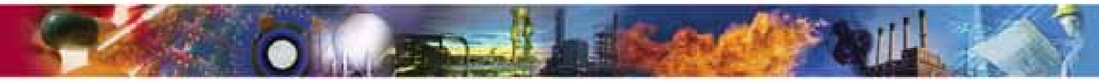

Heating Value Measurement of Natural Gas

using a Gas Chromatograph

Overview

The production and custody transfer of natural gas requires accurate measurement of the composition of the gas. Contractual requirements usually define the desired composition, heating value, relative density, and moisture content of the gas being sold. The sale of natural gas is based on the heating value per unit volume (kJ/m3 or BTU/Scf) of the gas. The industry uses instruments to monitor the characteristics of the gas at the point of sale.

The following instruments, used to measure the heating value of natural gas, are commonly found in the field and in the laboratory:

- Gas Chromatographs
- Gravitometers
- Moisture Analyzers
- Densitometers
- Hydrogen Sulfide Monitors
- Oxygen Monitors

Some of these instruments are portable and some are installed as on-line instruments at custody transfer points. Sample cylinders are used to take a sample of the gas to a lab chromatograph for analysis. An inaccurate sample will be obtained if the method used to capture a gaseous sample in the cylinder is not correct. The importance of well-designed sampling systems in portable and on-line instrumentation, in which analysis of the gas can easily take place in the field without transferring the sample to a laboratory, has increased.

This discussion is limited to the methods and application of gas chromatography used to measure the composition and heating value of natural gas. The equipment discussed is available for permanent installation or for portable application.

Gas Chromatography

Gas chromatography is a technique used to separate the components of a gas sample. The quantity of each component is accurately measured after separation. The heating value, relative density, and compressibility of the sample can be calculated once the gas composition has been determined. Typical natural gas components are nitrogen, carbon dioxide, methane, ethane, propane, iso- and n-butane, neo-pentane, iso- and n-pentane, and C6+. The industry requirement for chromatographic repeatability is ±0.10% commonly expressed as 1 BTU in 1000 Standard Cubic Foot (Scf) of gas. The accuracy of an instrument cannot exceed the accuracy of the associated calibration standard. The overall accuracy of the analyzer relies on the accuracy of the calibration gas blend. All chromatographs include the following major components:

- Sampling System
- Column Oven
  - Separation Columns
  - Sample Loop
  - Column Switching Valve(s)
  - Detector and associated electronics
- Carrier Gas
- Computer used for data acquisition, calibration, communication

The specific details and analyzer performance will vary among manufacturers, but the overall operational concepts are identical.

Sampling System

The chromatograph sampling system is probably the most important part of the analyzer. The sampling system must extract a representative gaseous sample from the pipeline, reduce the pressure, filter the sample, prevent sample condensation, and efficiently deliver the sample to the chromatograph. More measurement inaccuracies occur due to improper sampling systems than for any other reason.

Column Oven

The chromatograph oven usually contains two columns, the column switching valve(s), the sample loop, and the detector. The temperature of the oven must be precisely controlled since the performance of the columns and detector is affected by changes in temperature.

Separation Columns

The packed columns are usually 1 to 10 meter lengths of 4 or 8 mm stainless steel tubing that is filled with coated solid material. The choice of the column packing material depends on the sample being analyzed and the desired component separations. After sample injection, the time required for each component to pass through, or elute, the column is proportional to the molecular weight and boiling point of the component.

Capillary columns are also used in chromatographs. The advantage of capillary columns is speed of component separation; the disadvantages are column fragility, maintenance, and cost. The difference in the individual component travel times through the columns (elution time) results in component separation and the resulting component detection.

Valves

The sample valve introduces a fixed volume of the gas sample into the chromatograph column. The valve must inject a reproducible sample as rapidly as possible for reliable operation. The sample volume varies with the instrument but is usually less than 0.50 ml at low pressure (Figure 1).

