AMETEK®
PROCESS INSTRUMENTS

APPLICATION NOTE

CARBON DIOXIDE MEASUREMENTS IN NATURAL GAS PROCESSING USING TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS)

5100

5100 ATEX ZONE 1

5100HD GP, DIV 2 AND ATEX ZONE 2 VERSION

Natural gas is one of the world's most important sources of energy. In addition to its primary importance as a fuel, wellhead natural gas is also a source of low molecular weight hydrocarbons for petrochemical feed stocks. Although natural gas is considered a clean fuel when compared with other fossil fuels, wellhead gas contains dangerous impurities. Wellhead natural gas contains mainly methane (CH_4) together with heavier hydrocarbons, but can also contain problem contaminants such as carbon dioxide (CO_2), hydrogen sulfide (H_2S) and compounds containing mercury (Hg). The composition of the natural gas extracted from producing wells depends on the type, depth, and location of the underground deposit and the geology of the area.

CO_2 is one of the highest-level impurities found in wellhead natural gas – CO_2 concentrations of up to 50% are a reality. It must be removed to meet pipeline quality BTU standard specifications for consumer gas and to protect pipelines from the corrosion that occurs when CO_2 and water combine to form carbonic acid. When the natural gas needs transporting over a great distance, it is usually converted to liquefied natural gas (LNG). In an LNG processing plant, cooling the natural gas to a very low temperature causes excess CO_2 to freeze and it can block the LNG pipelines.

To meet the requirements of US pipeline quality standards for pipeline natural gas, the amount of CO_2 must be present at less than 2% by molecular volume. The processing of wellhead natural gas into pipeline quality gas involves several processes. A block diagram of a typical natural gas processing plant is shown in Figure 1.

Acid gas removal, also known as the gas sweetening process, is used to purify the natural gas by removal of acid gases such as CO_2 and H_2S. The technology that is widely used to remove CO_2 and H_2S from wellhead natural gas involves extracting these components into an amine containing liquid stream. The aqueous stream containing the acids is separated from the natural gas and sent to a sour water stripper unit. While there are several different technology approaches used to remove excess CO_2, each requires the measurement of the CO_2 level before and after the acid gas removal process, as shown in Figure 1.

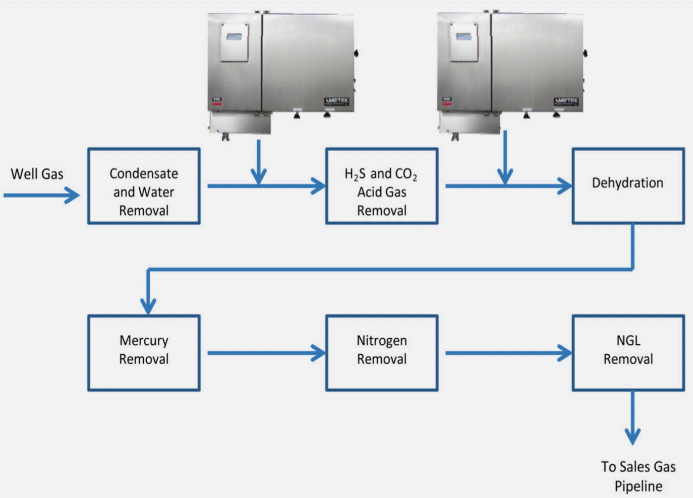

Figure 1. Diagram of a natural gas processing plant

PROCESS ANALYSIS ALTERNATIVES - GAS CHROMATOGRAPHY

The Gas Processors Association (GPA) method 2261 describes the analysis of natural gas using a gas chromatograph (GC). A GC analyzer 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 analyzer and travels down a hollow tube (column) packed with an adsorbent using a flowing carrier gas (usually N_2 or helium). The light components travel down the column more quickly and are "seen" first by the detector. Over the next few minutes, all the components exit the column and are measured by the detector. A diagram of the key components of a GC is shown in Figure 2.

A picture of a 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 11 components. Special column-switching techniques are used in natural gas chromatographs so that all the "heavy" C6+ components are measured as the first "peak". This is shown in the example as the C6+ peak. The "lightest" compound in natural gas sample is N_2, followed by CH_4, CO_2 and ethane.

