Fundamentals of Gas Chromatography
Class # 5170.1

Merle Bell
Project Manager
ABB, Inc.
7051 Industrial Blvd.
Bartlesville, OK U.S.A.

Introduction

"Btu" is the three letter acronym for British thermal unit. One Btu is the quantity of heat required to raise the temperature of one pound of water from 58.5° F to 59.5°F (about 1055.056 joules (SI)). Heat (Btu), is gained from the burning of Natural Gas otherwise known as Oxidation, which is shown in the chemical equations below:

- $CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O + HEAT$ (1010 Btu/CF)
- $2C_2H_6 + 7O_2 \Rightarrow 4CO_2 + 6H_2O + HEAT$ (1769 Btu/CF)
- $C_3H_8 + 5O_2 \Rightarrow 3CO_2 + 4H_2O + HEAT$ (2516 Btu/CF)

This "HEAT" is the valuable commodity that makes Natural Gas production, transmission and distribution profitable as an enterprise. The purpose of this paper is to describe how this heat amount can be obtained from the gas composition. The method for attaining this composition will also be discussed.

Gas chromatography is today being chosen more and more in the natural gas industry for monitoring of gas quality. The calculations of the gas volumes in modern electronic flow meters requires not only Btu information, but specific gravity, Mol. % CO_2 and Mol. % N_2 as well. In addition, the current AGA-8 compressibility equations for the "detailed method" of calculation of $F_{pv,,}$ the AGA 10 Speed of Sound equations and the SRK and Peng-Robinson Hydrocarbon Dew Point (HCDP) calculations also require a complete analysis. In the past, on line calorimeters were used to obtain heating value, but today, modern micro-packed columns are providing faster cycle times for "time critical" Btu measurement applications. For these reasons mentioned above, and the fact that the installation requirements for chromatographs are less stringent than calorimetric methods, the use of gas chromatographs has become standard practice.

There are two general classes of chromatography; laboratory chromatography and "At Line" or "on-line" or process chromatography. While both are discussed, the scope of this paper is primarily limited to on-line chromatography. Natural gas is a mixture in which the compounds vary in size from nitrogen, N_2, at the smallest, to the C6+ fraction at the largest, which can all be separated by Chromatography. The C6+ fraction is called that because it is composed of up to 200 different compounds (called Isomers). In order to get a more precise peak area and to clean off any residue left on the column the "C6 fraction" is backwashed out of the system. This concept will be discussed in detail in the following section.

How Chromatographs Work

The way that a modern microprocessor controlled at line/on-line chromatograph works has been thoroughly discussed in previous papers. However, it would be helpful to review briefly how a GC works. The sequence we will follow in this discussion starting with the sample probe is also the route the sample takes from the pipeline to the printer.

Theory

Chromatography is one of the most widely used means of performing chemical analysis. Russian botanist Mikhail Tswett is credited with discovering the technique of chromatography. Using alcohol as a mobile phase and chalk as a stationary phase, Tswett was able to separate various plant extracts.

Figure 1 shows how Tswett's experiment may have taken place. The vertical columns represent the chalk. At 0 minutes a mixture of plant extracts was placed at the top of the column. A steady rate of alcohol was then added to the top of the column. Over the next 10 minutes, as the extracts were pushed through the chalk by the alcohol, the extracts were separated into distinct bands.

A modern definition of the term chromatography is the ability to separate components based upon their affinities for separate phases. Several different types of chromatography exist including:

- Thin Layer Chromatography
- Liquid Chromatography
- Gas Chromatography

Reviewing the definition of chromatography, the ability to separate components based upon their affinities for two separate phases. These phases are known as the stationary phase and the mobile phase. In Tswett's experiments, the alcohol was the mobile phase and the chalk was the stationary phase. In gas chromatography, the mobile phase is the carrier gas and the stationary phase is the chromatograph column.

