

CHROMATOGRAPHIC ANALYSIS OF NATURAL GAS LIQUIDS

Class # 5060.1

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Scope

The analysis of natural gas liquids has become an integral part of the measurement process. Two methods that are commonly used in the gas industry to provide this analytical data are the GPA Standard 2177, "Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography" and the GPA Standard 2186, "Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography". The purpose of this paper is to provide an overview of the standards and the steps needed to obtain accurate results.

Introduction

With the changes in the economy as well as advances in technology in production of chemical, pharmaceuticals, and other products, the demand for NGL has changed which has a dramatic result in the value of NGL. The result of these conditions demands an accurate analysis and measurement of the NGL for the company's balance sheet and bottom line.

Sampling

One of the first steps in obtaining an accurate analysis is to provide a sample that is truly representative of the product being delivered in the pipeline. Sampling methods and equipment are not the topic of this class, but its importance in this process should be noted. To obtain a representative sample of the NGL, a composite sampler should be installed. The composite sampler should be programmed to operate proportional to flow; the pump stroke cycle will be determined by a volume of product, not a timed event. If possible, a sample probe should be installed in the pipeline. The use of a constant pressure cylinder is recommended to transport the sample from the sample point to the lab.

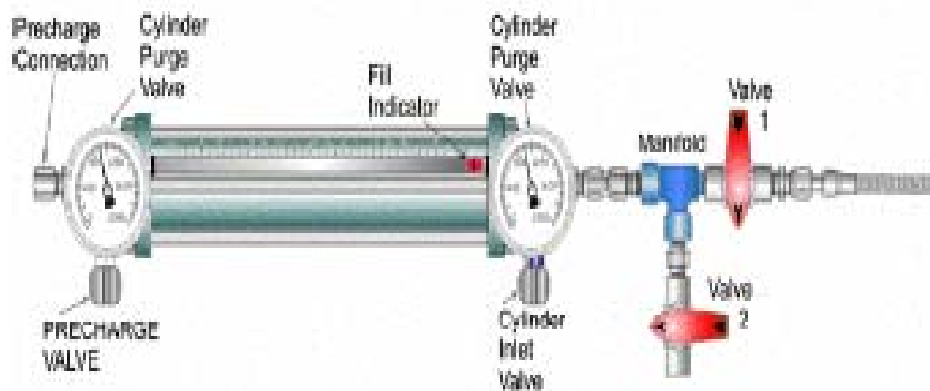
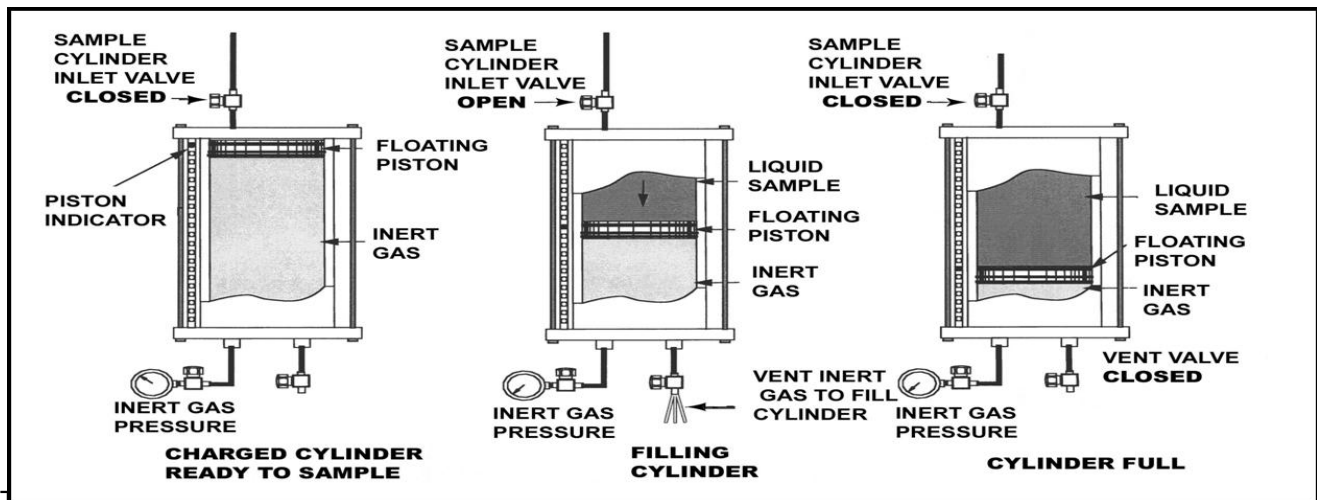
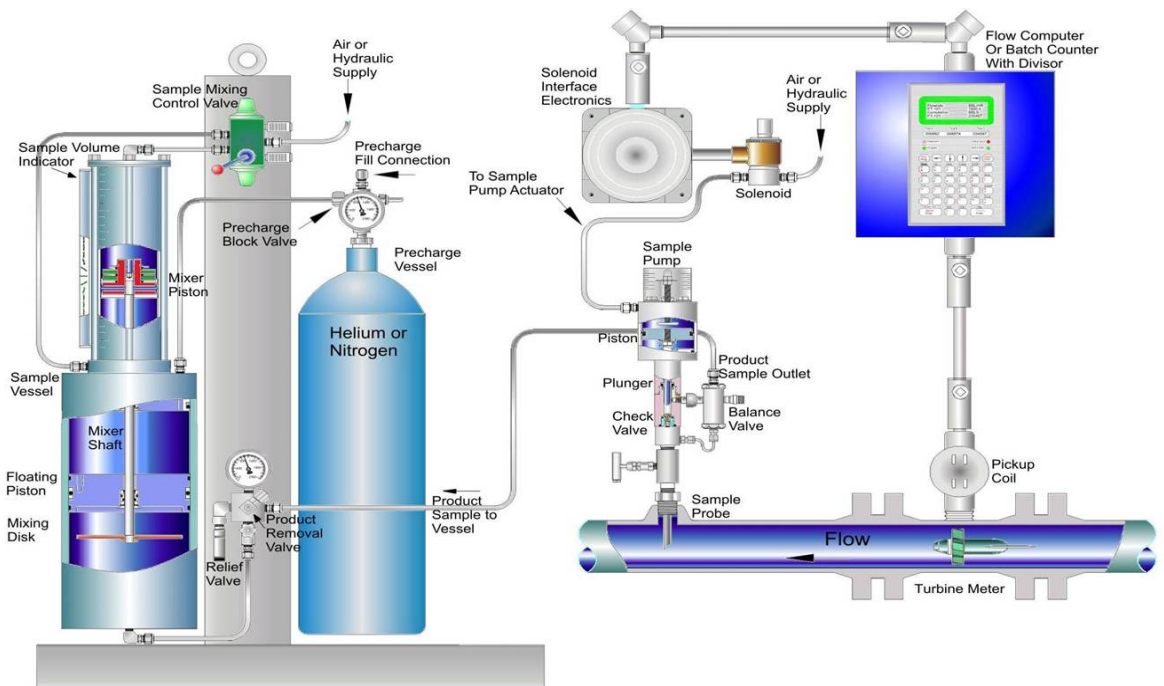


