Fundamentals of GC:

Introduction: If you are already familiar with gas chromatography, we would recommend you go visit the Links/References page for more in-depth discussion of chromatography. This page is intended as a brief (really brief) description of the broad principles of gas chromatography for the less experienced user.

Gas chromatography is the process of taking complex mixtures and separating them into their individual components. The process typically involves the introduction of a complex sample into column (more on that later), separating the mixture as it moves through the column, and detecting the individual components as they come out of the end of the column. The process can be broken down into three main functions: sample introduction, separation and columns, detectors.,. Finally, we break the process down in a manner which even we can understand, the high school analogy.

Sample introduction: The key to sample introduction in gas chromatography is the rapid transfer of the analytes of interest onto the front of the column. This will minimize any further issues with the separations that may take place further down stream of the injection port. Having said that, there are numerous ways to transfer the analytical sample into the system depending on the form the sample takes. Probably the simplest method to introduce samples into a GC is to use a gas sampling valve. These valves, typically between 6 and 10 ports, have a loop of a known volume installed. The sample is loaded into the loop and periodically the valve is rotated so that the loop is placed in line with the column. The contents of the loop are transferred to the column while the loop is in line. The valve is then switched back and a new sample is loaded into the loop.

Liquid samples require more complex sample introduction techniques in part because it is necessary to convert the liquid into a gaseous form before introducing the sample onto the analytical column. The important point here is to clearly separate the analytes of interest from the solvent without discriminating against any of the analytes of interest (more on that in a bit.) Liquid injectors vary widely depending on the application but the most common liquid injectors include packed column, split injector and splitless/split injection. Packed column injection, as the name implies, are intended to be used with packed columns which typically have high column flow rates and, as a result, these injectors tend to be the simplest. A packed column injector consists of a flow or pressure controller and a heated zone that the column is pushed into. Since packed columns are usually 1/4 to 1/8 in tubing, the needle is placed directly into the column so no injection port liner is required although they are sometimes used to create a more inert injection port (hot metal can be very catalytic and lead to analyte breakdown.)

Split injection ports are usually used with capillary columns. They also provide high injector flow rates but unlike packed ports much of the flow supplied to the injector is split away and discarded. As a result, split injectors provide very sharp chromatography which is valuable for difficult to separate constituents or analytes which elute early in the chromatographic analysis. The price you pay for the high quality chromatography is sensitivity. Since most of the analyte injected into a split port is discarded, it is a process only applicable to concentrated samples. For some samples, such as pure petroleum products, this is not an issue since there is more than enough analyte available. For others, such as environmental samples, this is not acceptable. The process of throwing away sample is the other main reason for split injections (other than really sharp separations.) Capillary columns, by their nature, have limited column capacity before the chromatographic process starts breaking down. If the amount of sample being introduced is too high for the column to successfully separate, a split injection is an excellent way to limit the amount of material getting to the column and maintain good chromatographic separations.

In order to combine the best features of the split injection without throwing away sample, a necessity when doing trace analysis, there is a third injection port design called a splitless/split injector. (Most people say split/splitless injector but that is actually backwards since, at the time of injection, the injector is splitless and then goes split) In the splitless/split injector a valve is turned on which greatly reduces the amount of flow going down the injection port towards the GC column. In this manner, time is given to vaporized sample to move on to the head of the column. After a time, typically about 1/2 minute, the valve is re-actuated and much more flow is directed down the injection port and out to waste. This additional gas flow is meant to sweep the injection port of any residual analyte or solvent which may be left in the port. Using this injection port, it is possible to get very low detection limits for trace analytical work, while still maintaining most of the advantages of a split injection port, that is, good quality

chromatography. The only disadvantage of splitless/split injection ports is that they require more maintenance, care, and feeding than either a packed injection port or a split injection port. As evidence of this, look at a chromatography supply house list of inlet liners for a splitless/split port compared to the split port liner selection.