There are two chromatographic techniques used to separate the components for the determination of gas heating value: the backflush (BF), and extended analysis (EA) methods.

Backflush Method

The backflush method is commonly used to reduce the total analysis time by backflushing the heavier components (C_6, C_7, C_8, etc.) to the detector. Since these components would pass through the long measuring column slowly, the backflushing technique reduces the analysis time without sacrificing accuracy. Using the backflush technique, the C_6, C_7, and C_8, components are combined and treated as a composite, commonly called C_6+ component. Refer to Figures 2 and 3.

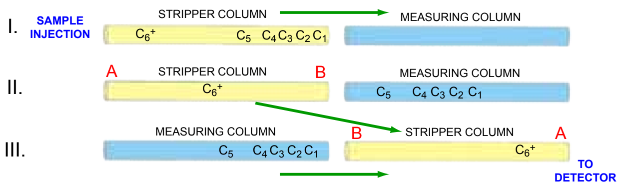

Figure 1: Backflush method

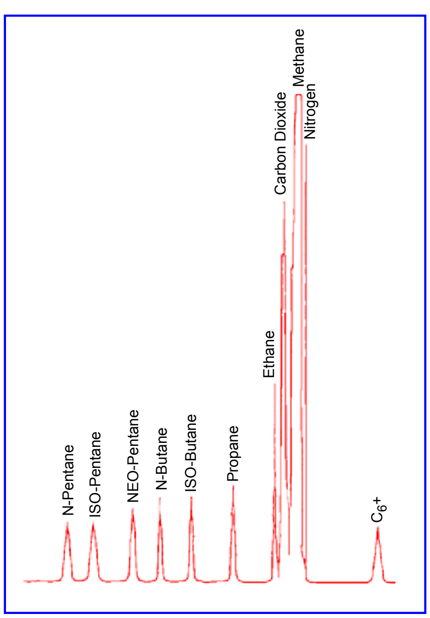

Figure 2: Typical chromatograph

Extended Analysis Method

The extended analysis method provides the same information as the backflush method except that the C_6+ composite is separated into the individual components. The extended analysis method, when using packed columns, results in long analysis times. When capillary columns are used, the extended analysis method can be used effectively. There are advantages to both chromatographic methods. In most cases, the relative composition of the C_6+ components does not vary sufficiently at a specific location to justify the longer analysis times or the expense of a capillary column chromatograph. The backflush technique is generally preferred in a field gas analyzer.

Carrier Gas

Helium carrier gas is typically used to transport the gas sample through the columns. The carrier gas must be pure (99.995%) or a reduction in sensitivity and other detection problems will occur.

Computer

An internal computer provides all of the instrument control and the integration of the chromatogram peak areas. Once the compositional analysis of the sample is completed, the computer calculates the heating value, relative density, and compressibility of the gas using ASTM, GPA, AGA, and ISO methods and component heating value data. This same computer provides the basis for the transmission of the data results.

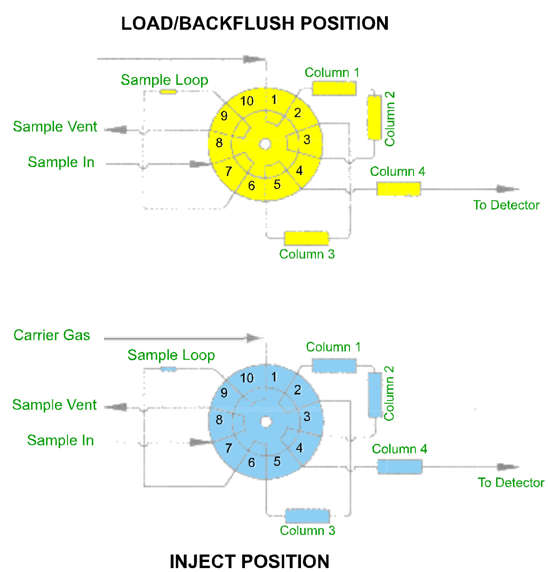

Figure 3: Typical chromatograph valve

Portable Analyzer

The Model 292 Natural Gas Analyzer is a lightweight, rugged chromatograph used to analyze a pipeline gas sample on-site to determine the gas composition and heating value. Portable analyzers have internal sampling system components that allow the analyzer to be connected directly to the gas pipeline sample probe. In all other respects, a portable analyzer provides all of the measurement features available in a single stream instrument. The analysis results are displayed using a digital display and stored in memory until they can be printed.