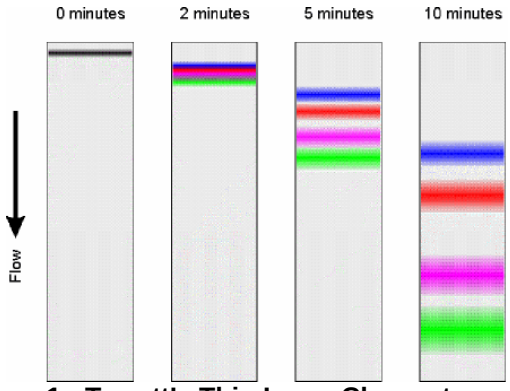

Figure 1 - Tswett's Thin Layer Chromatography

Separation of the components is achieved by placing a narrow band of the mixture on the tip of the column. The mixture is pushed through the column (stationary phase) by the carrier gas (mobile phase). As the components in the mixture interact with the stationary phase, they are separated into distinct bands which are detected as they exit the column. The primary mechanisms for separation by the stationary phase are surface adsorption, molecular size, and polarity.

Figure 2 shows how a modern gas chromatograph mimics Tswett's experiment. At 0 minutes, a mixture of components is injected into the flowing carrier gas. The mixture is then carried onto the column. As it is pushed through the column by the carrier gas, the mixture is separated into individual components.

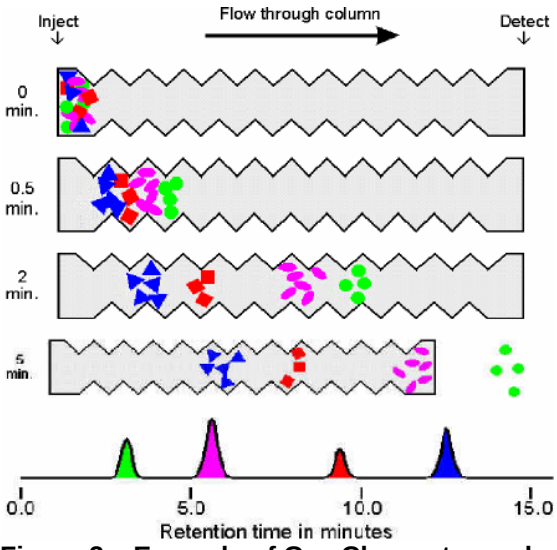

Figure 2 – Example of Gas Chromatography

The trace generated by the detector signal is called the chromatogram (Figure 3). The flow rate of the carrier gas (mobile phase) and the temperature of the column (stationary phase) must be carefully controlled to yield repeatable chromatograms.

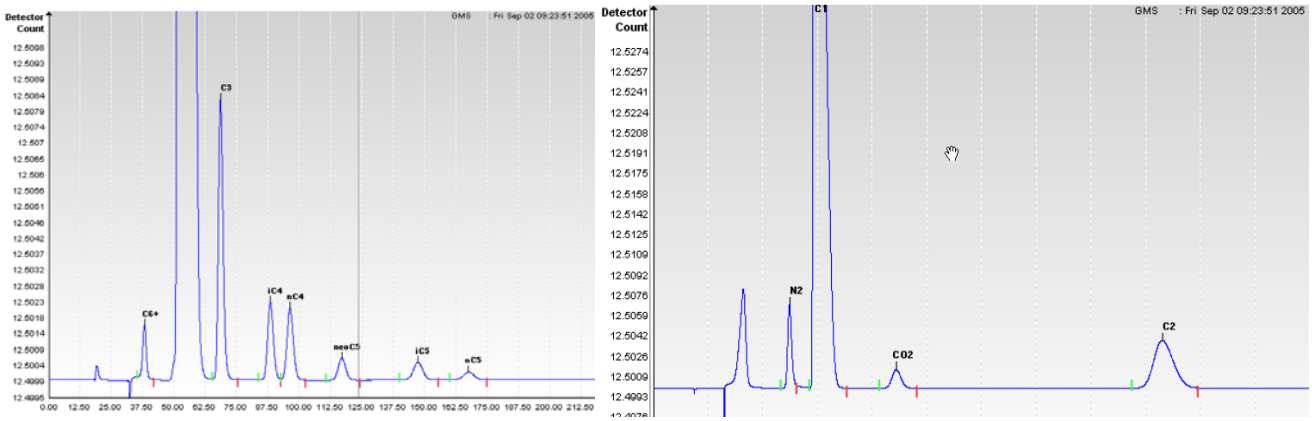

Figure 3 – Detector Trace or Chromatogram

It is necessary to control these parameters because components are identified by their retention time. The retention time is the amount of time from the beginning of the analysis until the component exits the column. If flow and temperature are held constant, the retention time is very repeatable. Retention time is the primary means of identification.

