DETERMINING THE COMPOSITION OF GASOLINES USING A GAS CHROMATOGRAPH

(Revised: 2-6-96)

BACKGROUND INFORMATION

TEL and Gasoline

"Knocking" or "pinging" in internal combustion engines is a complex phenomenon. For example, engine "knock" can be caused by incorrect compression ratios, pre-ignition of the gasoline-air mixture, or flaws in the engine design. These characteristics can disrupt piston speed and travel, and this can cause engine "knock".

Research on engine knock began in the early 1920's. The research suggested that the chemistry associated with the fuel (gasoline) was primarily responsible for engine knock. This led scientists to explore various "anti-knock" additives that could be combined with the fuel to either reduce or eliminate engine knock. One of the most effective "anti-knock" fuel additives that was



discovered was tetraethyl lead (TEL). This compound reduces engine knock because it increases the octane rating (see below) of the gasoline. Even though TEL was known to be extremely toxic, it did not take long before refineries started producing gasoline containing TEL. In May of 1925, forty-five cases of lead poisoning were discovered among workers at a gasoline-producing pilot plant. This caused the federal government to issue regulations that limited the amount of TEL that could be used in gasoline to

3 mL per gallon.

There were some other problems associated with the use of TEL in gasoline, too. For example, the use of gasoline containing TEL caused the accumulation of lead deposits in the engine which decreased engine performance. This problem was eventually solved by adding compounds like ethylene bromide and ethylene chloride to the TEL-containing gasoline. When the gasoline was burned in the engine, the TEL was converted to lead bromide and lead chloride. Lead bromide and lead chloride are sufficiently volatile at engine temperatures that these compounds could easily escape from the cylinders in the exhaust gases.

As mentioned above, the addition of TEL to gasoline increases the octane rating of the gasoline and reduces engine knock, but how is the octane rating of gasoline actually measured? The American Society of Testing and Materials (ASTM) has specified a procedure that is used for this purpose. The octane rating is determined by first burning the gasoline in a special one-cylinder engine. The results of these tests are then compared with two reference compounds

to determine the octane rating for the gasoline. The two reference compounds are *n*-heptane (C_7H_{16}) , which has been assigned an octane number equal to zero, and *iso*-octane, or 2,2,4-trimethylpentane (C_8H_{18}) , which has been assigned an octane number of one hundred.

Before 1970, TEL was the most widely used additive to increase the octane rating in gasoline. However, concerns about the toxicity of lead compounds in the atmosphere has resulted in the discontinued use of TEL in gasoline. Now, other compounds which do not contain lead are being used to boost the octane ratings of gasolines. For example, toluene (C_7H_8) is one of the most popular additives being used today. Toluene is advantageous for two reasons. First, it has an octane rating of about 120 which makes it a very effective anti-knock additive. Second, because toluene is a hydrocarbon (i.e., it contains only hydrogen and carbon atoms), it produces primarily carbon dioxide and water when it is burned. These compounds are much less hazardous than compounds containing lead. Finally, two other additives that are currently being used are methanol (CH₃OH) and ethanol (CH₃CH₂OH). These compounds are called "alcohols" because they contain an "-OH" group. Unfortunately, methanol-water mixtures are corrosive toward plastics and metals. This is problematic because small amounts of water can be introduced into gasoline tanks even under normal use (i.e., condensation of moisture from the atmosphere).

Thus, when methanol is used as an additive in gasoline, other higher molecular weight alcohols must also be added to reduce these corrosive properties.

In this experiment, you will use the method of "gas chromatography". First, you will study the chemical and physical properties of several of the common components in gasoline. Then, you will see if you can detect any differences in the chemical compositions of two different blends of gasoline (i.e., Blend A and Blend B). You should be aware of the fact that gasolines are known to contain over 150 different compounds; however, you will not attempt to separate and identify all of them. Finally, because methanol and ethanol are quite difficult to identify using gas chromatography, you will not study any blends of gasoline containing these compounds.

Gas Chromatography

Gas chromatography is a technique used to analyze mixtures. A **gas chromatograph** is an instrument that can be used to separate and to quantify each component in a mixture. One advantage of this technique is that very small samples (e.g., a few microliters) can be analyzed.

Samples to be analyzed in a gas chromatograph must vaporize easily. Once vaporized, the gaseous sample is carried through a long tube containing a porous material. The porous material is often called the **stationary phase**. This long tube is usually referred to as the **column**. Another relatively unreactive gas, such as helium, is used to carry the components of

the gaseous mixture through the column. This **carrier gas** is often called the **mobile phase**. However, the components of a mixture usually do not travel through the column at the same rate, and it is this characteristic that allows the components to be separated from one another.

