Gas Chromatography

"The second proposal, to look for halocarbons, was rejected as frivolous because it was 'obvious' that no apparatus existed sensitive enough to measure the few parts per trillion of chlorofluorocarbons I was proposing to seek."

James Lovelock, The Ages of Gaia
Introduction

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 — the first paper describing the use of a gaseous mobile phase was published by Martin and James in 1952 — GC is now used in all areas of science, medicine, and industry. Some typical analytical applications are trace hydrocarbons and other pollutants in air; petroleum refinery products; barbituates and other drugs in blood, breath, saliva, and urine samples; flavoring agents in foods; trace contaminants in beer, wine, and spirits; and pheromone sex attractants in insects.

Gas chromatography is a technique for the separation of volatile substances by percolating a sample mixture (in vapor form) in a gaseous mobile phase through a porous stationary phase contained in a long tube. The technique can be divided into two fundamental types: gas-solid chromatography (GSC) and gas-liquid chromatography (GLC). In GSC the separation is accomplished by passing the sample, in a carrier gas, over a solid stationary phase. The different components in the sample have different adsorption affinities for the stationary phase, and some are slowed down with respect to others. In GLC, components in the sample are separated by passing the sample and carrier gas over a stationary phase consisting of an inert solid support coated with a nonvolatile liquid. In GLC the distribution process between the mobile gas phase and liquid stationary phase is partition. GLC is by far the more versatile method because of the wide range of liquid stationary phases that are commercially available.
Background Chemistry

A general introduction to the theory of chromatography is given in the Background Chemistry section of Chapter 18, "Paper and Liquid Chromatography." If you are new to chromatography, it is probably advisable to read the section before you continue on into the Background Chemistry section of "Gas Chromatography."

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. The GC flow schematic is shown in Figure 19.1.

![Figure 19.1 Schematic of a Typical GC](image)

The carrier gas is usually a pure, inert gas (e.g., He, H₂, Ar, or N₂) stored in a pressurized tank. The flow rate of the mobile phase must be very carefully controlled in GC because the rates of migration of all components are dependent on it. Various pressure gauges, flow controllers, and meters accomplish exact carrier gas flow control.
The samples to be analyzed by GC may be gases, liquids, or solids. Solid and liquid samples must be volatilized; thus, they must be heated as they are introduced into the injection port. Generally, a very small sample volume is needed — on the order of 0.1 μL to 50 μL. The volatilized sample is swept onto the separating column by a flowing stream of carrier gas. The two main types of column in general use are shown in Figure 19.2.

![Diagram of Packed and Capillary Columns]

Figure 19.2 Two Types of GC Columns

Packed columns are relatively short because of the high pressure required to push the gases through the stationary phase. These columns are inexpensive and therefore widely used. Capillary columns are much narrower and can be much longer because of the hole all the way through the column. Capillary columns are tough to make and are expensive, although the increase in efficiency is worth the price, particularly for the analysis of very complex samples (e.g., gasoline).

Both types of columns are available with any one of several hundred different liquid stationary phases. Selection of the type of liquid stationary phase is based on the type of sample to be analyzed. The real power and flexibility of GC as a method of analysis rest on the fact that the stationary phase can almost be tailored at will to fit the separation problem. The choice is often made on the "like dissolves like" principle, or put in a more sophisticated way, the liquid is chosen on the basis of polarity index. The column is usually placed in an oven, the temperature of which can be raised or lowered (and monitored) in any predetermined manner. The separated components that leave the column are then quantitatively detected by a suitable detector or, in some instances, may be trapped and recovered. Again, one of the tremendous advantages of GC is the variety of sensitive, quantitative detectors that are available, e.g., thermal conductivity, mass spectrometry, and even live male insects (used as detectors of insect pheromones).

