

OPERATIONS OF ON-LINE CHROMATOGRAPHY

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INTRODUCTION

Since the early eighties it has become common in the United States, and elsewhere in the world, for natural gas to be bought and sold based on the amount of energy delivered. The quantity of energy delivered is calculated by multiplying the gas volume per unit time by the heating value (BTU) per unit volume.

Gas chromatography is normally employed for the calculation of the heating value. However, when the gas chromatograph runs an analysis we not only get the heating value, but other valuable information; such as gas composition and relative density. This additional information is used in the gas volume calculations. Gas Chromatographs (G.C.s) have been widely used in hydrocarbon processing facilities when high quality product specifications are required, or when rigid custody transfer standards are needed for natural gas trading.

Gas chromatography is a scientific method in which a gas sample is separated into its component parts for measurement. The gas chromatograph consists of subsystems that inject the sample, separate the sample, detect the components, integrate the peaks, and report the results. The injection, separation, and detection all occur in the heart of the GC known as the GC oven. The integration and calculation of results are done in the controller which can be considered the brains of the system.

This paper describes the basics of how a BTU analyzer works. In a typical natural gas application the gas is separated into eleven different components. Hexane's and heavier components such as heptane, octane, and nonane are combined together to form a single peak known as C6+. Because we separate up to these components, we call this a C6+ application. Typical ranges are as follows:

Component		Range
C6+	Hexanes and heavier	(0-0.7%)
C3	Propane	(0 -5%)
IC4	Isobutane	(0-1%)
NC4	Normal Butane	(0-1%)
NeoC5	Neopentane	(0-1%)
IC5	Isopentane	(0-1%)
NC5	Normal Pentane	(0-1%)
N2	Nitrogen	(0-15%)
C1	Methane	(0-100%)
CO2	Carbon Dioxide	(0-15%)
C2	Ethane	(0-15%)

The following section describes and illustrates what takes place in the GC oven.

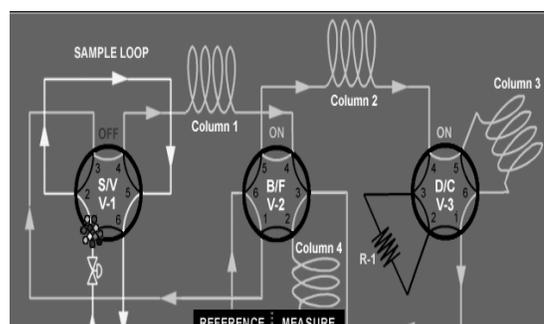
GC OVEN FOR C6+ NATURAL GAS APPLICATION

The GC oven is heated at a constant temperature (around 80C), and has a constant flow of carrier gas (usually high purity helium) flowing through it. The carrier gas is used for transporting the sample through the oven during the separation process. The oven consists of three valves and four columns, and a set of balanced thermal conductivity detectors.

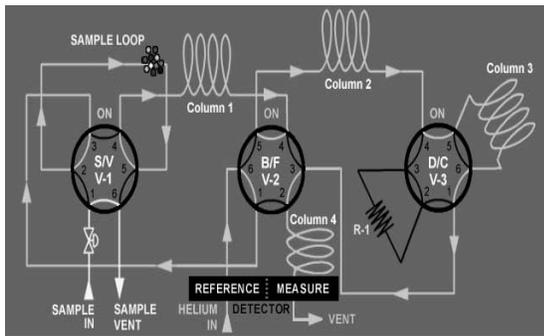
The first valve is the sample valve which is used for injecting the sample into the system. The second valve is called a backflush valve. The backflush valve is used for backing out the C6+ heavies so that they can be detected first without having to go through columns two and three. The third valve is a dual column valve which is used to trap the light components and allow the medium components to go around column three.

Of the four columns the first three are made up of tubing with special material inside called packing that is designed to separate the gas into its different components. The fourth column acts as a buffer to keep the flow steady when the valves are switched. The following steps illustrate the process taking place in the GC oven.

