BTU ANALYSIS USING A GAS CHROMATOGRAPH

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Introduction

The most widely used method to determine BTU content of natural gas is by gas chromatograph. The analytical data provided by this means represents over half of the weighted information needed for total energy determination. The potential financial impact of this data is tremendous. It is imperative that the quality of the data produced by laboratories using gas chromatographs for BTU determination is accurate.

Sample Procurement

The first step in the process is to obtain a sample that is representative of the flowing stream. The sample procurement phase offers much opportunity to invalidate the process of producing accurate analytical data. It is unlikely that an analysis of a compromised sample will provide meaningful data. The personnel responsible for sampling must understand hydrocarbon phase behavior and how to obtain a representative sample. There are eight methods listed in GPA Standard 2166 "*Obtaining Natural Gas Samples for Analysis by Gas Chromatograph"*. These techniques are for obtaining "spot" samples. Personnel must follow the method chosen precisely. The more desirable means of obtaining natural gas samples is to use a continuous sampler, taking sample "bites" proportional to flow rate. Regardless of the sampling technique chosen, the following requirements apply.   The sample point must have a sample probe installed or the quality of the sample procured will be of questionable validity.   The sampled stream must be of a single-phase fluid and should be flowing at its normal rate. During the sampling process it is important to remove all atmospheric air and to not alter the component composition of the sample.

Sample Handling

It is important that the sample arrive at the laboratory promptly after procurement. Sample tracking programs should provide a means of identifying samples for comparison purpose and helps ensure timely processing of analytical testing.   Natural gas samples are heated prior to analysis to return any condensable components to a vapor state. It is common practice to heat all samples to the same temperature for a specified period of time. If the equilibration temperature is not at least 20 degrees F above sample point temperature, it is necessary to heat these samples separately or the resulting BTU calculation will be in error. The equilibration time is at least two hours, and could be as great as twenty-four hours. Before sample analysis, confirm sample pressure to prevent analysis of a depressurized sample.   Representative samples that are mishandled prior to analysis will provide inaccurate analytical results.

Analytical Methods

The most common gas chromatographic method used in the United States for determination of BTU content of natural gas is GPA Standard 2261 "*Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography*". A Thermal Conductivity Detector, or TCD, measures compounds as they exit the analytical column, or columns. This detector is ideal for many analyses because it is sensitive to any compound whose thermal conductivity differs from the carrier gas. TCD's have a linear dynamic range of 10,000:1, which gives them a usable range of 0.01 to 100 mole percent.

Three column types are used in this method to separate components of interest. See *Table 1* for a list of columns. The first is the "partition column". This column is usually about thirty feet long and one-eighth inch in diameter, packed with DC 200/500 silicone oil at thirty weight percent on Chromosorb P, 80-100 mesh, acid-washed. This column has been found to adequately separate methane through pentanes carbon dioxide and air. Nitrogen, however is not resolved from oxygen on this column, and what is commonly called nitrogen on this column is actually nitrogen and oxygen. Sample injection volumes are usually from 250 to 500 microliters. The pre-column is an eighteen inch section of this same column and precuts and backflushes the

hexane and heavier fraction to the detector ahead of the rest of the components. This reduces the analysis time from the former method of reversing the flow through the entire long column to backflush hexanes plus, and provides more accurate quantitation of this fraction. The column temperature is usually about 120 degrees C, isothermal, and the carrier flow rate set at about 30 ml per minute of helium. A 40 inch column packed with 1 percent DC 200/500 on Chromosorb P is used as a surge column to reduce valve switching upsets to the detector.

If carbon dioxide content in the unknown samples is not close to the amount in the calibration standard, it may be necessary to use a "porous polymer" column to separate methane, carbon dioxide and ethane. This column is usually one-eighth inch in diameter by about ten feet in length. The column temperature is 100 degrees C, with helium flow set to about 30 ml per minute. Mesh size is normally 100-120 for columns less than 10 feet in length and 80-100 for longer lengths. Normally, the sample volume is 500 microliters. Propane and heavier components are commonly backflushed to vent and thereby ignored.

