Gas Chromatography*

Tara M. Lovestead, Applied Chemicals and Materials Division, National Institute of Standards and Technology

General Uses
- Analysis of complex mixtures made up of anything that can be heated to form stable vapors

Examples of Applications
- Mixtures of volatile compounds in petroleum oil, coal gasification and liquefaction products, oil shale, and tar sands;
- Pollutants and impurities in air, water, soil, and other solids;
- Drugs and metabolites;
- Pesticides;
- Additives, such as antioxidants and plasticizers in plastics

Samples
- *Form:* Solids, liquids, and gases; all organics and some inorganics
- *Size:* For liquid samples, a 0.1- to 10-µL injection depending on the sample concentration, inlet liner and split ratio. For gaseous samples, a gas-tight syringe can be used to inject 100 – 500 µL volumes.
- *Preparation:* Samples should be prepared to conform to the sample size restrictions given above and to the limitations of the detector response to concentration

Limitations
- Compound(s) must form stable vapors upon heating
- Detection limit is dependent on the detector. A thermal conductivity detector is ~ 1 ng whereas an electron capture detector can be as ~ 1 pg GC-MS operated in selected ion monitoring can achieve detection limits as low as 0.5 pg

Estimated Analysis Time
- When analyzing one compound, direct introduction of sample takes 1 to 20 min per analysis. For gas chromatography/mass spectrometry, analysis of 1 to 2 compounds takes approximately 15 min, while analysis of 20 or more compounds takes 180 min or more
- *Analysis and interpretation of data:* Variable (15 min to days depending on the number of compounds analyzed)

Capabilities of Related Techniques
- *Gas chromatography/Fourier-transform infrared spectroscopy:* Functional group analysis, but at least an order of magnitude less sensitive
- *Nuclear magnetic resonance:* At least two orders of magnitude less sensitive
- *Secondary ion mass spectroscopy:* A mass spectrometry method for looking only at surfaces of materials

Chromatography is about separating (often) closely related components (such as plant pigments or components of fuel). Modern chromatography is used to purify drugs, determine the level of pollutants in water or soil for environmental analyses, compare samples from a crime scene, determine the identity of unknown substances, and for process engineering quality control. A basic chromatographic separation requires the following:

1) sample
2) column/stationary phase
3) mobile phase
4) detector

To begin, the sample is introduced into the column. In gas chromatography, the column is typically long (from 10 to 60 meters). The column is wound into a coil and housed in a temperature-controlled oven. The column is coated with a stationary phase that is a solid (or a liquid supported on a solid). Chromatography also requires a mobile phase which can be a liquid or a gas that flows past the stationary phase and carries the components of the mixture. The movement of components through the column can be facilitated by heating the column or temperature ramping. The separation of the components in the sample depends on their interactions with the column stationary and mobile phases. The sample components ultimately arrive at a detector at different times (retention times) based on interactions with the column stationary and mobile phases.[1]

One way to classify a chromatographic technique is by the choice of mobile phase. The mobile phase can be either a liquid (liquid chromatography, LC) or a gas (gas chromatography, GC). This chapter is dedicated to gas chromatography. Gas chromatography is the method of choice for analyzing mixtures made up of anything that can be heated to form stable vapors. Gas chromatography is robust (can be used with minimal preparation), is rapid (minutes), and is efficient at separating complex mixtures of both organic and inorganic components.

The principles that govern separations are based on a molecule's affinity for the stationary phase. A component with no interaction with the stationary phase is simply carried by the gas and is said to be "non-retained". If a component strongly interacts with the stationary phase it will take longer to travel the entire length of the column. A component's affinity for the stationary phase is governed by *adsorption* (adhesion) onto a solid substrate; or by *absorption* or *partitioning* (dissolving and vaporizing) into and out of the liquid phase. *Enthalpy of adsorption, ΔH_{ads}*, describes the amount of energy required to move a molecule out of the solid substrate. Molecules with different ΔH_{ads} will move at different rates through a column determined by the instrumentation and adjustable parameters, for example, temperature ramping rate.

A chromatogram, a graph of the detector response as a function of time, is a way to visualize the molecule separations. A chromatogram shows the peaks which are representative of the response of a detector to a molecule; the area under the peak relates to the concentration of the molecule in the mixture. Chromatograms are used to determine a column's performance or resolving power (ability to separate two peaks). Resolving power is determined by the retention factor, the selectivity factor, and efficiency. These parameters can be optimized by changing pressure,

temperature, amount of sample introduced and heating profile and are dependent on the column length, stationary phase (chemistry) and on the molecule of interest.

