

Introduction to Gas Chromatography for Natural Gas Technicians

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Introduction

Gas chromatography is one of the most common analytical techniques employed in the natural gas industry. Gas chromatographs are widely used throughout the natural gas industry despite their reputation for being difficult to maintain, troubleshoot, and understand. To understand why chromatography is important, one must understand the significance of the many different compounds that are naturally present in natural gas and why they need to be measured.

Natural Gas is Natural

As extracted from the Earth, natural gas is composed of a mixture of energy-rich hydrocarbons and some undesirable contaminants. This mixture is rarely safe to deliver for sale to homes and businesses. To be deemed safe, gas processors and pipelines must control and monitor both the concentrations of contaminants and the heating energy that will be released when the gas is burned.

For natural gas to be safe for consumers, its heating value and density must be within ranges that are acceptable for use by industrial and household equipment. Contaminants must be reduced to concentrations that will not damage pipeline and consumer equipment in addition to being non-toxic to people. When safe for transport and consumption, the monetary value of a standard volume of natural gas is based upon its heating value: the amount of energy it will release when burned.

To confirm the safety and the monetary value of natural gas, it must be analyzed to determine both the concentrations of desirable hydrocarbons as well as undesirable contaminants. This requirement drives the use of gas analyzers at production connections, pipeline interchanges, city gates, and industrial facilities such as power plants and manufacturing facilities.

Why Use Gas Chromatography?

Other than gas chromatography, there are dozens of alternative gas analysis technologies such as IR-vis-UV and TDL absorption spectrometry, mass spectrometry, chemical cell sensors, capacitance sensors, atomic emission techniques, and many others. So, why does the natural gas industry utilize gas chromatographs as their primary analysis technology?

The simple answer is that all measurement technologies have strengths and limitations. When attempting to measure a component within a mixture, the measurement technology must be capable of avoiding, or eliminating, cross-interference from all other compounds present in the mixture. For a given application, a technology can be either interference-free or suffer from cross-interference between two or more compounds present in the sample.

In an 'Interference Free' situation, the change in signal being measured is only a function of the compound of interest. This permits the measured signal to be calibrated against the % of that compound present in the sample. For example, if the voltage emitted from a sensor only reacted to the % of CO₂ present in air, that voltage could be used to determine the % of CO₂ in a room. In a math sense, the voltage is a function of one unknown, the % CO₂.

In a 'Cross-Interference' situation, the change in signal being measured is a function of the compound of interest plus other unknown factors. An example of a sensor suffering from cross-interference is one where the sensor's voltage output varies when the % CO₂ in air changes and when the % O₂ changes. Due to the cross interference, it is impossible to know whether the sensor's output voltage changes are caused by a change in CO₂, a change in O₂, or a change in both. If the cross-interference between CO₂ and O₂ cannot be eliminated, that sensor's technology is unsuitable for the application of measuring CO₂ in air.

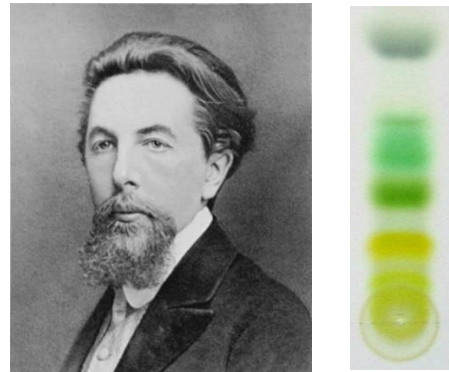
In a typical natural gas chromatograph (GC) application, the device is expected to detect and quantify the amounts of methane, ethane, propane, butanes, pentanes, hexanes-plus,

nitrogen, and carbon dioxide present in the natural gas. The natural gas industry uses gas chromatography because it is the only analytical method proven capable of measuring all the mentioned compounds with a sensitivity ranging from 100% methane to <10 ppmv hexanes-plus. Other technologies have not managed the cross interferences, or the wide range of sensitivities required.

How Chromatography Works

Mikhail Tsvet, a Russian botanist, began chromatography in 1903 as a technique to separate plant pigments. Because he was separating colors, he named his technique chromatography. Gas chromatography started in the 1940s with significant advancements in the 1950s and 80s.

In essence, chromatography is an analytical technique that eliminates cross-interference by separating a mixture into individual components prior to measurement. This is achieved by passing a gas-phase mixture through a medium in which the individual components move at different speeds. The medium is contained within a tube or capillary called a column.