Many commercial GCs have three types of built-in detectors: thermal conductivity (TCD), flame ionization (FID), and electron capture (ECD). The detector output (signal) is usually fed to a strip chart recorder or to a dedicated computer (are there any other kind?). A typical GC chromatogram is shown in Figure 19.3.
The various components do not have \( R_f \) values, in the same sense as in paper chromatography, because the components actually come out of the gas chromatograph, and the mobile phase is continuously flowing (compare PC). In GC the retention parameter is called the retention time \( (t_R) \) and is the time that elapses between the injection of the sample and when the center of the component band is detected by the detector. Almost always, the injection of the sample into a gas chromatograph results in air being injected. Air components (O\(_2\) and N\(_2\)) are generally unretained — i.e., have no affinity for the liquid stationary phase — and quickly appear in the detector. The time between sample injection and the detected air peak is called the retention time of air (even though it is not retained by the stationary phase). The detectors also produce a concentration profile that, with a suitable calibration line, can be used to quantitatively measure the amount or concentration of any sample component.

**A SMALL-SCALE GAS CHROMATOGRAPH**

The Department of Chemistry could not afford to buy a gas chromatograph for each of you (in spite of the current tuition trends!). However, you can build your own working GC for about $0.25. The GC design was developed by the author over a three-year period (between 1974–1977). The column stationary phase is constructed of a glass or straw tube filled with dry Tide detergent ("you can trust Tide!") and uses natural gas as carrier gas. The GC detector is rather unusual in that the principle has been known for 90 years and is only now beginning to be used in some modern instruments. You will be constructing a Beilstein detector — named after a famous German chemist, who incidentally didn't discover the principle; a Swedish chemist, Berthollet, did!
The detector is a copper coil that is placed in a small flame generated at the column exit by burning natural gas. One of the real reasons for using natural gas (methane) as a carrier gas is that it comes from a highly controlled valve and has a convenient useful line pressure of about 6–7 ounces per square inch. The normal gas tap serves as a fine-tuning regulator for the carrier gas flow. The methane is then used as a fuel source for the small-scale premix burner and Beilstein detector.

Normally in commercial GC instruments, the injection port is actually a little oven that quickly converts the liquid sample (often dissolved in a volatile solvent) into vapor. In your GC the samples are halocarbon vapors and, thus, heating is not necessary. The port is made from ordinary Bunsen burner tubing (latex tubing). Surprisingly, the latex is a self-sealing material that will take repeated injections without leaking. The separating column is a short (20 cm × 0.8 cm) tube of soft glass packed with activated Tide detergent. Tide detergent is a complex mixture of about twelve ingredients formulated to get clothes clean. However, from the GC viewpoint, it consists of an inorganic solid (Na5P3O10, sodium tripolyphosphate) coated with polar, high molecular weight, organic surfactant. The organic surfactant probably serves as the liquid stationary phase in GC. The Tide must be activated before use in order to remove the perfume and some water. Activation is carried out by placing a large tray of the detergent in an oven at 150°C for about 4 hours. The particle size of the powder is not ideal, but it is in the correct range to allow a reasonable carrier gas flow through the column (provided the column is not too long). The actual process of putting the Tide into the tube (packing the column) is critical to achieving successful separations. If the column is packed too tightly, there will be no carrier gas flow, and if the column is packed too loosely, channeling will occur, giving rise to poor or no separations. Of course, the larger the Tide column, the longer are the retention times for components and the greater is the band spreading of each component. A column length of 20–50 cm seems to be reasonable for the gas pressures encountered in most schools and universities.

It is worth noting that there are several reports in the scientific literature of the use of solid detergents as stationary phases in gas chromatography. In the GC that you will be building, the Tide-packed column will be used at ambient temperatures. The halocarbon samples that you will be separating have a relatively high vapor pressure at room temperature, and elevated column temperatures are not necessary. The Tide column will separate the sample mixture into individual halocarbon components that then must be sensed by some type of detector. You will be using a Beilstein detector, which is a sensitive device for the detection of compounds containing halogen atoms, but which is not very sensitive, or does not work at all, for other substances.