The area under each of the peaks is proportional to the concentration of the compound present in the sample. Like most analytical techniques, a calibration gas sample must be measured so that the process gas concentrations can be properly calculated. The accuracy of the results from a GC analyzer are 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 a source 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 10°C (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.

While the GC provides an accurate method to measure the CO_2 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, requiring 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, typically around five minutes.

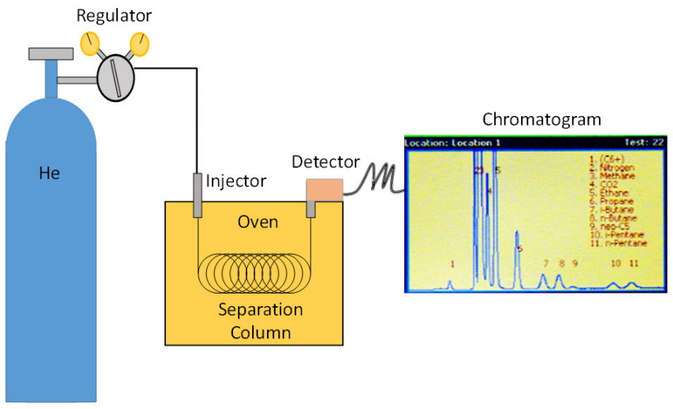

Figure 2. Gas chromatograph components

Figure 3. Control panel of a gas chromatograph

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 to determine the amount of light absorbed by a sample. The amount of light absorption is then directly related to the concentration of the component of interest through a calibration process.

Commercial infrared (IR) 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-IR region and are non-dispersive band pass filter-type instruments.

A filter-based spectrometer passes a narrow band of near-IR "light". The filter is designed to pass light in a region where CO_2 absorbs. The hydrocarbon components of natural gas have varying degrees of absorption in the region that is selected for CO_2 analysis. 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 CO_2 in one stream is removed with a scrubber. The analyzer then measures the response with no CO_2 present and the stream where it is present, and uses the scrubbed result to correct the results. This allows an accurate measurement of the CO_2 when the hydrocarbon composition of the natural gas changes.

Traditional near-IR absorption analysis of CO_2 is rapid (about 30 seconds) compared with GC. However, this approach requires a scrubbing cycle and materials used in the scrubbers must be periodically replaced. Limited-life switching valves are also required to alternate the measurement between the process gas before and after scrubbing.

TUNABLE DIODE LASER ABSORPTION SPECTROSCOPY (TDLAS)

TDLAS (Figure 4) uses a diode laser as a source. Near-IR TDLAS has gained much attention for use in industrial applications due to three key attributes: specificity for the analyte, high sensitivity, and fast response.

Specificity is the result of the extremely high spectral resolution achievable. Emission bandwidths for tunable diode lasers are on the order of 10^{-4} to 10^{-5} cm^{-1}, enabling the isolation of a single rotational-vibrational absorption line of an analyte species. The ability to rapidly tune the lasers allows implementation of techniques like wavelength modulation spectroscopy (WMS), which yield dramatic sensitivity enhancements over a direct absorption approach. Because TDLAS is an optical technique, it also offers a very fast response speed with an analysis time of two seconds. These qualities make TDLAS very suitable for a variety of process measurements, such as CO_2 in natural gas.

The specificity of TDLAS for an analyte is dependent on the sample matrix. For many applications, there is an absorption line for the analyte species that is free of interference from all other species in the sample matrix.

CO_2 measurement is performed with a distributed feedback laser, which produces an optical power of approximately ten milliwatts. The output of the laser is coupled into single-mode optical fiber and connected to a fiber-optic beam splitter. The splitter is used to divide the optical power for use in the sample and reference measurements. Gradient refractive index (GRIN) lenses, with a beam divergence of 1.8 milliradians, are used to collimate the output of the single-mode fibers and direct the resulting beams through the sample and reference cells. These cells each contain 0.5 mm^2 InGaAs-photodiode detectors, connected to separate input channels of the electronics unit.

A small portion of the laser source output is split out and passes through the reference cell. Data is collected simultaneously from both the natural gas stream and the CO_2 reference sample, providing real-time confirmation that the laser is locked on the CO_2 absorption line.