The concentration of the component is determined by comparing the peak area of the unknown to the peak area of a known standard. To calculate the amount of a given component, follow the equation:

$$Cunk = PAunk/PAstd * Cstd$$

Where

C_{unk} = Concentration of unknown

C_{std} = Concentration of standard

PA_{unk} = Peak Area of unknown

PA_{std} = Peak Area of standard

Sample Conditioning System

To obtain a representative sample of gas from a pipe line, a probe should be inserted into the flowing gas stream in the pipeline. This procedure is as essential for good sampling for on-line GC's as it is for spot or composite samples. With spot or composite samples care is taken to maintain pipeline conditions. Once in the lab, each sample must be pressure reduced and heated to 20 to 50° F above the dewpoint of the hydrocarbon sample before the analysis can be done. A major difference when sampling for an online chromatograph, however, is that the gas pressure is reduced to 15 PSIG at the probe for transport to the analyzer in order to prevent the loss of any part of the heavy component (C6+). Sometimes it is useful to have a sample bypass loop to reduce sample transport lag times. It is important to obtain a recent or fresh sample from the pipeline or other source of gas, so careful attention should be paid to the sample transport lag time.

In addition, filtering and liquid coalescing is done if needed to protect the integrity of the analyzer columns and to insure a single phase sample. Sometimes double block and bleed sample switching is used to prevent cross contamination by the standard or other sample streams.

Gas Chromatograph Oven

Since temperature control is critical for most chromatograph applications there is usually a mandrel type heater (air-less oven) and very good insulation to maintain this iso-thermal temperature control. The oven components,

such as, valves, columns, and detectors are usually attached to this mandrel. The temperature of these components is maintained by conduction through metal to metal contact.

Laboratory chromatographs or bench-top chromatographs require that the sample be brought to a central location. Great care must be taken by all involved in this process to reduce sample handling errors. It is very difficult to eliminate these errors all together.

On-line chromatographs or process chromatographs are actually installed at the process or on the meter run. While sample handling issues are not a great concern as with lab GC's, these instruments must have all utilities (such as power, instrument air, and carrier gases) supplied to them. Sometimes these analyzers must be installed in shelters to protect them from harsh environments.

These different types of chromatographs operate in different environments, but they all have the same three basic components; sampling, a column, and a detector.

Sampling into the GC Oven

There are 2 primary ways of introducing a sample into a chromatograph column. The first method is by injection using a syringe. This method is widely used in laboratories where most of the samples are liquids. The second method of sampling involves using a sampling valve, and uses a tube of a given volume known as the sample loop. This is the preferred method for sampling natural gas. It not only works well in the laboratory, but it also works well in the field where automation is required.

Once the natural gas enters the oven, a precise sample is measured by a sample inject valve. This valve must be repeatable to obtain the needed +/- 0.5 Btu or better precision. The chromatograph controller then blocks the sample flow and allows it to equilibrate to atmospheric pressure. This ensures even greater sample size precision. This sample is then swept on to a set of carefully selected chromatographic columns by a stream of helium gas for sequential separation of each component in the natural gas mixture.

Columns

Many types of columns are available, but they all fall into basically 2 categories, packed or capillary.

As the name implies, packed columns are hollow tubes which have been "packed" with the stationary phase. The diameter of packed columns generally ranges from 1/4" to 1/16". In some instances, 0.53mm capillary columns can be packed with good results. Many types of packing materials exist. Usually the column packing consists of a solid support coated with a liquid phase. Most natural gas applications use packed columns.