The **Beilstein detector** is a sensitive, selective GC detector that emits visible light when separated halocarbon components go through it. A quantitative analysis may be obtained by using some type of photodetector (e.g., a CdS cell or photodiode) to transduce emitted light into an electronic effect. Of course, a calibration line is required for each component because the detector and transducer response depend on the chemical structure of the detected substance. A Beilstein detector consists of a copper wire coil that is placed in the relatively cool part of a small flame. As the flame plays over the copper (and the surface copper(II) oxide), the surface reacts with free electrons in the
flame and is kept clean and reactive. This phenomenon is very beautiful to watch because the black surface ripples with a golden sheen as the flame reduces Cu\(^{2+}\) back to Cu\(^+\). If a halogen-containing vapor is burned in the flame, highly reactive halogen atoms are formed which then quickly react with the fresh copper surface to form volatile copper halides. The halides then rapidly react with OH radicals in the flame to give various copper species (e.g., CuOH\(^+\)) that are thermally excited by the heat of the flame. The excited copper species emit green-blue light as they return to the ground state. Emission of green-blue light is a definite indication that a halogen-containing component has arrived in the detector. By the way, the Beilstein effect has been used for many years in devices for detecting leaks in air conditioners and refrigerators!

Once you have built the GC, the best way to learn about the technique is to get involved in investigating a practical problem. The next section presents an interesting environmental sciences application that involves the analysis of industrial and commercial products and addresses the general problem of halocarbons in the environment.

HALOCARBONS AND THE ENVIRONMENT

A large number of chemical compounds containing carbon-halogen bonds have been made by the chemical industry and have proved to be extremely useful in industry, commerce, and agriculture. The uses are varied and include such applications as pesticides, hydraulic fluids, electrical transformer fluids, solvents, aerosol propellants, anesthetics, refrigerants, air conditioner fluids, foam expanders, plastics, etc., etc. Some specific examples follow.

Insecticide:

\[
\begin{align*}
\text{H} & \quad | \\
\text{Cl} & \quad | \\
\text{C} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad |
\end{align*}
\]

DDT, dichlorodiphenyltrichloroethane

Hydraulic fluids and transformer fluids:

\[
\begin{align*}
\text{Cl} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad | \\
\text{Cl} & \quad |
\end{align*}
\]

PCB, polychlorinatedbiphenyl

\[
\begin{align*}
\text{Br} & \quad | \\
\text{Br} & \quad | \\
\text{Br} & \quad | \\
\text{Br} & \quad | \\
\text{Br} & \quad | \\
\text{Br} & \quad |
\end{align*}
\]

PBB, polybrominatedbiphenyl
Solvents:

\[
\begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

Chloroform

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

Carbon tetrachloride

Solvents, propellants, refrigerants, foam expanders, air conditioner fluids, etc.:

\[
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\quad
\begin{array}{c}
\text{F} \\
\text{C} \\
\text{F} \\
\text{F} \\
\end{array}
\quad
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C} \\
\text{F} \\
\end{array}
\]

Freon 11
Freon 12
Freon 13
Freon 14
Freon 113

The use of many of these halocarbons has been restricted, and some of them have been banned outright because of environmental health problems. The environmental problems have arisen mostly from the chemical and biological properties of these halocarbons. Carbon-halogen covalent bonds are very stable, and these compounds do not break down easily under most environmental conditions. This chemical longevity, together with the fact that many of these compounds are fat soluble, means that halocarbons stay around a long time and concentrate up food chains. (For one interesting aspect, see Chapter 8, "An Introduction to Acids and Bases.")