The instrument parts and the relevant adjustable parameters (temperature, pressure, phase chemistry, and solvent choice) for obtaining the best possible chromatographic separation are discussed in detail and include 1) carrier gas cylinder; 2) flow controller and pressure regulator; 3) sample inlet and injection port; 4) column; 5) column oven; 6) detector (for example, a flame ionization detector), and 7) computer.

The mobile phase or carrier gas is supplied by a high-pressure gas cylinder through regulators and tubing. The sample is introduced into the GC instrument at the inlet or sample injection port. The molecules in the sample are vaporized in the injection port and the sample vapors (along with the carrier gas) travel through the column. The column is housed in a temperature-programmed. The gas stream is transported through tubing from the tank to the column exit and eventually, into a detector. GC relies on having an appropriate detector to measured and translated a signal response to useful data in the form of a chromatogram.

Common GC detectors are discussed, including the thermal conductivity cell detector (TCD), the flame ionization detector (FID), the electron capture detector (ECD), and the sulphur chemiluminescence detector (SCD). Mass spectrometry (MS) for detection is discussed in more detail in the following chapter of this handbook because it is a stand-alone experimental technique (does not require GC separation).

Gas Chromatography (GC) Method

Gas chromatography (GC) is the chromatographic method in which gas is the mobile phase and the column stationary phase is a solid or a non-volatile liquid attached to a solid support. GC can be used for analyzing mixtures made up of molecules (gases, liquids, and solids) that can be heated to form vapors (from solid or liquid into their gaseous form) and that don't break apart or decompose when heated. Gas chromatography is different from liquid chromatography because the mobile phase is essentially inert, and thus, is only used to carry the vapors; the vapors do not interact with the carrier gas. In LC, the liquid phase also interacts with molecules. Gas chromatography is advantageous because very small sample sizes can be used with minimal preparation, the technique is rapid (1-100 minutes), and it is efficient at separating complex mixtures into the individual components. Both organic and inorganic molecules (that can be vaporized in the inlet and are not immobilized in the column phase) can be separated. Also, GC can be automated to analyze hundreds of samples per day, and all for a very reasonable cost.[1]

Details on Molecule Separation
In gas chromatography, the principles that govern separations are based on a molecule's affinity for the stationary phase. A component with no interaction with the stationary phase is simply carried by the gas and is said to be "non-retained". If a component strongly interacts with the stationary phase it will take longer to travel the entire length of the column. If the stationary phase is a solid, a component's affinity for the stationary phase is governed by *adsorption*

(adhesion) onto the solid substrate; if the stationary phase is a liquid adhered to a solid support, the affinity is described by the molecule's *absorption* or *partitioning* (dissolving and vaporizing) into and out of the liquid phase.[1, 2]

The stronger the interaction between the stationary phase and the molecule, the larger the quantity of heat required to remove the molecule (sample molecule and carrier gas) from the surface of the stationary phase. A quantity can be assigned to this amount of heat and is referred to as the *enthalpy of adsorption, ΔH_{ads}*. A stationary phase needs to be selected so that the types of molecules to be separated have different adsorption or partitioning/absorption behaviors; additionally, the molecules can't adhere too well, or they won't leave the column. A GC separation is the process of molecules adsorbing (or partitioning) and releasing many times as they move through the column and separate out of the mixture. This process is often temperature dependent.