mixture

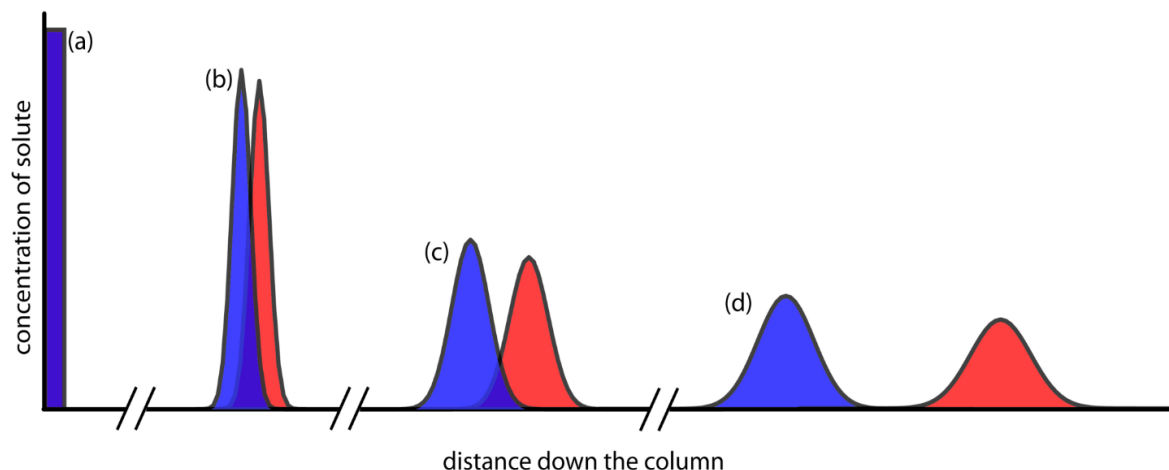


Figure 1 – When components move past a column's medium at different speeds, they can be separated

Figure 1 illustrates a two-component mixture being passes through a column containing a medium that reacts differently with the red and blue components. As the red component passes through the column faster than the blue component, the two can be fully separated from each other provided the column is long-enough.

Columns can be packed or capillary and contain various types of separation media as shown in Figure 2.

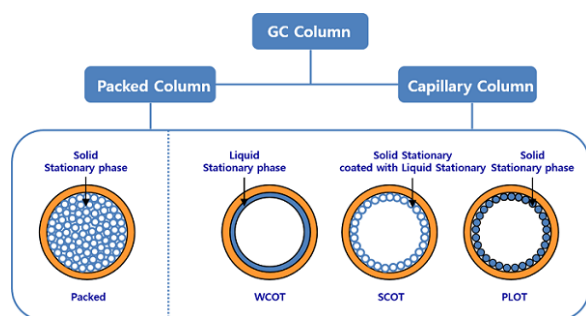


Figure 2 – Different Types of Gas Separation Media

The medium inside a column is called the stationary phase as it remains stationary in the column. Different mediums are selected based upon their ability to interact with the sample mixture to be analyzed. Different materials can result in separation based upon differences in solubility, affinity, and molecular size. For example, a natural gas chromatograph will often use different mediums for the separation of $N_2/CH_4/CO_2/C_2$ versus $C_3/C_4/C_5/C_6+$.

At a basic level, every GC consists of the functions illustrated in the following figure.

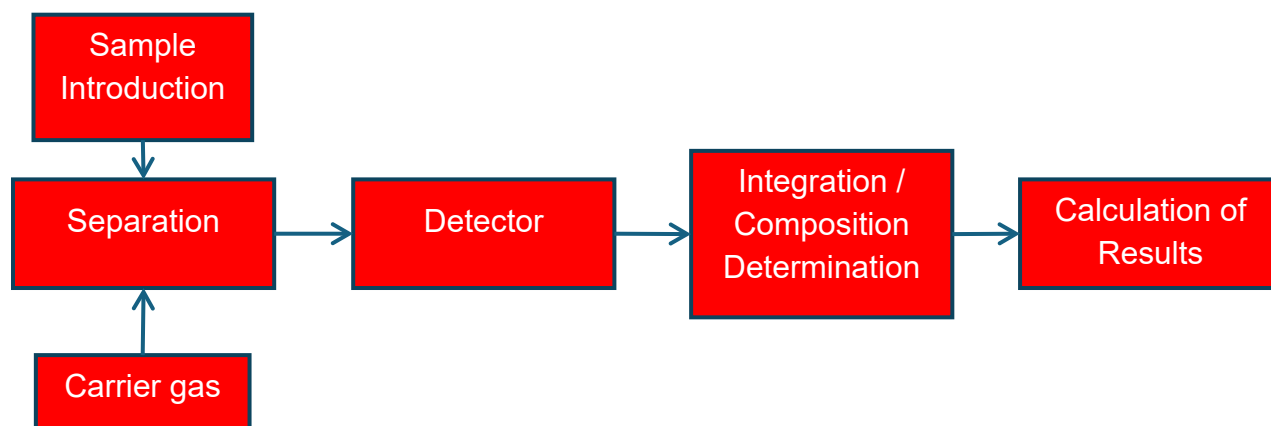


Figure 3 - Basic working principal of GCs

As shown in Figure 3, every chromatograph employs a system to introduce a sample into the separation columns. Carrier gas is also introduced to the columns to carry the sample through the columns' media. After the separation columns is a detector. The output of the detector goes into software that calculates the composition of the mixture from the detector's output. The final step is to use the determined composition of the mixture to calculate results such as heating value, density, Wobbe, and compressibility.