In this module, it is the smaller molar mass halocarbons (e.g., the Freons) that are of interest. The Freons, sometimes called chlorofluorocarbons (CFCs), are very stable, volatile, and cheap compounds. These characteristics make them valuable as refrigerants, propellants, and foam expanders. Their stability means that they persist in the air — the troposphere — for a long time (half-life is about 75 years; for Freon 12), eventually drifting into the stratosphere. Unfortunately, the stratosphere is a sink for Freons because at this high altitude, the high-energy ultraviolet (UV) light from the sun causes even stable compounds to break down. In a complex sequence of photochemical reactions, the Freons are decomposed by light into chlorine atoms:

\[
\text{CCl}_3\text{F} + \text{hv} \rightarrow \text{Cl} + \text{CCl}_2\text{F}
\]

\[
\text{CCl}_2\text{F}_2 + \text{hv} \rightarrow \text{Cl} + \text{CCIF}_2
\]

The chlorine atoms catalyze the destruction of ozone \((\text{O}_3)\) in a series of free radical reactions, one of which is:

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\]
Recently, it was discovered that each year, in September and October, the stratospheric ozone layer over Antarctica shrinks drastically and in many places disappears completely. Again, it appears that chlorofluorocarbons are the culprit. Unusual chemical reactions on the surface of polar stratospheric ice clouds generate chlorine from chlorofluorocarbons, and the ozone is destroyed. The maintenance of normal ozone concentrations in the stratosphere is critical to life on earth. The stratosphere ozone cycle removes most of the high-energy UV light that would otherwise reach the earth's surface. The consequences of a reduced ozone concentration in the stratosphere may vary from increased skin cancers to severe chromosome damage and dramatic climate changes.

A recent global conference of CFC producers, users, and scientists agreed that the problem of ozone destruction by chlorofluorocarbons is a real and severe environmental threat. In an unprecedented decision the conference announced CFC production restriction and eventual phase-out of CFCs altogether. This decision has stimulated several large companies to begin research on developing new CFC substitutes for refrigerants and foam-expanding agents. In spite of all the recent furor, it is important to note that most of the CFCs that have ever been produced are still present in the atmosphere. The ozone problem is not going to go away for many decades, if ever.

Gas chromatography has played a key role not only in the initial identification of CFCs in the atmosphere, but also in the current research on ozone "holes" in the polar regions. In fact, it could be said that the whole CFC story started about 20 years ago in an English country garden! In 1970 an independent scientist named James Lovelock, who now works in a barn-turned-laboratory in Cornwall, England, invented a new type of GC detector called the electron capture detector. He attached the detector to a GC, and his first sample for analysis was English garden air. The GC chromatogram revealed two previously unidentified peaks that were shown to be Freons 11 and 12. Lovelock did a rough calculation based on the Freon concentrations measured by the GC experiment and came to the conclusion that all of the Freons ever manufactured were still present in the atmosphere — the rest is history.

It is strange but true that the discovery of the CFC-global ozone problem relied on the invention and use of a GC detector. In this laboratory module, you have the opportunity to build your own sophisticated GC equipment, investigate its limitations, and carry out analyses on various samples containing halocarbons.
Pre-Laboratory Quiz

1. What is gas chromatography?

________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________

2. In GLC what is the name of the distribution process that occurs between the mobile and stationary phase?

________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________

3. In GC what is the retention parameter called?

________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________

4. What carrier gas will you use in your GC?

________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________

5. Give a brief description of the stationary phase you will be using in your packed-column GC.

________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
________________________________________________________________________________________
6. How does a Beilstein detector work?

7. Give the chemical formula for a Freon.

8. Give 2 chemical reactions that show how CFCs destroy ozone.

9. Who invented the electron capture detector?

10. Give one major use of a Freon.
Laboratory Experiments

Flowchart of the Experiments

Section A. The Construction of a Gas Chromatograph

Section B. Measurement of the Retention Time of Air and the Gas Flow Rate

Section C. Measurement of the Retention Times of Halocarbons

Section D. GC Separation of Halocarbon Mixtures

Section E. GC Analysis of Industrial Products

Section F. Optimizing a GC System: The Van Deemter Plot

Section G. Quantitative Analysis by GC with Photodetection

Requires one three-hour class period to complete
CAUTION: In this series of experiments, you will be using natural gas as a carrier gas in GC. Be aware that natural gas is flammable and in certain circumstances can be dangerous. Please remember that burning gas is hot, and so are metal objects (such as detectors and windbreaks) that come into contact with flames. Please sign out and in for the syringe sample injector you use during the experiment.