Separation is visualized in a chromatogram, which is a graph of the detector response as a function of time. Figure 1 presents an example of a chromatogram. A peak is the response of a detector to a molecule separated from the mixture. Two peaks have emerged, corresponding to two separated components. The area under the peak can be related to how much of a molecule is in the sample mixture. By use of standards, the identity of the peak can be determined by the time the it takes after sample injection for the peak to exit the column (the retention time, t).
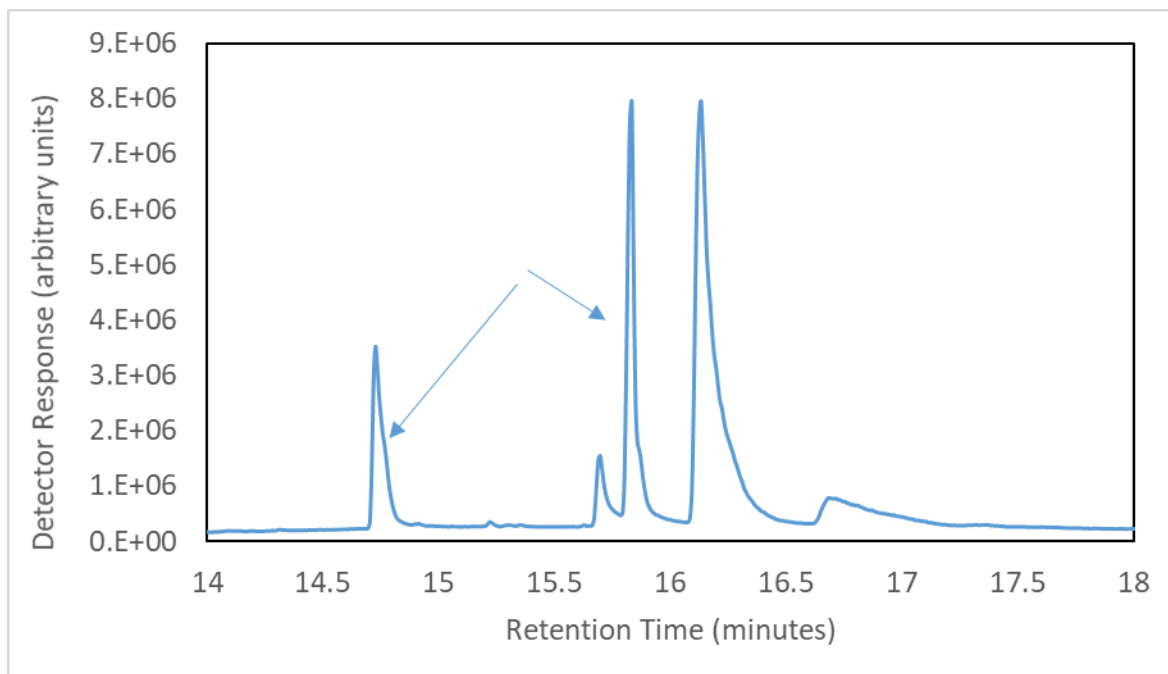

Figure 1: An example of a chromatogram is presented.

The chromatogram can be examined to determine a column's performance or resolving power, which is a column's ability to separate two peaks. Three chromatographic parameters that are used to evaluate a column's resolving power are: the retention factor, the selectivity factor, and efficiency. These parameters can be optimized by changing pressure, temperature, amount of sample introduced and heating profile and are dependent on the column length, stationary phase (chemistry) and on the molecule of interest. The retention factor and selectivity factor both describe the migration of solutes on the column. Equation 1 describes the retention factor for molecule A.

$$k_A = \frac{t_A - t_D}{t_D} \tag{1}$$

Here, t_A is the retention time for molecule A and t_D is the retention time for a non-retained solute to exit the column. The selectivity factor, α, is used to compare two eluting molecules and describes peak separation or isolation. It is the ratio of the retention factors of molecules A and B as shown in equation 2.

$$\alpha = \frac{k_B}{k_A} \tag{2}$$

Efficiency can be visualized on a chromatogram as a measure of a peak's width or sharpness. Efficiency can be measured by calculating the plate number, N, a dimensionless measurement based on the peak width at half the peak height and the retention time for a given molecule. A good column has a large N.[3]

Gas Chromatography Instrumentation

A schematic of a typical modern GC apparatus is shown in **Figure 2**, which consists of the following primary components:

1) carrier gas cylinder
2) flow controller and pressure regulator
3) sample inlet and injection port
4) column
5) column oven
6) detector (for example, a flame ionization detector)
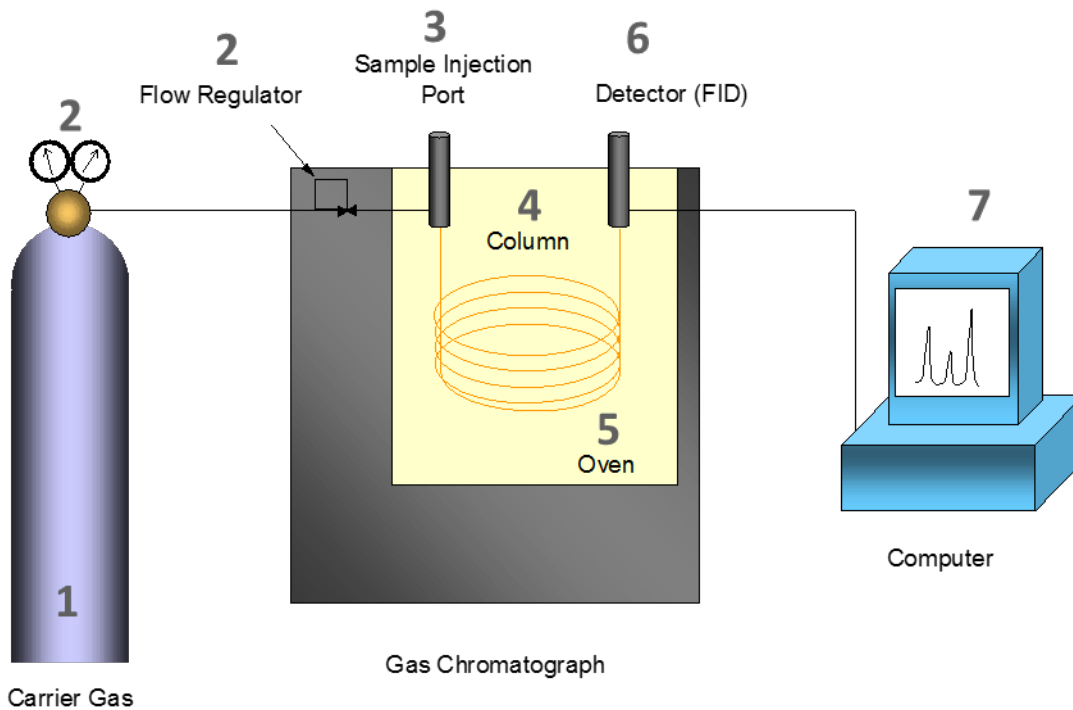7) computer

