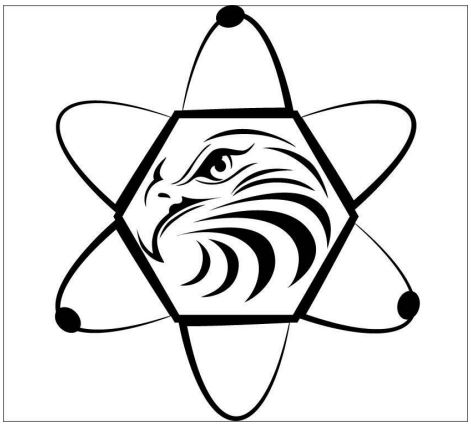


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## Basic Gas Chromatography Seminar

The following manual was produced by American Mobile Research, Inc. with the intent of educating those individuals who either deal with the hands-on operation of a gas chromatograph or those who simply wish to understand the dynamics behind chromatography for purposes of reviewing chromatographic data.

The material outlined in this manual was prepared and presented by American Mobile Research, Inc. with the assistance of various other chemists and published authors. This manual is prepared as a guide to those who deal with chromatographic analyses and data interpretation and wish to understand the complexity of obtaining accurate chromatographic data. Once you understand the chromatographic system and problems which can inhibit accuracy, you can begin to feel confident in performing quality analysis. The authors and chemists contributing to this manual (as well as American Mobile Research, Inc.) appreciate that education must be taught to those who deal with this type of analysis.

We hope that this will be a strong educational influence in the future of your chromatographic career.

# Lecture 1. Basic Gas Chromatography

### 1a) *Definition of Gas Chromatography*

The basis for gas chromatographic separation is the distribution of a sample between two different phases. One of the phases is a stationary, solid support bed with a large surface area and the other phase is a gas, which percolates through the stationary phase.

Gas chromatography is a technique used in separating volatile substances by percolating a gas stream over a stationary phase. If the stationary phase is a solid support, it is referred to as *Gas-Solid Chromatography* (GSC). GSC relies on the absorptive properties of the column packing to separate samples, primarily gases. Common packings used for this type of chromatograph include silica gel, molecular sieves, and activated charcoal.

If the stationary phase is a liquid, it is referred to as Gas-Liquid Chromatography (GLC). The liquid is spread as a thin film over an inert, solid support, such as Chromosorb P, and the basis for separation is the partitioning of the sample in and out of the liquid film. Since there are a wide range of liquid phases available, with usable temperatures up to 400 degrees Celsius, GLC is the most versatile and selective form of gas chromatography. The versatility makes GLC suitable for the analyses of gases, liquids, and solids.

### 1b) *History of Chromatography*

The first application of chromatography occurred in 1905 by a chemist named Ramsey. His first experiments used selective absorption on, or desorption from, solid absorbents such as activated charcoal. The following year, another chemist named Tswett obtained discrete color bands of plant pigmentation on a chromatographic column. He coined the development as “chromatography,” which literally means “color writing,” an obvious misnomer when applied to current methods.

Following the suggestion of two chemists, Martin and Synge, in a study for which they were later awarded the Nobel Prize, Martin and Synge introduced Gas-Liquid Chromatography in 1952. The sensitivity, speed, accuracy, and simplicity of this procedure for the separation, identification, and determination of volatile compounds resulted in phenomenal growth.

At the time of this writing, there are more than 18,000 gas chromatographic references and methods, with a growth rate of about 2,000 per year. It is estimated that there are well over 250,000 chromatographs in use worldwide.

**1c)** ***Chromatographic Apparatus***

The following is a list of basic parts of a chromatograph. Each is discussed in detail in section 1d.

a) Carrier Gas Supply, complete with flow controllers and flow regulators. Carrier is usually Helium, Argon, or Nitrogen.

b) Sample Inlet Injection Ports. Ports made of stainless steel where samples can be syringe-injected, or stainless steel sample valves (Valco) capable of delivering a reproducible amount of sample, usually steel sample loop pre-calibrated.

c) Column Systems

d) Detector Systems

e) Pyrometer controls for column oven, injectors, and detectors

f) Recording integrator or computer

1d) ***Basic Chromatographic Systems***

a) Carrier Gas Supply

A high-pressure gas cylinder serves as the source of containment for the carrier gas. During Isothermal Gas Chromatography, the permeability of a column does not change during the analysis. Pressure regulators are used to assure a uniformed flow of carrier to the inlet injector ports, and thereby a constant gas flow through the column system. At a given temperature, this constant flow rate will elute components at a characteristic time (the Retention Time). Since the flow rate is constant, the components also have a characteristic volume of carrier gas (the Retention Volume). Common carrier gases used are Hydrogen, Helium, Nitrogen, and Argon-Methane mixtures. The columns separating efficiency depends upon choosing the proper linear gas velocity. This means choosing the proper carrier for the percolating phase. A common value for a 1/4 inch O.D. is 75 mls per minute, versus an 1/8 inch column at 25 mls per minute flow.

Over the years, many chromatographers have inquired as to how pure the carrier gas must be, considering the economics of their operation and the varied cost of carriers based on purity. For the standard type of analysis we perform in the petroleum industry, a grade of 99.99% purity is more than adequate. Some companies wish to use 99.9999%

pure carriers, and this is fine (even recommended by many Chromatograph manufacturers.) However, the analysis of Hydrocarbon gases and liquids on Thermal Conductivity Detectors is not designed to determine low part per million ranges, where high purity carriers are necessary to reduce contaminant baseline noise such as water, oxygen, etc. A carrier with a purity of 99.99% is sufficient to perform daily analytical chromatography in our business. Moisture and water traps can be purchased and placed in-line between the carrier bottle and chromatograph if you wish to use cheaper carriers, allowing removal of these contaminants while still obtaining high resolution with minimal baseline noise.

