

COMPOSITION ANALYSIS IN PIPELINE GAS & NGL WITH PROCESS MASS SPECTROMETRY

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PREFACE

Mass Spectrometry (MS) can be found in most industrial laboratories for detailed compositional analysis of process fluids and gases. Though accurate, fast, and complete, laboratory analysis using MS can only provide process information regarding intermediate or final product analysis for quality control programs and production history.

MS is currently evolving from a laboratory instrument to an "on line" process analyzer so that a continuous compositional analysis can be utilized for process control purposes. There has been tremendous interest from the Natural Gas market, particularly in NGL production, for utilizing the speed of response and multi-component analysis that Mass Spectrometry can provide.

HISTORY

Since the 1950's, the Gas Chromatograph (GC) has been the workhorse for compositional analysis in pipeline gas and NGL recovery to measure gas composition in pipeline gas, fractionation overheads and bottom, and compute specific gravity, HC dew point, and fractionation ratio's for column control. The inherent speed of response of pipeline/ process gas separating through a GC column has been a hindrance in the control strategies for determining disruptions in pipeline gas quality and maximizing the fractionation process. Final product quality dependent on a GC measurement can be infrequent and delayed for several minutes. Conventional feed-back control action based on such a measurement must be strongly detuned to maintain stability of the process which results in sluggish response to disturbances

Implementation of "Advanced Process Control" (APC) in NGL fractionation to infer process upsets and compositional variations use strategies to maximize fractionation yields by monitoring process pressures, temperatures, flows, and expander speeds, which have been successful. However, their implementation and necessity has been to compensate for a slow compositional analysis that can not be used successfully in typical fractionation feedback control architectures. To maximize production yields and profits, today's producer is demanding a faster computational analysis in process feeds, pipeline gas, fractionation overheads and bottoms, than the traditional Gas Chromatography can provide.

NGL FRACTIONATION

NGL (natural gas liquids) fractionation is a process used in gas processing plants to remove NGLs from natural gas. These NGLs are Ethane, Propane, Butanes, and Pentanes plus. Since these various hydrocarbons are easily separated by their boiling point, the NGL feed is ran thru a series of fractionation towers where each tower separates one of the hydrocarbon products and sends the remaining product on to the next tower.

Once production gas has been dried and sweetened, it is first sent to the demethanizer where methane is removed from the overhead, than to the deethanizer for the ethane removal, and then on to the depropanizer, for the propane, etc.

Liquid fractionation towers are typically controlled by optimizing the inlet feed flow rate, reflux flow rate, reflux temperature, and tower pressure. Compositional analysis of the feed will dictate the optimization control parameters for the demethanizer. Overhead vapor composition provides feedback on the control scheme as to the validity of the control parameters, and a C1/C2 control ratio is computed off the bottoms liquid analysis to determine the quality of feed moving to the next tower. Further, market economics are entering in to the control scheme where decisions are made daily or even hourly to reject or recover ethane based on market prices.

It is evident that with a fast, accurate measure of feed composition, overhead product quality, and bottoms ratio, NGL fractionation can be finely tuned for economic benefit.

PROCESS MASS SPECTROMETER

Mass spectrometers use the difference in mass-to-charge ratio (m/e) of ionized atoms or molecules to separate them from each other. Mass spectrometry is therefore useful for quantization of atoms or molecules and also for determining chemical and structural information about molecules. Molecules have distinctive fragmentation patterns that provide structural information to identify structural components.

The general operation of a mass spectrometer is:

1. Create gas-phase ions
2. Separate the ions in space or time based on their mass-to-charge ratio
3. Measure the quantity of ions of each mass-to-charge ratio

COMPONENTS

In general a mass spectrometer consists of an ion source, a mass-selective filter such as a quadrupole, and an ion detector. Since mass spectrometers create and manipulate gas-phase ions, they operate at high vacuum to eliminate ion interaction. A turbo molecular pump is provided to generate the vacuum environment.