On-Line Analyzer - Permanent Installation

An on-line analyzer is basically the same as a portable analyzer with the following main differences (Figure 4):

- permanent installation
- automatic analysis cycling
- automatic calibration
- automatic sample selection
- remote control and data communication features (RS-232C)
- current loop (4-20 mA) outputs
- parameter alarm features

These analyzers and related sample switching systems are packaged in environmentally resistant enclosures (NEMA 4X or equivalent) to allow placement of the analyzer at pipeline custody transfer locations. The analysis results can be printed locally and the data can be automatically transferred to a central computer system using a data acquisition network.

Advanced systems provide features that allow full remote control and diagnostics for the chromatograph. The portable or on-line chromatograph and related equipment are located in Class I, Division 2, Group C&D hazardous environments. All equipment should be approved for use in these environments by a standards organization such as Factory Mutual Research (FMRC), Canadian Standards Association (CSA), Underwriters Laboratory (UL), or equivalent European Community recognized laboratories (CENELEC).

Sampling Systems

The importance of a well-designed and maintained sampling system must be emphasized. The sampling system for the analyzer must perform the following functions:

- Extract the sample from the pipeline.
- Resist the corrosive nature of the gas.
- Reduce the pressure of the sample.
- Filter the sample.
- Transport the sample to the analyzer.
- Control the sample flow rate and provide appropriate sample venting.

The sample probe must not be located near flow disruptions (orifice plate, elbow, etc.) which will induce flow turbulence and cause inaccurate samples to be collected. The end of the sample probe must be located in the center one-third of the pipeline. All components of the sampling system must be made from 300 series stainless steel to resist possible corrosive attack from H_2S, CO_2, and water. The sample pressure must be reduced using a heated sample regulator or a multistage regulator if the hydrogen dew point of the gas