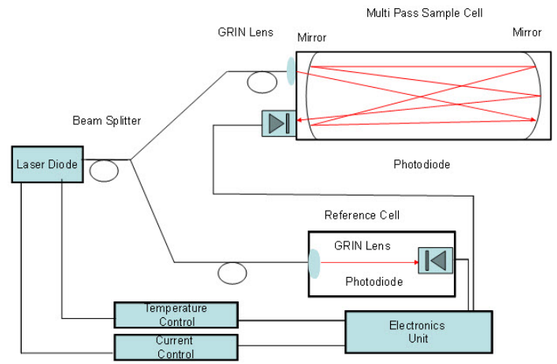

Figure 4. Diagram of a TDLAS analyzer

The CO_2 reference cell is also used to perform a reliability check on the quantitative measurement of the analyte measured in the sample cell. This is accomplished by using reference cell data to check the laser output and the proper operation of the data collection electronics. A mismatch between expected and calculated results returns an error. If an error is detected, an alarm is immediately generated.

Since there are no interferences from the other natural gas matrix compounds, a background measurement is not required, 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 minimize cost of ownership. Using two lasers in a single analyzer means both CO_2 and moisture in natural gas can be measured simultaneously. A single analyzer can be configured with two cells for measurements of CO_2 in two different.

The AMETEK 5100HD is an extractive-type CO_2 analyzer designed for hot/wet sample analysis. There is no sample conditioning, just fully integrated handling to transport the sample. The 5100HD uses a sealed reference cell for continuous on-line analyzer verification, and offers high specificity and sensitivity. It uses a digital implementation of the WMS, so changing the experimental protocol is simply a matter of uploading a file.

Sample cell temperature is controlled with accuracy of ±0.1°C and can be set in the range of 60 to 150°C (140 to 302°F). The reference cell temperature is maintained at 40°C (10°F) and is in the main electronics compartment with the laser, isolated from the heated sample oven.

Figure 5 represents the response of the instrument to a series of CO_2 challenges in the concentration range of 0 to 300 parts per million by volume (ppmv). The duration of each challenge was from 10 to 20 minutes. The speed of the response (T90) is 20 seconds at a flow rate of 2L/min. The data acquisition rate is two seconds per measurement.

Repeatability as a degree of agreement between replicate measurements of the same concentration was expressed in terms of standard deviation of the measurement results. The standard deviation of the CO_2 readings on each of the challenges was about 2 ppmv.

TDLAS-based technology for CO_2 measurements in natural gas stream offers much faster speed of response and lower maintenance costs than the GC. TDLAS also provides higher accuracy and selectivity than infrared photometry.

Additionally, the semiconductor laser used as the light source has a MTBF of more than eight years, while real-time verification algorithms and the internal reference cell provide a continuous indication that the analyzer is operating properly.

The wavelength modulation spectroscopy (WMS) data collection eliminates any concentration effects resulting from moderate cell contamination, and any major fouling of the analysis cell results in an alarm output. Also, the gas cell can be cleaned by plant technicians in less than an hour, minimizing down time in case of a condensation-related system upset.

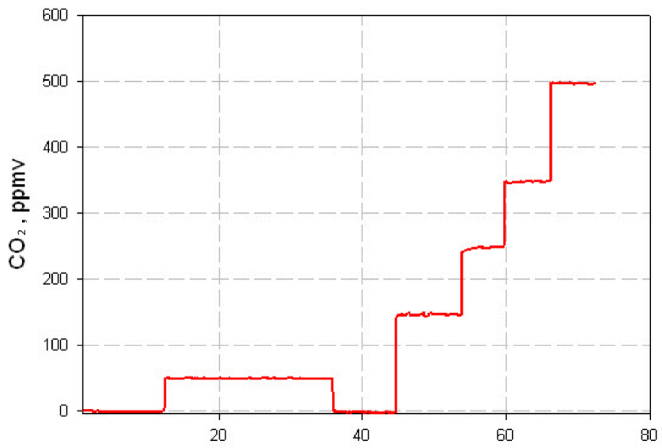

Figure 5. Response of the analyzer to a series of CO_2 challenges

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