Section A. The Construction of a Gas Chromatograph

Goal: To build a working small-scale gas chromatograph that is capable of separating several halocarbons.

Before You Begin: You are about to build the odd-looking device, actually a small-scale gas chromatograph, shown in the diagram below. As you work through Section A, refer to the diagram to compare with your own construction.

Experimental Steps:  
1. Obtain the following from Reagent Central: 1 x 20 cm piece of 8 mm glass tubing; 1 x 2 ft and 1 x 2 cm pieces of latex tubing; 1 glass Pasteur pipet; small bundle of polyester fiber; 1 piece of copper wire; 1 glass cutter or scorer; 1 box matches; 2 clothespins; 1 small cup of activated Tide detergent; 1 plastic scoop; and a windbreak made from a beverage can.

2. Do not wash the 20 cm piece of glass tubing or it will take a long time to dry. Place a small plug of polyester fiber 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 detergent and place the end of the scoop into the vertically-held glass tube.

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

   **NOTE:** If the scoop gets blocked, remove and invert it over the cup and tap. Do not attempt to poke it out or it will really clog.

6. Refill the scoop and keep pouring and tapping until the tube is completely filled with Tide. Remove the scoop.

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 into the end of the tube to keep the Tide in.

   You have now prepared a Tide-packed gas chromatography column. Since this is possibly the first time that you have attempted this high technology endeavor, there might be some probability that the column packing is not perfect. Don’t worry — diagnosis of “sick” columns is easy, and repacking takes only a few minutes. It is important that you handle the column carefully. Place it gently on the table and try not to bump it too much. Now you can construct the burner and Beilstein photoionization detector.

   **Beilstein Burner Construction**

10. Obtain a glass Pasteur pipet. Place the part where it narrows down in a small burner flame (or even a match flame). Keep rotating it until it starts to bend slowly. Stop rotating and let it bend, under gravity, until it forms a right angle. You can help it a little if you like!

11. Place the pipet on the table to cool.

12. Hold the large end firmly on the table and use a scorer (or file) to scratch and cut off the thin end so that you are left with a tip 2–3 cm long, as shown below.

   **CAUTION:** Glass can be dangerous so consult your instructor if you are uncertain about this step.
13. Likewise, cut off the larger diameter end about 2-3 cm from the bend with a scorer or file. This technique is not easy! If you have problems check with your instructor. Save the cutoff part.

14. Fire polish the sharp, large-diameter end. You have now made the burner.

**GC Detector Construction**

15. As demonstrated below, hold the straight, cutoff part of the pipet saved in Step 13 and tightly wind a copper wire coil 10 turns. As you wind, keep your thumb tightly on the end and put tension on the wire as you wind it. Leave a tail of copper wire about 3 cm long.

![Diagram]

16. 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.

17. Cut the tail off about 1 cm from the coil.

18. Now slide the tail into the narrow part of the glass burner.

Presto! You have created burner and detector! Now you are ready to assemble the gas chromatograph.

**Gas Chromatograph Construction**

19. Push one end of the latex tubing onto the natural gas tap and carefully push the other onto the column. Try to avoid pulling the polyester wad out.

20. Push the small piece of latex on the other end of the column.

21. 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.

22. Clip 2 clothespins onto the column as stabilizers.

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

Congratulations. You have just made a small-scale, packed-column gas chromatograph with a latex injection port and a Beilstein burner photoionization detector. The carrier gas is natural gas.
Section B. Measurement of the Retention Time of Air and the Gas Flow Rate

Goal: To "age" the Beilstein detector and measure the retention time for unretained air.

Discussion: The $t_R$ for air (retention time for air or air peak time) may be used to calculate the linear gas velocity of the carrier gas.