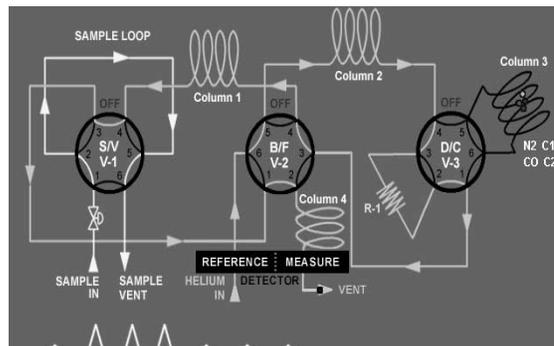
GC OVEN ILLUSTRATION



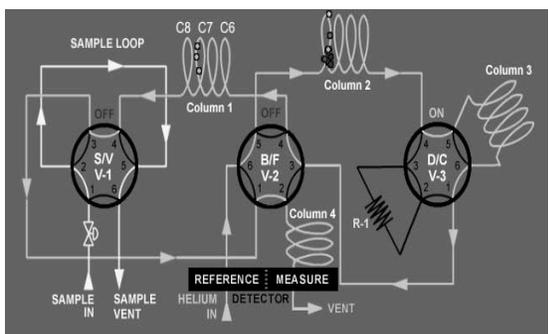
Step 1: Start of an analysis. Sample valve (V-1) OFF, backflush valve (V-2) ON, and dual column valve (V-3) ON. The sample purging system maintains a sample in the gaseous phase and passes the sample through transport tubing to the sample valve and through the sample loop.



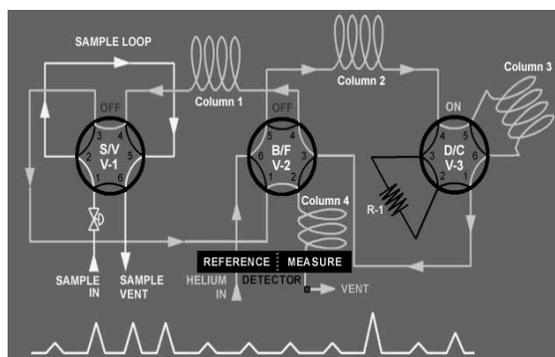
Step 2: The sample valve is turned ON to capture a precise volume of sample, and to allow the carrier gas (helium) to sweep the sample into column 1 to start the analysis.



Step 5: Dual column turns OFF after trapping the lightest components N₂, C₁, CO₂, and C₂. The medium components bypass column 3 by going through the restrictor column and follow C₆+ to the detector. Once again this helps speed up the analysis.



Step 3: The sample valve turns back OFF to start purging the next stream. The backflush valve turns OFF reversing the flow through column 1 so that C₆ and heavier components elute first (all combined as a single peak). Note: By switching the direction of flow through column 1 we bypass columns 2 and 3. This helps to expedite the analysis.



Step 6: After the heavy and medium components elute to the detector the dual column valve is turned back on freeing the light components and allowing them to cross the detector next.

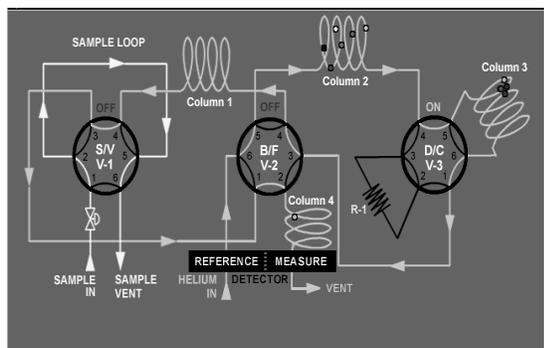
This ends the analysis and the next one is ready to begin. Typical analysis time is 4 minutes.

QUALITATIVE AND QUANTITATIVE INFORMATION

In a gas chromatograph it is vital that three things never change.

