Heating Value Measurement of Natural Gas using a Gas Chromatograph

This application note describes the methodology and practical application of the AMETEK model 292B portable gas chromatograph system used to measure the composition and heating value of natural gas.

Overview

The composition of natural gas varies but consists mainly of methane and varying amounts of heavier aliphatic hydrocarbons, nitrogen and carbon dioxide (CO_2). A typical commercial pipeline natural analysis compositional analysis by gas chromatography (GC) is shown in Table 1.

Compound	Mole %
Methane	90.988
Ethane	3.99
Propane	0.991
i-Butane	0.298
n-Butane	0.301
2,2-dimenthyl pentane	0.049
i-Pentane	0.151
n-Pentane	0.147
(C_6+)	0.075
H_2O	0
Nitrogen	1.51
CO_2	1.5

Table 1: GC Analysis of a Typical Natural Gas

Raw production natural gas must be purified to meet specified quality standards dictated by the major pipeline transmission and distribution companies. These quality standards vary and are usually a function of a pipeline system's design and the markets that it serves.

In general, the standards specify that the natural gas:

1. Have a certain minimum heating value (BTU). In the United States, it should be about 1000+/-50 BTU per cubic foot of gas at 1 atmosphere and 60 degrees Fahrenheit.

2. Be at or above a specified hydrocarbon dew point temperature. The hydrocarbon dew point is the temperature below which some of the hydrocarbons in the gas might condense in the pipeline. Condensation forms high pressure liquid slugs that could cause damage to the pipeline.

3. Free of particulate solids to prevent erosion, corrosion or other damage to the pipeline.

4. Have a sufficiently low water vapor to prevent the formation of methane hydrates within the gas. The maximum concentration should be less than around 150 ppm.

5. Contain no more than ~4 ppm hydrogen sulfide.

6. Contain no more than 2%-3% carbon dioxide.

7. That total inerts (CO_2, N_2, O_2) be less than 4%.

The production and custody transfer of natural gas requires accurate measurements of key components which affect the quantity and overall quality of the gas. Contractual requirements usually define the desired total energy flow (comprised of total gas flow and calorific value of the stream), composition, heating value, and relative density of the natural gas. Heating value per unit volume (expressed either in kJ/m3 or BTU/Scf) of the gas is a critical parameter used to determine final product price. Instruments used to determine the heating value and associated quality parameters may be found at the point of sale (custody transfer station), in the field (near the production or processing facility) or in central laboratories.

Examples of instruments and technologies commonly used to determine heating value or associated parameters of natural gas products include:

- Gas Chromatographs
- Gas Gravitometers
- Gas and Liquid Densitometers

Many of the instruments commonly used for the determination of gas quality and heating value (energy content) are designed for use as either stationary on-line (or at-line) analyzers installed in metering stations near the pipeline or process location. When the use of on-line instruments is not feasible or practical such as in remote locations or areas where there is limited access to utilities and other infrastructure, sample cylinders may be used to collect a sample in the field from the process location or pipeline. The sample is then transported to a laboratory for analysis. Proper sample handling techniques are crucial to ensure that a representative sample is obtained and transported to the lab on time.

The development of reliable, rugged and accurate field portable instruments for the determination of heating value (BTU content), in which analysis of the gas can easily take place in the field without transferring the sample to a laboratory has greatly enhanced sample accuracy and reliability, making it easier for process operators and pipeline companies to react quickly to changing process or gas quality conditions.

The Model 292B Natural Gas Analyzer (Figure 1) is a lightweight, rugged chromatograph used to analyze a pipeline gas sample on-site to determine the gas composition and heating value. The Model 292B is designed to be operated as a stand-alone unit capable of measuring samples directly in the field, and is suitable for installation in a mobile platform, such as a truck, van or car.

The analyzer features include internal sampling system and gas distribution components that allow for direct connection to a gas pipeline sample probe. In all other respects, this portable analyzer system provides all of the measurement features available in a single stream stationary analyzer.

