4. Gas Chromatography

GLOBE Teacher's Key:

Students should be able to:

1. Explain how scientists are able to detect the presence and amount of compounds in a mixture.
2. Describe how a principal separation and detection tool (gas chromatography) functions.

Appropriate grade levels: As a demonstration or in advanced placement high school classes.

Prerequisite skills: If students are going to construct the GC, they should know how to work with glass tubing and something about general laboratory procedures.

Time needed: two class periods (one for construction, one to use).

Notes to teachers:

I would suggest trying this on your own first, whether you are going to use this as a demonstration or allow the students to construct the GC. There are also a number of other experiments you can try in the reference.
We tried this in the lab with two students (ages 14 and 16). The construction of the GC went fairly well, although both students had some trouble working with glass tubing. (Neither had any previous experience in this area.) If you are going to have the students do the construction, I would suggest a separate session on working with glass tubing prior to this session.
Finding the right thickness of copper wire might take some experimenting; it must be thin enough to fit in the burner, but rigid enough to remain in a tight coil. The presence of a halogenated compound in the flame is marked by a brilliant green color, but we did not detect every compound we injected, and we got only one response from our mixture. We used a column that was only about 20 cm long; perhaps a longer one would work better.
We did not use the pop can windbreak, but it might be worth trying.

Introduction, Background

Gas chromatography (GC) is one of the most powerful and widely used methods for the qualitative and quantitative analysis of volatile components in sample mixtures. Although a relatively new method (1952), GC is now used in all areas of science. Typical applications include detection of trace hydrocarbons and other pollutants in air or water, petroleum refinery products, drugs in blood, breath, saliva, and urine, and sex attractants (pheromones) in insects.

GC is a technique for the separation of volatile substances by passing a sample mixture (in vapor form) in a gaseous mobile phase (carrier gas) through a porous stationary phase contained in a long tube, or column. The stationary phase most frequently consists of an inert solid support coated with a nonvolatile liquid. Different sample components have different affinities for the stationary, and move through the column at different rates, and thus are separated. The distribution of sample components between the mobile phase and the stationary phase is called partitioning.

A basic GC system consists of a carrier gas, a heated sample injection port, a separating column, and a detector. Commercially available instruments cost $5,000-$50,000 and often come with a dedicated computer for data collection, storage, and interpretation. A GC flow schematic is shown below.