When using Flame Ionization or Flame Photometric Chromatography, a high purity carrier is necessary since these instruments are used to determine low part per million range constituents. High purity carriers are necessary to produce a baseline which is quiet, so that noise and low level constituents can be easily differentiated, where the sensitivity of a Thermal Conductivity Detector does not see the lower levels of noise detection.

b) Inlet Injection Ports

The carrier gas enters the chromatograph at the flow controllers and is fed directly into the Injection Port through a “T” alignment. The gas enters the injector about 1/4” below the septum, forcing the flow to move from the injector through the column to the detector. There are two types of injections at the injectors. There is an “on column” injection, in which a gas or liquid is injected directly onto the column with a syringe, bypassing the actual injection port. There is also the “flash vaporizing” injection in which the gas or liquid is immediately flash-vaporized by the temperature of the heated injection ports, then swept into the column by the carrier gas.

The temperature of the injection ports is usually isothermal, around 200 to 250 degrees Celsius for gas analysis, and around 300 degrees Celsius for liquid analysis, allowing complete vaporization. If the temperature of the injector is too cool for the product being tested, incomplete vaporization will occur, causing the injection ports to become “coked” or causing condensable Hydrocarbons to accumulate at the entrance to the column. Coked material will eventually cause the injector’s liner to plug, causing erratic flow rates, and condensable Hydrocarbons will slowly elute as *ghost peaks* through the column. The injector temperature should always be set at least 50 degrees Celsius higher than the maximum column temperature.

Many chromatographs are equipped with an externally mounted gas sampling valve. This allows admission of large sample volumes, usually 1cc or higher, of gases to the chromatograph with the switch of a valve. The advantage of the loop injectors is that they are reproducible in volume delivered to the injection ports.

Likewise, internally-mounted liquid injection valves are used to assure completed vaporization of liquids and deliver a constant volume, usually 1 uL or larger, to the injection ports. Internally-mounted valves use the hot oven to provide the high temperatures needed to volatilize the liquids and sweep them into the injection port, then the column. Valves mounted on the outside of the chromatograph for liquid analysis are wrong. These valves do not provide the high temperatures needed to assure the volatility of the product in the loop, therefore, only part of the product (constituents with a boiling point less than room temperature) will be volatilized, leaving the heavier constituents in the loop, thus yielding an incomplete analysis.

c) Column Systems

The column is considered the "heart" of the chromatograph. Depending on the selection of the *stationary phase* and the *liquid phase*, the column system performs all of the separation capabilities for the instrument. Other factors such as the column's length, carrier flow rates, and temperature, can enhance the columns' separating efficiency, when relative to the tested product.

The proper selection of the stationary and liquid phases are the most important aspects when choosing the column system needed to perform the task of analyses. The stationary phase will provide a large, uniformed inert surface area for the distribution of the liquid phase. High crushing strength, large surface area, and uniformed size are all desirable characteristics of a good stationary phase.

The correct choice of the liquid phase to be used is probably the most important parameter in gas-liquid chromatographic separation. The ideal liquid phase should have the following characteristics: a negligible vapor pressure at operating temperatures, a different distribution coefficient than the samples being analyzed, and a reasonable solubility between the sample and the liquid phase. For the analysis of most petroleum products, a liquid phase composed of a silicon rubber. SE-30, OV-101, DC 200/500, and Carbowax are the most effective in hydrocarbon separations. The next step in providing the proper separation is in the amount of liquid phase to be used called the "loading." Too little or too much loading will yield a poor separation of the constituents. If there is

not enough liquid phase used in manufacturing the column, there will not be sufficient solubility between the sample and the liquid phase to allow separation of the lighter constituents such as Nitrogen, Methane and Carbon Dioxide. If too much loading is used, then the separation of heavier constituents, such as Butanes, Pentanes, and Hexanes will be eluted as long, broad, undefinable peaks, since the solubility between the liquid phase and the sample will result in increased retention of constituents as they are passed through the column. For most Hydrocarbon separations, a loading of between 10% to 20% liquid phase is adequate to provide a good light gas and heavier component separation. The highest loading which can be used is around 30%, however, “pooling” of the liquid phase will begin above 25 %, in which the high amount of liquid phase begins to channel in between the stationary phase, causing the column to plug, and the separation to be inadequate.

The column tubing can be made from copper, stainless steel, nickel, and glass, in a straight or coiled configuration. In general, stainless steel is used, packed while straight to obtain uniformed packing, then coiled to facilitate longer lengths. If coiled, the spiral diameter should be at least *ten times* the column diameter to minimize diffusion. Packed columns may vary in length from a few inches to more than 50 feet. Common analytical columns made with metal tubing usually range from 3 feet to 30 feet, using a 1/8” o.d. tube. The longer the column, the more theoretical plates and resolution will be achieved. The more theoretical plates, the better the separation capability you will maintain.

Glass column systems, which have become increasingly popular over-packed columns, offer greater lengths and separation capabilities. Wide-bore glass capillary columns are the most effective columns available for the separation of multi-constituent products. The wide-bore glass column is coated with the same liquid phases used in packed columns, without the solid support, just the glass walls of the column to disperse the liquid film. These columns are excellent for the separation of gas and liquid Hydrocarbons when used in lengths of between 30 and 60 meters. Although they are made of glass, these columns are durable and not as fragile as one might think. The wide-bore glass columns are fragile and require a sufficient amount of “lead line” from the injector to the column and from the column to the detector. The smaller bore glass is very flexible and easy to work with.

d) Detector Systems

The detector and associated electrometer systems indicate the presence and measures the amount of constituents in the column effluent. Some of the more desirable characteristics of a detector are high sensitivity, low noise levels, a wide linearity insensitive to flow and temperature changes, and an expensive cost.

There is no *ideal* detector system, however, the thermal conductivity and flame ionization detectors come close to being universal. In addition, specific detectors such as *flame photometric* and *electron-capture detectors* selectively detect certain compounds, such as Sulfur compounds and Poly-chlorinated Biphenyls, respectively. This makes them very useful in trace analyses of specific compounds.

