11

DETERMINATION OF THE COMPOSITION OF UNLEADED GASOLINE USING GAS CHROMATOGRAPHY

Purpose: To learn to use a capillary column gas chromatography system

To learn to use column retention times to identify compounds

To learn to calibrate a gas chromatograph and quantify the mass of each peak

BACKGROUND

Petroleum hydrocarbons may well be the most ubiquitous organic pollutant in the global environment. Every country uses some form of hydrocarbons as a fuel source, and accidental releases result in the spread and accumulation of these compounds in water, soil, sediments, and biota. The release of these compounds from underground storage tanks is the most common release to soil systems, and this is discussed in Chapter 16. The drilling, shipping, refining, and use of petroleum products all account for serious releases to the environment.

Crude oil consists of straight-chained and branched aliphatic and aromatic hydrocarbons. Upon release into the environment, some compounds undergo oxidation. Chemical and photochemical oxidation occur in the atmosphere; in water and soil systems, microorganisms are responsible for the oxidation. The analysis of crude oil, and organic compounds in general, has improved enormously with the advent of capillary column gas chromatography. In fact, capillary

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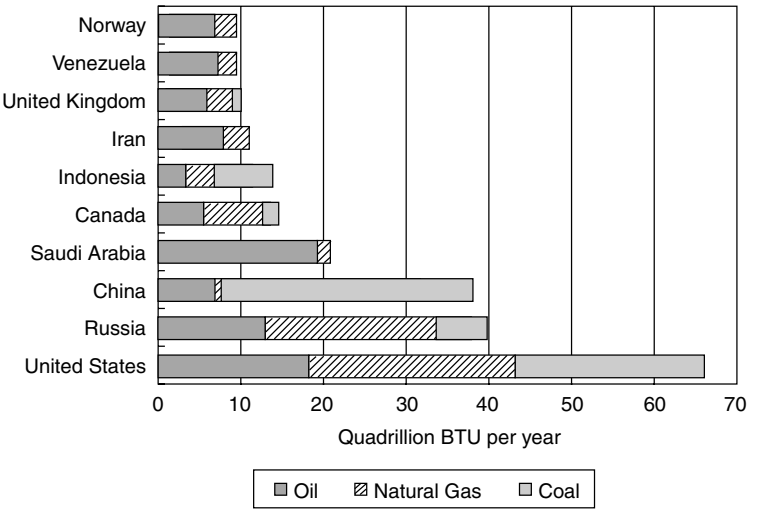

Figure 11-1. Energy production of selected countries. (U.S. EPA, 2002.)

column GC can even identify the country of origin of a crude oil sample based on the chemical/compound composition.

One of the largest problems with respect to the release of hydrocarbons in the environment is that they are hydrophobic (they do not like to be in water). Hydrocarbons are organic compounds and do not undergo hydrogen bonding, and thus do not readily interact with water. As a result, hydrocarbons bioaccumulate in the fatty tissue of plants and animals or associate with organic matter in soils and sediments. Compounds can be toxic at low levels, one of the most common examples being benzene, present in all gasoline products.

Our use of petroleum hydrocarbons is ever-increasing. Figure 11-1 summarizes the production rates for the highest-energy-consuming countries. You will note that the United States produces (and consumes) the most energy per year. But how do we use this energy? Figure 11-2 shows a breakdown of the energy use into

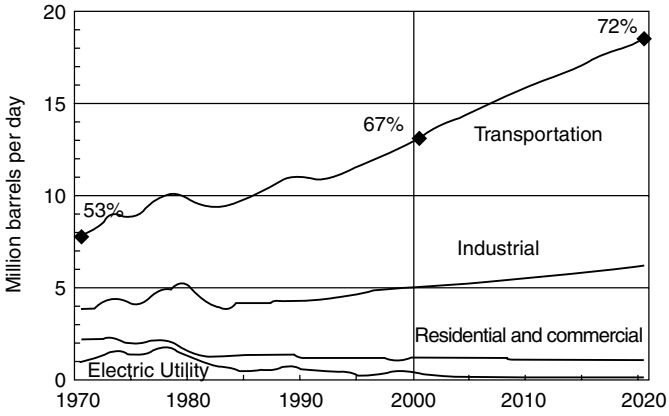

Figure 11-2. Current and predicted energy consumption in the United States. (U.S. EPA, 2002.)