Experimental Steps:

1. Turn the gas tap full on. Wait about 5 seconds, strike a match, and hold the flame to the top of the coil.
2. Adjust the gas tap so that the flame is about 0.5-1.0 cm above the top of the coil. Let the heat from the flame "age" the coil. The visible blackening of the copper surface is due to $2Cu + O_2 \rightarrow 2CuO(s)$.
3. Wait about 30 seconds, then remove the coil with a pair of tweezers and hold it for a moment to cool.
4. Place it carefully on the table.
   NOTE: Aged detectors are fragile.
5. Relight the burner flame if necessary.
   NOTE: From now on do not touch the gas tap. The flow is set.
6. Obtain a plastic, graduated 1.0 mL syringe from your instructor. Your instructor will have you sign for it.
7. Pull the plunger out to the 0.5 mL mark.
8. Push the needle into the latex injection port within a cm or so of the end of the column. Smoothly and quickly, push the plunger in.
   Watch the flame carefully and note that after a very short time, the flame will dip smaller and then go back to its regular size. The dip corresponds to a change in air-fuel ratio as the injected air arrives in the burner.
9. Repeat Step 8.
   - Measure the elapsed time from the injection to the flame dip.
   The elapsed time is the retention time for air — i.e., the time it takes for the injected air to travel unretained through the column and into the flame.
   - Carry out at least 3 measurements of the retention time for air and record your data.
   - Calculate the gas flow rate (linear gas velocity) by
     \[
     \bar{u} = \frac{L}{t_A}
     \]
     where $\bar{u}$ is the average linear gas velocity (in cm s$^{-1}$), $L$ is the length of the GC column (in cm), and $t_A$ is the retention time for air (in seconds). In any GC
experiment the carrier gas flow rate must be measured because all retention times for components will be dependent on it. The faster the carrier gas is flowing, the faster the sample components will move through the column.

NOTE: The carrier gas flow rate is sometimes measured in a different way (with a soap bubble flow meter) and is reported as a volumetric flow (i.e., mL per minute). If you have time, you might want to build a simple soap-bubble flow meter. Check with your instructor.

Section C. Measurement of the Retention Times of Halocarbons

Goal: To measure the GC retention times for a series of organic compounds containing carbon-halogen covalent bonds.

Experimental Steps:

1. Using tweezers slip the copper coil back into the burner. Relight the burner if necessary.

NOTE: It is very important that the flame be only on top of the coil. When the burner and detector are optimized, the flame will be steady, on top of the coil, and not very luminous. If the flame is burning from the glass tip or inside the coil, the coil will get too hot and the Beilstein effect will not work well. Try and adjust the coil with your tweezers, but do not change the gas flow rate!

2. At Reagent Central you will find 25 mL conical flasks stoppered with rubber septa. Take back to your place one of each of the 5 flasks labelled Freon 11 (CCl₃F), Freon 12 (CCl₂F₃), dichloromethane (CH₂Cl₂), chloroform (CHCl₃), and carbon tetrachloride (CCl₄).

3. Pump the syringe plunger several times to clean the syringe with air.

4. Pull the syringe out to the 0.1 mL mark.

5. Start with one of the Freons. Insert the needle into the septum.

NOTE: Do not tilt the flask — you are going to withdraw vapor, not liquid!
6. Push the plunger in and pull it out to the 0.1 mL mark. Remove the syringe and needle.

7. Stick the needle into the GC injection port. Be ready to begin timing.

8. Inject the vapor, using good injection technique, and immediately begin timing.

9. Watch the detector flame.
   - Record the elapsed time from injection to:
     (a) The first appearance of a green-blue color in the flame
     (b) The maximum intensity of green-blue flame

The first time you try this, everything generally happens too fast to get decent results (it took me 7 times!). Obtain another Freon sample and try again.

You have just measured the times shown in the diagram below.

![Diagram showing time to first color, time to maximum color, and intensity of green color](image)

The elapsed time from injection to the maximum green-blue flame color is the retention time $t_R$ for that halocarbon. Measuring the time to the first appearance of green-blue flame color will allow you to calculate $W_B$, the band width of the halocarbon peak.