The two most common detectors utilized in petroleum testing today are the *thermal conductivity* and *flame ionization systems*. The *Thermal Conductivity Detector* (TCD) employs a tungsten filament which is heated by passing constant current through it. Carrier gas flows continuously over the heated filament and dissipates heat at a constant rate. When sample molecules mixed with the carrier gas are passed over the heated filaments, the rate of heat-loss is reduced and the resistance of the filament is increased. The change in the resistance is easily measured by the *Wheatstone Bridge* and the signal is fed to a recorder where it appears as a peak. The principle operation is that the ability to conduct heat from a filament is a function of the molecular weight of the gas surrounding it.

In the *Flame Ionization Detector* (FID), Hydrogen and Oxygen are used to produce a flame within the detector. A collector electrode, with a DC potential applied, is placed above the flame and measures the conductivity of the flame. With pure Hydrogen, the conductivity is quite low, however, as organic compounds are ionized in the flame, the conductivity increases and the current which flows can be amplified and fed to a recorder. Later, these detectors will be discussed in more detail, as well as their current application to petroleum testing.

# Lecture 2. Product Sampling & Application in Analyses

*a) Introduction*

For many years, we have studied the effects of sampling versus analytical accuracy. We have determined that *good* sampling and analytical accuracy go hand-in-hand. The accuracy of the chromatograph can be determined with a series of standards: however, there are no standards to determine the accuracy of the sampling. Since the accuracy of the sampling depends entirely on the *sampler.* A repetitive sample style and understanding of the sampling points will aid in obtaining an accurate sample.

In a recent study between commercial laboratories in which a standard Hydrocarbon gas was sent to each lab for comparison, all labs reported the same distribution after analyzing the samples they received. The labs were then asked to secure a gas sample from the same sample point, ten minutes apart from each other.

Upon completing the analysis of the samples obtained by each lab (three different samplers), the results were compared and found to be quite different in Hydrocarbon content. While one lab reported 72.30 mole percent of Methane, another reported 76.80 mole percent of Methane on samples taken ten minutes apart. It was also noted that one lab indicated a 0.51 mole percentage of Hexanes and heavier hydrocarbons, while another lab reported 3.83 mole percentage Hexanes and heavier on the same sample point, ten minutes apart.

Since the Hexanes and heavier content was so far apart, a review of the sampling procedures commenced. It was determined that while one lab used the proper gas manifold set up for obtaining their samples, the others simply attached the cylinders directly to the sample point. The difference in sampling methods could easily explain the discrepancy in the data between the labs. By attaching the cylinder directly to the sample point a larger volume of liquids (condensable hydrocarbons) were taken into the cylinder upon opening the valve. The gas sampling manifold, outlined by the *National Gas Producers Association*, will allow condensable liquids to fall out and be removed before the cylinder. A more *representative and uniformed* sample is obtained using a manifold. In any case, this type of sampling error is common. Uniformed sampling of gas and liquid Hydrocarbons must be practiced routinely, just as often as instrumental standardization. Emphasis on the proper sampling techniques can assure the analyst that the proper results are obtained.

*b) Sampling of Hydrocarbon Gases for Chromatographic Analysis*

Begin by selecting the proper means to transport the samples for analysis. Unless a mobile laboratory is available to sample directly off the sample point, the proper cylinder must be selected to hold the gas until it may be sent to a lab for analysis. If the samples are to be shipped for analysis, it is advisable to use stainless steel or aluminum metal cylinders. The reactivity of Carbon steel to Hydrocarbons is low, however, its reactivity to Oxygen, Carbon Dioxide, and especially Sulfur compounds is very high. And in most instances, there are one or more of these compounds present in gases.

Also, the corrosive scaling inside a Carbon steel cylinder will be dislodged when high-pressure, high-velocity gas is passed through it. The particulate is blown out of the cylinder into the sampling valve, where it can cause etching on the surface of the Teflon coating on the valve. This problem is common when using Carbon steel, therefore, 10 micron sampling screens should be placed in-line between the cylinder and the valve. Replaceable screens will preserve the life of your valves, and stop unwanted particulates from depositing on your column inlet.

Stainless steel cylinders are the most common metal cylinders in use. However, the cost of these cylinders is considerably higher than any of the other metals used. Stainless steel cylinders are preferred because of their wall strength and the low reactivity with Carbon Dioxide and Oxygen. However, the reactivity with Sulfur compounds, such as Hydrogen Sulfide and Sulfur Dioxide, is high with stainless. Passivation of Sulfurs begins to occur instantly with both Carbon steel and stainless steel. Stainless has a slower passivation rate than Carbon steel, but most Sulfurs are passivated within *one hour* from the time of sample admission. Teflon-lined stainless steel cylinders offer the sampler the opportunity to sample corrosive gases and transport them for analysis, with little to no passivation. On the surface, this seems like the logical container for Sulfur gases to be kept in, however, as we discussed, high-velocity gas from a Carbon steel line (sample point) will blow particulate through the cylinder, scratching the micro-thin Teflon walls. Once the particulate scratches the Teflon, exposing the stainless steel, passivation begins immediately. Additionally, there is the cost to inspect and re-coat these cylinders continuously to assure no passivation. This cost usually forces samplers to use stainless steel or Carbon steel, without coating the internal walls to prevent passivation.

The Aluminum cylinder, which is our company choice for gases, has great advantages over stainless or even Teflon-lined stainless. These cylinders are about 1/3 the weight of stainless steel, with just as high wall strength as stainless. Unlike stainless

steel though, aluminum offers a very slow passivation rate to Sulfurs, holding Hydrogen Sulfide and Sulfur Dioxide *ten times longer* than stainless. The cost is about 1/3 that of stainless. Reactivity with Carbon Dioxide and Oxygen is practically non-existent. Therefore, we believe the Aluminum cylinder is an *excellent* metal container for transporting corrosive gases or liquids.

