ABSTRACT

The on-line gas chromatograph (GC) has been widely used for natural gas quality analysis and energy measurement at custody transfer locations since the early 80's. The energy measurement and relative density measurement provided by the GC can have a large effect on unaccounted for Gas because the gravity effects volume calculations and the heating value effects energy rates. The gas chromatograph measures component concentrations first and then calculates physical properties of the gas such as heating value and relative density. Units of energy measurement can be British Thermal Units (BTU) Mega Joules (MJ) or Kilo Calories (KJ). This paper will refer to BTU for energy units, ISO (KJ) or SI (MJ) metric units can be used interchangeably.

INTRODUCTION

The Gas Chromatograph (GC) can be a fairly complex instrument that requires a certain degree of specialization in order to maintain optimal measurement. Optimizing GC performance depends upon a thorough understanding of the chromatogram and its role in setting up a GC. The following paper will discuss the various operational components of a GC that need to be set up, in order of importance, to verify optimal measurement in a typical natural gas application.

PRINCIPLE OF OPERATION

The GC oven contains 3 main components mounted together in an electrically heated heat-sink-oven:

- GC Valves
- Micro-packed Columns
- TCD Detectors

The GC valves control sample injection and column switching. Components are separated into groups and diverted into specific columns for further separation. This creates a critical split between certain key components. Splits between Hexanes + (C₆+) and Normal Pentane (NC₅) are controlled by V-2 off time. Splits between Ethane (C₂) and Propane (C₃) are controlled by V-3 off time. The component separations are as follows in Table 1. The valve timing, inhibit on and off times, and other timed events must be properly configured to ensure that component groups are diverted to the proper columns and all relevant peaks are properly integrated. Chromatograms must be used in conjunction with raw data and analysis data to ensure that all timed events are optimized.

<table>
<thead>
<tr>
<th>Column Configuration</th>
<th>Components Separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column 1 (controlled by valve 2 off-time)</td>
<td>C₆+</td>
</tr>
<tr>
<td>Column 2 (controlled by valve 3 off-time)</td>
<td>C₂, IC₄, NC₄, NeoC₅, IC₅, NC₅</td>
</tr>
<tr>
<td>Column 3 (controlled by valve 3 on-time)</td>
<td>N, C₁, CO₂, C₂</td>
</tr>
</tbody>
</table>

TABLE 1.

SAMPLE CONDITIONING AND SAMPLE TRANSPORT

The sample conditioning system is a very important component in any analytical system. This is a frequently overlooked component that must deliver a representative sample from the pipeline to the GC without changing the composition. This is not a difficult task when low BTU gas is measured in warm climates. When high BTU gas is measured the potential exists to lose the heavier components as they drop into the liquid phase due to sample cooling. This cooling effect, commonly known as the Joules-Thompson (JT) effect, will bias energy readings low because the high BTU contributors drop out of the vapor-phase sample before the GC even has a chance to measure it. The JT effect occurs at the point where the greatest pressure drop occurs. Usually this is the point where line pressure is reduced to 20-50 PSIG for sample transport to the GC. In addition, ambient temperatures contribute to cooling in the sample transport lines if left unheated in winter conditions. If the JT effect causes a loss of some of these high BTU contributors energy measurement will be biased low as a result.

Site inspections should take into account the need for heating on sample transport lines in cooler climates. Potential exists for errors biased in the negative direction when sample pressure is reduced by more than 700 PSIG on 1100 BTU Gas or higher.

The Sample Transport System must include sample probes to ensure that a representative sample is collected from within the flowing stream rather than from the walls of the pipeline. Sample probes provide a dual function:

1-They minimize liquid-contaminants from entering the sample transport line from the pipeline walls.
2-They extract a representative sample from the middle of the flowing stream for the sample transport system.

Integral sample probe/regulators can be useful for high BTU samples because they reduce the pressure at the...
sample tip where higher gas temperatures can help minimize the JT effect.