Natural Gas – Pipeline Quality

As previously explained, natural gas is a naturally occurring mixture of hydrocarbons, inert compounds, and undesirable contaminants such as hydrogen sulfide. While the term 'pipeline quality' is commonly cited to describe natural gas that is safe for transport and consumption, the exact meaning of the term is not obvious.

The term 'pipeline quality' indicates whether the natural gas composition meets the requirements of a legal contract often called the Tariff. An example of a Tariff's gas quality requirements is shown in Figure 4 on the next page.

A natural gas chromatograph always provides measurements of Energy Content, Wobbe Number, Density, and Compressibility (Z) which are calculated from the compositional measurements of the hydrocarbons, carbon dioxide, and nitrogen.

Specially configured GCs would be required to measure special components such as hydrogen sulfide, oxygen, and common odorants. These special components and water vapor are typically measured using alternative analytical technologies.

Gas Quality Specification	Some Values Found in Tariffs
Energy Content (dry, HHV)	950 – 1,150 BTU/scf
Wobbe Number	1,279 – 1,400
Minimum Temperature	20° to 65°F
Maximum Temperature	80° to 140°F
Maximum Hydrocarbon Dew Point	0° – 25°F at either fixed or operating pressures
Cricondenthem HDP (CHDP)	15° – 20°F
C ₄₊	0.75 – 1.50%
Liquefiable Fraction (GPM) C ₅₊ ⁽⁶⁾	0.2 – 0.3 gallons/Mscf
C ₅₊	0.12 – 0.25%
Liquefiable Fraction (GPM) C ₆₊	0.05 gallons/Mscf
Maximum Water Vapor Content	4 – 7 lbm/MMscf
Maximum Total Sulfur Compounds, as Sulfur	0.5 – 20 grains per 100 scf
Maximum Hydrogen Sulfide (H ₂ S) ⁽⁵⁾	0.25 – 1 grain per 100 scf
Maximum Mercaptans (RSH)	0.20 – 2.0 grains per 100 scf
Maximum Solid Particles Size	3 – 15 microns
Maximum Hydrogen	400 – 1,000 ppm
Maximum Diluent Gases Total ^(2, 4)	3 – 6%
Carbon Dioxide (CO ₂)	1 – 3%
Nitrogen (N ₂) ⁽³⁾	1 – 4%
Oxygen (O ₂)	0.001 – 1%

Figure 4 - Gas quality parameters commonly included in a Tariff

The takeaway lesson is that GCs provide most quality measurements required at a custody transfer station. It is important to know that the results calculated from the measured gas composition come from one or more calculation Standards. It is important for a user to know both the Standard their company and tariff require as well as the base conditions of pressure and temperature at which the calculations are to be performed. Common Standards for heating value, and density in the USA include AGA-5 / GPA 2172, and ASTM D3588. ISO 6976 is used in the EU and other countries.

GC Terminology

When working with a natural gas chromatograph, one must know the meaning of certain terms:

Column A length of tubing or capillary (metal or glass) containing the separation medium (stationary phase) needed to separate the mixture to be analyzed. GCs often employ multiple columns each of which contains a different medium responsible for a specific range of separation tasks.

Carrier gas A pure gas that continuously flushes through the analytical columns and that serves as a carrier for the sample being injected. In most GCs this will be Helium gas although N₂, Ar, and H₂ may be used for some measurement applications. (Also referred to as the mobile phase as it travels through the column.)

Components of Natural Gas and GC Naming Conventions

C1 = Methane

C2 = Ethane

C3 = Propane

C4 = iso-, normal-Butanes

C5 = neo-, i-, n-Pentanes

C6 = Hexane, Cyclohexane, Methylcyclohexane, Benzene

C7 = Heptane, Toluene,...

C8 = Octanes

C9 = Nonanes

C6+ GC measures: N₂, CO₂, C1...C5. The + sign indicates two things:

- 1) Lighter weight Hydrocarbons (C1...C5) are individually measured
- 2) C6 plus heavier components are considered less important. They are measured only as a lump sum called C6+ using assumed physical properties.

(Note: O₂ is not separated from N₂ in the analysis of a standard GC.)

C9+ GC measures: N₂, CO₂, C1...C8

C9 plus heavier components are measured as a lump sum called C9+ using assumed physical properties.