Figure 2: A schematic of a typical gas chromatograph apparatus.

In summary, a high-pressure gas cylinder supplies the mobile phase (the carrier gas) to the GC instrument through regulators and tubing. The sample is introduced into the GC instrument at the inlet or sample injection port. The molecules in the sample are vaporized in the injection port and the sample vapors (along with the carrier gas) travel through the column. It is important to note that the injector port is typically maintained at a temperature 20 – 40 °C above the boiling point of the sample. The column phase is selected to optimize molecule separation. The forced-air oven that houses the column is programmed to either remain constant at a chosen temperature (isothermal), or more commonly, to change the temperature throughout the separation to control, speed up, or improve separation efficiency. Usually the temperature is increased or plateaued during the separation. The gas stream is transported through tubing from the tank to the column exit and eventually, into a detector. In Figure 2, a flame ionization detector (FID) is shown, however, there are many detector options that will be discussed below. Finally, GC software is used to control all of the adjustable parameters: the flow rate, sample injection volume, vaporization temperature, oven temperature ramping program, and the detector temperature. The computer software is also used to translate the detector's response (electrical signal) into interpretable results in the form of a chromatogram (shown in Figure 1).

Safety is always a concern in the analytical lab. The potential hazards to be aware of in gas chromatography are the use of compressed gases, the possibility of exposure to heated surfaces and potential exposure to the samples injected into the instrument. Good laboratory practice will minimize any of these hazards.

Carrier Gas

The purpose of the carrier gas (mobile phase) is to carry the sample from the inlet, through the tubing, column, and ultimately, to the detector. The carrier gas needs to be inert, meaning that it should not interact and/or react with the sample (analytes or solvent) that is being injected onto the column. The carrier gas also needs to be dry, non-reactive, safe, and suitable for the detector used (this will be discussed in the "Detectors" section). Among all the gas choices, there are advantages and disadvantages. For example, hydrogen gas, the gas that filled the Hindenburg airship that exploded in 1937, is sometimes used as a carrier gas. However, since it has the potential to explode, necessary safety controls must be put in place before it can be used as the carrier gas. Helium is more common.

Impurities in the gas stream (oxygen, water and particulates) also need to be removed before entering the GC instrument. These can attack the stationary phase and/or cause high background noise. This is typically accomplished by having the appropriate filter (adsorbent trap) in-line between the gas cylinder and the GC instrument or use of an ultra-high purity compressed gas source.

In addition to choosing an appropriate gas, the gas flow rate is also important. The higher the flow rate of the carrier gas the shorter the run time of the experiment and the lower the oven temperature needs to be to get a molecule through the column, but lower flow can be necessary for hard to separate compounds, e.g., samples with similar retention times. An optimum carrier gas flow rate will depend on the column diameter, mixture molecules to be separated and the type of detector.

Flow Control and Measurement

The carrier gas flow rate should be measured and controlled to identify molecules and achieve an efficient separation. Often identification is determined by the amount of time required to elute a given molecule from the column (retention time). If the flow rate is inconsistent between experiments, the retention times will be inconsistent. The appropriate gas flow rate will depend on the size of and type of column (packed or capillary) and the film thickness of the stationary phase. Packed columns are made from glass or metal (copper or stainless steel) with $1 - 4$ mm internal diameters, are $1 - 5$ meters long, and are typically operated with $20 - 30$ mL/min flow rates, whereas capillary columns are made from fused silica with $0.1 - 0.5$ mm internal diameters, are $10 - 150$ meters long, and are typically operated with $1 - 10$ mL/minute flow rates.