Capillary columns have become increasingly popular in recent years due to their superior resolution. Resolution is a measure of the columns ability to separate 2 adjacent peaks. As a general rule, the smaller the internal diameter of the column the more resolution it will have. The internal diameter of capillary columns can range from 0.1mm to 0.53mm.

The main type of capillary column is a "wall coated open tubular" or WCOT. A WCOT is a capillary tube with a liquid phase bonded to the wall of the tube. There is a variety of liquid phases available ranging from non-polar to polar.

Another popular capillary column is a porous layer open tubular or PLOT column. A PLOT column is basically a combination of a packed column and a capillary column. It uses capillary tubing with a porous polymer bonded to the wall of the tube. Porous polymers are very popular in packed columns. They are the primary packing material used to separate the lighter gases in natural gas.

Detectors

There are many different types of detectors for a gas chromatograph and they fall into two categories; specific, or universal. Specific detectors will only detect certain compounds based upon their chemical structure. A flame photometric detector (FPD) (Figure 7), is particularly useful for analyzing trace levels of sulfur compounds because it only detects components containing sulfur. As the separated components enter

the detector they are burned in a flame. When a sulfur containing compound is burned it produces a blue light. This light is transmitted to a photomultiplier tube that measures the number of photons passing through a 394nm filter.

Another common detector is a flame ionization detector (FID). An FID (Figure 8) is ideal for measuring low levels of hydrocarbons. Once again, as compounds exit the column they are burned. When hydrocarbons are burned in the flame they produce positive ions which are drawn to a negatively charged collector. This current is proportional to the amount of carbon atoms in the flame.

Universal detectors show a response to all compounds. The most common universal detector is the thermal conductivity detector (TCD). A TCD uses thermal conductivity to detect when a peak has reached the detector. Thermal conductivity is the ability of a compound to conduct heat. Today most Thermal conductivity detectors use thermistor beads arranged in a wheatstone bridge to generate the detector signal. One of the thermistors is the reference bead and is exposed to pure carrier gas. The other thermistor is the sense bead and is located at the end of the column. The beads are operated at a constant temperature. When a compound goes past the sensing bead, the bead is either heated up or cooled off, depending on the thermal conductivity of the gas. This changes the resistance in the bridge and a detector signal is generated. The TCD is typically used to measure components greater the 100 ppm. Figure 9 shows a typical Wheatstone bridge circuit employed in a TCD.

As each column does its specified separation job, it is switched out of the helium stream. The separated components make their way through the thermal conductivity cell detector where they can be measured. An example of a detector output is shown below in Fig 4a and 4b.