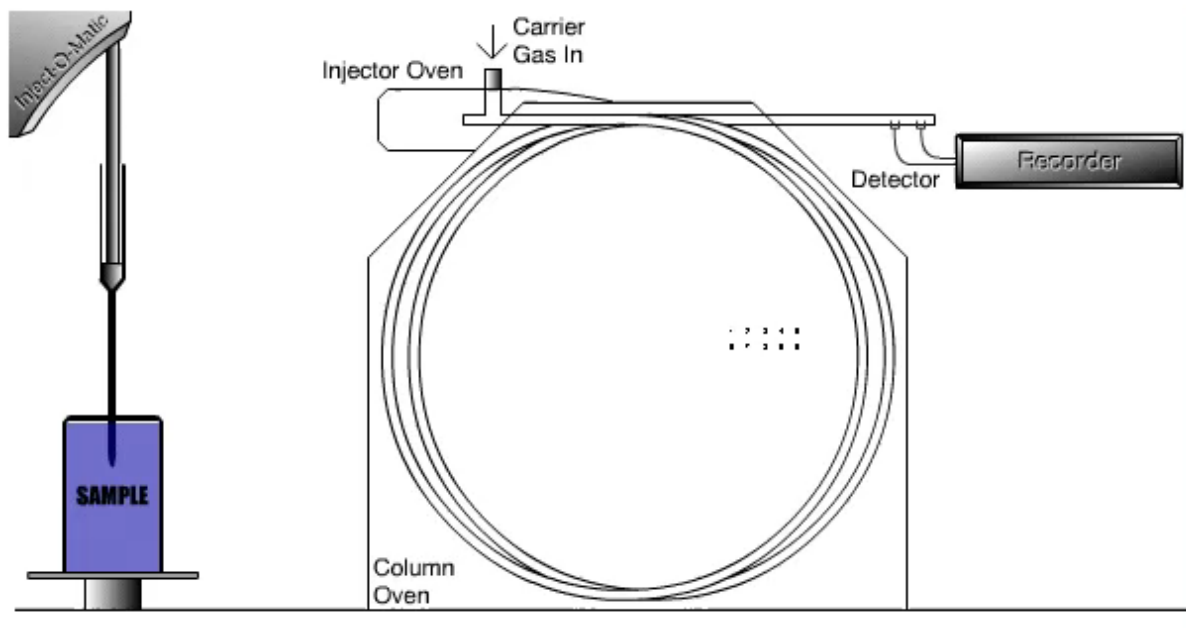
Retention (Elution) time The time at which a certain component reaches the detector. The retention time is measured from the point of injection to the top of the peak.

Thermal Conductivity Detector (TCD) A TCD's signal changes as the gas surrounding it cools, or insulates, a heated element of a Wheatstone bridge. Often called a 'universal' detector because it will generate a signal change from its baseline when any other compound passes by. Baseline is the signal state under conditions of pure carrier gas flow.

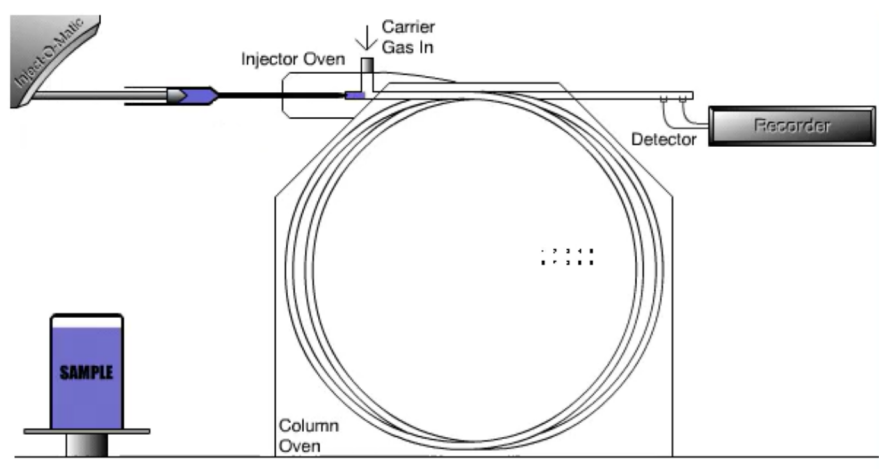
Response Factor (RF) A calibration factor that relates the TCD's signal to a %. RFs are unique to each measured component. Some GC RFs are based upon maximum signal (peak height) while other GCs use peak area (integrating the area under the response peak)

How it works – The Basics

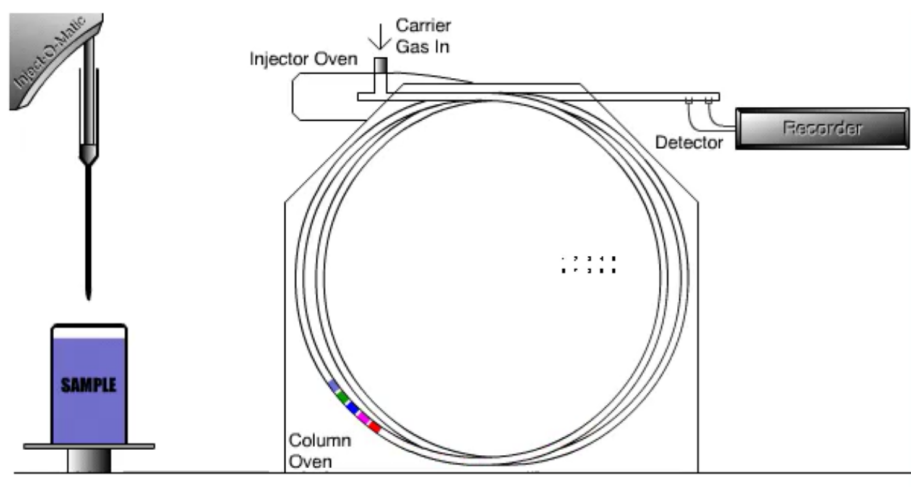
Carrier gas flows continuously at a constant velocity (controlled pressure) through the column and past a thermal conductivity detector (TCD) at the column's outlet. The column and TCD are maintained at controlled temperatures. The thermal conductivity of the carrier gas is the baseline (background) against which the natural gas' components are detected and measured.