If the sample is being drawn specifically for Sulfur compound studies, then Teflon-lined stainless steel or Aluminum would be preferred. However, we have found through many studies that any Sulfur study should be performed on location, with FPD Chromatography, to eliminate the probability of passivation. Mobile chromatography is becoming more accepted, despite its cost, because of the accuracy element. Anyone working on treater designs for Sulfur removal should consider the option of performing the analysis on-location with a mobile lab as opposed to submitting samples to an independent lab for analysis. From most locations around Wyoming, samples could not be transported to a central lab fast enough to prevent some degree of passivation. This is reason enough to utilize mobile Sulfur analyses.

Once the selection is made as to what type of container and analyses are required on the sample, the sample point should be reviewed carefully before taking a sample. Make any notations of irregularities in the sample valve, line, and location. We have had the experience over the past years to work in many facilities throughout our region, most of which maintain a corrosive product which causes Hydrogen embrittlement, causing sampling valves and taps to strip threading.

Valves should be inspected to assure they can maintain the pressure and cylinder, without the chance of leaking or cracking when opened and closed. If the sample valve is corroded, placing a sampling manifold on the line and opening the valve could induce outside air into the sample, yielding false Nitrogen values. Often, plants are designed, with sampling points considered low priority with sample points often located on the bottom or side of the line, not on top vertically. The location of the sample point could determine the validity of the sample. If the sample point is located under the line, condensable liquids will gather, yielding higher-than-normal Hexane plus values. If the sample point is located on the side of the line, again, the chances of erratic liquid contamination could nullify the sample validity.

The sample point should be located on the top of the line with a *stinger* or *sample probe* set down into the line to composite all levels. Hook the inlet to the sampling manifold into the sample point. Connect the cylinder to the manifold. Close the valve to

the cylinder and open the drain valve on the manifold. Allow the gas to purge through the manifold and then out the manifold drain for about *one minute*. This will give collective liquids time to purge through the manifold. Then, close the drain and open the cylinder to the sample source. Trap, then purge, the gas in the cylinder several times, (at least *ten times* for pressures below 100 psig and at least *three times* for high pressure gases over 500 psig. After the final trap, close the sample point valve and bleed the manifold through the drain. Remove the cylinder and cap the ends. Then, prepare the label and tag it.

Cylinders and valves should be pressure checked every *six months* to assure the integrity of the cylinder before field use. Be sure that you never over-tighten the brass valves on the cylinder with wrenches to prevent leaking. Over-tightened valves will split the Teflon or viton O-rings, causing the valve to leak continuously, despite efforts to hand tighten the valve.

There are several ways to prepare cylinders, depending on the analysis to be performed. The *Helium Pop* method is common among samplers. The cylinder is pressure tested, submerged underwater to verify no leaks, then all but about 10 psig of Helium is left in the cylinder. The positive pressure from the Helium will keep outside air from entering the cylinder before sampling. When the cylinder is attached to the sample manifold, the remaining Helium is released during the trap-and-purge procedure.

A sampler should be able to put his finger over the cylinder valve before sampling, open the valve, and feel the back-pressure from the cylinder against their finger. This will help assure you that the cylinder can maintain pressure during transit. If no pressure is felt, then the sample cylinder should be replaced because it will not hold its contents. Even a slight leak should invalidate the sample.

Often, sample cylinders are used for sampling contaminants in air. This type of analysis the cylinder is vacuum-pulled with a pump. The cylinder is allowed to sit on a vacuum pump for about *two minutes*, totally removing all traces of air. The cylinder is tested on location before sampling by placing a finger over the valve and opening the cylinder. If the cylinder is still vacuum pulled, your finger will be drawn to the valve and the cylinder should be closed, while your finger is still over the valve, to prevent outside air contamination. The vacuum cylinder is placed directly on the sample point, without a manifold. With the sample point opened, slowly open the cylinder valve and draw the sample into the cylinder. Close the cylinder valve as soon as a sample is obtained. Cap the cylinder before you transport it just to assure no leaking or outside interferences.

*c) Sampling Pressurized Hydrocarbon Liquids*

The *NGPA Method* for sampling liquid Hydrocarbons is a bit more complex than that of gases. Since Hydrocarbons, such as Ethane, Propane, and Butanes and Pentanes expand into vapor at room temperature and atmospheric pressure, the liquid hydrocarbons must be sampled using a *piston cylinder*.

The piston cylinder, manufactured by *Welkler and Y-Z Industries*, is designed to allow liquid hydrocarbons to enter the cylinder with a stainless piston. The backside of the piston cylinder is pre-pressurized above line pressure. Then, as the liquid Hydrocarbon enters the cylinder, the backside pressure is slowly released. When the backside pressure has equilibrated to the sample line pressure, the piston will slowly begin to slide back into the cylinder, allowing liquid Hydrocarbons to remain in compression while they are sampled. Maintaining a slow movement of the piston as the sample enters the cylinder is the *key* to maintaining good equilibrated compression on the liquid Hydrocarbons. Once the cylinder's magnetic indicator shows the volume to be about 80% of the total cylinder volume, the backside pressure is shut-in and the inlet valve is closed. The sample is now drawn in a cylinder that will maintain at least line pressure to stop the vaporization of volatile Hydrocarbons. When the cylinder is submitted to a lab for analysis, the backside pressure must be increased by at least 100 psig over the sample line pressure (most labs will re-pressurize the backside to at least 1000 psi, regardless of whether the line pressure is 100 psig or 500 psig.)

In conjunction with the piston cylinder, a sampling manifold should be made using high-strength, high-pressure stainless hosing and a T-valve so that the high-pressure line may be blown down after sampling and the liquid product can be purged through the line before sampling to remove moisture and air contamination. If the line is attached without a means of purging the air out, false Nitrogen contents will be obtained. When working with any high-pressure gas or liquids, safety dictates a blow-down valve to relieve pressure from the line. *Always wear protective glasses and gloves when working with high pressure liquids.* Propane and Butane can also cause severe damage (frostbite) to exposed skin. Always wear cryogenic gloves when sampling Propane or Butane products.