10. Repeat the above measurements (Steps 3 through 9) on the halocarbons that are available to you.

Use more vapor for some of the less volatile halocarbons — e.g., 0.2 mL CH$_2$Cl$_2$, 0.3 mL CHCl$_3$, and 0.5 mL CCl$_4$. You may use the same syringe provided that, after injecting each sample, you remove the plunger entirely, replace, and pump air several times to pump any residual vapor from the needle.
   - Measure and record the retention time for each halocarbon.
   - Record the retention time for air and flow rate.

If you think that for some reason the flow rate is changing (e.g., the building gas pressure might change), then redetermine the retention time for air.
   - Calculate the $W_B$ values for each halocarbon peak.
HINT: Assume that the peak is Gaussian, i.e., symmetrical. Note that the units of $t_R$ and $W_b$ (in this GC experiment) are seconds.

- Calculate an approximate value for the number of theoretical plates $N$ and the height equivalent to a theoretical plate $H$ for one of the halocarbons (e.g., dichloromethane).

Use the expressions suggested earlier for these calculations:

$$N = 16\left(\frac{1R}{W_b}\right)^2 \quad \text{and} \quad H = \frac{L}{N}$$

where $t_R$ is the retention time (seconds), $W_b$ is the width of the GC peak (in seconds), and $L$ is the length of the column (mm).

### Section D. GC Separation of Halocarbon Mixtures

**Goals:**

1. To make a homogeneous mixture of several halocarbons and to obtain a gas chromatographic separation of all of the components.
2. To measure halocarbon retention times and $W_b$ values in order to determine peak resolution.

**Experimental Steps:**

1. Clean the syringe by pumping with air.

2. Stick the needle into the septum of the Freon 12 flask. Pull the plunger out to the 0.1 mL mark.

3. *Leaving the plunger set,* stick the needle into the Freon 11 septum. Remove 0.1 mL of Freon 11 by pulling the plunger out to 0.2 mL. In the same way (in the same syringe), take 0.1 mL CH$_2$Cl$_2$ and 0.3 mL CCl$_4$.

   **NOTE:** Do not contaminate the individual halocarbons in the flasks by pushing the plunger in at any time.

   Be ready to record the elapsed times to the first and maximum green-blue flame color.

4. Inject the mixture into the gas chromatograph.

   - Record the elapsed times and describe what happens.
   - Why does the width of the peak $W_b$ increase as the $t_R$ increases?

One important parameter in any chromatographic systems is the *resolution* obtained between two successive components, which is defined by

$$\text{Resolution} = \frac{\text{band migration difference between 2 components}}{\text{component spreading}}$$
- Calculate the resolution obtained between Freon 12 and Freon 11. Note the diagram below.

\[
\text{Resolution between Freons 11 and 12} = \frac{t_{R(11)} - t_{R(12)}}{W_b(12) + W_b(11)}
\]

- What does a resolution of 1.0 tell you about the peaks in a chromatographic separation?

Section E. GC Analysis of Industrial Products

Goal: To use the gas chromatograph and your acquired knowledge of halocarbon separations to carry out a qualitative analysis of an industrial product containing halocarbons.

Discussion: Your instructor will provide you with an industrial product containing one or more of the halocarbons that you have studied in the GC laboratory module. Analyze the product by GC and report your result. Your instructor will then give you a brief product description indicating the uses and specifications of the product.

- How would you analyze a solid sample?

Section F. Optimizing a GC System: The Van Deemter Plot

Goal: To measure retention times and \( W_b \) values for dichloromethane at several different linear flow rates (of carrier gas).

Discussion: A plot of height equivalent to a theoretical plate (H) versus linear flow rate (\( u \)) is called a Van Deemter plot. This plot may be used to select flow rates at which optimum separations can be achieved.
Before You Begin: Make a table in your lab notebook similar to the one shown below. In Step 6 you will be asked to record your data and calculational results in this table.