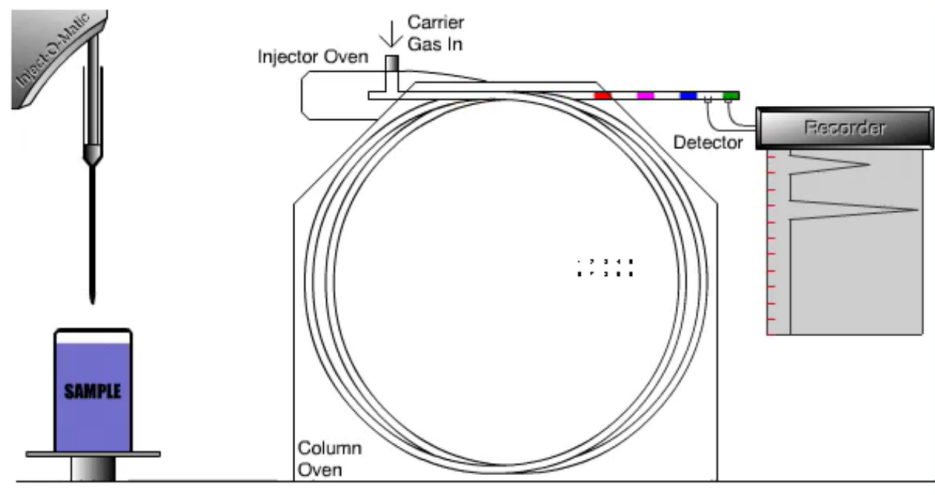
To start a new analysis, a controlled volume of unknown sample mixture is injected into the entrance of the column. The carrier gas flow then pushes the mixture through the column(s).



As the sample passes through the column, the components of the sample begin to separate from each other as they pass through the column at different velocities.



Making the column long enough provides separation between the individual components before they reach the TCD. This permits individual measurements of each component by the TCD.



A critical fact about gas chromatographs and their TCDs is that they do not automatically know what compound was responsible for a detected signal nor what concentration of that unknown component was present.

The TCD only senses a change from the background (carrier) gas, a peak. The electronics of the GC measure the time, called retention time, after injection at which the peak occurred. In short, the GC is only able to measure two things: 1) the magnitude of a change in thermal conductivity from the baseline (pure carrier gas) 2) the time after injection at which the change was detected (Retention Time).

Peaks to %

Translating a set of peaks and times into a comprehensive analysis requires knowledge of the order in which the sample's components will exit the column as well as how long it takes each component to exit the column after sample injection, Retention Times.

The GC's Peak Identification Table associates a name, such as Methane, with a specific Retention Time. The first step of processing a new chromatogram is to name each measured peak based upon its Retention Time.

Associated with each Name in the Peak Identification Table is a Response Factor (RF), also called a calibration factor. The RF is a conversion factor relating the size of a peak to a % concentration of the named component.

Multiplying a peak area against a RF provides what is called an **Unnormalized concentration**.

For example: A peak with an Area of 10,000 units is detected 2 seconds after injection.

- 1) The GC's electronics match the 2 seconds against the Peak ID Table to identify a name, such as Nitrogen.
- 2) The GC reads the RF associated with Nitrogen. The RF is a ratio such as (% per units of area). In this illustration the $RF = 1\% / 10,000$
- 3) The multiplies the Area x RF and reports Nitrogen = 1.00% as an unnormalized concentration

The process in the above example is repeated for every detected peak in an analysis. However, the resulting unnormalized concentrations are not yet ready for use in calculations for heating value, density, etc.

There are many hardware and environmental factors that impact a GC's results. Variations in ambient pressure, sample pressure, and injected sample volume cause unnormalized measurement estimates to add up to $>$ or $<$ 100%. Calculations should never be performed on anything other than 100% sample volume.

To eliminate the impact of these influences, GCs employ a process called Normalization.

Step 1: Sum all the unnormalized concentrations. The result should be between 97% and 103% in a well-running GC. It is sometimes referred to as the Sum External Standard (SumESTD) because each concentration is only based upon its RF.

Step 2: Multiple each unnormalized % by $(100 / \text{SumESTD})$. This mathematical process shifts the concentration of each compound by the same magnitude resulting in concentrations that always sum to 100%. These Normalized concentrations are used in all subsequent physical property calculations.

Why Normalization - A Thought Experiment:

Picture a GC sampling a mixture containing exactly 1% nitrogen. During a new sample injection, the volume of injected sample is 5% greater than the previous cycle.