In the realm of sample introduction, there are number of other ways to introduce samples into a gas chromatograph. For air samples, there are thermal desorber systems where the air sample is concentrated into a small volume, either through cryogenics or the use of an adsorbent, and then rapidly heated and transferred to the GC injector. In much the same way, water and soil samples can be analyzed by removing the analytes from the matrix, concentrating them on an adsorbent, and then rapidly heating the analytes to transfer them to the GC. This is a process known as purge-and-trap. It is also possible to place a sample in a small bottle or vial (about 1/2 full) and allow the analytes to distribute into the headspace above the sample. An aliquot of the headspace gas is then introduced into the GC. Known as headspace extraction, this is one of the simplest means of sample introduction although not usually the most sensitive. water and Samples can be introduced in a number of different ways. Solid phase micro-extraction is another means of introducing samples into a GC. This technique is between a purge-and-trap and headspace in functionality, with some concentration occuring (like purge-and-trap) on the SPME fiber but an equilibrium being established (like headspace.) SPME is a relatively simple and low cost technique to implement manually. It's main disadvantage is the fragility of the fibers that are used.

Separation and columns: Gas chromatography is a separation science. Since GC is a separation science, and the column performs the separation, columns are the heart of the gas chromatography system. Most GC separation is based on the principle of like dissolving like. To begin with, there is what is called a stationary phase. This is typically a chemical coating on the inside of a piece of narrow bore tubing. This coating stays put, thus the name stationary phase. The analytes of interest, having been introduced in the injection port, are pushed into the column in the mobile phase. Mobile phases in GC are gases, typically helium, hydrogen, nitrogen and sometimes argon, which move through the injection port and through the entire length of the column. Hence the name mobile phase. The separations occur when analytes dissolved in the mobile phase interact (dissolve) in the stationary phase. Analytes which spend little time dissolved in the stationary phase (poorly retained analytes) elute from the end of the chromatographic column quickly. Analytes which spend a lot of time dissolved in the stationary phase (well retained analytes) elute from the end of the column very slowly or not at all. In theory, a simple process and one with tremendous potential.

There are number of ways to effect this separation process. First, you can increase the speed at which the mobile phase is moving and decrease the opportunity of the analyte to interact with the stationary phase. A good thing to do for things that are well retained but there are a number of limitations to this approach. Second, you can increase the amount of heat applied to the system which also has the effect of decreasing the opportunity of the analyte to interact with the stationary phase. An excellent tool for changing the elution times. Third, you can change the stationary phase. The most sophisticated way of changing retention times but also one of the most complicated. More on this just a few paragraphs down!

Since they are so critical to GC systems, columns come in a wide variety of sizes and many forms. Columns can range in diameter from 1/4 inch outside diameter down to the very small 0.10 mm inside diameter columns used for high speed GC. In general, as the outside diameter gets smaller and smaller, the efficiency of the chromatography gets better and better. This comes at a price though. As the columns get smaller and smaller, their capacity gets lower and lower, meaning that the amount of analyte you can put on the column gets lower and lower which means that the detector has to be more and more sensitive. Not a problem with the DiDD detectors!

Column lengths also vary widely. When columns were 1/4 inch outside diameter, they were usually about 2-10 feet long to effect the necessary separations. As the outside diameter got smaller, the length got longer. Now, most capillary columns come in lengths ranging from 15 to 100 + meters in length with the most common length being 30 meters.

Columns started out using a packing material. This packing material was placed inside the 1/4 inch (or 1/8 inch) tubing. These packing materials were often coated with other compounds (such as squalane) to change the characteristics of the packing material and, therefore, change the retention characteristics of the column. It was not long before these same compounds were being placed on the inner wall of narrower bore tubing to create the same retention characteristics while improving the chromatography. It started with narrow bore glass tubing and rapidly advanced to coatings on the inside wall of fused silica tubing. Thus, capillary chromatog- raphy was born.