Alternatives to using a piston cylinder for sampling pressurized liquid Hydrocarbons include Water or Glycol-displacement cylinders. A stainless sampling cylinder is filled with water. The water-filled cylinder is placed on the sampling manifold

in a vertical position so that the liquid hydrocarbon enters through the top, and water can be removed through the bottom valve of the sampling cylinder. The manifold is purged to remove air, then the top valve of the cylinder is opened to receive product. After the top is opened, the bottom valve to the sampling cylinder is opened slowly. should flow out of the cylinder at about 100 cc per minute. The water should be caught in a graduated cylinder so that only 80% of the total cylinder volume of water is removed. Do not allow all of the water out of the cylinder, because you will lose compression immediately. A 20% outage of the remaining water in the cylinder can be taken after sampling to allow for any expansion of gases from the pressurized liquids when temperatures warm up. during transit. Once the cylinder is returned to the lab for analysis, it will be placed on a re-pressurization system which re-compresses the gases back into liquid. Any expansion of gas can be re-compressed if you maintain a *water piston* during transit and re-compress your cylinders at least 100 psi over sampling line pressure. We re-compress all of our liquid samples to 1000 psig, regardless of how low the line-pressure may be to assure a completed re-compression.

When sampling *Light Hydrocarbon Liquids* or NGLs, water displacement would not be an applicable method, since Propane and Butane, primarily, will flash-vaporize at room temperature. Re-compression of NGLs in a water-filled cylinder is very hard to accomplish. Using *piston cylinders* is the proper choice for sampling Propane and Butane products. Condensates and other heavier liquid Hydrocarbons can be sampled with water displacement cylinders since their vapor pressures are low compared to Ethane, Propane and Butanes.

There are those sampling instances in which neither piston cylinders nor water-displacement cylinders can be used. If the liquid being sampled is low pressure (under 100 psig which is the minimum pressure needed to operate a piston cylinder) and the composition of the liquid also contains reasonable amounts of gases like Methane and Ethane, then water displacement will cause the gases to expand, making re-compression virtually impossible. Samples such as compressor suction or discharges where the gases and liquids are combined under compression, tend to flash-vaporize upon entering the water-filled cylinder. Ideally, a piston cylinder is recommended, but, low pressure sample points are very difficult to sample with piston cylinders because they require a minimum amount of back-pressure to keep them in liquid phase and the line pressure at the sample point must maintain at least 50 to 100 psig from the sample inlet to move the piston.

Of all analytical testing currently available to the petroleum industry, an accurate separation and quantitation of Sulfur compounds in Hydrocarbons still offer today's chemists a challenging task. Since Sulfur corrosion is a major concern in the industry, costing billions of dollars per year to combat, Sulfur studies are becoming a greater analytical tool to determine the types of Sulfurs present, as well as quantitate the compounds for corrosion control.

Until recently, analytical procedures, such as *Tutweiler, Orsat*, and *Cadmium Sulfate Scrubbers* dominated the analytical scene by offering quick and fairly-accurate results. However, none of these procedures have the ability to differentiate Sulfur compounds, as most are reported as Hydrogen Sulfide. When a *Tutweiler* analysis is performed on a Hydrocarbon gas, the results are reported as *grains per 100 SCF H2S*. Many times, especially in gas streams with Carbon Dioxide and Moisture, additional Sulfur compounds can be formed, such as Carbonyl Sulfide. Tests such as the Tutweiler can not detect, nor quantitate, Carbonyl Sulfide. As with the *Orsat* (you can detect Hydrogen Sulfide and Mercaptans) and the *Cadmium Sulfate Scrubber*, the analyst is only able to determine one primary Sulfur: H2S.

Within the last decade, chemistry has produced a variety of new, more accurate tests, such as *gas tech tubes* (stain tubes), to make quick Sulfur determinations. Once again, these tubes are only an indicator of a specific Sulfur compound, such as Hydrogen Sulfide. They should never be used to make accurate quantitative decisions, like treater analysis or efficiency.

Of all the methods available to the analyst for Sulfur separation and quantitation, the *flame photometric detector gas chromatograph* (FPD) offers the only accurate means of differentiating and quantitating Sulfur Compounds in low concentrations. The basic concept in FPD is that sample gas is partitioned in a special column, usually a silica gel, then swept into a flame ionization chamber where each Sulfur compound is ionized. Attached to the detector is a photo-multiplier tube, equipped with a 394 nanometer filter specific for the wavelength of Sulfurs. This amplifies the ionzation process, allowing Sulfurs to be detected through the filter and recorded. With the proper flow adjustments to the air and column carrier, the FPD can effectively separate and quantitate Sulfurs down to about 0.5 ppm. There is interference from certain Hydrocarbons, such as Propane, which are also ionized and amplified along with the Sulfurs. Adjustments in

column length and the liquid film loading on the solid support will enhance the separation of Sulfurs from Hydrocarbons.

For instance, a 6 foot silica gel column can effectively separate most Sulfurs, but in the presence of Propane, Hydrogen Sulfide will be masked under the Propane peak. However, take a 30-foot Teflon column, packed with a Kel-F 40 liquid phase on a Teflon solid support will separate Hydrogen Sulfide and Propane, allowing for an accurate determination of the H2S. Also, reducing the Air or Oxygen to the flame, or increasing the Hydrogen to the flame will increase the sensitivity of the detector to Sulfurs while reducing its sensitivity to Hydrocarbons by using the Hydrogen produced in the flame from the ionization of Carbon and Hydrogen.

# Lecture 3. Detailed Chromatographic Detectors

In this section, I will detail the function of each of the four primary chromatograph detectors (ie, thermal conductivity, flame ionization, flame photometeric, and electron capture detectors). This section is intended to aid those analyst interested in further examining the functions and applications of chromatography. There are other detectors, such as photo-ionization, which are used within the industry, that will not be discussed since their application in the petroleum industry is relatively limited.

a) ***Introduction***

The chromatograph detector is a device which indicates and measures the amount of separated components in the carrier gas. Detectors can either be classified as an *integrating detector* or a *differentiating detector*.