That means there are 5% more nitrogen molecules being detected by the TCD. Hence, the peak will be larger even though the actual concentration of nitrogen in the sample has not changed. The unnormalized concentration will be reported as 1.05% nitrogen instead of the actual 1.00% in the mixture.

Calibration and RF

GCs are calibrated to determine the RF of each measured component. Calibration is essentially an analysis cycle with reverse logic. During calibration, the GC is told the concentration of every component in the mixture. This is possible through use of a man-made, certified cylinder of calibration gas.

During a calibration cycle, the GC measures a peak size (area) for each component and then reads the concentration % responsible for a peak. It calculates new response factors: $RF = \text{concentration} / \text{area}$.

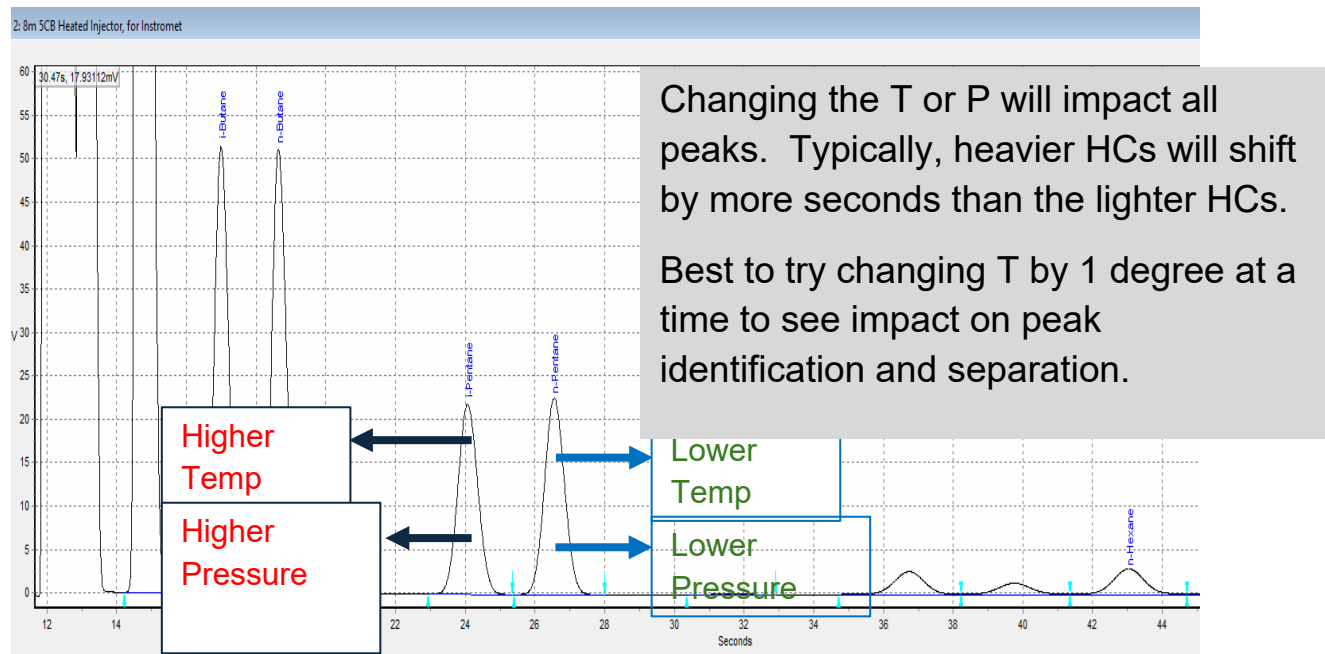
Technicians should bear in mind that the GC is stupid. It will not automatically know if there are mistakes made when programming a cal gas cert into the GC. It may also not know if a technician failed to program the new cal gas cert after a cylinder swap. The GC will simply calculate RFs based upon such errors; then produce analysis results using the erroneous RFs until the problem is discovered and corrected.

Retention Time Shifts

There are times when a peak will not be properly identified because there has been a shift in the RTs. Changes in Retention Time can occur for several reasons:

- Contamination in the column – prevents separation = faster elution
- Significant change in ambient pressure (elevation)
- Column temperature change
- Carrier gas pressure change in column = change in carrier gas velocity

Changes in carrier gas pressure or column temperature can also impact peak shape and separation.



When practicing with a GC, it is helpful for a technician to experience what happens when they change the column pressure or temperature. Such experiences can make tuning a GC in the field much easier.

Backflush & Column Switching

Natural gas analysis via a single, standard diameter column could take up to 60 minutes per analysis. To shorten this time, multiple column techniques, often with column switching and back-flushing, are employed.

