The Analysis of Carbon Dioxide in Natural Gas

Mike Fuller, AMETEK Process Instruments, 150 Freeport Road, Pittsburgh, PA. 15238

Natural Gas - Specifications

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 Figure 1.

Compound	Mole%
Methane	90.988
Ethane	3.99
Propane	0.991
i-Butane	0.298
n-Butane	0.301
2,2-dimethyl pentane	0.049
i-Pentane	0.151
n-Pentane	0.147
(C6+)	0.075
H2O	0
Nitrogen	1.51
CO2	1.5

Figure 1. GC Analysis of 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 at pipeline. Condensation forms pressure liquid slugs that could cause damage to the pipeline.
3. Free of particulate solids 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. Typically < 120 ppm or seven pounds of water per million cubic feet (MMCFD) of gas.
5. Contain no more than about 4 ppm hydrogen sulfide.
6. Contain no more than 2%-3% carbon dioxide.

Carbon dioxide is a naturally occurring diluent in oil and gas reservoirs and it can react with H_2S and H_2O to make corrosive compounds that threaten steel pipelines. It is therefore critical that pipeline levels of carbon dioxide are no more that 2%-3%. Well head natural gas can contain as much as 30% carbon dioxide. Removal of CO_2 from natural gas utilizes membrane technologies or larger amine plants. Measuring carbon dioxide concentration is required at processing plants and at natural gas custody transfer points to ensure the levels are low enough to meet quality specifications for pipeline transportation.

Methods of Analysis - Carbon Dioxide in Natural Gas

Historically there have been two major approaches for the analysis of carbon dioxide in natural gas, namely gas chromatography and absorption spectroscopy using infrared light sources.

Gas Chromatography

The Gas Processors Association (GPA) Method 2261 describes the analysis of natural gas using gas chromatography. A gas chromatograph can be used to separate the components of a natural gas such that each major component can be quantified. A sample is injected into the GC and travels down a hollow tube packed with an adsorbent using a flowing carrier gas (usually nitrogen or helium). The light 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 diagram of the key components of a gas chromatograph is shown in Figure 2.

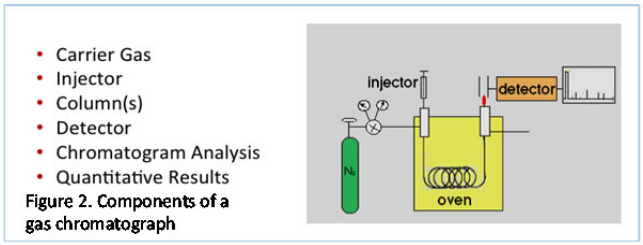

Figure 2. Components of a gas chromatograph

A picture of the control panel of the AMETEK 292B gas chromatograph is shown in Figure 3. The LCD display shows the detector response as a function of time. In this example the natural gas has been separated into eleven separate components. Special column switching techniques are used in GC natural gas chromatographs so that all of the "heavy" C6+ components actually are measured first "peak". This is shown in the Figure as the #1 C6+ peak. The "lightest" compound in natural gas sample is nitrogen followed next by methane, carbon dioxide and ethane, peaks 2-5 respectively.

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 process gas 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 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 certain locations.

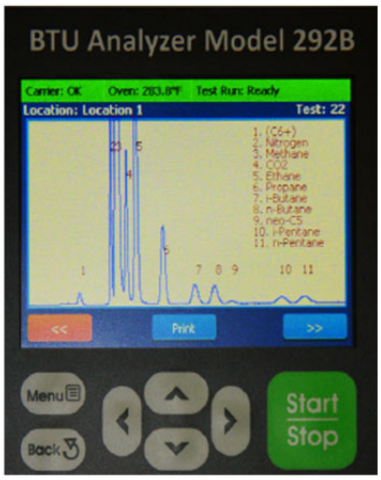

Figure 3

While gas chromatography provides and accurate method to measure the carbon dioxide content in a natural gas stream it does have several drawbacks. The GC approach requires periodic calibrations because the separation of the components changes over time as the column adsorbent ages. Eventually the columns must be replaced which requires a trained technician. The sample injection and column switching valves are reliable, but have a finite lifetime before replacement is required. Another disadvantage of this approach is the analysis time which is typically around five minutes.

Optical Measurements

TRADITIONAL NEAR INFRARED ABSORPTION MEASUREMENTS

Traditional absorption spectroscopy involves measuring the wavelength varying intensity of a source with and without a sample present. In this way the amount of light absorbed by sample can be determined. The amount of light absorption can then be directly related to the concentration of a component of interested through a calibration process. The absorption spectroscopy process is shown in Figure 4.

