CHE 226 EXPERIMENT 9

Gas Chromatographic Analysis of a Ternary Liquid System

Reference: D.A. Skoog, D.M West and F.J. Holler, Analytical Chemistry: An Introduction, 7th Ed., Chapters 25 and 25, pp. 638-698.

Unknown Sample Each student will receive an unknown mixture of organics in a small screw-capped septum vial. You do not need to turn in a container for unknown ahead of time.

Appartus.

A Shimadzu GC-17A gas chromatograph equipped with a mass spectrometer. Together the GC/MS is a QP5000 system and is controlled by a Micron PC. Other equipment required for the experiment includes: 5 µl Hamilton syringe and plastic cap sample vials. The GC/MS uses a 30 m 0.5 mm id capillary column paced with a relatively non-polar stationary phase (phenylmethylsiloxane, 0.5 µm thickness). The carrier gas is 99.999% Helium at an inlet pressure of 700 – 800 kPa and a flow rate of 1.1 mL/min. The GC/MS instruments are operated in a split mode with a split ration of 10.

Purpose.

The object of this experiment is to analyze an unknown three component mixture containing hexane, heptane and toluene by comparison of the areas of the three peaks in the chromatograms of the unknown to the areas of a known, standard mixture. The boiling points, molar masses and densities of the three chemicals are: n-Hexane – 69.0° C (bp), 86.17 g/mol (MW) and 0.6603 g/m (d), n-Heptane – 98.4° C (bp), 100.20 g/mol (MW) and 0.6838 g/mL (d) and Toluene – 110.6° C (bp), 92.13 g/mol (MW) and 0.8669 g/mL (d).

Use of Syringes

CAUTION Exercise care not to damage the syringes. If the syringe is operating properly and the attached plunger guide is properly aligned you do not have to push hard on the syringe. Syringes require proper cleaning and handling to give consistent results. After each use, pump the syringe repeatedly in acetone to clean it out. Dry by pumping air in and out of the syringe. The glass will appear frosted when dry. Be careful not to bang the tip of the needle against the bottom of the glass vials when filling or to bend the needle when inserting it into the GC or the septum vial. A syringe costs ~ $100.00 to replace.

Preparation of the Standard Mixture.

Prepare the following standard mixture in a plastic or screw-capped glass vial: toluene (~2.8 ml), n-heptane (~2.0 ml) and n-hexane (~1.3 ml). Try not to heat the vial with your hands and keep it tightly closed as much as possible to avoid loss of the volatile components.

Prepare the standard mixture by (1) accurately weighing (to within 0.1 mg) the empty, capped vial; (2) adding about 2.8 mL toluene using a 5 mL syringe, capping and weighting the vial and cap again, (3) adding 2 mL of heptane, capping and weighing again, (4) quickly adding 1.3 mL hexane, capping and weighing again.

Use a different pipette or syringe for each component. Keep the bottle with the prepared standard solution capped as much of the time as possible to avoid differential losses of the three components and a change in the ratios of the compounds.

Under the experimental conditions used this standard mixture should provide a chromatogram with roughly equal peak heights.

Procedure.

1. Obtain an unknown mixture from the TA.

2. Check with TA regarding operation of the chromatograph. Do not make any adjustments to the instrument. If you're having problems consult the TA.

3. Determination of retention times. Practice using the 5 μL syringe by separately injecting 2 μL of each of the three separate compounds. As soon as you inject a sample press "Start" on the GC.

After injecting each compound separately, you should know which peak corresponds to which compound in the mixture.

4. Now inject 2 μL of your standard. It is important to fill the syringe only immediately before you inject and to recap the vial immediately to avoid evaporation losses. Make sure there are no air bubbles.

Using the appropriate injection volume, obtain at least 3 nicely reproducible chromatograms each for your standard and for your unknown. You need a minimum of 3 values to obtain a reasonable estimate of the precision. "Nicely reproducible" means that the absolute peak area for a particular component reproduces to within about 2 to 3% relative.

EACH STUDENT MUST INJECT AND OBTAIN HIS/HER OWN CHROMATOGRAMS FOR THE COMMON STANDARD AND HIS/HER OWN UNKNOWN EVEN IF WORKING IN PAIRS. ATTACH THE ORIGINALS OF YOUR CHROMATOGRAMS TO YOUR LAB REPORT.

5. Having obtained all the necessary data, consult the instructor about shutting down the instrument. Clean and rinse with acetone and dry all syringes and vials used.

Hazardous Waste Disposal

Waste hydrocarbons (except acetone) are to be disposed of in appropriate labeled waste containers provided by the instrument. CAUTION: DOUBLE CHECK THAT THE WASTE IS GOING INTO THE CORRECTLY LABELED BOTTLES. DO NOT PLACE IN ACID WASTE BY MISTAKE. Place the various sample vials and caps you used in the container provided. Clean up the entire work area before you leave.

Analysis of Data

Individual components are recognized by the position of their peaks with respect to the point or time of injection. The time from injection to the peak maximum is called the retention time and the computer prints the retention time above each peak. The sample report prints the area for each peak. Average the values for each component, calculate the standard deviation and report these data.

For each run, the computer prints out a table that includes retention time (RT) and peak area for each of the components. These data are used as shown below.

For your report, state the retention times for the three components and the corresponding standard deviations in minutes and the mole percent of each component in the unknown mixture along with the respective standard deviations. With proper technique and careful measurement, the standard deviations for the retention times should be ± 0.05 min or less and ±4% relative standard deviation or better for mole percents.

Calculations in Gas Chromatography.

1. Quantitative analysis in gas chromatorgraphy depends on the direct relationship between the peak area in the chromatogram and the amount of material corresponding to that peak in the mixture examined. In more algebraic language this might be stated:

$$\frac{\dfrac{\text{Amt. Component A}}{\text{Total Amt. of Mixture}} \times 10^2}{\dfrac{\text{Area of Peak A}}{\text{Total Area for all peaks}} \times 10^2} = \text{A constant for each cmpd} = \frac{\text{Mole\%}}{\text{Area \%}}$$

This constant or response factor will be unique for each component and can be used to determine the fractional amount of that component in the mixture.

Since, in a ternary mixture such as this there is no clear solute or solvent, the composition of the mixture is best expressed in terms of the mole fraction or mole percent.

$$\text{Mole \% A in Mixture} = \frac{\text{Mole \% A in Std}}{\text{Area \% A in Std.}} \times \text{Area \% Peak A in Unknown}$$

The student should use such a technique to determine the mole % of each of the three compounds in the unknown sample in each of at least three injections and report the mean of those values and the associated standard deviations.