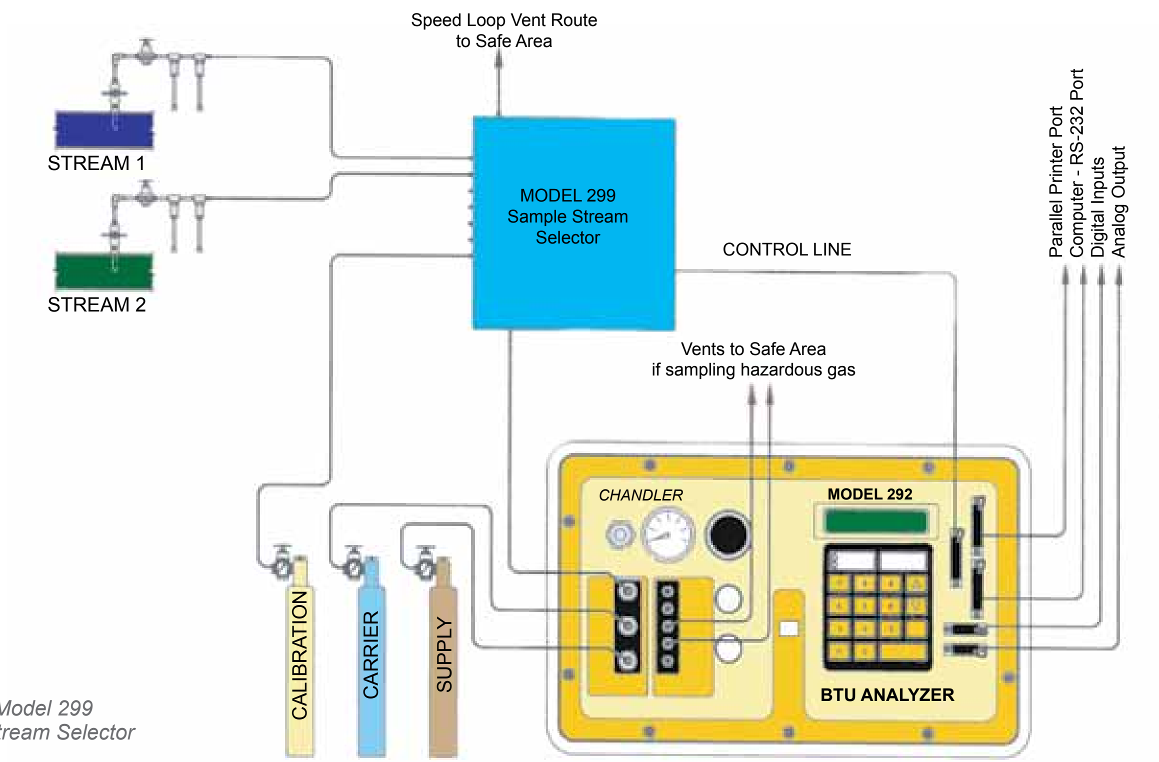

Figure 4: Model 299 Sample Stream Selector

is high enough to cause condensation of liquids due to the Joule-Thompson effect. A coalescing filter is normally used to remove particulates and entrained liquids from the sample. Under certain temperature conditions, liquids can condense in the sample line between the sample probe and analyzer. The sampling system must be heated or buried if the ambient temperature approaches the gas hydrocarbon dew point temperature. The sampling system design must also provide a shut-in valve, a sample flow control valve, bypass loop, and venting. The specific requirements vary with the choice of components and the analyzer requirements (Figure 5).

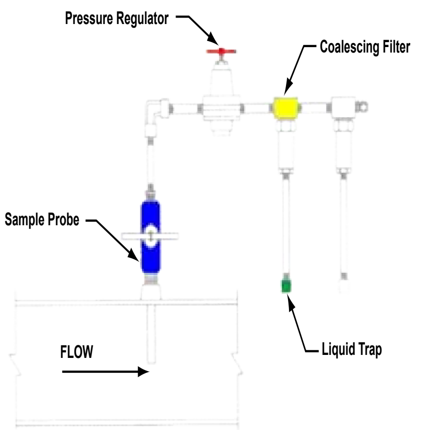

Figure 5: Typical pipeline sample system

Sample Switching

A single analyzer can be used to analyze samples from different pipelines using a sample switching system. Each pipeline must have a sample probe, regulator, filter, and related hardware. The design of the sample switching system varies with manufacturer but the principle of operation does not change.

The sample switching system must provide a sample from each pipeline sample probe to the analyzer without any mixing or carry-over from the previous sample. It must also provide a connection for the analyzer calibration gas and a connection for a sample cylinder, if required. The computer in the analyzer is programmed to sequence the sample solenoid valves as required.

Typical components used in a sample switching system are intrinsically safe 3-way solenoid valves. These solenoid valves can be used in the double block and bleed (DBB) configuration. The DBB method prevents sample mixing due to the possibility of an internally leaking solenoid valve. The disadvantage of the DBB method is cost and complexity because of the number of valves required. Using high-quality 3-way solenoid valves, reliable methods of low-pressure gas sample switching have been designed that do not require the DBB design (Figure 4).

Calibration

The accuracy of the results from an analyzer is totally dependent on the accuracy of the certified blend of gases known as calibration gas. A calibration gas blend can be obtained from equipment suppliers or sources with the appropriate gas mixing equipment. A certified analysis report is included with each bottle of calibration gas. Most analysis reports will include a statement of heating value and relative density at standard temperature and pressure. Ideally, these sources should provide proof of traceability to a primary standard.