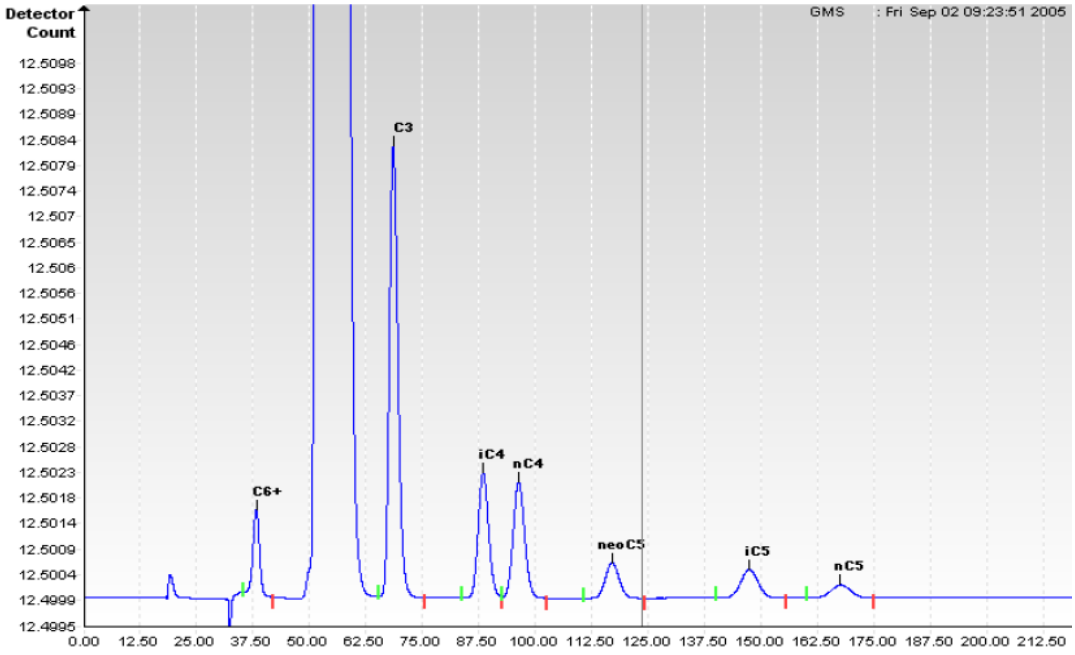

Figure 4a – Example Chromatogram from Detector 1

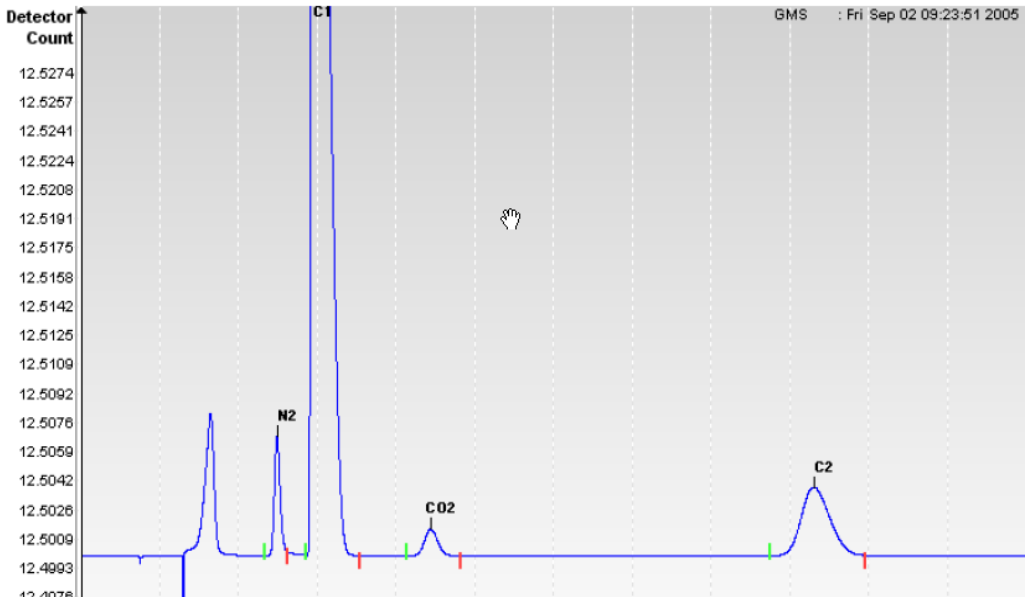

Figure 4b – Example Chromatogram from Detector 2

These peaks are "gated" and the area under each peak integrated in order to be quantified. All the timing functions, such as, sample inject, column reverse, auto calibration and results logging are done by the microprocessor controller board. In addition, this device will detect each peak, open and then close integration gates, identify the peak, and assign the correct response factor to it. The controller can then calculate the mole fraction of each component. Since these peaks are quite arbitrary in size due to variability of equipment setup and environment, high quality standards should be used to calibrate these instruments. Calibration assures the most accurate determination of mole fraction possible. Indeed, all Btu determination methods require high quality standard samples. On a Btu GC, the peaks should also be normalized to compensate for barometric pressure changes (which cause sample inject size variations). This allows the repeatability of the calculation to be as low as +/- 0.5 Btu or better at 1000 Btu/cf. The GC microprocessor may also calculate the specific gravity, compressibility, condensable liquids, Wobbe index, as well as the Btu.