An *integrating detector* gives response proportional to the total mass of components in the eluted zone. When pure carrier gas passes through the detector, the recorder indicates a straight baseline. As a component passes through the detector, the recorder pen moves across the chart by a distance proportional to the total mass of the component in the detection zone. When another component is eluted, the pen moves further across the chart. The chromatogram produced by an integrating detector consist of a series of steps in which the distance between consecutive level portions of the curve are proportional to the total mass of the component corresponding to that step. The *titrating buret* is an example of an integrating detector.

A *differentiating detector* gives a response proportional to the concentration or mass flow rate of the eluted component. The easiest example of a differentiating detector, which responds to concentration, is the *thermal conductivity detector chromatograph*. The flame ionization detector is an example of a detector responding to mass flow rate. The chromatogram produced by a differentiating detector consist of a series of peaks, each of which corresponds to a different component. The area under each peak is proportional to the total mass of that component. Differentiating detectors are more commonly used because of their convenience and accuracy.

b) ***Thermal Conductivity Detector Gas Chromatograph***

*Theory of Operation:* The *Thermal Conductivity Detector* (TCD) is based on the principal that a hot body will lose heat at a rate which depends upon the composition of the surrounding gas. Thus, the rate of heat loss can be used as a measure of gas composition. An early apparatus for determining the purity of gas streams was patented in 1915 by Shakespeare, and originally called a *Katharometer*. The *Thermal Conductivity Detector* was introduced into gas chromatography by *Claesson* in 1946 and has remained a major analytical tool ever since.

A typical thermal conductivity cell consists of a spiral tungsten filament supported inside a cavity within a stainless steel block. The heated filament can lose heat by the following processes:

1. Thermal conduction to the gas stream
2. Convection (Free or forced)
3. Radiation
4. Conduction through the metal contacts

The heat conduction through the metal filament contacts is negligible because of the small contact area. Calculations made to determine the heat loss by radiation of a typical filament temperature of 400 degrees Celsius, block temperature of 300 degrees Celsius, filament diameter of 0.001 cm, and a filament total length (uncoiled) of 10 cm show that the radiation heat loss is about 10 -6 calories per second. This number is negligible. Free convection is also negligible because of the small internal diameter of the filament cavity.

The major heat loss processes are gaseous thermal conduction and forced convection. *These two processes account for 75% or more of the total filament heat loss*.

The heat loss by forced convection could be minimized by proper geometry of the filament within the block cavity (called *diffusion filaments.*) However, diffusion-fed cells have an undesirably long response time. Use of carrier gases, such as Helium and Hydrogen, will cause heat loss by gaseous thermal conduction to predominate. It is assumed in the following discussion that thermal conduction by the carrier gas is the only mode of heat transfer.

Heat is transferred by conduction when gas molecules strike the heated filament and rebound with kinetic energy. The greater the number of molecular collisions with the filament per unit time, the greater the rate of heat loss. Differences in thermal conductivity of gases are based upon the mobility or speed at which the gas molecules can diffuse to and from the hot filament.

The speed of molecules is a function of molecular weight, and as a result the smaller the molecule the higher its speed and the higher its thermal conductivity. Since Hydrogen and Helium are the smallest molecules, they also have the lowest molecular weights, they have the highest thermal conductivity.

Thermal Conductivity (TC) Sensing Elements: As stated above, a TC cell consists of a spiral tungsten filament, similar to a light bulb filament, supported inside a cavity within a metal block. The filament is made of material whose electrical resistance varies greatly with temperature, that is to say, it has a high temperature coefficient of resistance. A constant current is passed through the filament causing its temperature to rise. In a typical TC cell, with a Helium carrier, and a filament current of 175 miliampheres, the filament may reach a temperature of 100 degrees Celsius above the block temperature.

The filament temperature is determined by the equilibrium between the electrical power input and the thermal loss due to heat conduction by the surrounding gas. With pure carrier gas flowing, the heat loss is constant, and thus the filament temperature is also constant. If the gas composition changes when a sample peak emerges, the filament temperature changes, causing a corresponding change in the electrical resistance. It is this resistance change which is measured by the *Wheatstone Bridge*.

c) ***Flame Ionization Detector Gas Chromatography***

In a typical flame ionization detector, the effluent gas from the column is mixed with Hydrogen and burned in air or Oxygen. electrons formed in the flame enter the *collector electrode* gap, decreasing the gap resistance, thus permitting a current to flow in the external circuit. When flame ionization was first introduced in 1958, it was

assumed that thermal ionization was the operating mechanism. Recent evidence indicates that thermal ionization may play only a minor role in the overall ionization mechanism.

The flame ionization detector responds to virtually all compounds, with the exception of of the following: All inert gases, Oxygen, Nitrogen, Sulfurs, Nitrogen Oxides, ammonia, water and silicates.

While other detectors are more universal, the flame ionization detector has the advantage of being able to detect concentrations as low as 10 -12gm/ml linearity of response is also a valuable asset of the FID. While linearity in the range of 10 to the $4^{th}$ power is not uncommon in detectors, the linearity of the flame ionization detector has been shown to cover a range of 10 to the $7^{th}$ power.

d) ***Flame Photometric Detector Gas Chromatography***

With the increasing interest in corrosion and environmental air pollutant in the oil field, this chromatograph is gaining quick popularity. *Flame photometeric detectors* (FPD) can be adjusted to obtain selectivity for either Sulfur or Phosphorus compounds, both of which are common constituents in air pollution. Not only are these machines selective, they are also sensitive enough to detect nanogram quantities of Organo-Phosphorus compounds.

e) ***Flame Photometeric Gas Chromatography***

The basic concept behind FPD is the measurement of emittance from the light of a Hydrogen flame. Carrier gas mixed with Oxygen-rich air enters a Hydrogen-filled chamber through a flame or burner tip. Light from the flame impinges on a mirror and is reflected to an optical filter. The optical filter allows only light either 526 mu (for Phosphorus compounds) or 394 mu (for Sulfur compounds), to pass through a photo-multiplier tube. Current from the photo-multiplier tube is sent to the electrometer for signal interpretation.