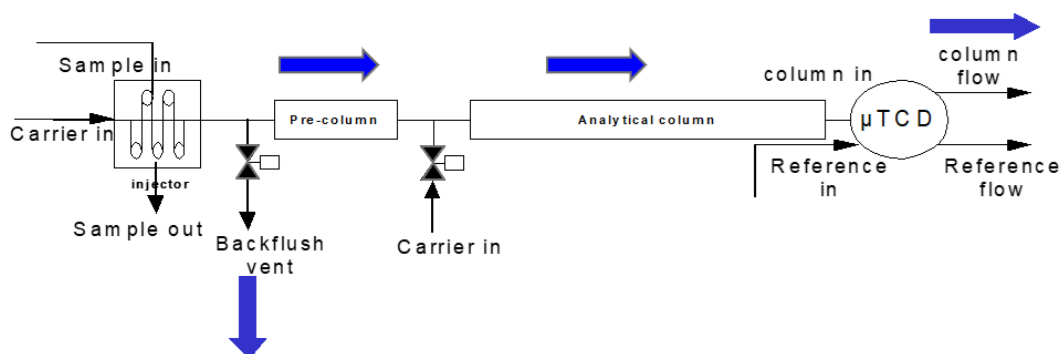
In chromatography, heavier components typically take much longer to pass through a column than lighter components. As previously mentioned, a C6+ GC is designed to detect and measure methane (C1) through the pentanes (C5). Hexane (C6) and heavier (+) components are not of interest which is why the GC does not attempt to separate them for individual measurement. Should the C6+ components pass into the measuring columns for the lighter hydrocarbons, they could cause measurement problems. In this way they could be considered contaminants to the GC's columns.

Back flushing is a technique used for either of two purposes:

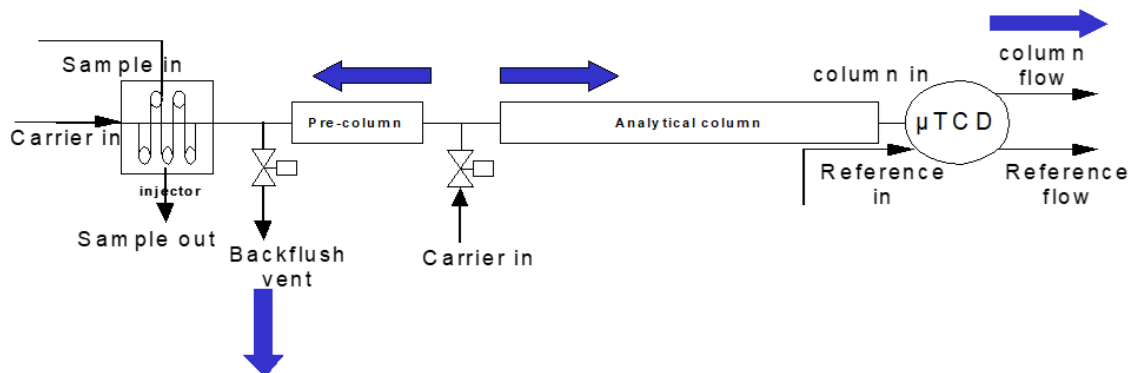
- 1) Compounds that elute after all components of interest, such as C6+
- 2) Contaminating compounds that must be kept out of the column, such as CO₂ from a molecular sieve column

Back flushing utilizes a pre-column as the first column after injection. It is the job of this material to quickly pass by the components of interest while slowing the contaminants or compounds that are not of interest, such as the C6+.

In the diagram below, upon injection the sample is pushed forward into the pre-column. The compounds of interest, such as C5 and lighter components, quickly pass through the pre-column to the downstream separation and analytical columns.



At a time when all compounds of interest (C5) passed through the pre-column but none of the undesirable components (C6+), the gas flow is reversed through the pre-column, backflushing its contents out.



If the pre-column was separating out contaminants, they would be pushed to a vent. If the back-flushed compounds were to be measured, like C6+, they would pass a TCD before going to vent.

Know Your GC

It is important for a technician to understand how his GC will actually perform its analysis as while all C6+ GCs provide the same measurements, the way they go about performing the separation of the natural gas components varies by manufacturer and GC model. Some basic differences are indicated below:

- An Emerson C6+ GC uses three interconnected 6-port switching valves to provide a single chromatogram with an elution order as follows: C6+, C3, C4, C5, N2, C1, CO2, C2
- An ABB GC C6+ GC uses different hardware. It has two 10-port valves that run as parallel analysis paths. One outputs C6+, a N2/C1/CO2/C2 composite peak (which is ignored), C3, C4, C5. The second path outputs a C3+ peak (which is ignored) followed by N2, C1, CO2, C2.
- Honeywell's EnCal 3000 proChain C6+ GC does not employ any rotary column switching valves. It provides two chromatograms: A C6+ peak and a complete N2...C5 analysis from a single non-isothermal column

Every approach has its pros and cons. It is the responsibility of the field technician to understand the GC he is working with. Regardless of GC model being used, a well-performed commissioning is the best first step to obtain the best long-term performance for a GC.