1. Oven temperature
2. Flow of carrier gas
3. Sample size

By keeping these three things constant we are able to run continuous analysis that repeat within ± 0.5 BTU / 1000 BTU's (± 0.25 BTU / 1000 BTU's when installed in a temperature controlled environment). By knowing this time (Retention Time) we can program the controller and have it identify the peaks as they come out. This identifying of the peaks is known as qualitative information.



Step 4: C₆+ (heavy) is on its way to the detector. Column 2 separates the mediums C₃, C₄'s and C₅'s while the lightest components N₂, C₁, CO₂, and C₂ continue traveling through column 2 into column 3

To find out quantitative information we use a set of matched thermal conductivity detectors (TCD's) integrated in a bridge circuit. One detector is the reference and is only exposed to the carrier gas. The other is called the measure detector and is exposed to both the carrier and the separated sample components. When carrier gas is flowing across both the reference and measure detectors at the same time the detector bridge is balanced and no signal is generated. When a component, other than carrier gas, is going across the measure detector the bridge is not balanced and a signal is generated, amplified, and sent to the controller. This raw signal is integrated by the controller which then calculates a raw area. A raw area is calculated for each peak (see Figure 1).

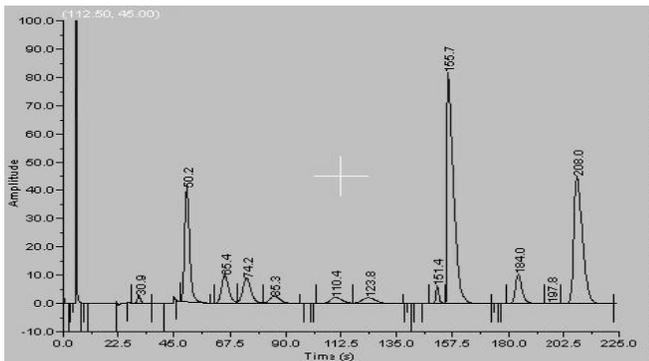


FIGURE 1. Chromatogram

Raw areas are calculated by integrating the area under each peak. Each raw area is directly proportional to the component concentration

During a calibration raw areas are divided by the known calibration concentrations and response factors (RF) are calculated. Each response factor is only changed during a calibration. The following formula shows how a response factor is used for calculating the mole percent of a sample stream component.

$$\text{Response Factor} = \frac{\text{Raw Area}}{\text{Calibration Concentration}}$$

$$\text{Mole \% of component} = \frac{\text{Raw Area}}{\text{Response Factor}}$$

The following is a simplified example of how the response factor is calculated and then used in the stream analysis.

Given: Calibration was run and a raw area for ethane calculated by the controller is 100.

Given: The calibration gas had a molecular concentration of 5% ethane in the bottle (this was programmed into the controller).

$$\text{RF} = \frac{\text{Raw Area}}{\text{Calibration Concentration}}$$

$$\text{RF} = \frac{100}{5} = 20$$

Given: Sample stream gas is run, and the raw area calculated by the controller is 200.

What is the quantity of ethane in the sample stream?

$$\text{Mole \% of Sample} = \frac{\text{Raw Area}}{\text{RF}}$$

$$\text{Mole \% ethane} = \frac{200}{20} = 10\%$$

Note: Realistically the Raw Area for the different components will typically be in the thousands.

BTU CALCULATIONS FROM MOLE PERCENT

After the controller has calculated the mole percent of each component, it normalizes the components so that the summation of all mole percentages equal one hundred. A simplified example of normalization using only four components instead of eleven is as follows:

Measured component	Normalized Component
N2 0.99%	1.0%
C1 89.1%	90%
CO2 0.99%	1.0%
C2 7.92	8.0%
Totals 99%	100%

To normalize mole %:

$$\text{CONCNn} = \left(\frac{\text{CONCn}}{\text{CONCt}} \right) \times 100$$

Where:

CONCNn = Normalized concentration of component n
 CONCn = Measured concentration of component n
 CONCt = Measured total concentration of components

After the mole percentages have been normalized the controller multiplies each of these percentages by a corresponding BTU value often taken from an internal table (GPA 2145). From the individual BTU calculations for each component the controller can then do a summation and calculate a total BTU per cubic foot of gas. This is an uncorrected or Ideal BTU value. To get a corrected or Real BTU value the controller multiplies the Ideal BTU by the compressibility factor. Figure 2 shows the results from an analysis report.