Which physical and/or chemical properties of the components in a mixture are important for being able to separate them in a gas chromatograph? Although there are many different properties of substances that we might consider, two of the most important properties are molecular weight and boiling point. Generally, components with high molecular weights tend to move more slowly through the column than those with low molecular weights. Moreover, components with high boiling points tend to move more slowly through the column than those with low boiling points. You should be aware of the fact that these are only general trends. Sometimes, factors other than molecular weight and boiling point will also play important roles in determining whether or not components can be separated in a gas chromatograph.

The **detector** in the gas chromatograph that you will use is called a **thermal conductivity detector**. As each of the gaseous components of the mixture pass through the detector, a change in conductivity is detected, and the detector sends a signal to a recorder. These signals create a series of **peaks** on the recorder. The collection of peaks for a particular sample is referred to as a **chromatogram**, and the time that is required for each component to reach the detector is called the **retention time** for that component. The retention time for each component is usually measured at the very top of the peak in the chromatogram. Finally, you should be aware of the fact that an **air peak** is also obtained in the chromatogram when a thermal conductivity detector is used. This peak results from the small amount of air that is injected along with the sample that is being analyzed.

Using the chromatogram, the relative abundance of each component in the mixture can be determined. For example, the relative abundance of each component is related to the area of each peak in the chromatogram. The area of each peak can be found by approximating each peak as a triangle:

Area of peak = (height of peak) x (width of peak at $\frac{1}{2}$ height) x attenuation

There is one additional factor that must also be considered when using the response from a thermal conductivity detector for determining the areas of peaks. The thermal conductivity of different substances tends to vary slightly so the response of the thermal conductivity detector will also vary slightly for different substances. Therefore, a correction factor will be used for each component in the mixture to account for any conductivity differences.

After the corrected peak areas have been determined, the relative abundance of each peak (i.e., component) can be calculated by: (1) dividing each peak area by the smallest peak area and

(2) comparing the resulting ratios.

INTRODUCTION TO THE EXPERIMENT

Gasoline is a complex mixture of over 150 different substances, consisting of alkanes, cycloalkanes, aromatic hydrocarbons, and additives. We will focus just on the six main components in gasoline. After we have analyzed some known compounds (standards), we will compare them with the results of our analyses on various samples of gasoline. Note that the alcohols that are found in some brands of gasoline have boiling points too close to some of the other components and thus cannot be analyzed in this procedure.

PURPOSE

To examine the composition of various grades of gasoline using gas chromatography.

SAFETY

Goggles/aprons

<u>*Caution*</u>: Injection port is <u>very hot</u>. Other parts of the instrument are also hot enough to cause burns.

Syringes are very delicate and sharp. They must be handled with extreme care.

The various controls on the instrument have been preset for you. **DO NOT MAKE ANY ADJUSTMENTS**.

GASOLINES ARE VERY VOLATILE AND VERY FLAMMABLE. DO NOT HAVE ANY OPEN FLAMES IN THE ROOM DURING THIS EXPERIMENT. VAPORS HAVE BEEN DETERMINED TO BE AN INHALATION HAZARD. DO NOT BREATH GASOLINE VAPORS.

PRE-LAB QUESTIONS

1a. Look up the chemical formulas, molecular weights, and boiling points for each of the following compounds. Some or all of these compounds may be in the sample you will be investigating. A table is provided on the next page.

PRE-LAB TABLE #1

compound	chemical formula	molecular weight (g/mol)	boiling point (°C)
<i>n</i> -pentane			
<i>n</i> -hexane			
<i>n</i> -heptane			
toluene			
benzene			
xylene			
methanol			
ethanol			

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b. Predict the order of separation based on both the molecular weights and the boiling points.

c. The mixture you will be analyzing will be carried through the column by the mobile phase. Identify the mobile phase.

2a. Read the *Scientific American* article, "Gas Chromatography," by Roy A. Keller. (Keller, Roy A. (1961). Gas Chromatography. *Scientific American*, **4**, 58-67.) Summarize in your own words the history of the gas chromatograph in a minimum of four well-developed paragraphs.

MATERIALS

Gas Chromatograph 10 µL syringe metric ruler

Standard compounds: *n*-pentane *n*-hexane

n-heptane benzene toluene xylene methanol ethanol

Gasoline Blend A Gasoline Blend B

PROCEDURE

Equipment Settings:

GC:

Gas pressure:	40 psi
Flow Rate:	45-50 mL/min
Injection Port Temperature:	As per instructions on the side of the GC
Column Temperature:	As per instructions on the side of the GC
Detector Temperature:	As per instructions on the side of the GC
Bridge Current:	100 mA
Attenuator:	8

Recorder:

Range: Speed: 2 mV/cm 2 cm/min

1. You will work in teams of four. Each team will first quietly work on parts 1 and 2 of the PRE-LAB QUESTIONS.

2. Your teacher will notify your team when it is time to use the gas chromatograph.

3. Gas chromatograms for the standard compounds will be completed by sharing data with another group using the <u>same</u> GC. Each person will inject one of the four standards assigned to your group.