Figure 1 – Typical Piston Sample Cylinder



The cylinder will consist of a cylindrical tube, piston, mixing device, piston position indicator, end caps, pressure gauges, valves, and a pressure relief disc. The cylinder should be pre-charged with an inert gas on the back side of the piston with enough pressure to prevent the sample from flashing during procurement. Prior to collection of the sample for analysis from a composite sample, the sample should be thoroughly mixed to avoid any stratification that might have occurred. The connection between the sample point and sample cylinder must be purged on either composite samples or spot samples. Once the connection is properly purged, the product inlet valve of the cylinder can be opened. Using the valve on the pre-charge side of the cylinder, slowly vent the pre-charge gas off. When the pressures match, the NGL should slowly move the piston allowing the NGL to fill the inlet side of the cylinder. When the piston indicator reaches 75-80% full, close the valve on the pre-charge side and then the inlet valve to the cylinder. The source valve should then be closed and the line safely vented. Using Teflon tape, cap or plug the valves of the cylinder. A sample tag should be attached with as much information that can be provided including sample source, sample date, time, pressure, temperature, cylinder number and the sampler's name. The cylinder is then transported to the lab for testing.



D.O.T. Regulat

When transporting natural gas liquids, it is important that you follow the regulations of the D.O.I. and your company's policies. This issue is again outside the scope of the paper but should be mentioned.