	MolPct	WgtPct	LiqVol	Gal/1000	BTUGross	BTUNet	RelDens.
C6+ 50/50/00	0.0817	0.4292	0.2045	0.0396	4.20	3.89	0.0026
PROPANE	0.7427	1.8473	1.1737	0.2047	18.73	17.23	0.0113
iBUTANE	0.1313	0.4303	0.2463	0.0429	4.28	3.95	0.0026
nBUTANE	0.1486	0.4871	0.2687	0.0469	4.86	4.48	0.0030
iPENTANE	0.0575	0.2340	0.1207	0.0211	2.31	2.13	0.0014
nPENTANE	0.0381	0.1552	0.0792	0.0138	1.53	1.42	0.0010
NITROGEN	1.5539	2.4547	0.9769	0.1703	0.00	0.00	0.0150
METHANE	91.3020	82.5942	88.7254	0.0000	924.25	832.22	0.5057
CARBON DIOXIDE	1.6375	4.0644	1.6005	0.2790	0.00	0.00	0.0249
ETHANE	4.3066	7.3036	6.6042	1.1520	76.39	69.87	0.0447
TOTAL	100.0000	100.0000	100.0000	1.5170	1036.54	935.19	0.6123
Compressibility Factor	1.0023						
Heating Value Gross BTU Dry	1038.92						
Heating Value Gross BTU Sat.	1020.84						
Heating Value Gross BTU Act.	1038.92						
Heating Value Net BTU Dry	937.34						
Heating Value Net BTU Sat.	921.03						
Heating Value Net BTU Act.	937.34						
Relative Density Gas Corr.	0.6134						

FIGURE 2. Analysis Report

The analysis report gives the BTU values as well as gas composition, and relative density which can be used for volumetric calculations.

CONCLUSION

Gas Chromatographs have been used for process and BTU measurement for many years. They have proven to be an accurate and reliable source for gas energy measurement needs. During the gas analysis the chromatograph uses columns to separate the gas into its constituents, and uses thermal conductivity detectors to quantify the mole percentage of each component present. A BTU value is then calculated for each constituent based on this mole percentage. By summing up these individual values we can find the total BTU value of the gas.

GLOSSARY:

1. *Carrier Gas* – the gas supply, regulated to a specific pressure, which carries the sample through the columns to the detector. The most common carrier gas used for natural gas applications is pure helium.
2. *Columns* – various tubes or capillaries mounted in a chromatograph oven that are packed with solid material, combinations of liquid and solid material, or liquid material.
3. *Analytical valves* are installed in the chromatograph oven both to inject a sample for analysis and to divert it or its separated components as per the application schedule (timed events).
4. *Detectors* are devices or assemblies of instruments that transmit electronic signals proportional to the

concentration of a component. The Thermal Conductivity Detector (TCD) is the most widely used detector for natural gas analysis.

5. A *Calibration cylinder* is used as the basis of comparison for the each of the components measured on a stream(s). The components and ranges blended in the cylinder are roughly comparable to the stream.
6. *Retention time* — the amount of time elapsed from the start of an analysis to the maximum moment of influence a component makes on the detector.
7. The *chromatogram* is the graphic depiction of the chromatograph analysis. It is used to allow the technician to view the baseline integrity and peak separation as a part of quality assurance.
8. The *Molecular percentage* (mole %) is the volumetric measurement of the percentage of a component in a sample (also known as the percentage by volume.)
9. *Response factor* — used for quantitative measurement. $RF = RA / CC$
Where:
RF = Response Factor
RA = Raw Area
CC = Calibration Concentration from calibration gas.