A "molecular sieve" column will separate nitrogen from oxygen. This column is the same dimensions as the porous polymer column. Mesh size is usually 40-60, and the packing 13X Molecular Sieve. The column temperature is about 40 degrees C, and the helium flow rate is 25 ml per minute. This column will also quantify carbon monoxide. Compounds eluting after Carbon monoxide are backflushed to vent and not quantified. It is important to keep water vapor and carbon dioxide contact with this column to a minimum. If the column begins to lose separation of oxygen and nitrogen, cure the column at 250 degrees C for about four hours and it will regenerate.

A 20 foot long by one-eighth inch 5A molecular sieve column, using argon carrier at 15 ml per minute, will separate helium and hydrogen. Mesh size is 40-60 and column temperature 40 degrees C.

Another method is GPA Standard 2286, "*Tentative Method of Extended Analysis for Natural Gas and Similar Gaseous Mixtures by Temperature Programmed Gas Chromatography*". The non-hydrocarbons, and hydrocarbons lighter than hexanes are determined by GPA Standard 2261, but hexanes and heavier are determined on a separate chromatographic run. The detector for this analysis is the Flame Ionization Detector, or FID. This detector has greater sensitivity than the TCD, but does not respond to non-hydrocarbon compounds. The linear dynamic range of an FID is 10,000,000:1.

The preferred column in this method is sixty meters long, 0.32 millimeter diameter, with a one micron film thickness of methyl silicone. This is a partition column similar to the DC 200/500 packed column in GPA 2261, but is a fused-silica open tubular type or capillary column. The column temperature starts at forty degrees C, or less, and is temperature programmed up to over two-hundred degrees C. This temperature program allows the lower boiling point compounds to separate, and the high boilers to elute more quickly than by isothermal means. The late eluting compounds peak shapes are also improved. The hexanes plus fraction is separated into individual compounds in GPA 2286. This additional component separation allows the physical characteristics of hexanes plus to be calculated rather than assumed. By using GPA 2286 to determine hexanes plus physical characteristics for the GPA 2261 analysis, a more accurate determination of BTU is accomplished.

Purpose	Column
CO_2, N_2, and C_1-C_5 's	1/8" x 30' 30% DC 200/500 on Chromosorb P, 80-100 mesh, AW
Pre-cut of C_{6+}	1/8" x 18" 30% DC 200/500 on Chromosorb P, 80-100 mesh, AW
Surge delay	1/8" x 40" 1% DC 200/500 on Chromosorb P, 80-100 mesh, AW
O_2-N_2 separation	1/8" x 10' 13X Molecular Sieve, 40-60 mesh
CO_2-Ethane separation	1/8" x 10' (Hayesep or Porapak), 100-120 mesh
He_2-H_2 separation	1/8" x 20' 5A Molecular Sieve, 40-60 mesh
C_{6+} speciation (extended)	0.32 mm x 60 m , (0.5 - 5 micron film) methyl silicon capillary

Table 1

Gas chromatographs not using the aforementioned methods for BTU determination include on-line gas chromatographs, portable gas chromatographs and benchtop laboratory gas chromatographs. On-line GC's offer the advantage of performing many analyses during an accounting period and supplying data to electronic flow meters frequently. Portable GC's can eliminate the potential errors of sampling and handling samples. It is not uncommon to find benchtop GC's not configured according to GPA 2261. These GC applications should be verified by instruments that are configured according to the aforementioned methods.
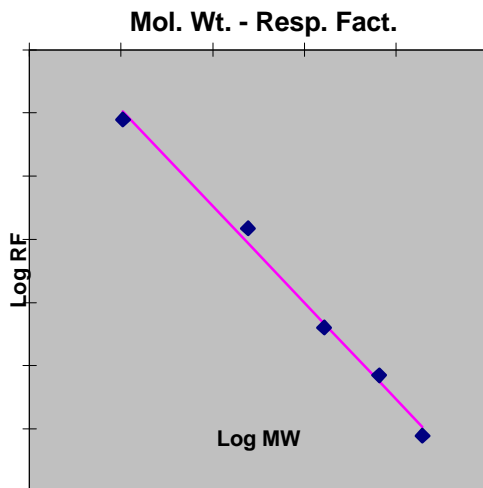
Quality Assurance