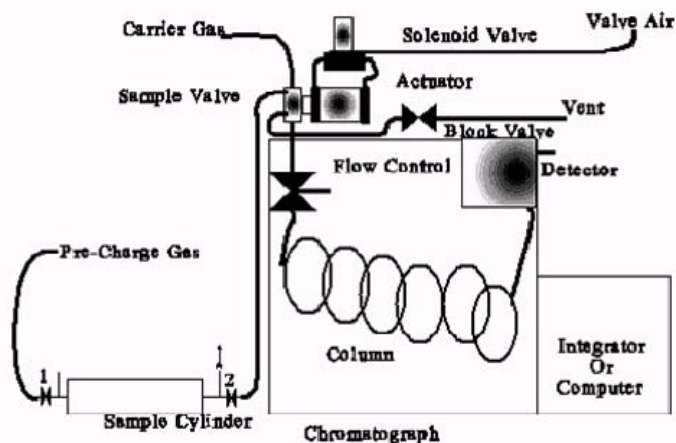


Figure 4 – Chromatograph

Apparatus

Any GC that meets the following specifications may be used to obtain a C7+ precut Natural Gas Liquid Analysis (GPA 2177). The gas chromatograph consists of several systems including:

Sample Injection - The sample injection system is designed to take a very small fraction of the sample to analyze on the GC. To accomplish this, the inert pre-charge side of the transport cylinder is pressurized to a pressure above the bubble point of the product at the highest temperature of the injection system. The transport cylinder is rocked to allow mixing of the product. The sample end of the cylinder is then connected to the sample inlet tubing, which is connected to the liquid sampling valve. A purge block valve is downstream of the liquid sampling valve. The block valve is closed and the product valve is opened to allow the product to pressurize the injection system. The block valve is opened slightly to purge the sample through the lines. The flow is controlled to avoid the pressure dropping below the bubble point, compromising the sample. At this point, the liquid sample valve will be rotated, either manually or automatically by solenoids. A typical sample size for a packed column is between 0.5 to 1.0 micro-liters or 0.06 to 0.5 micro-liters for a capillary column.

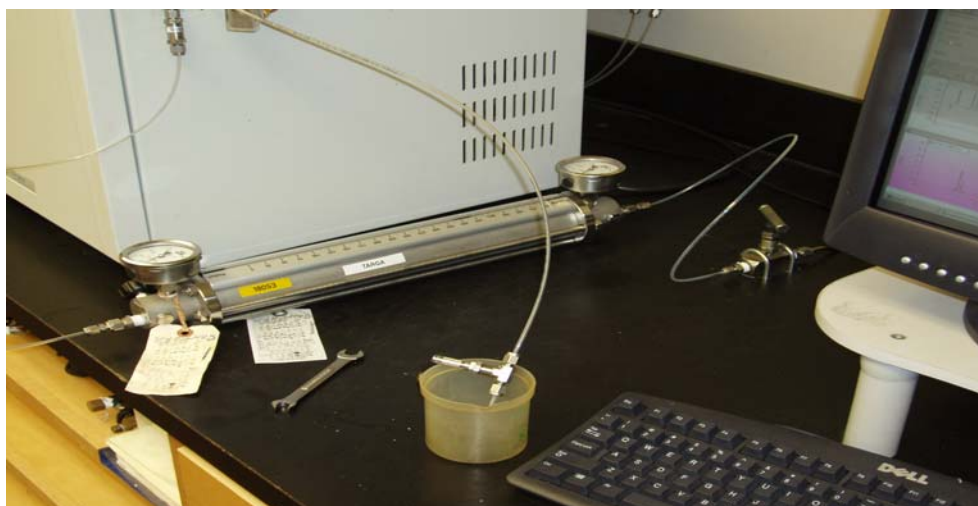


Figure 5 – Sample Purge Line

Pressure, Flow, & Temperature Controllers – The sample is carried through the column by the carrier gas. The flow rate of the carrier gas, the temperature of the columns, and the length of the columns all can affect the time that each component takes to flow through the system and the amount of separation seen between each component. A typical flow rate of the helium carrier gas in a packed column GPA 2177 analysis is 30 cc's/min with a temperature of 100-120C. The GPA 2186 extended analysis is performed by using a capillary column with the analysis starting at a low temperature that is ramped up as the run progresses.