<table>
<thead>
<tr>
<th>Retention Time for Air</th>
<th>$\bar{u}$ (cm s(^{-1}))</th>
<th>Time for 1st $t_R$ (s)</th>
<th>Appearance</th>
<th>$W_B$ (s)</th>
<th>N</th>
<th>H (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental Steps:

1. Make a new 3-turn copper wire coil detector for your gas chromatograph.
2. Adjust the gas flow rate so that the retention time for air is about 2–3 seconds. Leave the flow rate set at this value.
3. Inject 0.2 mL CH\(_2\)Cl\(_2\) vapor.
   - Time the first and maximum appearance of green-blue color and record.
4. Decrease the flow rate slightly by turning the gas tap and again determine the retention time for air at this new flow rate. Leave the flow rate set at this new rate.
5. Inject 0.2 mL CH\(_2\)Cl\(_2\) vapor.
   - Measure and record times as before.
6. Carry out one more set of time measurements at a slightly lower rate. Try to obtain about a 1 second difference in the retention time for air at the different flow rates.
   - Record your data and calculational results in the table you made in your lab notebook.
   - Measure and record the length of Tide packing in the column (L) in mm.
   - Make a graph of H (vertical axis) versus $\bar{u}$.

This plot is called a Van Deemter, Von Klinkenberg, and Zuiderweg plot, or Van Deemter plot. The plot will often show a minimum in H at some flow rate. A minimum in H means a maximum in chromatographic efficiency. The flow rate at which this occurs is called the optimum flow rate.

Section G. Quantitative Analysis by GC with Photodetection

Goals:

(1) To add a quantitative emitted-light detector (a cadmium sulfide cell and digital multimeter) to the GC. (2) To use the instrumental combination to obtain a calibration for the quantitative analysis of dichloromethane.

Experimental Steps:

1. Obtain a cadmium sulfide (CdS) cell light detector from your instructor.
2. Build a straw holder and stand for the cell.
NOTE: Replace the 3-turn coil with the original 10-turn coil.

3. Position the cell horizontally and at a convenient height about 4 cm away from, and pointed directly at, the detector flame. Use the cutout can as a windbreak and flame stabilizer.

4. Connect the CdS cell to a multimeter and set the meter to measure resistance. If you can, adjust the sensitivity of the meter to give reasonably stable readings.

5. Inject 0.6 mL CH₂Cl₂ vapor into the GC and measure the maximum emission of light — i.e., minimum resistance on the meter — as the halocarbon goes into the flame and causes the emission of green-blue light.
   • Record the measurement in your lab notebook.

6. Now inject 0.5 mL CH₂Cl₂ vapor into the GC. Determine the minimum resistance on the meter for this volume of CH₂Cl₂ vapor.
   • Record the minimum resistance on the meter for this volume of CH₂Cl₂.

7. Perform Step 6 again with each of the following amounts of CH₂Cl₂: 0.4 mL, 0.3 mL, 0.2 mL, 0.1 mL, and 0.05 mL.
   • Plot mL CH₂Cl₂ vapor versus minimum resistance on the CdS cell. Draw a smooth curve through the experimental points.

If you know the temperature of the CH₂Cl₂ liquid/vapor sample, the ambient atmospheric pressure, and the following vapor pressure expression, then you can calculate the exact number of moles of CH₂Cl₂ injected into the GC. The vapor pressure expression is

\[ \log_{10} P = (-0.2185 \times \frac{A}{T}) + B \]

For CH₂Cl₂, A = 7572.3 and B = 8.1833; for 25°C, T = 298 K (valid from -70°C to 41°C). Then the vapor pressure of CH₂Cl₂ is 428 Torr. You can now use the ideal gas law PV = nRT to calculate the number of moles.

Once you have obtained a calibration line at a particular flow rate with a particular detector and CdS cell, etc., etc., then you can carry out a quantitative analysis for that substance on the GC system.

8. Obtain an unknown from your instructor and have a go.