The concentration of each component in the calibration gas should be similar to the pipeline gas being measured. Condensation of the heavier components in the calibration gas will occur if the temperature of the calibration gas blend drops below the hydrocarbon dew point. The temperature of the gas should never be allowed to drop below 50 °F, although the actual minimal temperature will depend on the composition and pressure of the blend. With some blends, the calibration bottle may require a heater when used in certain locations.

An analyzer is calibrated by analyzing the calibration gas and relating the individual component peak areas to the known component concentration in the calibration gas. A constant or response factor (RF) is determined for each component in the calibration gas. The following equation describes the response factor calculation:

Response Factor,

$$\mathbf{R} = \frac{\textbf{Component Concentration}}{\textbf{PeakArea}}$$

The individual response factors are used to determine unknown component concentration from measured peak areas once the analyzer has been calibrated. The frequency of calibration of an analyzer will depend on manufacturers' recommendations. Advanced on-line analyzers are programmed to automatically recalibrate at predetermined time intervals. Custody transfer contracts typically require analyzer recalibration every 24 hours, although most chromatographs do not require this frequency of calibration. Calibration every 30 days is adequate in most cases.

Heating Value Calculation

The heating value, relative density, and compressibility values are calculated using a computer once the pipeline gas composition has been determined by the analyzer. Each pure component in the natural gas has a known heating value and density. The heating values are obtained from tables published in current GPA, AGA, and ISO standards. The heating value can be determined from the gas compositional analysis using the following equations:

$$H_{ideal} = \sum_{i=1} x_i H_i$$

$$\text{Heating Value} = \frac{H_{ideal}}{Z}$$

where:

H_{ideal} = Ideal Heating value

x_i = Component concentration

H_i = Component heating value/unit volume

Z = Compressibility of sample

Similarly, the relative density can be determined from the gas compositional analysis using the following equations:

$$G_{ideal} = \sum_{i=1}^{n} x_i G_i$$

$$\text{Relative Density} = G_{ideal} \frac{Z_{air}}{Z}$$

where:

G_{ideal} = Ideal relative density

x_i = Component concentration

G_i = Component relative density

Z_a = Compressibility of air

Z = Compressibility of sample

The compressibility of gas can be determined using an older method defined as NX-19 or using a more recently developed method defined in the AGA 8 standard. The AGA 8 method uses the composition of the gas in the determination of gas compressibility. The AGA 8 method requires a lengthy and complex calculation and is normally done on a computer with computational capabilities.

Since the heating value is expressed as kJ/m^3 or BTU/Scf, the column of the gas must be considered in regard to the standard temperature and pressure. Unfortunately, there is no wide agreement for the value of standard temperature and pressure.

In the U.S., the *standard* or base pressure standard can vary from 14.65 to 14.73 PSIA depending on location. In Europe, even that standard temperature standard varies. Most analyzer computers are configurable for different standard temperatures and pressures. For this reason, before comparing heating value results from different analyzer systems, verify that the standard conditions at which the gas volume is calculated are the same.

The heating value of natural gas is reported as gross or net values.

Gross Heating Values

The gross gas heating values are reported either as dry or saturated values. The dry result assumes that the gas contained no water prior to combustion. The saturated result assumes that the gas is saturated with moisture at standard temperature and pressure prior to combustion. The saturated result accounts for the difference in energy released during a complete and ideal combustion of the gas that includes the heating value (enthalpy of condensation) of water. All water formed by the reaction condenses to a liquid. Refer to the sample analysis report (Figure 6) for a comparison of the gross dry and saturated results.

Net Heating Values

The net heating value represents the energy released from the total, ideal combustion of the gas at standard temperature and pressure where all the water formed by the reaction remains in the vapor stage. The condensation of excess water vapor does not contribute to the heating value.