As the particular sample of interest enters the analyzer for measurement, it is bombarded by electrons generated by the ion source. The electrons ionize the molecules in the sample, thereby, with the ionized charge, they can be electrically manipulated.

The quadrupole filter is excited by a variable frequency and voltage. At a particular voltage-frequency, only one particular atomic mass can pass through the quadrupole filter to the detector. All other atomic masses can not get through the filter and are swept away. The atomic masses of interest that pass through the quadrupole mass filter are counted by a faraday cup type detector. Concentration of the sample can then be derived by the quantitative analysis of the atomic masses in the sample. Software provided with the mass spectrometer provides the interface to the operation, calibration, and outputs to the control system.

SPECIFICATIONS

Typical specification for a Mass Spectrometer:

Detection Range: 1 PPM to 100%
Sample Ports: 8, 16, or 32 way selection manifold
Inlet Pressure: 2-20 psig
Accuracy: Better than 0.1% of range
Speed of response: Seconds

SAMPLE SYSTEM

Samples may be transmitted to the Mass Spectrometer in either gas or liquids phase, but they will ultimately be analyzed in the gas phase only. Vaporizing regulators are typically used near the Mass Spectrometer to insure a gaseous sample. The Mass Spectrometer requires only a minute amount of gas to measure and is not affected by variable sample volume. Since the response time of the Mass Spectrometer is virtually instantaneous, sample transport time will ultimately determine the particular

applications speed of response. Centrally locating the analyzer and small diameter tubing such as 1/8" to reduce sample volume is recommended.

The sample manifold of a Mass Spectrometer is typically three way solenoids valves exhausting to a common exhaust header. Sample input selection can be manipulated via the analyzer software to multiplex all sample inputs sequentially or can be programmed to sample some inputs more frequently than others. When specifying the amount of sample ports, additional ports other than process points must be added to accommodate calibration gas inlets.

CALIBRATION GAS REQUIREMENTS

Due to the ionization of the sample gas, fragments are also created where a few the molecules of interest is broken apart and create additional mass to charge ratio molecules that must be compensated for to get a true compositional analysis. Mass Spectrometers will require binary gas calibration standards where the target component concentration is blended with an inert gas for a primary calibration and a blend gas which is a mixture of multiple process gases to provide a fragment calibration to compensate for the molecules created by fragments. Though some binary gases can be combined into one bottle, some installation might require up to 9 calibration standards for proper operation.

LIMITATIONS IN NATURAL GAS

Though the speed of response and multiple channels on Mass Spectrometers seems ideal for natural gas measurements and NGL fractionation, there are limitations that must be considered.

1. Due to molecule fragment creation, mass spectrometry measurement gets more complex with many components in the sample stream. Further, unknowns in the sample which are not compensated for can cause measurement errors. Mass spectrometers in natural gas applications typically quantify up to C5+. Detailed analysis of C6 and higher is not usually recommended.

2. It can be difficult to quantify Iso and Normal concentrations in Butane and Pentane, depending on the complexity of the sample. Overhead and bottoms concentrations on Butane splitters can be accomplished with a mass spectrometer, but only if heavier components are fairly small.

3. Due to the nature of H₂S, concentrations below 25 PPM are difficult to detect reliably, such as after the sweetening process or in pipeline gas. Larger concentrations of H₂S and CO₂, such as in producer gas, are easily measured.

4. Due to the difficulty in Iso and Normal separation and the complexity in C6+ measurement, custody transfer measurements and the resultant calculations such as BTU, SGU, HC Dew point are not normally recommended.

SUMMARY

The Mass Spectrometer does have applications in the natural gas industry, specifically for improved process control. The fast analysis can provide real time measurements of CH₄, CO₂, H₂S, & inerts in producer gas, Feed gas composition to the fractionation plant to determine control parameters as well as feedback compositions on the tower overhead and bottoms. The multiple input capabilities can do multiple measurement points with different compositions with one instrument.

Mass spectrometry continues it's evolution to the process environment, with configurations and cost comparable to Gas Chromatograph installations. It should be considered in future plant upgrades to improve control and plant economics.