The flow rate is determined by the desired separation, the size of the column and the choice of detector. It is selected to not only optimize separation, but also to be sufficient for the detector operation. For example, GC-MS requires the flow rate to be approximately 1 mL/min, while GC-FID can handle flow rates up to 20 mL/min.

Sample Introduction

There are several methods by which sample (both liquid and gas) can be introduced into the gas chromatograph. A liquid sample can be manually introduced into the injector by pushing a known volume of solution directly into the inlet with a small volume syringe (1-10 µL). The syringe needle pierces a gas-tight rubber seal (septum). A gaseous sample can be introduced by directly flowing a gas into the inlet, a gas sampling valve, or by use of a gas-tight syringe (100 – 500 µL). Liquid samples amenable to syringe injection can be injected manually or with an automatic liquid sampler (ALS). An ALS is often employed because it is much more accurate at injecting consistent solution volumes into the injection port with repeat injections. Reproducible volumes are necessary for quantitative results because the area under the peak on the chromatogram relates to the concentration of the molecule in the sample solution.

The main function of the injection port is to properly place the sample onto the beginning of the column. Typically, the injection port is heated to above the boiling point of the molecules of interest so that they can be applied to the column in vapor form. When choosing a proper GC inlet there are several aspects of the GC setup to consider, including: the diameter of the column that follows the sample inlet, the sample concentration, and the injection volume. The most common inlet encountered today is the split-splitless. This inlet allows some of the vaporized sample volume to be deposited onto the column and the remainder of the vaporized sample to be vented. The splitting of the sample is achieved by selecting an appropriate inlet liner, with sufficient volume to contain the vapor volume (upon injection of the sample into the heated chamber), and the correct gold seal. The vapor is formed in the inlet liner. Splits in the gold seal (at the base of the inlet liner) allow a path for some of the vapor volume to be diverted between the liner and the inlet body and out the split vent. Splitting the vapor volume injected onto the column avoids column overload and improves reproducibility. One disadvantage to splitting the injection volume is that higher boiling point molecules may not be accurately represented in the injection volume. Splitless injection is also possible with this inlet. In this case, the split vent is closed, and all the vapor volume is injected onto the capillary column.

Some additional aspects of sample introduction that need to be mentioned are the proper choice of sample solvent, injection volume and inlet temperature. These three parameters need to be optimized so that the solvent vapor volume does not exceed the total volume that the inlet liner can contain.

Columns for Gas Chromatography

The stationary phase is held in a tube that we call the column. Typically, there are two types of columns that are used; either a packed column with small particles coated with a stationary phase or a capillary column that is hollow and contains the stationary phase on the inner wall. Packed columns are used in separation of permanent gases and when standard methods (such as ASTM or EPA) call for their use. Most modern gas chromatography methods utilize capillary columns because they are far more efficient and sensitive than similar applications of packed columns. The remainder of this text will focus on instrumentation for capillary columns with liquid stationary phases.

Capillary columns can be classified further into porous layer open tubular (PLOT) columns or wall coated open tubular (WCOT) columns. WCOT columns are so ubiquitous that they are

often referred to as simply capillary columns. Capillary columns are made from fused silica. The columns are usually coated on the outside with polyimide (a strong, flexible and durable polymer or plastic that protects the more brittle fused silica from scratches) and coated on the inside with a stationary phase. The column is housed in the temperature-controlled oven. A stationary phase is selected to achieve the desired separation of mixtures. Stationary phases should reasonably solubilize the sample molecules and should have a negligible vapor pressure at the GC operating temperatures.[2]

All the molecules eventually exit the column to be analyzed by the detector. The separation of the molecules is dependent on many factors, for example, the chemical properties of the molecules being separated, such as their molecular weights, boiling temperatures, volatility, and polarities, as well as the physical and chemical properties of the stationary phase (density, surface area, and polarity). For example, a non-polar stationary phase will separate non-polar compounds with increasing retention times corresponding to increasing boiling temperatures, whereas, a polar stationary phase should be selected to separate polar molecules. Many other factors affect the separation, which we will discuss in more detail below.

Molecules are generally separated based on their polarity and volatility. To separate polar molecules a polar stationary phase should be selected. Some common stationary phase chemistries are dimethylpolysiloxane and polyethylene glycol (PEG) polymers. Dimethylpolysiloxane has a silicone oxide backbone with methyl substitution. When the backbone is completely substituted with methyl groups, this is the least polar stationary phase. The methyl groups can be replaced with either phenyl or cyanopropyl groups to increase the polarity of the stationary phase. The stationary phase can also be entirely made up of PEG polymer to obtain the most polar stationary phase.