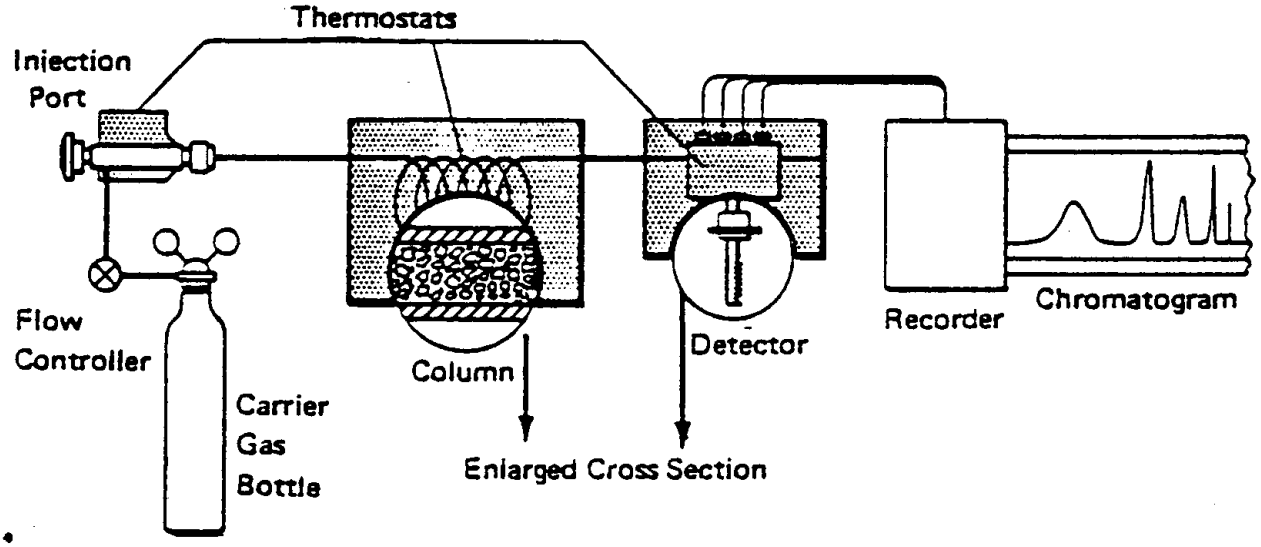


FIGURE I-1—SCHEMATIC DRAWING OF A GAS CHROMATOGRAPHIC SYSTEM

The carrier gas is usually a pure, inert gas (such as helium or nitrogen) stored in a pressurized tank. The flow rate is carefully controlled because the rates of migration of all components through the column are dependent on it.

The samples to be analyzed can be solids, liquids, or gases. Solid and liquid samples must be volatilized; thus, they must be heated as they are introduced into the injection port. Normally, a very small volume of sample (on the order of 0.1 µL to 50 µL) is used. The volatilized sample is swept onto the column by the flow of carrier gas.

The two primary types of chromatographic columns exist. Packed columns are relatively short because of the high pressure required to move gases through the stationary phase. They are inexpensive and can be packed in the laboratory. Capillary columns are much narrower and can be made much longer because of the hole all the way through the column. They are difficult to make and expensive, although the

increase in performance is often worth the price, especially in the analysis of complex samples. Both types of columns are available with any one of several hundred different stationary phases. The stationary phase can frequently be tailored to fit the separation problem.

The column is normally placed in an oven, the temperature of which can be controlled and varied quite accurately. The separated components that leave the column are detected by a suitable detector. A variety of sensitive, quantitative detectors are available; the choice depends on the type of compound(s) present and the level of sensitivity required. (Live male insects have even been used to detect insect pheromones.)

A Small-Scale Gas Chromatograph

Your school could not afford to buy a GC for each student (possibly not even one for the entire school). However, you can build your own working GC very cheaply. The column consists of a piece of glass tubing; the stationary phase is Tide detergent; and the mobile phase (carrier gas) is natural gas. You will be using a Beilstein detector, made from a piece of copper wire twisted into a coil and placed in a small flame generated at the column exit by burning natural gas.

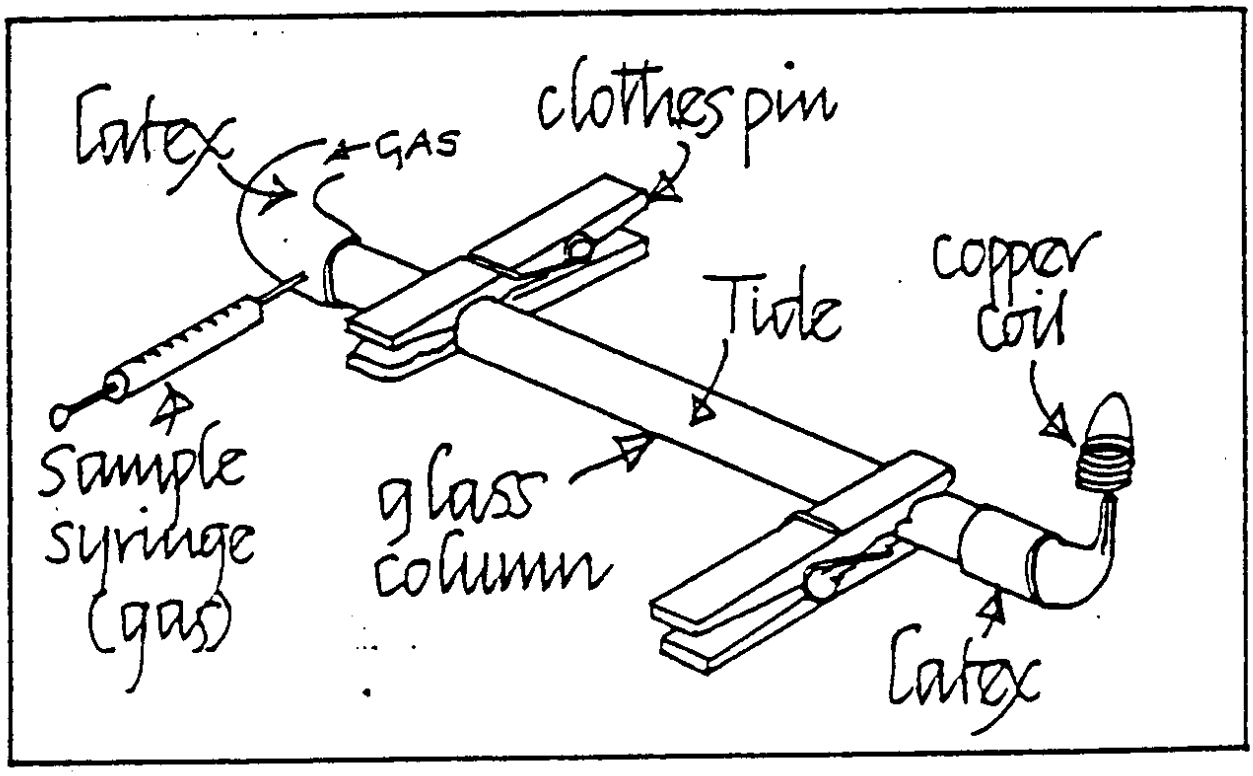
Normally, in commercial GCs, the injection port is a small oven that quickly converts the liquid sample into a vapor. In your GC, the samples are already in the vapor state; therefore, heating is not necessary. Your injection port is made from ordinary latex tubing; latex is a self-sealing material that will take repeated injections without leaking.

