire structure using one set of analytical tests. The most common type of NMR is proton NMR (^{1}H NMR). The medical technique of magnetic resonance imaging (MRI) uses similar principles for molecules inside the body.

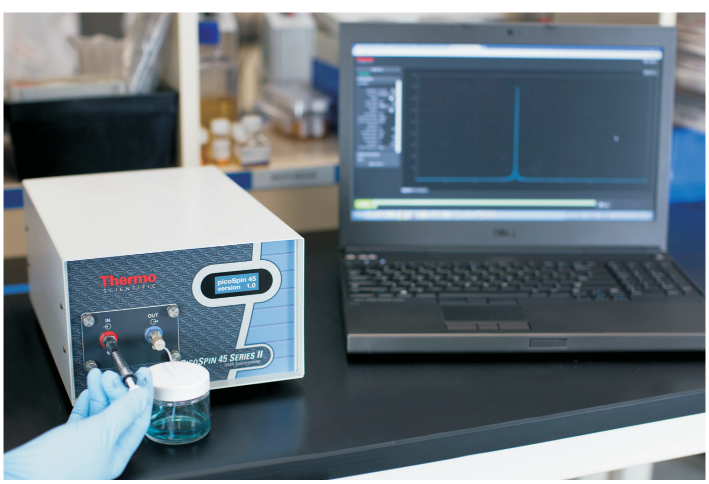
All atomic particles possess a property know as nuclear spin. In isotopes with an odd number of protons and neutrons, the nucleus is said to have a "half integer spin" and it is observable by NMR spectroscopy. Ordinary ^{1}H with only a single proton in the nucleus has a nuclear spin of ½ and can be detected by NMR. The spinning, positively-charged protons create a magnetic field, making the nucleus of ^{1}H behave like tiny magnet.

When these nuclei are placed between the poles of a powerful magnet, they align their magnetic fields either with or against the field of the larger magnet. When radio waves are applied at a specific frequency, known as the Larmor frequency, the orientation of the nuclei can be changed into an excited state. This is known as spin flip. When the radio frequency is turned off, the nuclei spin flip back to their original orientation. We can observe this relaxation using an NMR spectrometer, and a computer to analyze the results.

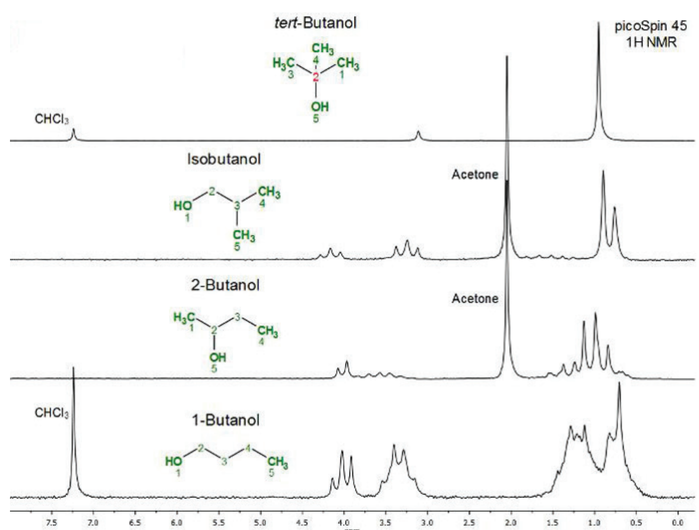
The key is that not all ^{1}H nuclei flip their spins at precisely the same frequency in the radiowave spectrum. Hydrogen molecules in different chemical environments (where they are bonded to different atoms or have different atoms surrounding them) will spin flip at different frequencies of energy. Because of this, different hydrogen environments will produce unique peaks in the NMR spectrum, which is how it is used to identify organic molecules.

NMR spectra of four different molecules

Another valuable aspect of ^{1}H NMR is that the area under each peak is ideally proportional to the number of hydrogens producing that peak. A convenient way of analyzing peak areas is to "integrate" the peak intensity, to convert the area of the peak into a distance. This distance is routinely printed onto a ^{1}H NMR spectrum as a vertically stretched S-shaped curve. The height of the integration line is proportional to the number of hydrogens. The ratio of the number of hydrogens is determined by measuring the height of each integration line in the spectrum. This



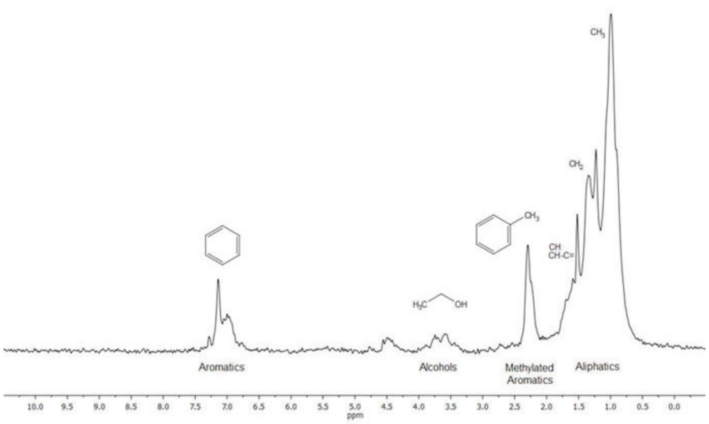
Thermo Scientific™ picoSpin™ 45 Series II NMR Spectrometer



ratio can be very helpful in determining the structure of an unknown substance using NMR. Note that for the purposes of this lab, integrations are only approximate values.