Accuracy is the sum of the bias error and precision error. The most common cause of "bias" error is invalid calibration blends. Typical causes of "precision" errors are improper instrument configuration and inconsistent operator technique. GPA 2261, Section 8 "Precision", states the component precision data determined in 1982. *Table 2* is taken from GPA 2261.

Component	Mol % Range	Repeatability % Relative	Reproducibility % Relative
Nitrogen	1.0-7.7	2	7
CO2	0.14-7.9	3	12
Methane	71.6-86.4	0.2	0.7
Ethane	4.9-9.7	1	2
Propane	2.3-4.3	1	2
Iso-butane	0.26-1.0	2	4
n-Butane	0.6-1.9	2	4
Iso-Pentane	0.12-0.42	3	6
n-Pentane	0.14-0.42	3	6
Hexanes Plus	0.10-0.35	10	30

Table 2

It is good laboratory practice to order a new standard before replacement is required. The old blend and the new blend can be compared while the old blend is still valid. It is prudent to have multiple calibration blends available. Comparing blends of different composition demonstrates detector linearity.

Mol. Wt. - Resp. Fact.

The best means of monitoring calibration blends is to plot response factors on a control chart. The initial response factor or peak area is the starting baseline on the graph. After enough data points have been acquired, about seventeen, the baseline can be changed to the mean value. Using the relative percentages in the previous chart, one multiplied times the percent relative plus and minus the baseline value is the warning limit line for the chart. Two times the percent relative plus and minus the baseline value is the control limit line for the chart. Three times the percent relative plus and minus the baseline value is the scale of the chart. Three consecutive data points outside the same warning limit line or any point outside the control limit line indicate the need for further examination. Do not use the blend or instrument until the problem has been identified and corrected. Refer to *Figure 2*.

GPA 2261, Section 4, outlines the procedure for a detector linearity check. Partial pressures, from 100 to 700 millimeters of mercury at 100 millimeter intervals, of methane are plotted against peak area on a linear scale graph. If the plot is linear, no adjustments are necessary. If the graph is not linear, the sample loop size needs to be adjusted. To properly size the sample loop, take the highest reading that is linear and divide it by barometric pressure in millimeters of mercury. Measure the sample loop and multiply the length by the previous calculated fraction and adjust the loop to this length. For example,
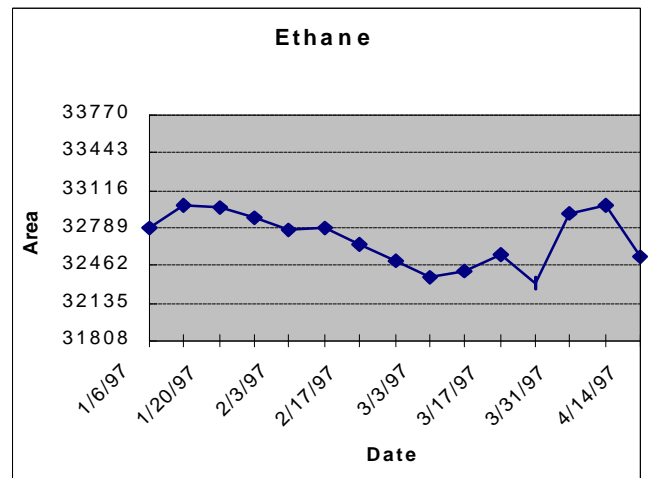