Commercial infrared absorption based instruments consist of a heated pressure regulator to reduce the pipeline pressure a gas cell sealed with sapphire windows, detector and associated electronics. Most commercial instruments operate in the near infrared region and are non-dispersive band pass filter type instruments. A filter based spectrometer passes a narrow band of near infrared "light". The filter is designed to pass light in a region where carbon dioxide absorbs. The hydrocarbon components of natural gas have varying degrees of absorption in the region that is selected for carbon dioxide analysis. In order to compensate for this varying background interference analyzer suppliers have developed scrubbing techniques. In an external sample handling system the sample gas stream is split and the carbon dioxide in one stream is removed with a scrubber. The analyzer then measures the response with no carbon dioxide present and the stream where it is present and uses the scrubbed result to correct the results. This allows an accurate measurement of the carbon dioxide when the hydrocarbon composition of the natural gas changes.

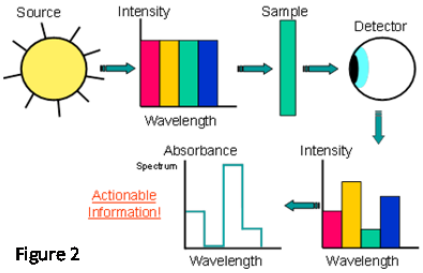

Figure 2

The traditional near infrared absorption approach to analyzing carbon dioxide is rapid (about 30 seconds) compared with gas chromatography. On the negative side this approach requires a scrubbing cycle and the materials used in the scrubbers must be periodically replaced. This approach also requires limited life switching valves to alternate the measurement between the process gas before and after scrubbing.

TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS)

TDLAS involves using a diode laser as a source. Over the past several years, near-infrared TDLAS has gained much attention for use in industrial applications. Three key attributes of the technique are responsible: specificity for the analyte, high sensitivity, and fast response speed. TLDAS's specificity is the result of the extremely high spectral resolution achievable. Emission bandwidths for tunable diode lasers are on the order of 10^{-4} – 10^{-5} cm^{-1}, which results in the ability to isolate a single rotational-vibrational absorption line of an analyte species. A second advantage of TDLAS is the ability to rapidly tune the lasers, so techniques like wavelength modulation spectroscopy (WMS), which yield dramatic sensitivity enhancements over a direct absorption approach, are easily implemented. Because TDLAS is an optical technique, it also offers a very fast response speed with an analysis time of two seconds. The high specificity, sensitivity, and response speed of TDLAS make it very suitable for a variety of process measurements such as carbon dioxide in natural gas.

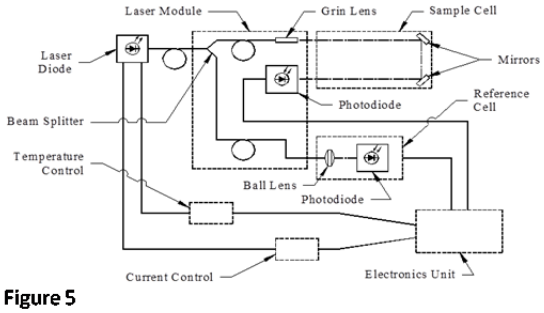

Figure 5

The specificity of TDLAS for an analyte is dependent on the sample matrix. For many applications such as the analysis of carbon dioxide in natural gas there is an absorption line for the analyte species that is free of interference from all other species in the sample matrix.

A schematic of the AMETEK 5100HD Div. 1 TDLAS analyzer is shown in Figure 5 and a photograph of the analyzer is shown in Figure 6. A small portion of the laser source output is split out and passes through the reference cell. Data is essentially collected simultaneously from both the natural gas stream and the carbon dioxide reference sample providing a real-time confirmation that the laser is locked on the carbon dioxide absorption line. The carbon dioxide reference cell is also used to perform a reliability check on the quantitative measurement of the analyte measured in the sample cell. This verification is accomplished by using the reference cell data to check the output of the laser and the proper operation of the data collection electronics. If there is a mismatch between the expected and calculated results an error is reported. If such an error is detected an alarm is immediately generated and sent to the host computer or through the built in Web interface to a remote computer anywhere on the system network.

Figure 6

Since there are no interferences due to the natural gas matrix compounds, a background measurement is not required thus reducing the complexity of the design. The simplicity of the design, the precision of the laser wavelength and the extremely long life of diode lasers (+10 years) minimize cost of ownership. It's also possible to use two lasers in a single analyzer so both carbon dioxide and moisture in natural gas can be measured simultaneously.