The analysis results are displayed using a color LED display and stored in memory until they are either retrieved via the on- board USB port or printed directly when a printer is connected to the USB printer port. Internal memory stores past results as well as calibration data and previously created reports. The GC may be supplied with an optional DC to AC inverter so it can be operated with DC power from a car/truck or a DC power source at a remote location.

The Model 292B was designed around field-proven chromatographic techniques defined by GPA, ASTM, ISO and AGA

Figure 1: The AMETEK 292B Portable BTU Analyzer

Gas Chromatography

Gas chromatography is a technique used to separate the components of a gas sample. The quantity of each component is accurately determined using a sensitive thermal conductivity detector. Fully integrated gas chromatograph (GC) analytical systems such as the AMETEK model 292B BTU analyzer provide all the necessary functionality to ensure repeatable and reliable results that meet or exceed reporting requirements for the BTU analysis of natural gas.

The AMETEK 292B analyzer measurements are made with a configurable base pressure and are in accordance with the following standard methods

ISO 6568, 6569, 6976
ASTM D3588, D1945
GPA 2261, 2172, 2145
AGA 8 (Direct Method)

Figure 2. A Typical Natural Gas Chromatogram

These methods describe the analysis of natural gas using gas chromatography. A gas chromatograph is used to separate the components of a natural gas so that each major component can be quantified. A sample is injected into the GC and travels down a hollow tube packed with an adsorbent. The low molecular weight components travel down the tube more quickly and are the first “seen” by the detector. Over the next few minutes all of the components exit the column and are measured by the detector.

A screen shot of a natural gas GC separation, called a chromatogram, is shown in Figure 2. Special column switching techniques are used in the 292B gas chromatograph and all of the “heavy” C_6+ components actually are measured first. This is shown in the figure as the #1 C_6+ peak. The “lightest” compound in natural gas sample is nitrogen followed next by methane, carbon dioxide and ethane, peaks 2-5 respectively.

The major components of the model 292B include:

- Sample handling and gas distribution system
- Column/analyzer sample oven including
  - Separation columns
  - Sample loop
  - Column switching valve(s)
  - Detector and associated electronics
- Carrier Gas

Sample Handling and Distribution System

The GC sample handling and gas distribution system is an extremely critical part of the analyzer system. A sample probe is highly recommended for sample gas extraction. As a general rule, a sample probe should not be located near flow disruptions (orifice plate, elbow, etc.) where there is a possibility to induce flow turbulence and cause inaccurate samples to be collected. The sample probe should be inserted in the flowing gas stream approximately in the center of the gas pipeline. The model 292B can be configured with an AMETEK sample probe which extracts a representative sample form the process and transports it to the inlet manifold of the GC. Several probe designs are available to meet requirements for service in even the most challenging of natural gas applications.

Sample pressure reduction is required to meet the inlet manifold operating pressure of the 292B analyzer (maximum 3500 PSIG). AMETEK Process Instruments offers several pressure reduction options to reduce the sample pressure and minimize Joule-Thompson cooling effect. Sample filtration may also be provided to prevent condensation and maintain the sample above the water or hydrocarbon dew point temperature (Figure 3). Careful selection of approved sample handling components and proper design ensures that a representative sample is delivered for analysis. Suitable materials of construction (generally series 300 stainless steel) are chosen to ensure reliable service in natural gas applications. The sampling system design should also include 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.