NMR spectrum for ethanol/gas mixture

If compounds are present in a bulk mixture containing hydrogen nuclei that spin-flip in a unique NMR region, rapid identification of these compounds can be made. Using integration, the concentration of that substance in the mixture can also be determined.

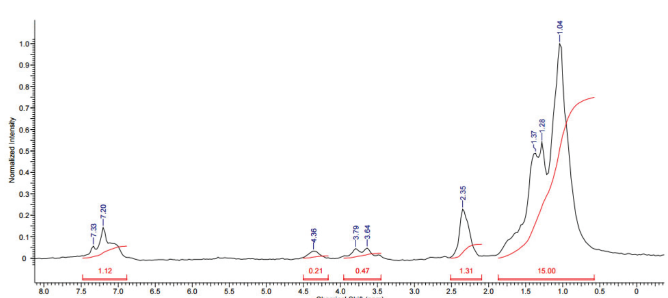


The position of a signal in the 3.5–3.75 ppm range is unique to alcohols, incuding ethanol in gasoline samples (see NMR above). Therefore, the integration of the NMR peak area between 3.5–3.75 ppm is directly proportional to the concentration of the ethanol in the gasoline sample (see NMR below).

By plotting peak area versus ethanol percentages for a known set of standards into a graph of standards (standard curve), you can determine the percentage of total peak area in an unknown. Use the peak area produced by ethanol in a gas mixture from the NMR integration values above to calculate (see calculation in the next column).

Gasoline spectrum with integration

Using NMR integration:

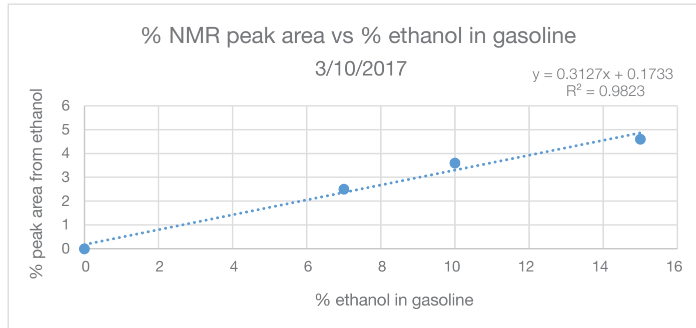


Peak area from ethanol = 0.47

Total peak area = 1.12 + 0.21 + 0.47 + 1.31 + 15.00 = 18.11

$$\frac{\text{peak area from ethanol}}{\text{total peak area}} \times 100 = \frac{0.47}{18.11} \times 100 = 2.5\%$$

Using the equation of the line from the graph of standards to find the percentage of ethanol:



Using 2.5% as y (the integrated peak area from ethanol in the NMR in the previous column) as y, the equation for the graph of standards provided above, and solve for x:

y = 0.3127x + 0.1733

2.5% = 0.3127x + 0.1733

2.3267 = 0.3127x

7.440% ethanol = x

Part B: Determining the percentage of alcohol in a gasoline mixture using NMR spectroscopy

1. With the help of your instructor, determine the NMR spectrum for your gasoline mixture.
2. Using the integration from the spectra, find and record the peak area from the alcohol.
3. Using the integration, find and record the total peak area from the sample (see example above).
4. Calculate the percentage of the peak area caused by the alcohol (see example above).
5. Using the graph of standards provided above (% peak area vs % alcohol graph), calculate the percentage of alcohol in the gas mixture (see example above).
6. Print and include spectrum with lab.

Lab Data Part B

Name ______________________________

Peak area from alcohol	__________
Total peak area	__________
% peak area from alcohol	__________
% alcohol in gasoline	__________

Show your work for calculating % peak area from alcohol:

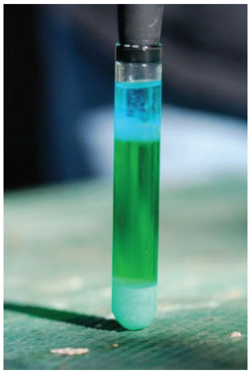
Show your work for calculating % alcohol in gasoline mixture:

Part C: Proof that alcohol was removed using NMR spectroscopy

1. With the help of your instructor, determine the NMR spectrum of the remaining gasoline layer following your separation in Part A.
2. Print the spectrum and, using a pen or pencil, identify where you would find the ethanol peaks on the NMR spectrum.
3. Print and include the NMR spectrum with the lab.