As noted above, the coating on the inside diameter of capillary columns is called the stationary phase. Stationary phases range from the non-polar (oil like) to the polar (water like) with a vast range of stationary phases in between. The choice of stationary phase is very application specific but some examples are provided here for information purposes. If a pure hydrocarbon stream such as diesel fuel is being analyzed, then a non-polar stationary phase like a DB-1 (EC-1, SE-54, RTX-1, BP-1,) will do the job nicely. This stationary phase is considered a boiling point phase meaning that the compounds eluting off the column will come off in the same order as their boiling points. However, if a polar range of compounds is being analyzed, alcohols for example, then a more polar stationary phase would be used. An example of this would be the polyethylene glycol stationary phase typically known of as a wax (DB-Wax, Carbowax, EC-Wax, ...) In between these two extremes are a number of options such as phenyl, cyanopropyl, cyanophenyl, trifluoropropyl, and cyclodextrin as well as a number of secret recipes unique to specific column manufacturers. Each of these stationary phases will have different retention characteristics which will allow the chromatographer to obtain the necessary separations. A partial list of column manufacturers would include Agilent, Alltech, Chrompack, Phenomenex, Quadrex, Restek, and Supelco all of which have web sites you can get more information from.

Detectors: Detection is the process of converting the presence of the analyte in some place into an electrical signal. GC detectors a , there are a couple of different ways of characterizing detectors, bulk property detectors vs specific property detectors or unifversal detector versus specific detectors. Bulk property detectors rely on some change in the bulk characteristics of the analytical system By far, the most common detector in this category is the thermal conductivity detector or TCD. This detector relies on the change in the overall thermal characteristics of the carrier gas system as compounds elute from the column.

Specific property detectors rely on a specific characteristic of the analyte of interest. The most common example here is the flame ionization detector (FID) which relies on the creation of specific ions as hydrocarbons are burned in a hydrogen flame. These two detectors represent about 80% of the GC detector market.

The TCD is also considered a universal detector since it responds to everything that has a thermal conductivity different from that of the carrier gas. The nitrogen phosphorous detector is a good example of a detector that is selective since it selectively responds to compounds containing N and P in their structure. ,

The decision about which detector to use depends on several factors. The ability to detect the analyte of interest, obviously, has to come first but in most cases that is not that hard to figure out. Sensitivity generally comes right after that, which is to say, can I measure the analyte(s) I need to at the levels I need to. If you are talking about very high levels of analytes, almost any detector will meet these requirements but if you are talking about very low levels of analytes, the decisions get a little more complicated.

Price and ease of use generally form the next set of questions and, at this point, trade offs almost always occur at this point. Under the price category, detectors run from a few thousand dollars for an FID, TCD or DiDD up to the $50+ thousand dollar range for mass spectrometers. Operating costs also play into this consideration. Since the TCD usually requires only one gas for operation it is one of the least expensive detectors to operate while FID's and NPD's will require two or three operating gases which increases the overall cost of ownership. While mass spectrometers only require one gas to operate, they generally have many more ancillary support needs and their hardware replacement costs are high enough that they would be placed at the higher end of the cost of ownership scale. At the same time, ease of use is important. Again, the TCD wins this one since it is one of the easiest detectors to use although its sensitivity is the worst. Also in the easy to use category would be the DiDD operating in the AID mode since it is easy to start, windowless and only requires one reaction gas. FID's are also generally thought to fall into the easy to use category as long as you are not having trouble getting them to light! In the middle of this category are detectors like the ECD, the PID, and the DiDD HID and ECD. These detectors require