By visually inspecting the sample transport system (including sample probes) and noting maximum pressure drops relative to the energy content of the gas an engineer/technician can get a feel for the potential for Joules-Thompson effect.

The Stream Switching System can be double block and bleed, solenoid purge or single block with no bleed. In in custody transfer applications the latter is more common (see Figure 1). In this case each stream should be pressure balanced to minimize changes in sample loop volume due to pressure changes on differing streams. By halting GC operation and manually actuating each stream the engineer/technician can verify proper setup (pressure balancing) on the sample system. For example: Stream 1 pressure should be set at the pressure regulator (usually mounted at the sample probe) to indicate the same sample flow at F1 as streams 2,3 and the calibration stream (Cal Std). All stream flow rates can be adjusted in this manner with pressure using the common sample roto-meter to balance flow. Sample flow rate is not critical, so any point roughly mid scale (0-100cc/min) is adequate. When streams are pressure balanced the amount of normalization required during the analysis will be minimized. Sample filters should also be checked and replaced at least once per year.

INSTRUMENT PERFORMANCE

Linearity

Linearity can be verified with the use of three known standards. The on-site calibration standard may suffice as one of the three standards, preferably the middle one. Each standard should have component concentrations that yield a BTU value over the full operational range for a given installation. A meter station that may have BTU swings from 1020 on stream 1 to 1250 BTU on stream 3 should have a component mix roughly as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Std #1 Value</th>
<th>Std #2 Value</th>
<th>Std #3 Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanes +</td>
<td>0.01</td>
<td>0.03</td>
<td>1.59</td>
</tr>
<tr>
<td>Propane</td>
<td>1</td>
<td>3</td>
<td>75.48</td>
</tr>
<tr>
<td>Iso-Butane</td>
<td>0.5</td>
<td>0.1</td>
<td>3.26</td>
</tr>
<tr>
<td>N-Butane</td>
<td>0.5</td>
<td>0.1</td>
<td>3.26</td>
</tr>
<tr>
<td>Neo-Pentane</td>
<td>0.08</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iso-Pentane</td>
<td>0.08</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>N-Pentane</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.31</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>89.5</td>
<td>87.6</td>
<td>77.4</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>2.9</td>
<td>1.5</td>
<td>11</td>
</tr>
<tr>
<td>Ethane</td>
<td>2</td>
<td>35.99</td>
<td>194.66</td>
</tr>
</tbody>
</table>

**TABLE 2.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Std Value</th>
<th>Mol % Range</th>
<th>Repeatability</th>
<th>Reproducibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>1.0-7.7</td>
<td>7</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.14-7.9</td>
<td>12</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>71.6-86.4</td>
<td>7</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>4.9-9.3</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>2.3-4.3</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Iso-Butane</td>
<td>26.1-10</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>N-Butane</td>
<td>6-1.9</td>
<td>6</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Iso-Pentane</td>
<td>.12-45</td>
<td>6</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>N-Pentane</td>
<td>14.42</td>
<td>6</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Hexanes +</td>
<td>.1-.35</td>
<td>30</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 3.**

Note: GPA-2186-95 Section 9 Precision

REPEATABILITY

Several consecutive runs with on-site calibration gas will yield results that will determine the analyzer repeatability. As a general rule the first run should be disregarded. The next 5 or 10 consecutive runs should yield BTU results that are within at least ±0.5 BTU, ±.25 BTU is not uncommon. The same repeatability test over a 24-hour period in a temperature-controlled environment should yield no worse than ±1 BTU. If the installation is in an uncontrolled environment a test over 24 hours should yield results no worse than ±1 BTU. Once repeatability has been established careful review of historical calibration reports can reveal a lot about the instrument performance. GPA report 2286-95 serves as a useful guideline for mole % repeatability standards.