In addition to stationary phase chemistry, the separation can be controlled by the stationary phase film (or particle film) layer thickness (0.1 – 1 μm), capillary column length and tube internal diameter. A typical specification, for example, would be 30 meters (coiled into a 6-inch diameter configuration) with a 250 μm internal diameter and a film thickness of 0.25 μm.

Chromatography configurations are not limited to only one column. A guard column, a short column placed between the inlet and the analytical column to remove impurities and particulate matter, is sometimes used to protect the column. Additionally, two capillary columns can be used in series. This practice was originally developed for the identification of hundreds of hydrocarbons in fuel mixtures in the 1990s. Today it is referred to as comprehensive two-dimensional chromatography (GCxGC) and is used to analyze very complex sample mixtures for fuels, environmental analyses, and food and fragrance applications. It works by pairing two GC columns, connected in series through a modulator, which is sometimes cooled. The carrier gas and sample molecules are carried from the first column to the modulator and are held there for a fixed period of time before being focused and injected into the second column. The first column typically is nonpolar and thus separates non-polar compounds essentially by boiling point. The second column is typically polar (to separate by polarity) and shorter, and thus, separation is more rapid. The chromatograms obtained through repeated trapping and injecting are rendered in two dimensions with boiling point on one axis and polarity on the other. Understanding and interpreting the resulting chromatogram requires complex software and a great deal of training.

Column Oven

Gas chromatography ovens are temperature programmable although operation at room temperature and/or constant temperature (isothermal) is possible and sometimes necessary. The temperature range can include temperatures less than zero (down to -100 °C) if a source of cool air (liquid nitrogen boil-off) or refrigeration is available and temperatures up to 450 °C. The oven temperatures are often restricted based on the column stationary phase. If the oven temperature is too low, the stationary phase will solidify (for liquid supported on a solid), making it difficult for absorption to take place. If the oven temperature is too high, the stationary phase will vaporize, potentially increasing the background signal and possibly fouling the detector.

In general, the oven is programmed to have a low initial temperature to resolve the low-boiling molecules and the temperature is increased during the separation to resolve the less volatile molecules.

Detectors

The detector indicates what and how much is in the carrier gas that exits the column. Detectors need to have the following characteristics:

1) high sensitivity
2) low noise
3) linear response to concentration
4) response to the types of chemicals the user is interested in
5) cost effectiveness

A detector should be selected with sufficient sensitivity for the intended analysis. Sensitivity is a measure of the smallest detectable quantity that can be measured above the noise divided by the width of the peak base in seconds. In general, sensitivity increases as the noise (the background electrical response inherent in the detector and electronics) decreases. Detectors are further defined by a range of compound concentrations for which the response of the detector can be fit with a straight line when plotted on a graph, for example, see Figure 3. In the linear response range the detector response can be converted to the compounds concentration, providing a quantitative analysis of a sample with a previously unknown analyte concentration. Different detectors also respond differently to the types of chemicals the user is interested in.
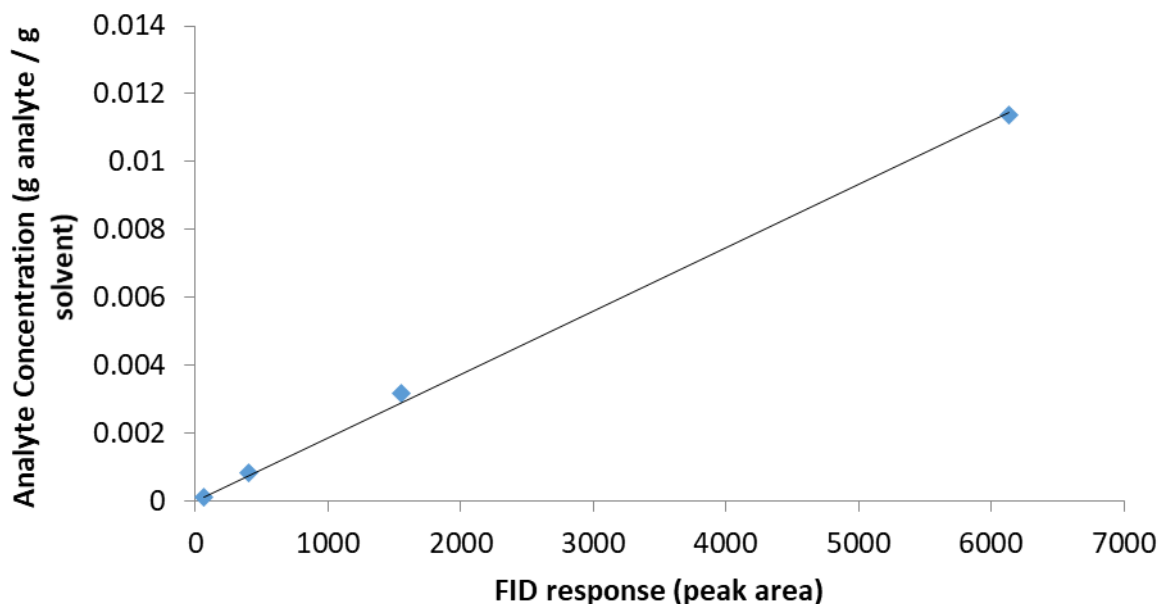
Figure 3: A graph of analyte concentration in solvent versus a flame ionization detector (FID) response. A linear increase in FID response with increased analyte concentration is observed.