Data Communications

On-line analyzers must be able to transmit data to a host computer, flow computer, or other process using serial and current loop (4-20 mA) interfaces.

Serial (RS-232 or RS-485) communication and software are used in advanced analyzers to remotely control the analyzer and acquire data. The current loop outputs from the on-line analyzer can also be used to transmit defined data values to a host computer, flow computer, control room, process, or SCADA system. The data gathering system design varies with installation and analyzer capabilities.

Troubleshooting

Analyzers are inherently reliable instruments provided they are operated and maintained properly. The following items must be considered as a part of operating and maintaining an analyzer.

Carrier Gas

Poor quality carrier gas is responsible for more analyzer problems than any other cause. Analyzers used for natural gas analysis require zero-grade (99.995%) helium as a carrier gas for trouble-free operation. Problems sometimes occur when a depleted carrier gas bottle is replaced. Other problems can be the result of a carrier gas leak that entrains air, low-purity helium, contaminants, or air trapped in the carrier gas tubing and regulator. Air in the carrier gas will change the chromatogram baseline and can oxidize the filaments in the detector causing premature detector failure or loss of sensitivity and stability.

Temperature

All analyzers have an internal oven that is maintained at a constant temperature. Optimum accuracy can be achieved if wide variations in ambient temperatures are avoided. As a general rule, a temperature-controlled environment (±10°F) will improve the accuracy and longevity of the analyzer.

Sampling System

If the sampling system is deficient, you can get unpredictable analysis results and the analyzer may be open to contamination from samples that contain liquids (heavy hydrocarbons, water, glycol, etc.). Repairing an analyzer contaminated using an inadequate sampling system requires complete disassembly and cleaning of the analyzer. The analyzer columns may also require replacement if they are contaminated. A well-designed sampling system will improve accuracy, prevent contamination of the analyzer, and reduce maintenance costs.

Vents

All analyzers have vent ports for the carrier gas and sample. Some analyzers require a constant flow of the sample through the sample loop. Other analyzers require brief sample flow times. Proper venting of the sample to a safe area is essential. Major variations in the backpressure of the venting systems can cause operational problems with the analyzer since the sample loop volume used by the analyzer is dependent on the sample pressure. The sample loop pressure will be affected by changes in vent backpressure, atmospheric pressure, or a change in the flow rate of the sample through the sample loop. Minor changes in the sample volume do not cause inaccurate analyses since the effect of sample volume is removed by "normalizing" the data.

Flow Adjustments

The carrier gas flow rates may require periodic adjustments. These flow rates typically measure less than 30 ml/min and adjustments require the use of a low-flow measurement instrument. Usually there are two adjustments of the carrier gas flow rates: the *measuring* adjustment and the *reference* adjustment. Although the specific requirements will vary with equipment, the measuring and reference flow rates are adjusted to be equal. Changes in these flow rates can cause misidentification of components, changes in sample analysis time, valve timing shifts, and calibration changes. Changes in the carrier gas flow rates should be avoided once an analyzer has been installed and calibrated.

Valve Timing

Some analyzers require valve timing adjustments. These analyzers can be more difficult to maintain due to the critical nature of these adjustments and the number of valves. The valve timing adjustments define the time intervals after which multiple column valve switches occur. These adjustments must be made after the carrier gas flow rates are set. Analyzers that use a single chromatography valve have one valve adjustment time - the backflush time - resulting in simplified adjustments.

Conclusion

Gas chromatography has replaced other techniques used for the direct measurement of the heating value of natural gas. The advantages of gas chromatography include improved repeatability and accuracy, and the ability to measure the gas composition directly. Once the gas composition is known, the gas heating values, relative density, compressibility, and liquid volumes can be determined.

Well-designed, on-line or portable analyzers can be used in Class I, Division 2, Group C&D environments that are found near gas pipeline installations. Analyzer designs that have been approved by FMRC, CSA, UL, or CENELEC are usually the best choice.