electric, residential and commercial, industrial, and transportation. Transportation, the largest form of consumption, is increasing at an alarming rate. This not only explains the intensive research programs in fuel cell technology but also the geopolitical conflicts in the Middle East.

THEORY

Although it takes months to years to become a good chromatographer, this laboratory exercise will introduce you to the basics of chromatography. There are many highly technical parts to a capillary column GC, including the ultrapure carrier and makeup gases, flow controller values, injector, column, oven, a variety of detectors, and a variety of data control systems. You should consult a textbook on instrumental methods of analysis for details on each of these systems. The basic theory important to understand for this laboratory exercise is that there is generally a separation column for every semivolatile compound in existence. We limit the GC technique to volatile or semivolatile compounds since the compound must travel through the system as a gas. Nonvolatile or heat-sensitive compounds are normally analyzed by high-performance liquid chromatography (HPLC). Compounds are separated in the GC (or HPLC) column by interacting (temporarily adsorbing) with the stationary phase (the coating on the inside wall of the column). The more interaction a compound undergoes with the stationary phase, the later the compound will elute from the column and be detected. This approach allows for the separation of both very similar and vastly different compounds. Vastly different compounds can be separated by relying on the diversity of intermolecular forces available in column coatings (hydrogen bonding, dipole interactions, induced dipole interactions, etc.). Similar compounds are separated using long columns (up to 60 m).

The most important parameter we have for separating compounds in GC is the oven temperature program. If we analyze a complex mixture of compounds at a high temperature (above the boiling point of all of the compounds in the mixture), we do not get adequate separation, and the mixture of compounds will probably exit the system as a single peak. But if we take the same mixture and start the separation (GC run) at a low temperature and slowly increase the oven temperature, we will usually achieve adequate separation of most or all of the compounds. This works by gradually reaching the boiling point (or vaporization point) of each compound and allowing it to pass through the column individually. In this manner, very similar compounds can be separated and analyzed.

You will be using external standard calibration for your analysis. This is the common way that standards are analyzed, in which you analyze each concentration of standard separately and create a calibration curve using peak height or peak area versus known analyte concentration. However, capillary column GC requires that you account for errors in your injections. This is accomplished by having an internal standard, in our case decane, at the same concentration in every sample and standard that you inject. By having the same concentration in every

injection, you can correct for injection losses. (The peak area for the decane sample should be the same; if it is not, modern GC systems correct for any losses.)

For a good summary of the theory and use of a gas chromatography system, see the down loadable GC Tutorial (`http://www.edusoln.com`). Your instructor will have this available on a computer for your viewing.

REFERENCE

U.S. EPA, `http://www.epa.org`, accessed July 2003.

IN THE LABORATORY

This laboratory is divided into two exercises. During the first laboratory period, you will determine the retention times of analytes in an unleaded gasoline sample. For the second laboratory period, you will measure the concentration of several components in the gasoline using external and internal standard calibration.

Safety and Precautions

- Safety glasses should be worn at all times during the laboratory exercise.
- This laboratory uses chemicals that you are exposed to every time you fill your car with gasoline. But this does not reduce the toxic nature of the compounds you will be handling. Many of these are known carcinogens and should be treated with care.
- Use all chemicals in the fume hood and avoid inhaling their vapors.
- Use gloves when handling organic compounds.