Figure 2

the highest linear reading is 650 mm Hg, the barometric pressure is 745 mm Hg, and the sample loop is eight inches long. Then, 650 divided by 745 is 0.8725, and 0.8725 multiplied times eight is approximately seven inches. See *Figure 3*.
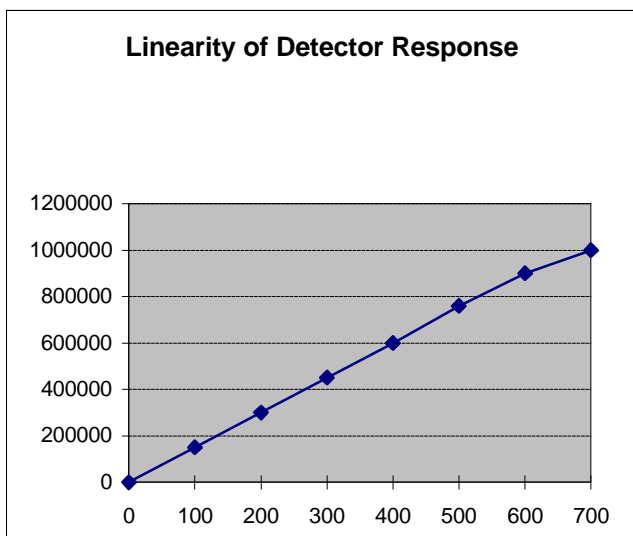
Linearity of Detector Response

Figure 3

Quality Control

After the sample is analyzed, the data must be checked to determine its validity and the quality of the analysis which was performed. The unnormalized total of the molecular percentages of compounds analyzed should be within plus or minus one percent of one-hundred percent. If not, then either instrument conditions have changed since calibration, a compound or compounds present in the sample was not detected, or detector linearity is not adequate to compare the range of compounds with the existing calibration blend. Check instrument conditions to determine if they have changed. Check the range of concentrations for components in the unknown sample to determine if they are close to the composition of the calibration blend. If neither of the above are the case, there may be components present in the unknown that were not detected, normally the same component as the carrier gas.

The sample validation portion of a Laboratory Information Management System, or LIMS, should provide a means of comparing the current sample to previous analyses of that sample. If the composition varies noticeably, the cause should be determined. It is good analytical practice to compare individual component values statistically. The LIMS calculates the mean and standard deviation of previous analyses. Outlier values, or bad data determined staistically, are not included in future evaluations. Upper and lower component limits are calculated using the mean plus or minus the tolerance. If the new value is not between specified limits, it is flagged for scrutinization.

Integration

The signal from the thermal conductivity detector is a voltage output. The higher the concentration of analyte in the detector cell, the greater the voltage signal output. When only carrier gas is present in the detector, the signal is fairly constant and the output is at baseline. As compounds elute from the column and enter the cell, the signal changes. The signal is plotted over time and a device called an integrator interprets this data. Each component has a different thermal conductivity and therefore a different detector response. It is important that only one compound enters the detector cell at a time. This is called baseline separation. Integration settings do not overcome poor chromatography.

The signal plotted over time produces a "triangular" peak shape. The area under the peak is compared to the concentration. This is the response factor. There are two types of response factors, relative and absolute. Relative response factors compare detector response of all compounds to that of the reference compound. In natural gas samples, methane is used as a reference peak and in natural gas liquid samples propane is used. Absolute response factors are divided into "area / concentration" and "concentration / area". The calculated concentration does not change with response factor method change. See *Table 3*.