Columns – The column separates the individual components of the sample from the original mixture. The column must be capable of separating nitrogen, carbon dioxide, and the hydrocarbons methane through normal hexane. A column with a support of 30% DC 200/500 and a length of approximately 30' will provide the separation required. The separation is accomplished by the adsorbing/absorbing of the components through the column materials. Larger components are retained longer than smaller components and the elution time from the column is slower than the smaller components resulting in peaks broadening out as the run time increases.

Methods and techniques are used to minimize run time and aid in the integration of the peaks. The backflush method simply reverses the carrier flow through the column. The heavier components then elute in a broad ill-defined peak. The precut method uses a short precut column similar to the main partition column, which is placed before the partition column at injection. When the lighter components have passed into the partition column, a valve switch will happen that will reverse the carrier flow through the precut column and position it to the front of the partition column. The result of this is the heavy components elute at the first of the analysis in a sharp defined peak. Temperature programming is typically used with capillary columns to facilitate separation of components and rapid elution times.

Detector – The two most common detector types used for the analysis of natural gas liquids is the TCD and the FID.

The TCD (thermal conductivity detector) measures the difference in the thermal conductivity of the carrier gas and the components as they elute from the column. The carrier gas (typically helium or hydrogen) conducts the heat of the element more than the eluting components. The result is the filaments will warm as a component elutes from the column, producing an electrical signal. The TCD is considered a universal detector as it will detect any component with a different thermal conductivity than the carrier gas.

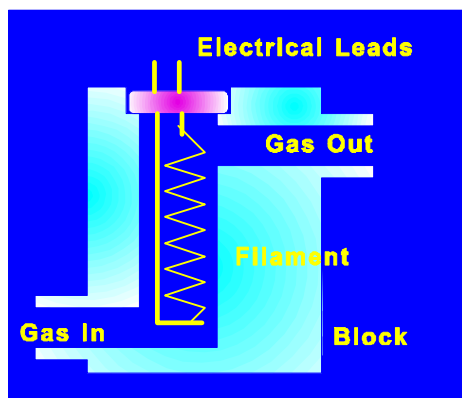


Figure 6 – Thermal Conductivity Detector

The FID (flame ionization detector) consists of a jet and collector. Hydrogen and air are mixed with the column effluent and ignited. As hydrocarbons elute, the heat of the flame breaks up the molecules. The flame jet has an electrical charge that ionizes the molecule fragments. These fragments are carried by the carrier gas inside a cylindrical collector. The collector is electrically charged. The flow of current between the jet and the collector is proportional to the concentration of the component. The FID is more sensitive than the TCD and more linear. The FID has a limit in that it does not detect all of the components in the natural gas liquid stream.

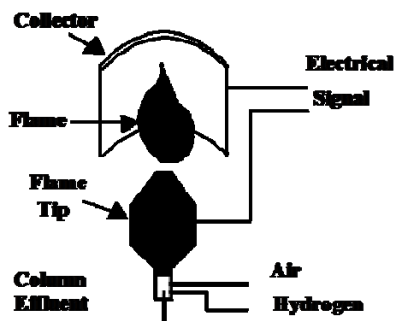


Figure 7 – Flame Ionization Detector

Integration System – The electrical signal produced by the detectors must be converted into a usable value that can represent the concentration of the component. Digital integrators and computer software are the most accurate and precise way to integrate the data from the detector signals. The integration system computes the area of each peak. This is used to calculate the concentration of the component. The elution time is used to identify components. Each brand and style of integration system has parameters that must be properly adjusted to verify each peak is identified and the area interpreted for the peak is correct. These values will be used for calibration calculations of the GC and component concentrations of the samples being analyzed.

Calibration – Even with a properly procured sample and the test performed to perfection, an improperly calibrated machine will result in an inaccurate analysis. Calibration of a GC starts with a properly prepared standard containing the appropriate concentrations of the components expected in the sample. The standard should be gravimetrically prepared – each component will be weighed in. Before using a new standard, the concentrations should be evaluated prior to using this blend for calibration. Some of the methods to validate a new standard include a mole weight / detector response plot, an analysis by an independent lab, and running the standard as an unknown.