Table 1: Review of Detectors commonly used in Gas Chromatography

Name	Type/operating characteristic	detection limit	relative merits	disadvantages
TCD	Universal/change in gas thermal characteristics	low-mid nanogram	detects everything, simple to use	not very sensitive
FID	Almost universal/ creation of ions from burning hydrocarbons	low nanogram	large linear range, excellent carbon counter	uses a hydrogen flame, multiple support gases, won't detect some compounds
PID	Selective/ionization of compounds with low enough ionization potentials	mid-picogram	selective, sensitive	window maintenance, won't detect some compounds
ECD	Selective/capture of free electrons in the detector	low-picogram	selective, extremely sensitive	radioactive source, fussy
NPD/TSD	Selective/ionization of nitrogen and phosphorous containing compounds	low to mid-picogram	sensitive, excellent nitrogen and phosphorous selectivity	very fussy, multiple support gases
MSD	Universal/electron impact ionization	low nanogram (scan) low picogram (SIM)	structural information is available	cost, cost, cost, complexity, vacuum system
DBD AID	Selective/ionization of compounds with low enough ionization potentials	low picogram	sensitive, easy to use, flameless	compound dependent response, won't detect some compounds
DBD HID	Universal/helium ionization	mid to high-picogram	detects everything	fussy, about as fussy as a standard ECD
DBD ECD	Selective/capture of free electrons in the detector	low picogram	ECD w/o radioactive source	extra dopant gas required

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more system maintenance such as window cleaning and they require more attention to details such as gas quality and system leak tightness. However, once these items are addressed, these detectors are easy to use. At the extreme of this category, in our opinion, are detectors like the mass spectrometer and nitrogen phosphorous detector which require attention more often than others listed above. Source cleanliness, tuning factors, bead voltages, appropriate solvents and flow rates must be strictly observed for these detectors to provide reliable and stable performance.

The last set of questions that come into play when deciding on detectors is the need for specificity or selectivity. If you have plenty of chromatographic separation between you analyte and the interferences that may be present, a TCD, FID or HID will all do the job nicely. If, however, you need to pick your analyte out of a large amount of sample interference, you might need a specific detector such as the ECD, NPD or mass spectrometer to resolve the analyte of interest from the matrix interferences.

Examples of different types of detectors appear in Table 1 above with the relative merits of each and their approximate detection limits. This list is by no means exhaustive, but rather an indication of the number of different types of detectors that are utilized depending on the application. In the honorable mention category of GC detectors, we would toss out some other types that are less familiar. These include the ultrasonic detector, the electrolytic conductivity detector, the reductive gas detector, the surface ionization detector, the sulfur chemiluminescent detector, the HAFID detector, and many, many more. For much more information on detectors, please look on the links/references page or contact us. Since detectors is one of the most important things that we do, we would sincerely appreciate the opportunity to talk your ear off when it comes to detectors and the applicability in the world of GC!

The high school analogy:

The analogy we like to use is this. If you take a high school student body and ring of the bell between classes, you have a good model for the process of gas chromatography. The least popular students are not as likely to get held up in the hallway and, as a result, will get to their next class quickly. The more popular students might end up talking to someone and get there slightly later. The really popular students might end up in a round table discussion at a locker and get to class much later. This is the essence of chromatography. Those compounds which do not interact strongly with the stationary phase (the lockers) will arrive at the detector first. Those compounds which interact more strongly will arrive later and those compounds which interact strongly (the around-the-locker discussion) will arrive much later or not at all.

Using this analogy, we can also discuss the ways in which chromatography can be modified. If we increase the pressure on the students (a principal in the hall) we can increase the speed at which the students make it to the next class with some loss in the resolution. We can also increase the temperature and get the same effect (sorry, no analogy there!) We can also vary the stationary phase of the column to change the way the compounds elute. For example, if we do not have lockers to meet at, then the separation becomes one of simple walking speed and distance between classes and the order of elution (who gets to class first and last) may be vastly different than it was in the first example.

In summary, the bell becomes the injector, the lockers in the hallway become the stationary phase, and the teacher becomes the detector. The bell has the effect of quickly releasing all of the students into the hallway much the same way an injector is intended to quickly release the sample onto the analytical column. Depending on the configuration of the hallway, students will be separated according to their interaction with the the lockers in the hallway much the same way that the stationary phase will separate the analytes. The teacher becomes the detector. That is, they will measure the signal coming in and put it in a recordable format. If the teacher is not sensitive, much of the information (who is getting to class first, second, third, etc.) is lost and only the crudest form of information (overall presence or absence) is available (analogous to the TCD) If you have a really sensitive teacher, they will record when each student arrives in class (like the DiDD detectors.) Pretty straight forward when you think about it that way!