1 Name	2 Mol %	4 Ref. Area	6 (2/5) ARF	8 Unk. Area	10 (6x9) Mol. %	11 (*) Norm. Mol %
N_2	3.54	6224	0.0005688	13378	7.609	7.710
CO_2	2.24	4397	0.0005094	286	0.146	0.148
C_1	72.40	92053	0.0007865	91499	71.964	72.921
C_2	7.96	16432	0.0004844	17004	8.237	8.347
C_3	5.54	14292	0.0003876	16851	6.532	6.619
IC_4	2.63	7854	0.0003349	2029	0.679	0.688
NC_4	3.69	11335	0.0003255	7291	2.374	2.406
IC_5	1.00	3409	0.0002933	1603	0.470	0.476
NC_5	1.00	3487	0.0002868	2358	0.676	0.685
$C6^+$	0.00	2627		3866	0.000	0.000
Total	100.00				98.687	100.000

Table 3

Table 4 (top)

2.384	31.791	0.750	2.0068	0.0478	3262.3	77.8	0.0478	0.0011
0.472	27.380	0.172	2.4912	0.0118	4000.9	18.9	0.0581	0.0003
0.679	27.673	0.245	2.4912	0.0169	4008.9	27.2	0.0631	0.0004
0.879	23.274	0.378	3.1765	0.0279	5065.8	44.5	0.0873	0.0008
100.000		5.779		0.7804		1232.1		0.0159

Z	0.9963
Real Sp.Gr.	0.7830
Real Dry Btu	1236.7

Table 4

Calculations

The concentration calculation most commonly used in BTU determination is molecular percentage. Molecular percentage is "vapor volume percentage". BTU per cubic foot calculation is the sum of the products of each component's BTU heating value per cubic foot and the "molecular fraction" of each component. The result is the BTU per *ideal* cubic foot. Natural gas is a *real* gas and therefore the heating value must be corrected. The compressibility factor corrects the volume of a cubic foot as an ideal gas to that of a real gas. The BTU per ideal cubic foot value is divided by the compessibility factor to obtain the BTU per real cubic foot. Calculations are performed according to GPA Standard 2172, "*Calculation of Gross Heating Value, Relative Density and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis*". Physical constants are taken from GPA Standard 2145, "*Table of Physical Constants of Paraffun Hydrocarbons and Other Components of Natural Gas*". Physical constants for the compounds determined by extended analysis can be found in GPA TP-17. See *Table 4*.

The BTU per cubic foot multiplied by the volume yields the total energy of the stream. The unit of energy measurement is the dekatherm, or MMBTU. The heating value and volume calculations must be at the same base conditions. To change pressure base of the calculated heating value, divide the existing heating value by the existing pressure base and multiply by the desired pressure base. To change pressure base of the calculated volume, divide the existing volume by the desired pressure base and multiply by the existing pressure base.

Two other energy measurement parameters that are sometimes confused are "Gross" versus "Net" and "Dry" versus "Saturated". "Gross" heating values assume the water produced by the complete, ideal combustion of the gas and oxygen is condensed to liquid. "Net" heating values consider the water as a vapor. "Gross" heating values are used for custody transfer calculations and "Net" heating values for actual energy considerations. "Dry" heating value calculations ignore water vapor as a component of natural gas. "Saturated", or "Wet", heating value calculations assume the water vapor at base conditions to be at saturation. The contract conditions should be verified to determine heating value for custody transfer.

11 (*)	12	13	14	15	16	17	18	19
Norm. Mol %	Cu. ft./gal. Liquid	(11x10/12) GPM	Ideal Sp. Grav.	Sp. Grav.	Ideal Btu/ Cu.Ft.	(11x16/100)	Comp. Summ. Fact.	(11x18/100) Summ. Fact.
7.642			0.9672	0.0739			0.0044	0.0003
0.147			1.5196	0.0022			0.0197	0.0000
72.281			0.5539	0.4004	1010	730.0	0.0116	0.0084
8.273	37.476	2.208	1.0382	0.0859	1769.6	146.4	0.0239	0.0020
6.561	36.375	1.804	1.5226	0.0999	2516.1	165.1	0.0344	0.0023
0.682	30.639	0.223	2.0068	0.0137	3251.9	22.2	0.0458	0.0003