Accuracy

Repeatability is necessary in order to obtain accuracy. Once repeatability has been determined instrument calibration...
will improve accuracy. The calibration updates *retention times* and *response factors* for each component. New response factors can deviate from the old response factors by up to 10%. Response factor (RF) deviations in excess of roughly 5% indicate that performance may be deteriorating slightly during on-line operation. There is a very important relationship between components that are on either side of a column split. If Response Factor (RF) deviations in excess of 2% are over time over time it is an indication that something may not be right. The critical component splits on a 4 or 6 minute Danalyzer are \( \text{C}_2/\text{C}_3 \) and \( \text{IC}_5/\text{C}_6+ \). A problem can be revealed by careful attention to the RF deviations for each pair. For instance, high RF deviations for \( \text{NC}_5 \) and \( \text{C}_6+ \) may indicate a problem with V2 off time (see Table 1). If there is a problem of this nature instrument linearity will be adversely effected. A single point repeatability check will not indicate a problem. In addition, calibration will do nothing to correct the problem. As time progresses these types of set up problems will show up as RF Deviation alarms. These are factory set to default values of 10% RF deviation for any component.

**PHYSICAL PROPERTY CALCULATIONS**

**HEATING VALUES FOR IDEAL GASES USING GPA 2145 1996 VS. 2000 FOR IDEAL GASES**

Once the preceding GC components have been optimized there are some minor configuration parameters that can be checked to ensure that contractual obligations are in compliance. Every few years the GPA publishes new values for physical properties of select hydrocarbons. At the bottom of the table is a statement of accuracy that reads:

“Numbers in this table do not have accuracy’s greater than 1 part in 1000. In some cases, extra digits have been added to calculated values to achieve internal consistency or to permit recalculation of experimental values.”

The largest % change made to any BTU value in the 2000 table is for ethane and it is changed by 1 part in 17,696. This is a change that is more than 17 times less than the stated accuracy. The stated accuracy has not changed with the 2000 data. The net effect on component concentrations is minimal, is well below the repeatability of all TCD based field GCs. In addition, the changes have an even smaller effect on relative density calculations.

These updated values have very little effect on the accuracy of the heating value calculation in natural gas when measured on a GC. The 2000 GPA data included very minor constituent changes in natural gas, the overall BTU change is negligible. The difference in physical property measurement can be seen in table 4 using two identical natural gas streams with the 96 data and the 2000 data. The GPA 2000 data is currently under review.

<table>
<thead>
<tr>
<th>Typical Natural Gas</th>
<th>GPA 2145-96</th>
<th>GPA 2145-2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich Gas</td>
<td>1300 BTU</td>
<td>+0.0138 BTU</td>
</tr>
<tr>
<td>Typical US</td>
<td>1078 BTU</td>
<td>+0.0032 BTU</td>
</tr>
<tr>
<td>Gulf Coast</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4.**

Most GCs operate with a stated repeatability of no better than 0.1 BTU at ideal conditions. 1 BTU is more common. There is questionable value in updating ideal gas heating values that are 10-100 times less than the repeatability of the instrument that is using the numbers.

**PRESSURE BASE FOR BTU CALCULATIONS**

Pressure base, on the other hand, can have a large effect on the BTU calculation. Care must be taken to ensure that the pressure base for BTU calculations is the same as the pressure base used in ancillary computers that rely on the GC data for volume and flowing energy calculations.

<table>
<thead>
<tr>
<th>Typical Natural Gas</th>
<th>Composition</th>
<th>Pressure Base @</th>
<th>Pressure Base @</th>
<th>Pressure Base @</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>2.46</td>
<td>14.73</td>
<td>14.696</td>
<td>15.023</td>
</tr>
<tr>
<td>Methane</td>
<td>89.709</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>5.001</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>.999</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Butane</td>
<td>.300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Butane</td>
<td>.300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iso-Pentane</td>
<td>.100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Pentane</td>
<td>.100</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆+</td>
<td>.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative Density</td>
<td>.6222</td>
<td>.6222</td>
<td>.6223</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 5.**

Note: Base temperature @ 60 F

**SUMMARY**

To verify GC operation, historical calibration reports and configuration reports are necessary to ensure that all configuration parameters and calibration parameters are correct and within specifications. Three certified standards should be used to check repeatability, linearity and accuracy throughout the measured heating value range for all streams. Sample conditioning and sample transport systems should be carefully considered for possible JT effect on rich gas samples.
APPENDIX A

General description a typical audit procedure using two certified standards:
A second cylinder of certified calibration gas can be used. Temporary tubing to the chromatograph should be installed along with a bleed vent to allow for purging. Gas will be introduced to the unit and the resulting “As-found” analysis reports to be saved. The unit will be re-calibrated and the second standard can be introduced to record “As-left” measurements.