4. Each group will analyze a sample of each of the two blended gasolines. You will need to change the chart speed to 6 cm/min for the blended gasolines.

CLEANING THE SYRINGE

5. Clean the syringe by inserting the needle into the sample to be analyzed and drawing up 5-10 μ L of the liquid. Depress the plunger of the syringe to discard the liquid onto paper towel as described by your instructor.

6. Repeat step 5 at least three times.

PREPARATION FOR INJECTING SAMPLE

7. Draw 10 μ L of the sample into the syringe.

8. While holding the tip of the needle over the waste container, depress the plunger to exactly 1 μ L (no more than 1 μ L should be injected into the GC; when injecting pure substances, use only 0.5 μ L samples).

9. Carefully pull back the plunger to the 8 μ L mark to draw up some air. The air in the syringe will produce the **air peak** in the chromatogram.

INJECTION OF SAMPLE

10. Prior to injection, check the baseline on the recorder for alignment. If it is not properly aligned, obtain help from your instructor.

11. Carefully insert the needle into the injection port. **REMEMBER THE INJECTION PORT IS VERY HOT**. Quickly depress the plunger and remove the syringe.

12. Examine the chromatogram as it is being plotted. Your chromatogram should begin with an air peak. Also, your chromatogram should end with a flat, continuous baseline after each component (peak) has passed through the detector. On your chromatogram record the following information:

- a. Attenuator setting
- b. Sample size
- c. Identity of sample
- d. Chart speed
- 13. When your chromatogram is complete, remove it from the chart recorder.
- 14. Return to your work area.

15. Disregarding the air peak, label each successive peak at its top, beginning with #1, #2, ..., etc.

Record each peak number in the appropriate space on your data table.

16. Using a metric ruler, draw the baseline of the chromatogram through the bottom of each peak.

17. Measure the peak height and the peak width at $\frac{1}{2}$ height to the nearest tenth of a centimeter for each peak. Record these measurements in the appropriate space in the DATA/CALCULATION TABLE #1.

CALCULATIONS SHOW ALL WORK!

1. Using the chromatograms for the standard compounds, measure the retention time for each standard. To do this, measure the distance from the top of the air peak to the top of the each standard's peak. Then, calculate the retention time (in minutes) for each peak using the chart speed that you recorded previously. Record your results in the appropriate space on REFERENCE TABLE #1. Repeat using your data for Gasoline Blend A and Gasoline Blend B and record your results in the appropriate spaces in DATA/CALCULATION TABLE #1.

2. Compare the retention times of the standards with the peaks in your chromatograms for Gasoline Blend A and Gasoline Blend . Identify each component in your gasoline samples and record this information in the appropriate space in DATA/CALCULATIONS TABLE #1.

3. Calculate the area of each peak (in cm^2) for Gasoline Blend A. Do this by multiplying the peak height times the peak width at $\frac{1}{2}$ height times the attenuation. Record your results in the appropriate space on the DATA/CALCULATION TABLE #1. Repeat using your data for Gasoline Blend B.

4. For Gasoline Blend A, correct each peak area using the correction factor for each substance given in Reference Table #1. To do this, multiply each peak area by the correction factor for that substance. This is the corrected peak area and it should be recorded on CALCULATION TABLE #2. Repeat these calculations using your data for Gasoline Blend B.

REFERENCE TABLE #1

substance	correction	octane	retention
	factor	rating	time (min)

<i>n</i> -pentane	0.705	91	
<i>n</i> -hexane	0.637	25	
<i>n</i> -heptane	0.592	0	
benzene	0.525	106	
toluene	0.669	120	
xylene	0.551	118	

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DATA/CALCULATION TABLE #1 Gasoline Blend A

peak #	name of substance	peak height (cm)	peak width at ½ height (cm)	attenuation	peak area (cm ²)	retention time (min)

CALCULATION TABLE #2

peak #	name of substance	peak area (cm ²)	correction factor	corrected peak area (cm ²)	percentage of total

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DATA/CALCULATION TABLE #1 Gasoline Blend B

peak #	name of substance	peak height (cm)	peak width at ½ height (cm)	attenuation	peak area (cm ²)	retention time (min)

CALCULATION TABLE #2

peak #	name of substance	peak area (cm ²)	correction factor	corrected peak area (cm ²)	percentage of total

CONCLUSIONS

1. Why do you pull back on the plunger to 8 µL before you inject the sample? Explain.

2. Differences in which physical property, boiling point or molecular weight, best explains the distribution of peaks on your chromatogram. Explain.