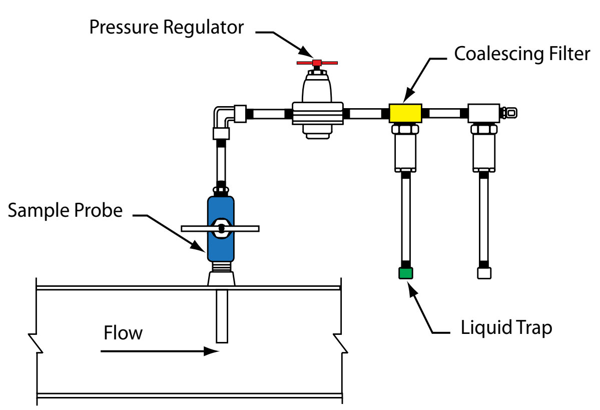

Figure 3. A Typical Sample Handling and Gas Distribution System

Details of the GC Module design and Component Detection

The AMETEK 292B GC oven contains four columns, column switching valves, sample transport loop and the detector assembly (Figure 4). The temperature of the oven must be precisely controlled since the performance of the columns and detector is affected by changes in temperature. The AMETEK model 292B maintains careful control of temperature in varying ambient temperatures, ensuring tight control and accurate results. The analyzer's packed separation columns are 1 to 30 feet in length and are constructed of 1/16th inch stainless steel tubing filled with specially coated solid material. The analyzer columns are made up of tubing that contains solid support material coated with a liquid phase that have a selective affinity for the sample components. The time required for each component to pass through the column, or elute, is proportional to the oven temperature and the carrier gas flow rate. This difference in the elution times for individual components provides the separation of the components.

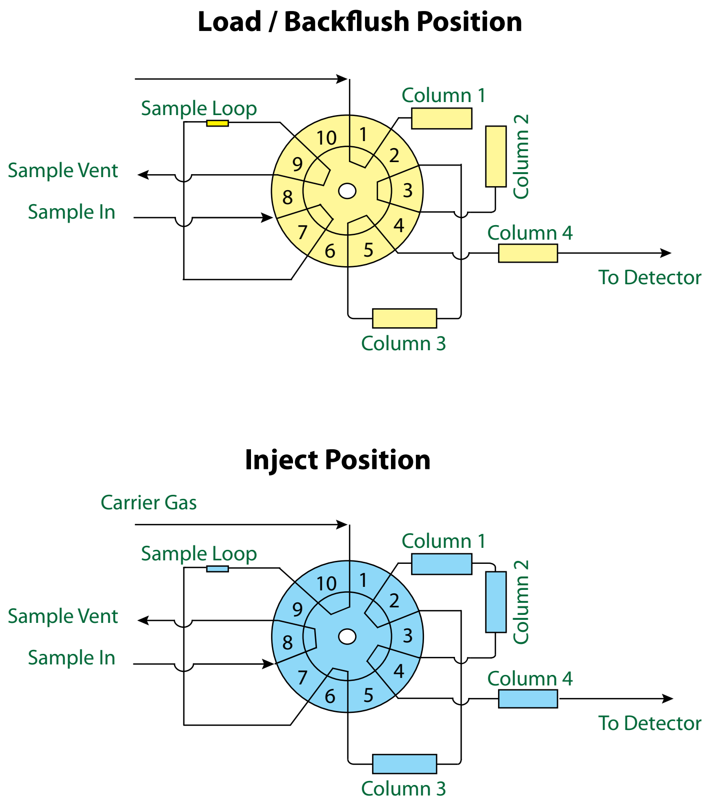

Figure 4. Diagram of the Separation Columns and Switching Valve

A sample valve installed in the sample oven injects a fixed volume of the gas sample into the GC column of the model 292B analyzer. The valve must inject a reproducible sample as quickly as possible for reliable operation. The sample volume is less than 0.50 mL at low pressure. The AMETEK designed and manufactured 10 port gas valve ensures a rapid and accurate distribution of sample gas within the GC system.

Back Flush Sampling and Separation Method

Since the C_6, C_7, C_8 and heavier components (called C_6+) can take ten minutes to elute from the columns, a technique known as back flushing is used to reduce the total analysis time for the sample. In back flushing, the two main columns are connected in a series to a 10-port gas sampling valve. The first column (the stripper) is very short; the second column (the measuring column) is 20 times longer. The lighter components nitrogen through n-pentane, pass quickly through the stripper and onto the measuring column. The heavier components remain in the stripper. After a predetermined time period, known as back flush time, the valve is actuated to back flush the heavy components to the detector. The back flush takes the stripper and instantly puts it at the end of the measuring column so that all heavy components will elute quickly. The model 292B utilizes the back flush method and is designed to provide the fastest possible response and accuracy in a field portable type analyzer. The back flush methodology is described in Figure 5.