How the Btu is calculated

Most gas contracts today have at least a Btu specification and many use MMBtu (million Btu) rather than gas volume for custody transfer measurement. The higher the Btu content, the more energy can be obtained from burning the gas. It just doesn't take as many cubic feet of gas to heat the home hot water tank if the gas is 1090 Btu instead of 940 Btu per Scf. The Btu, then, is the measure of the actual amount of heat energy contained in a cubic foot (cf) of this natural gas. Total flowing energy is defined as:

E= H*q

Where:

E= Energy flow rate

H= Heating Value/unit volume or mass Q= Volume or mass flow rate

In North America, the prevalent unit for energy measurement is the MMBtu or the dekaTherm. An $MMBtu^2$ is calculated by:

Btu/cf * MMcf = MMBtu

The financial benefit for keeping track of energy rather than just flow rate is substantial. If we postulate 1000 Btu/cf as fairly average for natural gas, and define a +/- 5% error between doing a lab determination of the heating value on a spot sample of the gas once per month, and an on-line (nearly continuous) monitor of the heating value, this results in a +/- 50 Btu difference. On a station that has 50 MMcf per day at $2.50 per Mcf or

MMBtu, this is $125,000.00 worth of gas per day. Five percent of this is $6,250.00 per day. If a process chromatograph is used to determine the energy content and this chromatograph has a $25,000 installed cost, one can easily see a pay out of about 4 days on this 50 MMcf/day station. Most major interconnects have on-line Btu measurement of some sort today. We anticipate even smaller volume stations justifying GC's as the installed costs are pushed downward by new developments.

Calculation Methods

The methods for calculation of the natural gas Btu from analysis data are well documented in GPA 2172-96, ASTM 3588, ISO 6976 and others, and example calculations have been published previously.

C_6 Plus Component Considerations

The C6 and heavier component values are of interest in the calculation of the detailed method of the AGA-8 compressibility calculation procedure15, the calculation of Hydrocarbon Dew Point (HCDP), and the AGA 10 Speed of Sound. They are also of concern when calculating the heating value, Btu or CV, of the natural gas. This is because the molar heat content increases dramatically with increasing carbon number (C6, C7, C8, etc.). Certain Industry standards pertaining to the calculation of gas flow and heating value from the AGA and API allow the use of individual concentration values for the heavier components of natural gas such as C6, C7, C8, and C9. These each represent a “family” of components of the same Carbon number, called Isomers. There are nearly 200 of these Isomer families between 2,2 diMehtyl Butane and Normal Decane. These families are usually represented by only the Normal or NCX because the Isomers are not included in the GPA 2145 constants document. This is another source of error that should be considered.

The word “allow” is specifically chosen as opposed to the word “require”. Using C6+ is also allowed, and is perhaps more precise. While it may seem intuitive that "more is better" when it comes to values entered into the AGA-8, HCDP and AGA 10 formulae, however this is not necessarily correct.

A gas chromatograph that is designed to analyze C6+ does exactly that. Everything that may happen to be in the gas sample being analyzed gets measured. This is because the first chromatographic column that the gas sample is put onto is actually turned around and flushed backwards with carrier gas until all the heavier components are washed through the chromatographic detector. This means that the C6, C7, C8, and C9 and any thing else that is on the chromatographic column gets measured by the analyzer. The components are all lumped together, but definitely all measured. This allows all the heavier components to be accounted for in the Btu calculation. This also provides a very useful service to the chromatograph itself. Any residual heavy contamination that may be left from the injection of the first sample is purged before the next sample is introduced. This allows a chromatograph to operate over and over, day in and day out without the stability of the baseline being adversely affected. If the base line creeps up because of residual left over from previous sample injections this can cause subsequent inaccurate analyses.