From the GC's standpoint, Tide consists of an inorganic solid (sodium tripolyphosphate) coated with a polar, high-molecular-weight, organic surfactant, which serves as the liquid stationary phase. The Tide must be activated before use in order to remove water and perfume. Activate by placing about half a cup in a tray or large beaker (made of Pyrex) and heating in an oven at 150°C for about 4 hours.

The Beilstein detector produces a brilliant green-blue flame in the presence of halogenated compounds (compounds containing fluorine, chlorine, bromine, iodine). The halogen atoms react with the copper detector to form volatile copper halides, which in turn react with OH radicals in the flame to produce the colored copper species (e.g., $CuOH^+$) that are visible in the flame. The Beilstein effect has been used for many years to detect leaks in air conditioners and refrigerators.

The Construction of a Gas Chromatograph

You are about to build a small-scale GC; as you work through this process, refer to the figure below and compare it with your own construction.



1. The following supplies are needed:
1 piece of 8-mm glass tubing (cut to length)
1 piece of latex tubing, 1 ft long
1 piece of latex tubing, 1 in long
1 glass Pasteur pipet
1 glass cutter or scorer
1 Bunsen burner
1 box of matches or 1 striker
a small bundle of polyester fiber or glass wool
1 piece of copper wire
2 clothespins
1 plastic or metal scoop
1 windbreak made from a beverage can
1 cork (to fit inside the 8-mm glass tubing)

Column

2. Do not wash the glass tubing; it will take too long to dry. Cut the tubing to about 30-50 cm in length and fire polish both ends. (Have your teacher show you how. Be careful when working with glass.) Place a small plug of polyester fiber or glass wool inside one end of the glass tube.

3. Insert a small cork at the end of the tube with the plug.

4. Scoop up some of the activated Tide and place the end of the scoop into the open end of the glass tube (held vertically). You can use insert a small funnel into the glass tube if that makes the job easier.

