

Determination of Alcohols by Gas Chromatography

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Introduction

The term *chromatography* applies to the separation of chemical constituents in a sample so they can be either detected or utilized individually. *Gas chromatography* (GC) is a method of separating “volatile” compounds (those with a high-vapor pressure or a relatively low boiling point) so that they may be detected individually in complex mixtures. Compounds are separated based on differences in their vapor pressures and their attraction to solid materials inside the instrument (a gas chromatograph or GC). Because the vapor pressure of a given compound is a function of the intermolecular forces between molecules, GC takes advantages in differences in at least one of the properties of matter discussed in lectures and in the text.

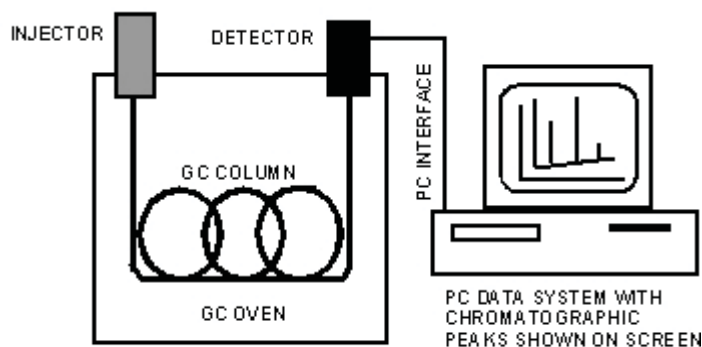
In GC, the sample is injected into the instrument (the gas chromatograph) using a small syringe. The sample is swept into the instrument using a *carrier gas* (usually He) where the sample is separated into its individual chemical components, called *analytes*. Separation is achieved by both attraction to the *stationary phase* (the coating on the inside of the column) and differences in vapor pressure. Because vapor pressure varies with temperature, the temperature of the instrument is often adjusted during the chromatographic run. A detector, which is designed to “sense” analyte molecules as they exit the GC, is at the exit of the column.

We will be using a *thermal conductivity detector* (TCD), in which changes in the properties of the carrier gas are measured. The changes are due to the presence of the separated analyte molecules in the carrier gas stream.

Because the analyte molecules bind differently to the stationary phase, they travel through the GC column at different rates. That is, they have different *retention times* on the column. As an analyte appears in the detector, its presence is signaled by a peak. Thus, a *gas chromatogram* consists of a series of peaks, one for each of the components of the sample. The chromatogram is displayed on a chart recorder or computer screen.

Vapor Pressure

To learn about the vapor pressure of liquids and intermolecular forces, see Chapter 13 of *Chemistry & Chemical Reactivity*.



SCHEMATIC OF A GAS CHROMATOGRAPHY SYSTEM

A chemist would normally inject a sample into the GC and watch as the signals produced by the instrument are displayed on the screen as the chromatogram. Modern instruments save these data on a computer and print it out for later use. They can also *integrate* the signal associated with a given compound. That is, they can determine the area of each peak, an area that reflects the relative amount of the component in the sample. This means that one can perform quantitative analyses using gas chromatography.

An alternative to computer analysis is to record the chromatogram on a chart recorder. The areas can be determined by calculating the area of the peaks based on the assumption that they are triangular in shape.

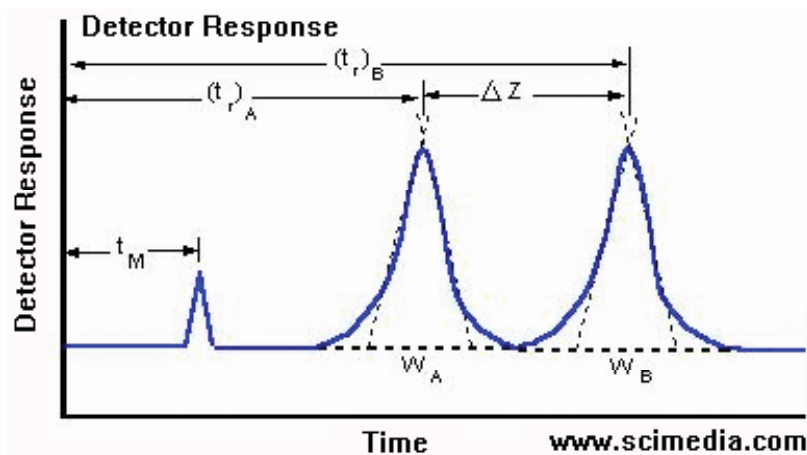
By comparing the areas of the chromatographic peaks the instrument records for both the sample and a standard containing a known concentration of the analyte, one can determine the concentration of the analyte in the sample. Chromatographic peaks can be quantified easily if certain variables are kept constant (e.g. extraction efficiency, amount injected into the GC). Quantitative calculations are often made according to the following relationship, which eliminates the need for a calibration curve if the analyte response is directly proportional to analyte concentration over a wide range.

$$\frac{[\text{Analyte}]_{\text{sample}}}{\text{Peak area of sample}} = \frac{[\text{Analyte}]_{\text{standard}}}{\text{Peak area of standard}}$$

or

$$[\text{Analyte}]_{\text{sample}} = \frac{[\text{Analyte}]_{\text{standard}}}{\text{Peak area of standard}} \cdot \text{Peak area of sample}$$

An example chromatogram is also shown below.