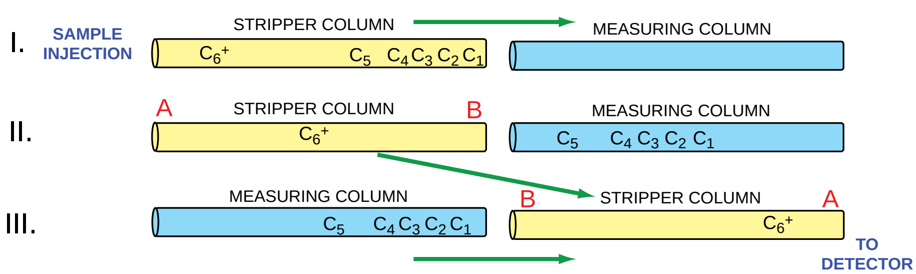

Figure 5: AMETEK 292B Back Flush Methodology

Individual Component Detection/Quantification

A pure carrier gas (helium) carries the sample through the columns. As the components elute from the columns, a Thermal Conductivity Detector (TCD). A TCD consists of a metal block with two small internal volumes that contain hot wire filaments, and detects the components. The difference in thermal conductivity for each component as it passes through a volume and over the hot wire filament is determined by the change in temperature of the hot wire filament. The second chamber has carrier gas only and is used as a reference signal. The resulting bridge imbalance detects the presence of a component and provides a voltage output change from the detection electronics. The voltage is output as a graph and is called a chromatogram.

The model 292B analyzer system is capable of measuring the following components:

- Hydrocarbons (C_1 – C_5, C_6+)
- Nitrogen (N_2)
- Carbon Dioxide (CO_2)

On Board Electronics and User Interface

For many custody transfer and metering applications, the calculation of heating value, compressibility and relative density are required. The on-board microprocessor of the AMETEK model 292B performs all necessary calculations and all values may be obtained via the user interface of the instrument, recorded and printed using the analyzer's external reporting capability or downloaded using the USB port provided on the front panel of the analyzer. The required calculations may be output in variety of engineering units to meet reporting requirements. Calculations are performed to meet the requirements as per standards published by ISO, GPA ISO and ASTM.

Carrier Gas and Drive Gas Distribution

Helium carrier gas is 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. Carrier gas distribution and flow control is optimized in the model 292B to ensure minimal losses of valuable carrier gas and optimum performance. Bottled nitrogen or dry instrument air is used to automatically actuate the internal valves. Pressure and flow control of the drive gas (used to drive the GC valve automation) is provided on the front panel of the instrument (Figure 6).

Figure 6. The Front Panel of the AMETEK 292B

Calibration

The area under each of the peaks is proportional to the concentration of the compound present in the sample. Like most analytical techniques calibration gas sample must be measured so that the concentrations can be properly calculated. The accuracy of the results from a GC is dependent on the accuracy of the certified blend of gases known as the 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. 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 cold weather locations.

The AMETEK model 292B 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 is determined for each component in the calibration gas. The following equation describes the response factor calculation:

$$\text{Response Factor} = \frac{\text{Component Concentration}}{\text{Peak Area}}$$

The individual response factors are used to determine unknown component concentration from measured peak areas once the analyzer has been calibrated. Advanced analyzers such as the model 292B 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. Re-calibration every 30 days is adequate in most cases.

Calculated Values

Heating Value Calculation

The heating value, relative density, and compressibility values are calculated using the analyzer's on board microcontroller 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:

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

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

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:

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

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

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 is determined using the 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 performed using the 292B on-board microprocessor.