5. Deliver the detergent at an even rate, tapping the tube gently as you fill it.

6. Repeat step 5 until the tube is completely filled with Tide.

7. Keep the tube vertical and very gently bounce the tube on the table (at the cork end). The Tide will settle a little.

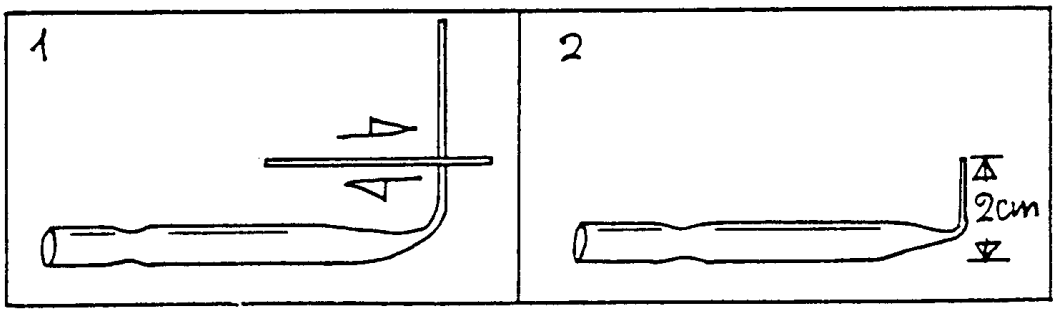
8. Add more Tide until it is about 0.5 cm from the end.

9. Place a plug of polyester fiber or glass wool into the end of the tube to keep the Tide in. Place the completed column gently on the table and move on to the construction of the detector.

Burner

10. Obtain a Pasteur pipet and place the part where it narrows in a small burner flame (or even a match flame). Rotate it until it starts to bend slowly. Stop rotating and let it bend until it forms a right angle. Place it on the table to cool.

11. Hold the large end of the pipet on the table and use a scorer (or file) to score and cut off the thin end so that you are left with a tip 2-3 cm long, as shown below.

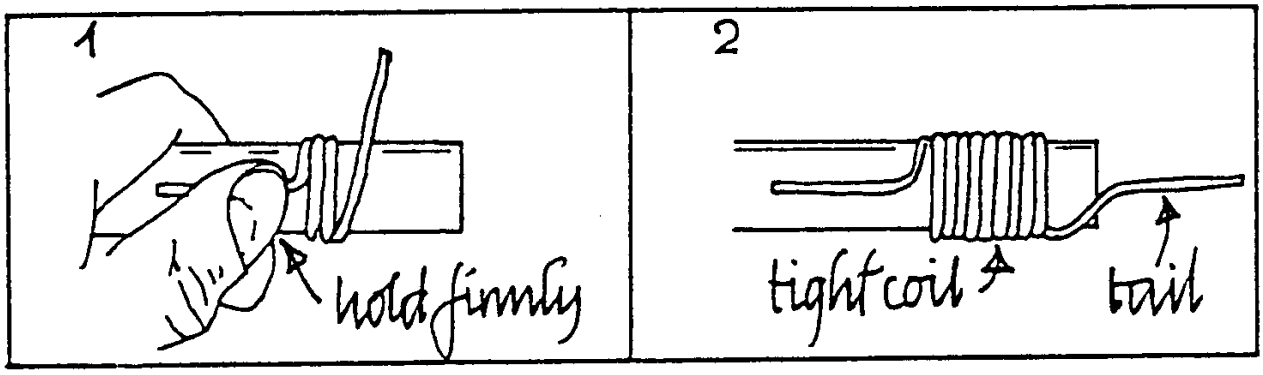


12. Similarly, cut off the larger diameter end about an inch (2-3 cm) from the bend with a scorer or file. Save the cutoff part.

13. Fire polish the sharp, large-diameter end of the pipet. The burner is now complete.

Detector

14. As demonstrated in the figure below, hold the straight, cut-off part of the pipet saved earlier and tightly wind a copper wire 10 turns. As you wind, keep your thumb on the end and put tension on the wire. Leave a tail of copper wire about 3 cm long.



15. Slip the tight coil off the glass tube and adjust the tail so that it bends and then is positioned down the axis of the coil.
16. Cut the tail off about 1 cm from the coil, and slide the tail into the narrow part of the glass burner. You have now completed the detector and are ready to assemble the gas chromatograph.

GC Construction

17. Push one end of the longer piece of latex tubing onto the natural gas tap and carefully push the other end onto the column. Avoid pulling the polyester or glass wool plug out.

18. Push the small piece of latex tubing onto the other end of the column.

19. Attach the burner to the small piece of latex. Rotate it if necessary to ensure that the column will lie naturally on the table with the burner vertical. Use the clothespins as stabilizers.

20. Place a windbreak made from a beverage can around the burner so that the flame exhaust can exit through the tab hole in the top. This also acts as a flame stabilizer.