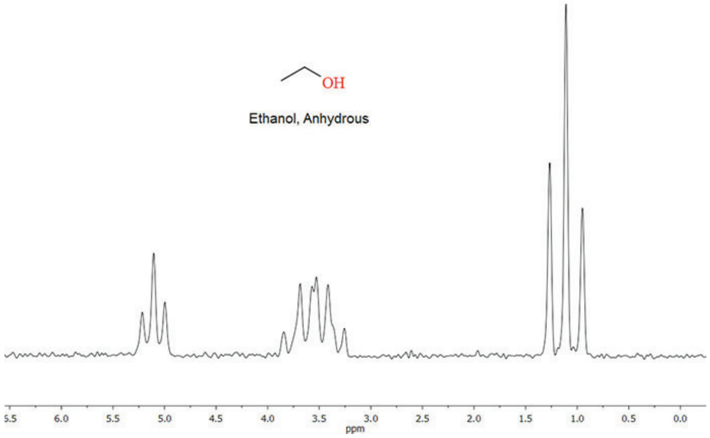
Optional Part D: Removal of the ethanol from the water

Salting out



When the salt concentration (ionic compound) in a solution is increased, some of the water molecules are attracted by the salt ions. This attraction decreases the number of water molecules available to interact with the charged part of other polar molecules. As a result of the increased demand for water molecules, the solubility of nonionic (nonpolar) substances decreases. Nonionic substances are literally pushed out of the water solution and create their own organic layer. This process, known as salting out, is used in this lab to separate ethanol from water.

1. In a test tube, add 2.0 grams of potassium carbonate (K_2CO_3) to the water/alcohol mixture.
2. Stopper and shake vigorously for several minutes.
3. Rest the mixture, which should separate into two layers. If layers do not form, add 1.0 gram more of potassium carbonate to the mixture and repeat Steps 2 and 3.
4. Allow ample time for the two layers to completely form, then separate the top layer containing ethanol from the bottom layer containing salt water using a pipette.
5. To verify the successful isolation of ethanol, remove 2–3 mL of the ethanol layer using a pipette and test the purity of the sample using the Thermo Scientific™ picoSpin™ NMR spectrometer.
6. Include your sprectrum with the lab.



Lab conclusions*

1. **What percentage of alcohol did you find in your gasoline sample?**

   Burette ________________ %

   NMR ________________ %

2. **Do the two methods of determining % alcohol correlate with each other?**

3. **What proof do you have that you actually removed the alcohol from the gasoline?**

4. **If a person uses an gas/ethanol blend in their car and water gets into the gas tank, what will happen inside the gas tank and how will it affect the performance of the car? You may want to draw a diagram.**

5. **There are many commercial products, like HEET® Gas Line Antifreeze, on the market to "remove" water from the gas tank. If this additive contains an alcohol (methanol), does it really remove the water? If not, what does it do to increase the performance of the car?**

6. **Design a "homemade" method for creating premium gasoline.**

*Be sure to include the NMR spectra with these conclusions.

Prelab questions

Name ______________________

1. **What is the structural formula for 2,2,4-trimethylpentane (isooctane)?**

2. **Is octane:**

   - ☐ ionic?
   - ☐ polar covalent?
   - ☐ pure covalent?

3. **What is the structural formula for ethanol?**

4. **Is ethanol:**

   - ☐ ionic?
   - ☐ polar covalent?
   - ☐ pure covalent?

5. **What is the structural formula for water?**

6. **Is water:**

   - ☐ ionic?
   - ☐ polar covalent?
   - ☐ pure covalent?

7. **If gasoline, ethanol, and water are added to a container and mixed, based on the rule of "like dissolves like" what do you expect to happen? You may want to draw a diagram.**

8. **Why is ethanol added to gasoline mixtures?**

9. **What disadvantages, if any, are there for using a gas/ethanol mixture in your car?**

10. **What disadvantages, if any, are there for using a gas/ethanol mixture in small engines (lawn mowers, ATVs, boat engines)?**

11. **What is NMR spectroscopy?**

12. **What element does proton NMR spectroscopy detect?**

thermoscientific

13. **What makes NMR such a valuable tool for organic chemistry?**

14. **Identify two ways you will be using NMR spectroscopy in this lab.**

15. **A gasoline sample produces an NMR spectrum and 2.95% of the peak area comes from ethanol in the gas mixture. Use the graph of standards provided to determine the percentage of alcohol in the gas sample.**

16. **What is "salting out"?**

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