Gas analyzers are available as portable or on-line instruments. The portable version of the instrument is used to make on-site gas composition measurements, eliminating the need for sample cylinders and possible sampling problems. The analysis results are stored internally and can be sent to a computer or printed. Portable analyzers are easy to use, reliable, and designed to withstand rough treatment.

Gas analyzers, like other natural gas measurement instrumentation, must have well-designed and maintained sample conditioning systems. Potential problems with gas chromatograph can be avoided through attention to the sampling system design.

Advanced systems have computers and data communication features. It is possible to have complete control of a remote on-line analyzer by using a computer, modems, and communication software.

The heating value calculation methods and individual component heating values have evolved over the years. The methods and heating values adopted by AGA, GPA, ASTM, and ISO are similar. The principal differences are the values for standard temperature and pressure. During the last several years the method used to calculate the compressibility of natural gas has been improved (AGA 8), although a computer is required for calculation.

The choice of a specific on-line or portable analyzer should be made on the basis of performance, reliability, manufacturer support, ease of use, and cost.

The performance issue usually involves a decision on repeatability, C_6+ backflush analysis, extended analysis, and analysis cycle time. The reliability issue is paramount since the analyzer may be used continuously 24-hours per day for years and downtime is unacceptable and repairs expensive.

The ease-of-use of the analyzer is important since it reduces the time required to train the operator to use the analyzer efficiently and the chance of operator error. Ideally, the gas analyzer operator will not require extensive training in chromatography. The cost of the analyzer system varies with product complexity. The most expensive analyzer systems are not always the best choice of equipment when all factors are considered.

Glossary

BTU (British Thermal Unit)

A measure of energy. The amount of energy required to raise the temperature of one pound of water from 58.5°F to 59.5°F.

Coalescing Filter

A filter type that will cause liquids and solids to be removed from a gas stream. Moisture in the gaseous state will not be removed by this type of filter.

Dead Volume

The volume of any system flow passage where a dead-end or cavity could retain materials to contaminate subsequent samples. The quantity of the former sample that remains inside the component after flushing with some specified volume is defined as dead volume.

The dead volume or the unswept volume must be minimized. The smallest tubing size (1/8", 1/4", 4mm, or 6mm) should be used as a part of the sampling system. Large dead volumes will cause long instrument stabilization times and inaccuracies. Unless absolutely necessary, avoid a Bourbon tube pressure gauge or other components that increase the dead volume. An instrument bypass circuit, know as a speed loop, is typically used to reduce the stabilization time of the instrument readings if low sample flow rates are required.

Dew Point

The dew point represents the temperature and pressure at which water vapor or hydrocarbons condense from a gas. The dew point for water and hydrocarbons in natural gas exists at different temperatures and pressures. The relationship between dew point and moisture (water content) can be obtained from ASTM Method D1142.

Filters

A filter is used to remove particulates and liquids from the sample line. Filter elements that do not retain moisture must be chosen. A properly specified coalescing filter is recommended as part of the sampling system. Other filters downstream of the coalescing filter are usually designed to remove liquids, glycols, and other contaminants from the sample. The choice of filters must be made after considering the pressure drop across the filter(s) and the required sample flow rate of the instrument.

Gas Composition

The chemical content of the natural gas. A natural gas will contain varying amounts of methane, ethane, propane, nitrogen, carbon dioxide, and other components.

Heating Value

The energy content of the natural gas. This value is determined from the natural gas composition using a chromatograph, or from calorimetry. The units are BTU/Scf or kJ/m3 and reported as net, dry, or saturated values depending on the natural gas moisture content.

IR Light: Infrared Light

A specific range of wavelengths of light that are not in the visible range.

Joule-Thompson Effect

The cooling that occurs when a natural gas at high pressure is passed through an orifice to a lower pressure. This cooling can cause the condensation of liquids (water and liquid hydrocarbons).