Also, the precision of the measurement of the heavier components is greatly enhanced when the relatively small amounts of all the heavy ends are lumped. In pipeline quality natural gas the relative amounts of each component decreases dramatically as the carbon chain length increases. This is shown in the typical natural gas standard blend analysis listed below:

Component	Mole %
N_2	2.5%
CO_2	1.00%
C_1	89.564%
C2	4.99%
C3	0.999%
iC_4	0.305%
nC_4	0.309%
NeoC5	0.101%
iC_5	0.100%
nC_5	0.102%
C_6+	0.030%

The question one must ask is how precisely the device detect peaks so small that 200 of them add up to 0.03 Mol. %? Do the errors in Btu calculation due to slight changes in the composition of the C_6+ fraction outweigh the inherent errors of integration due to the ever decreasing peak sizes and the problem of not detecting everything that went onto the chromatograph because of not backwashing?

One very well accepted method to adjust for the variable component content of the C_6+ fraction would be to have a laboratory do what is called an "extended analysis" from time to time to adjust the C_6, C_7, C_8, etc molar contribution characteristics of this C_6+ fraction. For a complete discussion of this method in developing a custom Btu factor see references.

However, the calculation below outlines how this composite C_6+ Btu value can be obtained from an extended analysis:

$Btu/cf = X_1 * C_1 + X_2 * C_2 + X_3 * C_3 \ldots\ldots\ldots X_{11} * C_{11}$

Where:

X_1 = Mole fraction of C_1 or methane

X_2 = Mole fraction of C_2 or ethane

X_3 = Mole fraction of C_3 or propane

X_{11} =Mole fraction of C_6 + hexane's and heavier

and:

C_1 = Molar heating value of C_1, or methane (1010 Btu/cf)

C_2 = Molar heating value of C_2, or ethane (1769 Btu/cf)

C_{11} = Molar heating value of C_6+ or Hexane's and heavier (~4943 Btu/cf)[1] (made up of C_W,C_X,C_Y, and C_Z)

C_W = Molar heating value of nC_6, or normal Hexane [4755.9 Btu/cf]

C_X = Molar heating value of nC_7, or normal Heptane [5502.5 Btu/cf]

C_Y = Molar heating value of nC_8, or normal Octane [6248.9 Btu/cf]

C_Z = Molar heating value of nC_9, or normal Nonane [6996.5 Btu/cf]

The composite concentrations of C_6, C_7, C_8, and C_9 can be easily calculated from an extended analysis of the sample gas. The Specific Gravity and compressibility are calculated in similar ways to the method above.

Conclusion

Gas Chromatography has become the device of choice to determine the Btu of natural gas. The additional composition information is now demanded for the AGA gas volume calculations, the AGA 8 compressibility calculations, the HCDP calculations and the AGA 10 Speed of Sound calculations. Sampling system design is as important to analytical for on-line or spot analysis precision as analyzer design itself. The analyzer should back flush the C_6+ fraction and this type of analysis is preferred for Btu precision. Summing C_6, C_7, C_8, and C_9 peaks from anything less than an FID extended analysis GC can lead to errors due to the difficulty of detecting and summing of the 200 isomers that form the composite NC_6 through $_{NC10}$ carbon numbers. Unique features of power, remote communication, remote troubleshooting, and environmental protection of the GC and calibration blend are required to install online GC's with ◦ 0.5 Btu @ 1000 Btu precision in remote locations.

References

1. GPA Standard 2145-2009
2. "Sampling and Analysis of Natural Gas", Schepens, Kilmer and Bernos, GPA proceedings #61
3. "Btu Measurement in Natural Gas Using Process Gas Chromatography", Kizer and Sund, Proc. of Gulf Coast Meas. Soc. #24, 1989, p. 72 ff.
4. "Calculations of Gross Heating Value, Relative Density and Compressibility Factor For Natural Gas Mixtures From Compositional Analysis", GPA Std. 2172-96
5. "Gas Heating Value: What It Is and How To Measure, Calculate", D. N. McClanahan, Oil and Gas Journal, Feb. 20, 1967, P. 84 ff.
6. Kizer, "Natural Gas Energy Determination Review", ISA Proceedings, 1991, p. 777
7. “Energy Measurement Using On-Line Chromatography”, Kizer, Proc. Of the71 st International school of Hydrocarbon Measurement, 1996, p. 544 ff.
8. AGA Report No. 8
9. Speed of Sound in Natural Gas; AGA Report No. 10