Common GC detectors include the thermal conductivity cell detector (TCD), the flame ionization detector (FID), the electron capture detector (ECD), the sulphur chemiluminescence detector (SCD), and mass spectrometry (MS) detectors. Descriptions of each of these detectors, the operating principles, limit of detections, linear range, advantages, and disadvantages are presented next. GC-MS will be treated in more detail in the next article of this Handbook.

Thermal Conductivity Cell Detector (TCD)

The first gas chromatographs were built around the middle of the 1950s. Typically, the thermal conductivity cell detector (TCD) was the detector used for these instruments because it is rugged, reliable and easy to use.[4]

The TCD works based on the principle that a hot body will lose heat at a rate depending on the composition of the surrounding gas. For a hot wire-based detector, the flow of carrier gas (typically helium or hydrogen) through the wires (across the filament) removes heat at a specific rate depending on the thermal conductivity of the reference gas. When a sample is present, there is a change in the thermal conductivity of the gas mixture (a decrease in the rate of heat removal), which raises the temperature of the wire. The change in temperature causes an electrical resistance change, which can be measured and translated into a signal response in the form of a chromatogram.[5, 6]

An advantage to the TCD is that it uses a nondestructive process, so it is often used for prep scale chromatography application. A disadvantage is that it is not as sensitive as other GC detectors.

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The TCD is very useful for analyzing inorganic gases (argon, nitrogen, hydrogen, carbon monoxide, carbon dioxide, ammonia, carbon disulfide, etc.) and small hydrocarbon molecules (that might be found in natural gas, for example). The TCD is not very useful if the sample has water or oxygen impurities in it. These impurities can interact with the stationary phase and cause high baseline noise, which is problematic for the TCD because of its low sensitivity.

Flame Ionization Detection (FID)

The limitations of the TCD (its lack of sensitivity and use of helium gas, which was difficult to procure outside of the United States in the 1950s) led researchers to develop other detectors. In 1958, two detectors were introduced, one of which is the flame ionization detector (FID), the other is the electron capture detector, discussed later. With high sensitivity, an extended linear range, and lack of a radioactive source, it became the most widely used detector within a few years.[4]

The FID is based on the principle that the electrical resistance of a flame changes with the composition of the gases being combusted.[4] The FID is highly sensitive to carbon containing molecules and, in fact, has been referred to as a carbon counter. The FID typically uses a hydrogen and air flame, which has a high electrical resistance (it is very difficult to pass an electrical current through the flame). When a substance with carbon-hydrogen bonds exits the column, and enters the flame, carbon atoms produce an ion which decrease the resistance (increase the current across two electrodes). The corresponding chromatographic response is proportional to the change in resistance. It is important to note that since hydrogen gas is used, there is a significant explosion hazard when operating a FID.

The FID responds well to organic and combustible gases. It is not sensitive to the noble gases (helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)), carbonyls (compounds with C=O group(s)), alcohols (compounds with C−OH group(s)), halogens (compounds with fluorine (F), chlorine (Cl), bromine (Br), or iodine (I)), nitrogen-containing compounds, and noncombustible gasses such as water (H_2O), carbon dioxide (CO_2), sulfur dioxide (SO_2), and oxides of nitrogen (NO_x). The combination of sensitivity towards organics and insensitivity towards water make the FID particularly well suited for detection of pollutants in water samples.[3]

Electron Capture Detector (ECD)

At the same time that the FID was introduced, the argon ionization detector was also introduced, which was later modified to become the electron capture detector (ECD). This detector is most sensitive when measuring molecules that contain halogens, for example, pesticides and polychlorinated biphenyls (PCBs), toxic substances that were used widely as heat transfer fluids. The ECD uses a radioactive energy source to charge, or ionize, the carrier gas. The radioactive energy source is a β-emitter (β-rays or particles are electrons). The electrons emitted ionize the carrier gas, generating a standard current between a pair of electrodes. Molecules in the gas stream that capture or "absorb" electrons, such as halogens, cause the current to decrease sharply. The response signal is proportional to this decrease.