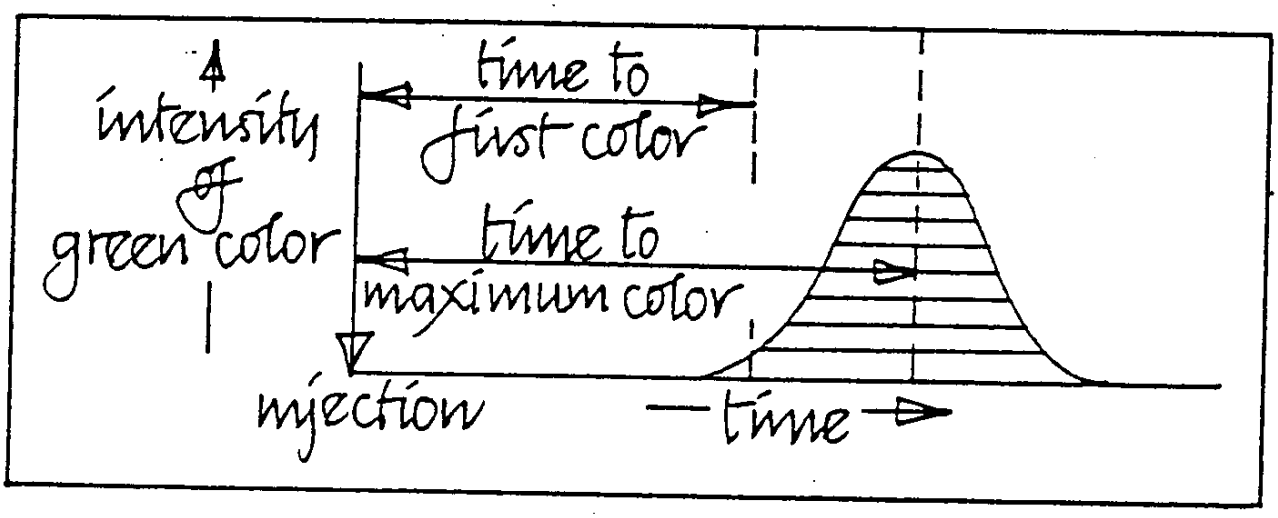
You have now constructed a small-scale, packed-column GC with a latex injector port and a Beilstein detector.

Using the Gas Chromatograph

Turn the gas tap full on. Wait about 5 seconds, strike a match, and hold the flame to the top of the coil. Adjust the gas tap so that the flame is about 0.5-1.0 cm above the top of the coil. The flame should sit on top of the coil. Let the heat from the flame "age" the coil. The visible blackening of the copper is due to the formation of cupric oxide.

Obtain a gas-tight syringe and several conical flasks stoppered with rubber septa, each containing a different halogenated volatile organic compound. Pump the syringe several times to clean the syringe with air. Pull the plunger out to the 0.1 mL mark. Insert the needle into the septum of one of the flasks. Do not tilt the flask - you are going to withdraw vapor, not liquid. Push the plunger in and pull it out to the 0.1 mL mark. Remove the syringe and needle.

Stick the needle into the GC injection port. Inject the vapor, and immediately begin timing. Watch the detector flame; record the elapsed time from injection to (a) the first appearance of a green-blue color in the flame and (b) the maximum intensity of the green-blue flame. Perform several injections with the same compound, timing each one. You have measured the times shown in the diagram below.



Repeat the injections and measurements with the other available compounds. You may need to use more vapor for some of the less volatile compounds. You can use the same syringe for different compounds, but after each injection, remove the plunger entirely from the syringe, replace, and pump air several times to remove any residual vapor from the needle.

You should note different retention times for different compounds. Now try injecting all compounds in one injection:

1. Clean the syringe by pumping with air.

2. Stick the needle into the septum of the first compound. Pull the plunger out to the 0.1 mL mark.

3. Leaving the plunger set, stick the needle into the septum of the second compound. Remove 0.1 mL of that compound by pulling the plunger out to the 0.2 mL mark. Similarly, take 0.1 mL of the other compounds. Do not contaminate the individual compounds by pushing the plunger in at any time.

4. Inject the mixture into the GC. Record the elapsed times and explain the results.

Reference

Stephen Thompson, 1989. Chemtrek: small-scale experiments for general chemistry. pp 420-442. ISBN 0-205-11913-1