OPERATIONS OF ONLINE CHROMATOGRAPHS

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Introduction

Gas Chromatographs have become vitally important in today’s gas industry for one very important reason. The reason is they provide the data that tells us how much energy in contained in a given sample of gas. With the escalating costs of natural gas, the capability of calculating the full energy of the gas sample has also increased in value.

Currently, gas is exchanged based on the amount of energy contained in natural gas, not just the volume of that gas. The energy of a given gas quantity is derived by multiplying the gas volume by the quality or Btu value of the gas. The energy value is called a deka Therm or MM Btu.

An online gas chromatograph is a device that is used typically at fairly large volume metering stations to provide not only the heating value (Btu) of the gas but also the compressibility, relative density, and Wobbe Index. Additionally, a gas chromatograph can calculate full AGA-8 compressibility equations, hydrocarbon dew point, and AGA-10 speed of sound equations. These are all valuable items of data that can and are used in custody transfer gas measurement applications.

Online Gas Chromatograph Basics

Gas chromatography calculates the energy of a gas sample by separating the sample into its various components. Almost all natural gas is made up of many different components bringing their own heating value to the overall energy value of the sample.

A fairly typical natural gas blend would be:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂ Nitrogen</td>
<td>0.24 %</td>
</tr>
<tr>
<td>CO₂ Carbon Dioxide</td>
<td>1.31 %</td>
</tr>
<tr>
<td>C₁ Methane</td>
<td>86.39 %</td>
</tr>
<tr>
<td>C₂ Ethane</td>
<td>6.16 %</td>
</tr>
<tr>
<td>C₃ Propane</td>
<td>3.46 %</td>
</tr>
<tr>
<td>IC₄ Iso Butane</td>
<td>1.08 %</td>
</tr>
<tr>
<td>NC₄ Normal Butane</td>
<td>0.80 %</td>
</tr>
<tr>
<td>IC₅ Iso Pentane</td>
<td>0.27 %</td>
</tr>
<tr>
<td>NC₅ Normal Pentane</td>
<td>0.15 %</td>
</tr>
<tr>
<td>C₆+ Hexanes Plus</td>
<td>0.14 %</td>
</tr>
</tbody>
</table>

In the sample above, it should be noted that the largest component by mole percent is methane. However, the heavier carbon components have much higher heating value and are very important in deriving the overall energy value of the sample. Methane, for example, has a heating value of 1,010 Btu/CF while propane, C₃, has a heating value of 2,516 Btu/CF.

The C₆+ value is a combined peak made up of hexane (C₆), heptane (C₇), octane (C₈), nonane (C₉), and any other components heavier than C₉.

A graphical depiction of the components as they are separated and measured is called a chromatogram. The peaks are an indication of how much of each component is in the gas sample while the time that the peaks appear during the detection process identifies what the component is.

The components are separated by a 1/32” tubing that is filled with compacted particulate which is coated with a liquid phase. That substance captures the components based on their molecular structure then releases them as a partitioned component that is then measured by the detection system of the chromatograph. The gas sample is propelled through the separation columns by a carrier gas, typically, helium. After separation, the gas sample components move over a detector. In most online chromatographs, the detector is a thermal conductivity detector or TCD. TCDs are glass encapsulated heated beads that are held at a specific temperature, usually 140°F. As the various components move across the TCD, they remove heat from the detector, which causes the system to apply more power to the TCD to keep it at required temperature. This power draw to the TCD is measured very accurately by the chromatograph and correlates to the amount of the components that caused the temperature change.

The amount of each component is shown as a series of peaks above a baseline on a chromatogram. The height of the peak and the area under the peak are used by the chromatograph to calculate the amount of each component in the sample.
Here is a chromatogram representing a split sample:

Heavier components are shown on this chromatogram.

Lighter components are shown on this chromatogram.

Sample Conditioning

One of the most important aspects in the day-to-day operation of an online gas chromatograph is the sample conditioning system. No chromatograph can produce a representative analysis if the gas in the pipeline does not reach the analyzer.

Particulates and liquids in the pipeline need to be prevented from getting into the chromatograph for one simple reason, they are not gas. Sample conditioning systems are in place to insure that what is in the pipeline is what gets into the analyzer.

There are various methods for sample conditioning. It starts at the sample point where it is the job of the sample probe regulator to get the sample from the pipeline and reduce the pressure without causing liquids to form. Due to the cooling effect of reducing gas pressure, it is possible for some sample components to fall out at their hydrocarbon dew point.

Some sample conditioning systems such as the one shown below are more specialized. Low-pressure landfill gas is a popular source of gas that needs to be pressurized before it can be used in an online chromatograph. These systems have pressure pumps as well as liquid rejection and particulate filters condition the gas sample prior to analysis.

In order to get a repeatable result from the above operation all the components in the chromatograph must be kept at a uniform temperature. The oven components
such as valves, columns, and detectors are all maintained at the temperature by their contact with the mandrel type heater. The entire unit is housed within a heavily insulated package.

Gas chromatograph internal operation sequence:

**Step One:** Sample valve opens to let in the sample of gas enter the two sample loops.

**Step Two:** The pilot valve is actuated and the GC module switches to inject mode. The helium carrier gas is regulated by the pressure regulators.

**Step Three:** The carrier gas flows into the GC valve and carries the gas sample out of the sample loop.

**Step Four:** The gas sample flows onto the GC Column A. The heaviest components C_{6+} on GC Valve 1 and C_{3+} on GC Valve 2 are trapped on Column A.

**Step Five:** The lighter components pass through Column A into Column B. At the end of the forward flow time, the pilot valve activates to return the GC valves to the Backflush mode.

**Step Six:** The lighter components continue to move forward through Column B while the heavier components are back flushed from Column A and over the detector.
Step Seven: The lighter components are separated on Column B and pass again through Column A. They are then back flushed to the detector beads and then vented to atmosphere.

Step Eight: The chromatograms are integrated and the component concentrations are calculated. It is from these calculations that the heating value and other values are calculated.

In the peak depiction in the chromatogram, the mole percent of each component is calculated by the height of the peak as well as the area under the peak. Once the mole percentage is obtained then the heating value for each component is multiplied by that percent to arrive at the overall heating value of the sample.

Analysis Report

Once the component mole percents are calculated, the component total is normalized. In normalization, the total of all percentages is brought to 100% by allocating the difference between the un-normalized total and 100% to the components based on their percentage participation in the whole sample.

After normalization, the chromatograph produces an analysis report, which provides an over all view of the sample, including heating value, density, and GPM.

Summary

The online Btu gas chromatograph is one of the most important devices in natural gas measurement today. The analysis of the various components makes up the energy in a given gas sample and energy is the way gas is bought and sold these days. With careful sample conditioning and installation, a modern gas chromatograph will provide accurate, reliable gas analysis for many years.