The width of the peak at the base is shown above as W_A and W_B , and the height of the peak is the height above the baseline (the horizontal dashed line above).

In today's experiment, you will be presented with a scenario in which you have been approached by the owner of a chemical products company who is concerned about the quality of his starting materials. He wants to supply a shampoo manufacturer with hexanol and octanol (two materials used to make hair gels), but needs to be sure that his products are free from impurities so he isn't fined by US-SMOB (United States Shampoo Manufacturers Oversight Board). You need to determine which, if any contaminant(s) are in his samples of starting material and how much is there. Any contaminant (any non-hexanol or non-octanol compounds) must be there at concentrations less than 250,000 ppm (parts per million) by volume.

PROCEDURES

NOTE: you should work in a group of three students. The data should be entered in your laboratory notebook.

Part 1: Preparation of the Standard

NOTE: Only one person in the group needs to do this.

1. In a small beaker, prepare a mixture of 1 mL each of pentanol, hexanol, heptanol, and octanol and using a transfer pipet. *These materials are in the fumehood!*
2. Mix well and cover with a watch glass.
3. This is your *Standard*, containing approximately equal concentrations of each analyte (250,000 $\mu\text{g/mL}$ of each analyte). (Each component is 25% by volume of the sample.)

Part 2: Analysis (all three lab partners):

Your instructor will assist you with the operation of the GC.

1. Your instructor will provide you with three *Unknown Samples*, which are mixtures of the four possible alcohols. You will also receive three *Pure Solutions*, each containing one of the possible compounds (pentanol, hexanol and octanol).
2. Inject 10 μL of *Standard* into the "B" injector on the right of the GC.
3. Inject each of the three *Pure Solutions* into the GC. Inject 10 μL volumes. Collect the chromatograms on the chart paper. At the start of each run, mark on the chart paper where the run started. The chart paper moves at a rate of 1 cm/minute. At the end of each run, label the chromatogram with the sample name, injection volume, and other parameters.

You should now know what the retention time is for each of the four alcohols. By comparing the three *Pure Solution* chromatograms with the chromatogram of the *Standard*, you can identify the peaks. The peak for heptanol will be the one in your *Standard* that does not correspond to any of the three *Pure Solution* peaks!

◆ Volumes Injected

Note: your instructor will tell you the exact volumes to be injected if it is not 10 μL .

- Analyze the three *Unknown Samples* by injecting 10 μL of each into the GC. Your *Unknown Samples* may contain one, two, or three of the compounds!

CALCULATIONS:

Two data tables appear below for your convenience.

- For the chromatogram of your *Standard*, measure the distance from the time of injection to the center of each peak in cm. Knowing that the chart moves 2 cm/minute, calculate the retention time for each peak (analyte). Use your *Pure Solution* chromatograms to assign identities to each peak. Record this in Table 1.
- On the *Standard*, Sample 1, Sample 2 and Sample 3 chromatograms, calculate the area of each peak by first assuming it is a triangle. Then, draw a triangle, with all three sides within the peak. Remember that the area of a triangle is $(1/2)(\text{base})(\text{height})$. Calculate the area (in cm^2) for each peak. Record this information in Table 1 and Table 2.
- Using the *Standard Solution*, calculate a "response factor" by dividing the concentration of the *Standard* by the peak area. Your final answer will be in ppm/cm^2 . Record this in Table 1.
- Calculate the concentration of the analytes you observed in *Unknown Samples* 1-3 by multiplying the peak area for those samples times the response factor. Be sure to use the unique peak areas and response factors for each analyte (refer to **Table 1** for this information). If an analyte is not present in the sample, you would not see a peak, and would not calculate a concentration for it. It would be "not detected".
- Finally, calculate the *percent composition* of each sample.

POST-LAB QUESTIONS:

- Did any of your samples exceed the 250,000 $\mu\text{g}/\text{L}$ contaminant concentration threshold? If so, which ones?
- Since GC separations are based on (among other things), boiling point differences in compounds, the compound with the lowest boiling point usually elutes (comes off the column) first and has the shortest retention time. What are the boiling points for the compounds you are interested in? Do their retention times make sense when compared to the order of their boiling points? [Hint: Boiling points can often be found in sources such as the *Merck Index* or the *Handbook of Chemistry and Physics*.]
- Include in your report (taped or stapled into your laboratory notebook), the structures of the compounds. You may draw them by hand or get them from a source such as CAChe or the *General Chemistry Interactive CD*.

Parts Per Million

Note that mg/L is the same as $\mu\text{g}/\text{mL}$ is the same as parts per million.

Table 1: Initial Concentrations and Chromatographic Results (mg/mL = ppm)

Standard	Retention Time minutes	Concentration (ppm)	Area (cm ²)	Response Factor (ppm/cm ²)
1		250,000		
2		250,000		
3		250,000		
4		250,000		

Table 2: Compositions and Concentrations

$$\text{Concentration (ppm)} = \text{Area (cm}^2\text{)} \times \text{Response factor (ppm/cm}^2\text{)}$$

Unknown 1	Area (cm ²)	Concentration (ppm)	Percent Composition
Component 1			
Component 2			
Component 3			
Actual composition			

Unknown 2	Area (cm ²)	Concentration (ppm)	Percent Composition
Component 1			
Component 2			
Component 3			
Actual composition			

Unknown 3	Area (cm²)	Concentration (ppm)	Percent Composition
Component 1			
Component 2			
Component 3			
Actual composition			