3. At the bottom of each peak in your chromatogram, write the name of the compound most likely indicated by that peak and the percent composition calculated for that compound.

FOLLOW-UP QUESTION

1. Based on the availability of hydrocarbons, how does a refinery manufacture gasolines with different octane ratings?

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TEACHERS' GUIDE DETERMINING THE COMPOSITION OF GASOLINES USING A GAS CHROMATOGRAPH (Revised 2-6-96)

CLASSROOM USAGE Chemistry I, Chemistry II, AP Chemistry

CURRICULUM INTEGRATION

Solutions Percent Composition Physical Properties Molecular weight Bonding/Polarity

REQUIRED KNOWLEDGE

Metric measurement Percent calculation Significant digits Definition of solution Molecular weight Boiling point Operations of a gas chromatograph and underlying principles

PREPARATION

The teacher should use a sample chromatogram to instruct students on mathematical calculations for area determinations of peaks and % composition of a mixture. It is suggested that students be given a practice problem for guided instruction the day prior to the lab. Use a chromatogram which you have obtained previously.

A major consideration in determining retention time in chromatography is polarity. In this experiment, the polarities of all the substances are very similar. Because of this similarity, the students are led to looking at molecular weights and boiling points as other considerations.

In this experiment, the column (stationary phase) used is DNP (2,4-Dinitrophenylhydrazine). DNP is slightly less polar than Carbowax. **PLEASE NOTE:**

THE COLUMN FOR USE WITH GASOLINES IS NOT THE SAME AS USED BY OTHER EXPERIMENTS. BE SURE TO COORDINATE THIS LAB WITH THE PURDUE VAN DRIVER. The mobile phase is helium.

SAMPLES

Samples of references and gasoline Blend A and Blend B will be available from the Chemobile.

<u>TIME</u> Each sample takes approximately 5 minutes to run through the GC.

SUGGESTION

Have students work in rotations by groups of four. Pair two groups together to run the eight standards for sharing between those two groups. Each group then can run one sample of each gasoline blend.

SAFETY AND DISPOSAL

Students should be warned of the hazards of the syringe needle and the hot injection port. Solutions should be disposed of according to Flinn disposal 27J – evaporation in a fume hood.

PRE-LAB ANSWERS

1a. Data Table:

compounds	chemical formula	molecular weight (g/mol)	boiling point (°C)
<i>n</i> -pentane	$C_{5}H_{12}$	72	36.1
<i>n</i> -hexane	$C_{6}H_{14}$	86	69.0
<i>n</i> -heptane	C ₇ H ₁₆	100	98.4
toluene	C ₆ H ₅ CH ₃	92	110.6
benzene	C_6H_6	78	80.1

xylene	CH ₃ C ₆ H ₄ CH ₃	106	139
methanol	CH ₃ OH	32	65
ethanol	C ₂ H ₅ OH	46	78.5

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ANALYSIS

There are two ways to determine the identity of each peak. One way is to run a chromatogram of each standard and compare retention times. The other way is to "spike" the mixture with each standard and observe which peak increases in area. This latter method is called **co-injection**.

CONCLUSIONS

1. The air peak is used as an event marker or a reference point for the time that the sample was injected into the gas chromatograph. By using an event marker we are able to measure the retention time of a particular substance.

2. Boiling point. Because the molecular weights are all approximately the same, the separations must have been due to the differences in boiling points.

3. Refer to student's chromatogram.

FOLLOW-UP QUESTION

ASSESSMENT

A. Activities:

1. Have a chromatogram prepared that consists of an air peak followed by 4 other peaks. Have the areas of each peak already calculated - the students are to calculate the mass percent composition for each of the peaks.

B. Final-portfolio – Report on the history of the gas chromatograph.

CONTRIBUTIONS TO THIS LAB BY: Carol Chen, Chris Fields, Henry Looft, Barrie McClain, James Miner, Carl Schulenberg, and Maria Walsh

REVISED BY: Dr. John Nash, Department of Chemistry, Purdue University

References: GOW-MAC Instructional Manual Model 69-350.
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Experiment #50, Modern Experimental Organic Chemistry by Miller & Neuzil, Western Washington University, D.C. Heath.
Experiment #18, Introduction to Organic Laboratory Techniques by Pavia, Lampman & Kriz, Western Washington State College, W.B. Saunders.