GC Commissioning Tips

The following are the tips I always follow myself and provide to technicians during training and measurement schools. Of course, the most important tip to follow is:

READ THE MANUAL

Because no two GC models are identical, there will be differences in pressure settings, installation recommendations, PC software, etc.. Only by reading the manual for the GC can you be certain you are taking the correct steps. Failing to read the manual and mistakenly applying too high a carrier or sample pressure, the wrong power voltage, or other commissioning steps could potentially damage that brand new GC before it ever sees a day of service. Also be certain to install the GC's PC software on your computer before arriving onsite for commissioning.

Before or upon arriving onsite, confirm that there is a good sample handling and conditioning system in place that is designed for the sample gas. Typical components include:

- 1) **Sample Probe** – to extract a representative sample from the center 2/3 of the pipe
- 2) **Sample Conditioning System** - Maintain gas-phase of sample while conditioning sample. Reduce pressure before transport for fastest system response speed. Exclude solids & liquids
- 3) **Heat-Traced Sample Transport Tubing** – to maintain gas-phase of sample during transport to analyzer and deliver a 'timely' sample. Tubing diameter should be matched to the sample consumption of the GC. If the GC has an 1/8" tubing inlet, do not use 1/4" diameter sample line. (Note – If your GC is to measure trace sulfur

compounds such as H₂S or odorants, **always** use sulfur service tubing for both sample and calibration gases.)

- 4) **GC Enclosure** – To ensure transition from #3 to GC has no cold spots. Keep cal gas and cal gas tubing at a warm, stable temperature

For most natural gas GC applications, I prefer to see the GC kept in temperatures >40 F to avoid possible HC and water condensation, especially the possible ice-trapping that can occur when passing pipeline quality gas through sub-freezing tubing.

All GCs will need troubleshooting and maintenance at some time. Having the GC in a protected enclosure or an instrument building will make it much easier to work on, even during inclement weather.

Calibration gas is a critical part of a GC system. This mixture is how the GC will generate those RFs upon which all the GCs measurements are based. My tips for calibration gas are:

- Always use the most accurate calibration gas mixture available. The slight savings from using a less accurate gas is far more costly than the mis-measurement that can result.
- The calibration gas should contain a representative amount of each component being measured by the chromatograph. Never include components that are not measured by the GC (eg. Hydrogen, Oxygen).
- Calibration gas must always be maintained above its HC dew point. Never use a calibration gas mixture that is 2-phase within the cylinder as the boil-off composition is not stable.

Purging Gas Connections

Start up is a critical time for every GC. It is critical that the pipeline, sampling lines, and cal gas lines are properly flushed and free of air and water, especially if the pipeline was hydrotested. Should one be following a hydrotest, be certain the natural gas has flowed through the station for at least three or four hours. Pulling gas from a packed, but static pipeline can be a risky chance which could possibly damage a GC.

During installation of the accessories supplying the GC, keep in mind that transport tubing, pressure regulators, and filters will contain air. Properly flushing the air from these components can greatly reduce the time needed to commission the GC. The following are the steps I follow to flush carrier and calibration gas tubing.

1. Loosen the tube fitting at the GC to permit a leak
2. Crack open the valve on the gas cylinder, to pressurize the regulator; then immediately close the valve.
3. Set regulator's outlet pressure while gas slowly leaks from loose fitting at GC.
4. Repeat Step 2 at least two additional times.
5. Fully open cylinder valve and verify pressure setting.
6. Tighten tube fittings at GC and ensure there are no leaks.

Flushing pipeline gas lines is often a matter of flushing a lot of gas through the system upstream of the GC. As mentioned before, be certain that gas has been flowing through the pipeline for at least a few hours before pulling a sample to the GC.

Starting the GC

All GCs will need some run time before they provide their best performance. If a GC is still 'stabilizing', you should not attempt to perform a calibration. Once the installation has been looked over and all the lines properly flushed, it is time to put gas and power to the GC.

Recommendations (after physical installation)

1. Do not turn GCs ON and OFF. It is always best to leave a GC powered with carrier gas flow.
2. Program the GC to perform repeated analysis runs on the calibration gas while gathering detailed results data on your PC
3. Start running repeated analyses on the cal gas. Then perform / validate all GC programming and Comm performance.
4. Program the calibration gas' certified concentrations into the GC.

5. Verify that you entered the correct % in the correct locations. It can be easy to transpose i- and n- component entries.
6. Now, check your most recent four or five analysis runs for stability / consistency of component measurements.
7. If good repeatability, VERIFY that the GCs measurements (with factory calibration) reasonably match the cal gas certification.
8. Perform an Initial Calibration with the cal gas.
9. Reprogram GC to measure pipeline gas, no longer cal gas.
10. UPLOAD and SAVE all configuration files from the GC.
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11. Ensure that you have saved, READ ONLY commissioning files. You would be surprised how many GC problems are fixed by reverting to the 'last known good' configuration and calibration.

Conclusion

Gas chromatographs are an indispensable tool of the natural gas industry. I hope that by learning a bit about why we use GCs and how they work, you will find the challenges of working with GCs a bit less intimidating. Should you have any questions, I can be contacted on LinkedIn or reached at my Honeywell email:

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