Specifications for the second standard as follows:
1) Hydrocarbon dew point: 20 degrees F. or lower.
2) Cylinder contents to include all components that are measured by the on-line gas chromatograph.
3) The component concentrations will be higher than those in the station calibration gas, except methane — which must be the balancing component.

Handling the cylinder
4) The cylinder will be heated for __ hours if/when exposed to temperature below the hydrocarbon dew point __ degrees F.
5) The cylinder must not be used below 25 p.s.i.g.
6) The cylinder regulator must be equipped with the inlet CGA fitting that corresponds to the gender and the left hand thread direction.

Suggested guidelines for sample system tubing and fittings:
1) Maximum 1/8” stainless steel tubing must be used.
2) Tubing must be clean (free of any/all contaminants) and dry.
3) Temporarily install a manual three-way valve to select the calibration gas or the referee without allowing air to enter the system.

Suggested purging procedure:
1) Install the regulator and open the cylinder block valve and purge the air from the system.
2) While the gas is slightly purging, tighten the “CGA” fitting into the regulator block valve.
3) Connect the delivery tubing from the cylinder regulator to the three-way manual valve.
4) Attach the second standard as seen in Figure 2.
5) Use the purge valves to eliminate air.
6) Adjust the pressure regulator to deliver the same pressure as that used for the existing calibration cylinder (see pressure balance procedure on page 2).
7) Set the temporary three-way valve to allow the existing calibration gas to flow to the sample flow-meter.

Testing the chromatograph:
1) Idle the chromatograph.
2) Using the keypad or the personal computer, issue the proper command to run the calibration gas as an unknown sample. Do not calibrate the GC yet.

Verifying repeatability to obtain the “As-found” results on the station calibration gas:
3) Observe the results and pay particular attention to the measured results for nitrogen. As soon as the nitrogen measurements are repeated for at least three consecutive runs, then reports are to be saved as “As-found” documentation.
4) Idle the GC.

Preparing to run the second standard:
5) Using the three-way selector valve, select the second cylinder. Make sure that the flow rate is the same for the referee cylinder as for the existing calibration cylinder.
6) Using the keypad or the personal computer, issue the proper command to run the referee gas as an unknown. Do not calibrate the GC yet.

Verifying repeatability to obtain the “As-found” results on the referee gas:
7) Observe the results and once again verify that the referee gas is repeating the nitrogen measurement. Once repeatability is established, save the reports as “As-found” documentation.
8) Switch the selector valve back to the existing calibration gas.
9) Idle the chromatograph.
10) Run the unit to establish repeatability checking the nitrogen measurement as seen above.

Calibrating the GC:
11) Calibrate the unit now.

Obtaining as-left results:
12) Check the repeatability of the GC on the existing station calibration gas and save the reports as “As-left” documentation.
13) Idle the chromatograph.
14) Switch the selector to the referee cylinder.
15) Issue the command to run the referee gas as an unknown and verify repeatability as above.
16) Save the reports of the referee as “As-left documentation.”
17) Issue the proper command to return the GC to automatic service.
18) Remove the temporary tubing and reinstall the delivery tubing from the existing station calibration cylinder.
19) Purge the calibration gas delivery line of air.

APPENDIX B

Base conditions – The conditions of temperature and pressure to which measured volumes are to be corrected. In the case of energy, the base conditions affect the volume of gas in a cubic foot that contained the measured volume for a BTU determination.