Chemicals and Solutions

- One or more unleaded gasoline samples
- Neat samples of *m*-xylene, *o*-xylene, benzene, ethyl benzene, isooctane, toluene, and *n*-heptane

Equipment and Glassware

- Several class A volumetric flasks
- 10-, 50-, 100-, and 500-μL syringes for making dilutions
- 1-, 5-, and 10-mL pipets
- a column gas chromatograph equipped with a DB-1 or HP-1 capillary column (a DB-5 or HP-5 will also work, but retention times will change

GC Settings

- Splitless for the first 2 minutes, split mode for the remainder of the run
- Injector temp.: 250°C
- Detector temp.: 310°C
- Oven:

Oven:	Initial temp.:	40°C
	Hold for:	5 minutes
	Ramp:	10 to 200°C
	Hold for:	20 minutes or less

PROCEDURE

Week 1: Determining the Retention Times

1. Turn on the GC, adjust all settings, and allow the instrument to go through a blank temperature run to clean the system. You may also inject pure pentane for this run.
2. While the GC completes the first blank run, prepare a set of reference standards for determining the retention times on your instrument (with the temperature program given in the equipment and glassware section). You will be using decane (C-10) as your internal standard for all solutions. Absolute retention times may vary slightly between GC runs, and the internal standard will allow you to calculate relative retention times (relative to that of decane) and allow you to identify each peak in subsequent GC runs. This first set of standards does not have to be quantitative since you are only checking the retention time, not the concentration of compound in any of the mixtures. To make the standards, place 2 drops of each compound in an individual vial, and add 2 drops of decane and 5 to 10 mL of pentane to each vial. Pentane serves as a good dilution solvent for this procedure since it is very volatile and will exit the GC early to leave a clean window for your analytes to elute.
3. Analyze each solution using the same temperature program and determine the absolute retention time and the relative retention time with respect to decane.
4. Copy the chromatographs for each member in your group and place them in your laboratory manual.
5. There will be plenty of time to spare during this laboratory period, but in order to finish on time, you should keep the GC in use constantly. While you are waiting for each GC run to finish, you should make your quantitative standards for next week's lab. If you wait until next week to make these standards, you will be leaving lab very late. These standards will contain all of your compounds in each solution, but at different concentrations. Analyte concentrations should be 2, 5, 10, 15, and 25 mg/L in pentane. Each solution must also contain the internal standard, decane (at 30 to 50 mg/L). The internal standard will allow you to identify each analyte based on relative retention time and allow you to correct for any injection errors (see the theory section). Seal the standards well and store them in the refrigerator.

Week 2: Determining the Composition of Unleaded Gasoline

1. Turn on the GC, adjust all settings, and allow the instrument to go through a blank temperature run to clean the system. You may also inject pure pentane for this run.

2. While the GC completes the first blank run, arrange a set of reference standards for determining the retention times on your instrument (with the temperature program given in the equipment and glassware section). Since you used pentane as your solvent, some may have evaporated. Allow your standards to come to room temperature and adjust the volume of pentane in each vial. It is unlikely that any of the other compounds evaporated since pentane is the most volatile compound in the mixture, so you do not have to worry about a change in the concentration of your analytes.
3. Make a pure pentane injection, followed by each standard. Run the standards from low to high concentration. Calibrate the GC or store the chromatograms and use your linear least squares spreadsheet.
4. While the standards are running, make dilutions of the pure gasoline for analysis on the GC. Prepare 100- and 250-mg/L solutions of your gasoline in pentane. You will need only a few microliters of this solution, so do not waste solvent by preparing large volumes.
5. Determine the concentration of each analyte in your samples.
6. While you are waiting for the GC runs to finish, your instructor may have some literature work for you. If not, enjoy the free time and clean the lab.

Waste Disposal

Dispose of all wastes in an organic solvent waste container.

ASSIGNMENT

1. Prepare a labeled chromatogram of a midrange calibration standard.
2. Summarize the concentrations of analytes in your gasoline sample and correct for the internal standard.

ADVANCED STUDY ASSIGNMENT

1. Research the operation of a gas chromatograph in the library or on the Internet. Draw and explain each major component of a capillary column system.
2. How does temperature programming affect the elution of compounds from the GC system?