Pressure Regulator(s)

A low internal volume, stainless steel diaphragm regulator is optimum for reducing the pipeline pressure to the inlet pressure rating of the instrument. Care must be used to avoid problems due to liquid condensation caused by rapid gas expansion through the regulator and the Joule-Thompson effect. In some cases, a heated sample regulator or multiple pressure reduction stages may be required to avoid the condensation.

Relative Density (Specific Gravity)

The ratio of the gas to the density of air standard temperature and pressure.

Sample Valve

A suitable valve should exist downstream of the sample probe to allow the sampling system to be disconnected. This valve may be part of the sample probe assembly.

Standard Temperature and Pressure (STP)

The standard (reference) temperature and pressure at which gas volumes are calculated. In the U.S., the base temperature is 60°F and the base pressure will vary (14.65, 14.696, 14.73 PSIA) depending on local standards. When comparing gas volumes, verify that the base conditions are the same.

Temperature Control

In cold climates, the sampling system temperature must be maintained above the dew point of the natural gas. In these climates, the use of a heated sample regulator and heated (or buried) sample tubing must be used to prevent condensation from forming in the sampling system. The most accurate moisture measurements are made if the temperature of the sampling system is stable.

Chandler
Model 292 BTU Analyzer

Test time: Jan. 06 05 18:11 **Calibration #: 3**
Test #165 **Stream #1** **Location No. 050108**

	Standard / Dry Analysis				Saturated / Wet Analysis		
	Mole %	BTU*	R.Den*	GPM**	Mole %	BTU*	R.Den*
Methane	95.027	962.02	0.5264		93.373	945.28	0.5172
Ethane	2.42	42.92	0.0251	0.6471	2.378	42.17	0.0247
Propane	0.667	16.83	0.0102	0.1839	0.656	16.53	0.0100
i-Butane	0.16	5.21	0.0032	0.0523	0.157	5.12	0.0032
n-Butane	0.134	4.37	0.0027	0.0421	0.131	4.29	0.0026
i-Pentane	0.051	2.03	0.0013	0.0185	0.05	1.99	0.0012
n-Pentane	0.023	0.93	0.0006	0.0084	0.023	0.91	0.0006
(C6+)	0.079	3.99	0.0025	0.0339	0.077	3.92	0.0025
Moisture	0.000	0.00	0.0000		1.74	0.88	0.0108
Nitrogen	0.371	0.00	0.0036		0.365	0.00	0.0035
(CO2)	1.070	0.00	0.0163		1.051	0.00	0.0160
Total	100.00	1038.3	0.5917	0.9861	100.00	1021.1	0.5922

***: Uncorrected for compressibility at 60.0F & 14.730PSIA**
****: Liquid Volume report at 60.0F**

Standard / Dry Analysis Saturated / Wet Analysis			
Molar Mass	=	17.138	17.153
Relative Density	=	0.5928	0.5934
Compressibility Factor	=	0.9978	0.9977
Heating Value	=	22938 BTU/lb	22538.BTU/lb
Heating Value	=	1040.6 BTU/CF	1023.5 BTU/lb
Absolute Gas Density	=	45.3666 lbm/1000CF	45.4117 lbm/1000CF
Unnormalized Total: 100.038	=		
Last Calibrated with Calgas of	=	1050.3 BTU/CL Jan 06 05 16:31	
C6+ Last Update:	=	Jan 02 05 14:11	
C6+ BTU/CF 5065.8, C6+ Lbm/Gal	=	5.6425, and C6+ Mil. Wt. 92.00	

Figure 6: Typical BTU analysis report. The report can be printed in SI (metric) units or in English units.

Value	English	SI / Metric
Temperature	ºF	ºC
Pressure	Psig	KPa
Heating Value	BTU/CF	KJ/m^3
Heating Value	BTU/Lbm	KJ/kg
Gas Density	Lbm/1000CF	Kg/m^3
Relative Density	No units	No units
Liquid Volume	GPM	L/m^3

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