BTU (British Thermal Unit) – a measure of the quantity of heat contained within 1 cubic foot of volume. The “classic” definition is that one BTU will raise the temperature of water one degree Fahrenheit at or near 60°F (15°C). The AGA has defined a BTU as equal to...
BTU net – The term net quantity subtracts the heat required to vaporize the water and represents actual useful heat energy. Gross BTU is commonly used in the United States for custody transfer; net BTU in Europe. During combustion water is formed. If that water remains in the ideal gas state the heating value is termed net. Once net BTU is determined gross BTU can then be calculated on a dry and wet basis. Other terms sometimes used for net and gross are: inferior(net) and superior (gross) or lower and higher heat value.

Saturated gas – for the purpose of maximum lawful price calculations under the NGPA, the gas tested contains the maximum amount of water vapor possible under conditions of 14.73 psia and 60°F.

The total quantity of heat is determined by multiplying a volume of gas at a specified pressure and temperature by the heating value per unit volume saturated with water at the same pressure and temperature base. No further corrections for the presence of water shall be made.

The BTU content of one cubic foot of natural gas at defined conditions is the number of BTU's produced by the complete combustion of such cubic foot of gas at constant pressure with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of the gas and air and when water formed by such combustion is condensed to a liquid state at the initial temperature of the gas.

critical temperature and pressure – temperature above which a fluid cannot exist as a liquid; vapor pressure of a fluid at the critical temperature. These values are used to calculate compressibility.

Dekatherm – 1 dekatherm = 1 MMBTU (1 million BTU's) or 1000 SCF x 1000BTU.

density, relative (gas) – The ratio of a specific weight of a gas to the specific weight of air at the same base conditions.

density, relative (liquid) – The relative density of a liquid is the ratio of the fluid at a temperature to the density of pure water at a specified base temperature. (Also known as specific gravity)

dew point – temperature at which water vapor will begin to condense. A typical pipeline spec for maximum water vapor content is 7 lbs/MMSCF. At 100 psia, the dew point is 32°F. At 100 psia, the dew point drops to ~15°F (and water droplets wold form with possible line freezing).

mole % – the amount of a substance expressed as the percentage of its molecular volume compared to the total of molecular volume for all substances in a sample. The relative percentage of a component in a mixture of components in the sample stream is determined by comparing the peak area to the sum of peak areas for all components. Mole % = peak area / response factor.
response factor – the factor that defines how much detector output will be generated for a given amount of a sample component. (RF equals peak area for a known component in the cal gas divided by the known amount of the component.)

retention time – the time measured between the start of analysis to the top of a peak.

specific gravity (SG) – (see relative density) The ratio of the density of a substance to the density of a “standard” (normally water for liquids and air for gasses). SG is the reciprocal of relative density. Density is mass per unit volume of a fluid, but typically expressed as weight per unit volume — lb/gal, lb/bbl, grams/cubic cm, etc.).

water vapor – defined as pounds of water per MMSCF in the U.S. As pressure increases, water vapor is compressed into its liquid state. For example, at 60°F, a natural gas stream holding 17.9 lbs/MMSCF of water at 1000 psia will hold 128 lbs/MMSCF at 100 psia. Lowering the temperature from 60° to 40° F at 100 psia will reduce water content to 61 lbs/MMSCF.

Wobbe Index – An index, used to determine the size of a gas burner tip, calculated by dividing total saturated BTU by the square root of specific gravity.

CONVERSION FACTORS
BTU = 252.2 calories
BTU = 0.252 kilocalories
BTU = 1055 Joule
1000 BTU/MMSCF = 37.27 megaJ/m³
Gallon (Imperial) = 1.2 Gallon (US)
ft³/sec = 0.000589 liters/min
°F = 9/5(°C) + 32
°C = 5/9(°F -32)

For the “NGPA Pricing Method” ...

REFERENCES
GPA Engineering Data Book Volume 11 section 23
GPA Report 2145 & 2286-95

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Charlie Cook, Daniel Measurement & Control, Appendix A

Murray Fraser