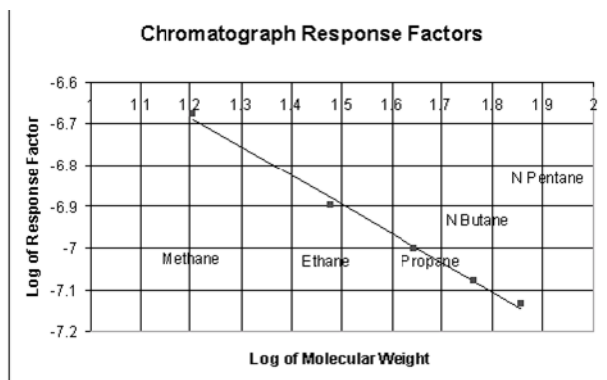


Figure 8 – Example of Detector Response Plot

The above graph shows a standard plot. The log of the response factor of the TCD is graphed on the Y axis while the X axis is the log of the mole weight of the straight chain hydrocarbons. To obtain the response factor, the standard is injected as an unknown. The areas for methane, ethane, propane, n-butane, & n-pentane are noted. (On a C7+ analysis, the area of n-hexane is also recorded). The response factor of each component is calculated by dividing the mole % from the certification paper by the area count. The log of this number is used for the y-axis value.

If the standard is run on a calibrated machine as an unknown, the values should fall within the GPA 2177 tolerances for repeatability. If it does, the standard can be assumed to be good.

A third-party lab can also evaluate the standard by running as an unknown.

Storage, handling, and care of the standard should be observed as to never compromise the standard blend. The pre-charge side should always be kept at the pressure recommended by the vendor.

Once the standard is known to be valid, the standard is used to calibrate the machine by performing back to back runs. The values of the runs should fall within the tolerances outlined in GPA 2177. Response factors are calculated for each component by the formula $RF_{(x)} = \text{Mole } \%_{(x)} / \text{Area Count}_{(x)}$.

Calculations

The raw % of a component in a sample is calculated as $\text{Raw Mole } \%_{(x)} = \text{Area}_{(x)} * RF_{(x)}$. The raw mole percents of each component are added to give a total raw mole percent. Each component's raw % is divided by the total raw mole % and multiplied by 100 to obtain the mole % of the component in the sample.

Extended Analysis

An extended analysis is performed when a more detailed breakdown of the heavy components is required. The analysis is actually the combining of 2 analyses. The lighter components are separated easily in GPA 2177 and GPA 2145 lists the physical property values for these components to be used in the calculations. The C6+ or C7+ peak will contain many components therefore no physical property values are listed for this peak. The components that make up this peak need to be separated to achieve an accurate mole weight, gravity, and heating value of the combined components. Since the peak has many heavy components, a different GC setup is used for the analysis because the packed column would not give the resolution needed and the TCD may not see the components at the small concentration. The GPA Method 2186 uses a capillary column, flame ionization detector, and temperature programming of the column oven to obtain the necessary resolution and detection levels required for this test. The capillary column is typically a 60m *0.26 mm ID fused silica DB1 bonded Methyl Silicone, 1.0 micron film thickness. The temperature of the column oven is ramped to expedite the time of the heavier components travelling through the column. The method requires calculations similar to GPA 2177, but on more components. GPA Technical Publication TP-17 provides the physical properties for the components that comprise the C6+ or C7+ peak.

The drawback is the FID doesn't see all the components in the sample, this requires a separate injection on a TCD system. The two chromatograms are mathematically combined to produce a complete analysis. Calculation methods are described in GPA Standard 2186.

Conclusion

In order to obtain an accurate analysis of a natural gas liquid sample, careful attention to detail on each step of the process must be observed. The sample must be a representative of the stream to be analyzed. The sample must be procured, transported, prepared, and injected into the chromatograph in a way that will not compromise the sample. The chromatograph must be installed with operating parameters set to allow for separation of the desired components to be easily detected, integrated, and measured. The standard must be verified and handled properly to determine the correct response factors for the detector. The instrument must be properly calibrated by an accurate standard and proper mathematical formulas used to calculate the components and physical properties of an unknown sample. Careful attention to detail will ensure an accurate representation of the product being delivered.

References:

GPA Standard 2177 – Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography

GPA Standard 2186 – Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography

GPA Standard 2198 – Selection, Preparation, Validation, Care, and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends

GPA Standard 2174 – Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography

I would like to give special thanks to Bob Armbruster, Joe Landes, Dee Orr, and PTEX for their information and diagrams that were used in this paper.