Aside from its specificity, other factors keep the FPD from being used more frequently. First, the FPD exhibits little or no linearity. For accurate quantitation, a calibration curve must be developed on each Sulfur compound. Due to the arrangement of the flame and the large amount of Hydrogen present, sample solvents are likely to extinguish the flame.

f) ***Electron Capture Detector Gas Chromatography***

The *Electron Capture Detector* (ECD) was developed in 1960 by Lovelock and Lipsky. Another type of ionization detector, the ECD uses a radioactive source to generate the ions measured in these detectors. Rapidly moving free electrons from the radioactive source (usually Nickle-63, Krypton-85, or H3 Tritium) will be captured by molecules in the detector to form a stable negative ion or charged atom.

Not all molecules exhibit the same capability to capture free electrons. This is a measure of the electron affinity for a specific molecule. Those molecules showing lower capability for capturing free electrons are said to possess a lower electron affinity.

In the ECD, a carrier gas, usually 95% Argon and 5% Methane, is flowing past an ion source. The free electrons ionize in Nitrogen creating a current flow. As samples with higher electron affinity enter the detection chamber, the current flow is reduced. Unfortunately, the amount of current reduction is not only a function of the amount of sample present, but also the electron affinity of the sample. For quantitation then, a calibration curve must be made on each of the components being tested.

The ECD exhibits considerable selectivity. It is highly sensitive to halogenated compounds (Iodine, Bromine, Chlorine, and Fluorine), and Nitrates. Also conjugated Carbonyls and certain Organo-metallic compounds are detectable It is not sensitive, however, to compounds with low electron affinities, such as alcohols and aliphatic compounds. The linearity if the ECD will vary according to the radioactive source used. Tritium (H3) provides the widest linear range. Nickel 63 provides a linear range of about 50 picograms, compared to over 100 for Tritium.

# Lecture 4. Instrument Calibration and Routine Audits

As discussed earlier, all chromatographs require a regular calibration procedure to determine the detectors response to each constituent being analyzed. Likewise, routine audits between labs are necessary to confirm the accuracy of our calibration.

In the case of the thermal conductivity detectors, a gas and liquid standard must be manufactured by a *National Bureau of Standards*-certified company, such as *Phillips Chemical* or *Matheson Scientific*, with a known concentration of the constituents to be analyzed. Gas standard will be a detailed mole percentage distribution of the compounds Accompanying the purchased contained in the standard. This *Certificate of Analysis* is needed so that an accurate calibration can be achieved. Without it the standard is invalid.

Standards for gas and liquid analysis come in varying concentrations of the constituents, and it is up to the chromatographer to select the proper one for the calibration desired. As a general rule, the calibration standard should be as close in composition, as possible, to the gas being analyzed. In other words, if the Methane content of the gas to be analyzed is 90%, then the standard should be purchased with 90% Methane. If a gas sample has 10% Carbon Dioxide, then the standard should be near the same composition. Since thermal conductivity has a good range of linearity to Hydrocarbons, it would not be wrong to use a standard with 70% Methane when calibrating a gas sample with 90% Methane. However, thermal conductivity has a low range of linearity to compounds such as Carbon Dioxide, therefore, it would be inaccurate to analyze a gas sample with 10%+ Carbon Dioxide with a standard that contains only 1% Carbon Dioxide. Most standard manufacturers can make a standard with constituents in the range of those being analyzed, which will likely be more expensive than a stock standard, but are truly necessary to provide *accurate* calibration.

Once the standard's composition is determined and purchased, calibration of the chromatograph may begin. For discussion's sake, let us assume a certified gas standard with roughly the same concentration of constituents being tested has been purchased. To begin, the standard must be submitted to the chromatograph in the exact same procedure the samples being analyzed will. By GPA guidelines, the gas standard must be heated to at least 120 degrees Fahrenheit, although many companies are changing this to 140 degrees Fahrenheit, so that a completed volatilization of the condensable Hydrocarbons (Pentanes and Hexanes+) is achieved. Without heating the standard, the calibration of these Hydrocarbons will be inconsistent and inaccurate. Many companies in the past have used standards made with Methane, Ethane, and Propane to calibrate instruments in which Butanes, Pentanes, and Hexanes are present in the gas sample. This allows them to bypass heating the Standard since C1 to C3 are gases at room temperature. However, when they try to accurately determine the concentration of C4 and heavier, they fail because the detectors linearity begins to drop around Butane. Unless you have known concentrations of Butanes and heavier in the standard, then calibration for those Hydrocarbons can not be accurately determined, and analysis should not be performed based on the linearity of lighter Hydrocarbons.

So, assuming you have a standard gas made up of Nitrogen, Carbon Dioxide, and Methane to Hexane Hydrocarbons in the range you need, and the calibration standard has

been heated to the proper temperature (140 F), you may now begin to determine your chromatograph detector's response to each constituent with accuracy.

The standard gas is passed through a heated line to the sample loop on the chromatograph. Flow through the loop can be determined by using many different techniques, such as rotometers or flow meters, however, the flow should be about the same for samples as they are for the standard so that the loop can charge with same volumes for comparison. After flowing the standard through the loop for a few seconds (about ten to thirty seconds depending on the traveling distance of the heated line) the gas flow is stopped, *three seconds* are counted off to allow the loop to equilibrate to atmospheric pressure, then the gas is injected into the chromatograph. The three seconds are necessary to allow equilibration to atmospheric pressure in the loop, otherwise the sample volume will not be reproduceable from injection to injection. Shooting the standard or sample gas while it is flowing through the loop will administer a partial pressure sample to the chromatograph. Unless the flows are exactly the same on partial pressure injections, or you are using flow meters to assure the same volume, the comparative analysis will be inaccurate.