Sulfur Chemiluminescence Detector (SCD)

Sulfur molecules are ubiquitous in refining and petrochemical products. Sulfur has a negative impact on product quality, causes corrosion, poisons catalysts, and pollutes the air. For example, higher sulfur content in diesel fuels leads to higher emissions of particulate from diesel engines. A sulfur chemiluminescence detector (SCD) can be used to determine the sulfur concentration of diesel fuel, and thus determine the impact of the diesel fuel emissions on the environment.

In the SCD, the gas mixture flowing out of the end of the column is mixed with hydrogen and air and is burned just as in the FID. The resulting gases are then mixed with ozone, trioxygen (O_3). It is a pale blue gas with a distinctively pungent smell. It is present in the Earth's atmosphere in low concentrations and prevents damaging ultraviolet light from reaching the Earth's surface. It is also a powerful oxidant that reacts with sulfur molecules. When sulfur molecules encounter ozone, they react and luminesce (emit light). The intensity of the luminescence is proportional to the sulfur concentration. In an SCD, the luminescence is due to a chemical reaction, and thus, is termed chemiluminescence. Some disadvantages to SCD is that it requires stabilization (on the order of days) and can be tricky to operate. Also, the ceramic reaction tubes are costly and are prone to contamination from hydrocarbon residue.

Nitrogen Phosphorous Detector (NPD)

Another detector for GC is the nitrogen phosphorous detector (NPD). This detector is basically an FID with a bead of metal (rubidium or cesium) just above the flame. The hydrogen to air ratio is optimized to minimize hydrocarbon ionization, while the alkali ions on the bead surface facilitate ionization of nitrogen and phosphorous containing molecules, so it can detect the things that the FID is bad for. This detector is well suited for environmental and forensic applications, for example, detecting pesticide residues in food and water.

Conclusion

Gas chromatography is the method of choice for analyzing mixtures made up of anything that can be heated to form stable vapors Gas chromatography is robust (can be used with minimal preparation), is rapid (minutes), and is efficient at separating complex mixtures of both organic and inorganic components. The principles that govern separations are based on a molecule's affinity for the stationary phase. A component with no interaction with the stationary phase is simply carried by the gas and is said to be "non-retained". If a component strongly interacts with the stationary phase it will take longer to travel the entire length of the column. A component's affinity for the stationary phase is governed by *adsorption* (adhesion) onto a solid substrate; or by *absorption* or *partitioning* (dissolving and vaporizing) into and out of the liquid phase. *Enthalpy of adsorption, ΔH_{ads}*, describes the amount of energy required to move a molecule out of the solid substrate. Molecules with different ΔH_{ads} will move at different rates through a column determined by the instrumentation and adjustable parameters, for example, temperature ramping rate.

Separations are visualized by a chromatogram, a graph of the detector response as a function of time. A peak is the response of a detector to a molecule separated from the mixture and the area under the peak provides quantitative information. The chromatogram can be examined to determine a column's performance or resolving power (ability to separate two peaks). Resolving power is determined by the retention factor, the selectivity factor, and efficiency. These parameters can be optimized by changing pressure, temperature, amount of sample introduced and heating profile and are dependent on the column length, stationary phase (chemistry) and on the molecule of interest.

The instrument parts and the relevant adjustable parameters (temperature, pressure, phase chemistry, and solvent choice) for obtaining the best possible chromatographic separation are discussed in detail. The mobile phase or carrier gas is supplied by a high-pressure gas cylinder through regulators and tubing. The sample is introduced into the GC instrument at the inlet or sample injection port. The molecules in the sample are vaporized in the injection port and the sample vapors (along with the carrier gas) travel through the column. The column is housed in a temperature-programmed. The gas stream is transported through tubing from the tank to the column exit and eventually, into a detector. GC relies on having an appropriate detector to measured and translated a signal response to useful data in the form of a chromatogram.

Common GC detectors include the thermal conductivity cell detector (TCD), the flame ionization detector (FID), the electron capture detector (ECD), and the sulphur chemiluminescence detector (SCD). Mass spectrometry is another extremely powerful detector commonly available for GC analyses. Gas chromatography Mass spectrometry (GC-MS) is a much more complicated an experimental technique than GC with the aforementioned detectors, and thus, it is treated in more detail in the next article of this Handbook.

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