Since the heating value is expressed as kJ/m3 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. The default value used by the 292B is 14.73 PSIA. In Europe, the standard temperature value varies from country to country. The AMETEK 292B is configurable for different standard temperatures and pressures. For this reason, before comparing heating value results from different analyzer systems, it is important to verify that the standard conditions at which the gas volume is calculated are the same.

Gross Heating Values

The 292B gross gas heating values can be 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 7) for a comparison of the gross dry and saturated results.

Test Details

Name	Validation Run #3
Start Date/Time:	5/14/2013 16:35
End Date/Time	5/14/2013 16:53
Operator:	John Smith
Comments:	Validation Run Sequence
Instrument S/N:	SN-575-001-4765
Calibration Number:	2
Test Number:	5
Location:	Tulsa, OK - Chandler Lab

Analysis Details

	Dry Analysis				Wet Analysis		
	Mole %	BTU	R. Den.	GPM	Mole%	BTU	R. Den.
C6+	0.065	3.30	0.0021	0.0283	0.064	3.24	0.0020
Nitrogen	1.508	0.00	0.0146	0.1658	1.481	0.00	0.0143
Methane	90.994	921.16	0.5040	15.4222	89.410	905.13	0.4952
CO2	1.502	0.00	0.0228	0.2563	1.476	0.00	0.0224
Ethane	3.992	70.81	0.0414	1.0674	3.923	69.58	0.0407
Propane	0.987	24.90	0.0150	0.2720	0.970	24.47	0.0148
i-Butane	0.292	9.52	0.0059	0.0955	0.287	9.35	0.0058
n-Butane	0.300	9.82	0.0060	0.0946	0.295	9.65	0.0059
neo - C5	0.0580	2.32	0.0014	0.0211	0.057	2.28	0.0014
i-Pentane	0.1610	6.47	0.0040	0.0585	0.159	6.36	0.0039
n-Pentane	0.1410	5.65	0.0035	0.0514	0.138	5.56	0.0034
Moisture	0.0000	0.00	0.0000	0.0000	1.740	0.88	0.0108
Ideal	100.000	1053.95	0.6207	17.5331			

Cumulative Analysis Detail

	Dry Analysis Results		Wet Analysis Results	
Molar Mass	17.981		17.98	
Relative Density	0.6223		0.6223	
Compressibility Factor	0.9976		0.9973	
Gross Heating Value	23154.1	BTU/lb	22752.1	BTU/lb
Gross Heating Value	1056.4	BTU/CF	1038.9	BTU/CF
Absolute Gas Density	47.605	lbm/1000CF	47.6049	lbm/1000CF
Wobbe Index	1316.99	BTU/CF		
Un Normalized Total	100.007			

Figure 7. Example AMETEK 292B Report

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.

Conclusion

Gas chromatography is the most commonly used technique 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, calculations may be performed which include gas heating values, relative density, compressibility and liquid volume.

Well-designed, rugged and reliable portable analyzers can be used for measurement of the gas composition near gas pipeline installations. Portable gas analyzers, including GCs, must have a well-designed and maintained sample conditioning system. Potential problems with gas chromatographs can be avoided if basic sample system techniques are adhered to and suitable hardware is used throughout the entire sample handling and gas distribution system.

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. Performance requirements for on-line and portable GC technology are based on repeatability, C_6+ back flush analysis, extended analysis, and analysis cycle time. Fully integrated portable analyzers such as the AMETEK model 292B provide a direct measurement of the gas composition and calculations on site, eliminating the need for sample cylinders and possible sampling problems. The analysis results are stored internally and can be sent to a PC or printed directly on site. The AMETEK 292B analyzer is easy to use, reliable, and designed to withstand rough treatment. The AMETEK model 292B offers an easy-to-use alternative to stationary devices and eliminates the requirements for taking batch samples in the field. The instrument is designed to be operated at a single touch of a button, eliminating the need for extensive operator training, adjustments, and complex field setup.

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.