Once the standard has been injected, a chromatogram of the peaks and their respective retention times and associated areas must be obtained. It is important to understand the position of each compound based on its retention time. Many errors are caused when the wrong peak is identified with the wrong constituent, which is most common when integrating computers are programmed to identify constituents based on a retention time and the time is moved due to flow or temperature changes. Once you have obtained the proper constituents and the area produced by the integrator for each peak, then you may plot the response factor needed to correct the detector's response to each constituent. By taking the known mole percentage concentration of each compound from the standard's *Certificate of Analysis* and dividing each by their respective area, a *response factor* is produced. This response factor is usually expressed in exponential form, such as 0.00042 or 4.2 X 10-4. Once produced, it is entered into the computer or integrator and all subsequent areas produced at that retention time are multiplied by the response factor, then re-normalized to 100.00%. As mentioned above, if the flow or temperature should change for any of a number of reasons, the retention times will shift and an integrator programmed to call Methane at a retention time of 2.00 minutes may see Carbon Dioxide instead and calculate it as such. Therefore, calibration with a standard must be performed at least *daily*, if not *more* frequently, to confirm the retention

times have remained the same, otherwise re-calibration must be performed before any more analysis can be obtained. Whenever a carrier gas bottle is changed, or if the chromatograph has been turned off, then restarted, re-calibration must be done to assure the analyst that the retention times and response factors are determined properly for the integrators calculating purposes.

In the case of Hydrocarbon gas analysis, as mentioned earlier, the sample must be submitted to the chromatograph with the same techniques used to analyze the calibration standard. The sample cylinder must be heated to the same temperature (140 degrees Fahrenheit) as the standard before it is run. There are some exceptions to this rule. In the analysis of samples containing high amounts of Carbon Dioxide (usually above 20 Mole %), heating the cylinder will cause the Carbon Dioxide to expand. Since Hydrocarbons will expand in a relatively linear fashion within the cylinder when heated, Carbon Dioxide will not. If a sample contains high Carbon Dioxide (above 80%) the cylinder will probably blow its rupture disk, discharging the sample. If a sample of high Carbon Dioxide is taken at a line pressure of 500+ psig and a temperature of -30 degrees Fahrenheit, heating the cylinder to 80 degrees Fahrenheit alone will raise the cylinders pressure above 2000+ psig, causing the rupture disk to discharge since they are only rated at 1800 psig. Therefore, both calibration with high Carbon Dioxide and the analysis of samples containing high Carbon Dioxide should be perform at no greater than room temperature.

Once the Hydrocarbon gas sample is heated to the proper temperature and it is submitted to the sample loop in the same manner as the Standard, data may be obtained from the chromatograph. This data is compared to the standard response factors and a re-normalized report is produced. Calibration is complete and the sample data is accurate.

There are several ways to check the integrity of your analysis. One way is to run your standard as an unknown sample and compare the results to the actual values produced on the Standards Certificate of Analysis. If the un-normalized results are within 1% of the normalized values, then your calibration is still good. If your un-normalized results are outside the 1 % threshold, re-calibration should be performed before any samples are run. Another way to assure integrity is to run unknown calibration standards from another source, such as another lab's standards, and compare the results to the actual values of that standard. This is usually done in *round robin* exchanges between several consenting labs, at least on a quarterly basis. This gives the analyst a chance to compare his accuracy with fellow labs and to review his chromatographic operations for

problems. It is unlikely that all companies participating will have exactly the same results when compared to the actual standard values, and corrections can be made to bring labs that fall outside the standard *means of deviation* back into alignment with the others.

Audits are becoming increasing popular among some of the larger oil and pipeline companies due to the fact that prices are based on BTU content. During an audit, your analytical accuracy is necessary to fall within the tight BTU ranges required by these companies. If your calibration is off, then the final results will show a different BTU value than the correct one. If the BTU value is off by more than two BTU of the actual, then there is reason for the company giving the audit to insist that you make the needed adjustments to conform to the audit specifications.

When placed under the scrutiny of a gas or liquid audit by a company, the chromatographer is often defensive of his/her analysis, especially if they are out of compliance. Remember that these audits, like the *round robin* exchanges, are necessary to determine any discrepancies in your technique and final data compilation versus other chromatographers. They should be viewed as an opportunity to test your skills and accept all errors as a chance to review your accuracy and make any necessary changes to bring you into line with other chromatographers in your related field.

Although only some laboratories are requested to perform these annual audits, it is a good idea to establish some type of round robin exchange with other companies, or inner company, to assure your quality. Most companies that buy and sell to each other will usually cooperate in this type of quality assurance program. Sampling and analytical errors are easily determined by these exchanges and corrections can be made more frequently when they are detected. These exchanges should not be viewed as *pass-or-fail*, but simply how accurate your data is when compared to those who participate.

Preparation for liquid calibrations are performed slightly different in the fact that the cylinder of liquid standard, as well as samples, should not be heated. Liquid standards and Hydrocarbon liquid samples, such as Propane, Butanes, NGL, and gasoline are analyzed at *room temperature*, *never* heated. Once again, liquid standards and Hydrocarbon liquid samples must be submitted to the chromatograph in the same manner. This refers to to the back-pressure used for re-compression. A liquid standard run at 1000 psig can not be compared to a liquid sample with 100 psig. To guarantee a complete re-compression of expanded gases back into a liquid phase, it's important to apply an adequate amount of back-pressure. The NGPA recommends re-compression at least 100 psig above the line pressure sampled. Most Labs will re-compress all liquid samples to at

least 1000 to 1200 psig, regardless of the line pressure, to assure a good re-compression of expanded vapors.

## Conclusion:

Chromatography is as much an art as it is a science. The artistic side of chromatography is developed over time and with repetition. Anyone who views chromatography as simply injecting a sample and reviewing data that is calculated by a computer is mistaken. Replication in both the analytical presentation and there must be sampling, respectively. An understanding of how the chromatograph operates, what problems to look for in your analytical accuracy, and how to perform analytical task with reproducablity are all necessary when trying to develop the artistic style. The science of chromatography come in determining the proper columns, temperatures, data interpretations, and calculations.