

PROPER SAMPLING IN ACCORDANCE WITH INDUSTRY STANDARDS AND ACCEPTABLE DEVIATIONS FOR COMMON APPLICATIONS AND CONSIDERATIONS

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Introduction

This paper will discuss the fundamental ways to properly design and sample for common analyses, such as BTU determination, Moisture and H₂S. It will also outline alternative systems for these applications, considerations for sampling a supercritical fluid as well as different sampling configurations specific for various contaminants. All of the systems for the various analyses will have some commonalities but each will have minor to major alternatives to consider that could significantly change the components. The application (which includes the purpose of the analysis, gas composition and operating condition), will be the driving force when selecting the proper components. This includes coatings, membrane location, regulator placement and elastomer selection just to name a few.

API 14.1 and GPA 2166 standards will be used as guidelines when designing the proper system. The scope of the standards identifies a representative sample as a sample in the vapor state that has been separated from entrained liquids under the operating conditions. This paper will continue to explore and explain sampling considerations and alternatives beyond the scope of the standards that allow for the best analysis possible when the conditions and contaminants are such that fundamental methods will either not be possible or create an unrealistic demand of servicing of the sample system. Identifying an unconventional system that will both balance the purpose and type of analysis with system upkeep in applications that occur throughout the industry.

Industry Standards and Probe Placement

The American Petroleum Institute, the Gas Processors Association and the International Standards Organization have published the following standards that address natural gas sampling:

API Manual of Petroleum Measurement Standards, Chapter 14 – Natural Gas Fluids Measurement, Section 1 - Collecting & Handling of Natural Gas Samples for Custody Transfer, a.k.a. API 14.1

GPA 2166-05 Obtaining Natural Gas Samples for Analysis by Gas Chromatography

ISO 10715 Natural Gas Sampling Guidelines

It is important to be familiar with the contents of these standards since commercial contracts commonly require adherence to the practices specified in one or more of them.

The API 14.1 and GPA 2166 standards state that placement of the collection end of the sample probe in the center one-third of the pipe cross-section is an industry practice. Caution is given to possible probe breakage resulting from resonant vibration triggered by vortex shedding at high gas velocities. A table and calculation provide a means for determining the maximum probe insertion depth for a given probe design. For more information on this subject refer to section 7.5.2 in the GPA 2166 standard or section 7.4.1 in the API 14.1 standard. Both standards recommend using probes less than ten inches in length. The length referenced is not the distance between the inner pipe wall and probe tip but rather the length between the point of attachment and the probe tip. (Figure 1) It should be clarified that that center 1/3 is the recommendation of the standards but that does not mean center of the pipe. Proper insertion on a 12" pipeline should be 4.1".

There is also another school of thought throughout the industry that questions the need for such an insertion. The measurement community identifies 10-20% depth from the pipe wall as the start of laminar flow. The purpose of every probe is to be inserted into the flowing gas to extract a representative sample. There is no test that has identified that greater than a 20% insertion provides a more representative sample than a 15-20% insertion. The best practice in sample system design is to use the smallest and least amount of components possible to extract and condition a representative sample. This applies to probe length as well.

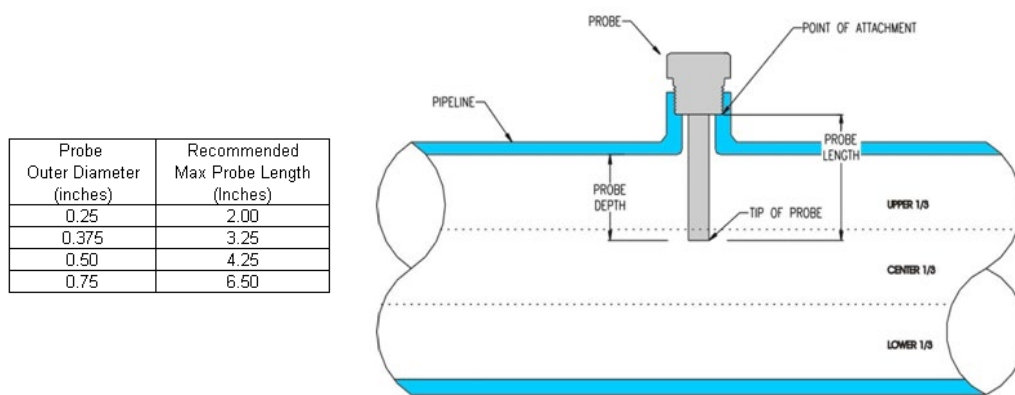


FIGURE 1. Probe dimensions used to determine recommended probe length -taken from API 14.1 and GPA 2166 Standards.

The point of attachment in some cases can be several inches from the pipe wall. It should be noted that as probe length increases its natural resonate frequency is lowered thereby lowering the gas velocity required to trigger potentially destructive vibration.

The conclusion is that one must consider the maximum source gas velocity anticipated and probe design characteristics before selecting the insertion depth of a sample probe for a specific sample location.

The probe location recommended by the API 14.1 and GPA 2166 standards is vertical mounting at the top of a horizontal pipe run. It is also recommended that the probe be placed at least five diameters downstream of a disturbing element. The referenced diameters are of the disturbing element, not pipe diameters when the disturbing element is a tube-like protrusion such as a thermocouple well. However, if the disturbing element is an orifice plate, pipe tee or elbow, filter, strainer, etc then the disturbing element diameter is considered to be the inside source gas pipe diameter.

These standards apply to transmission quality gas. All of them stress the importance of sampling above the hydrocarbon dew point and that obtaining a representative sample from a gas source near the hydrocarbon dew point is difficult. All of them acknowledge the reality that natural gas can contain hydrocarbon liquids at conditions below the hydrocarbon dew point and that natural gas can contain liquids such as oil, water, glycol, amines, or other contaminants. Clearly indicated in the scope section of each of the three standards is that none of them cover sampling from multiphase natural gas, more commonly known as wet gas. (Sampling Challenges Associated with Unconventional Sources – Mark Firmin)

Wet Gas

The term **Wet Gas** is widely used in the natural gas industry to describe anything that is not dry gas. It has not been quantitatively defined by any codes or standards body. Compliments to the flow measurement community for identifying the rudiments of a definition by assigning the term **Multiphase** to liquid dominant flow with a gas volume fraction (GVF) <80% and the term **Wet Gas** to a gas dominant flow with a GVF >80%. This definition of wet gas includes everything from a saturated vapor up to gas with up to 20% liquid by volume entrained, with no distinction between liquid contaminants and condensates. Since the range of this definition is too broad for gas sampling purposes it would behoove the analytical community to assign terms to multiple segments of the range and quantitatively define each term.

Wet gas is not always wet because it contains natural gas liquids. Sometimes it's wet because it contains liquid water or liquid contaminants such as corrosion inhibitors, treatment chemicals such as amines and even compressor oil. The lack of definition combined with the variety of possible liquids makes it difficult to determine proper sampling methods for "wet gas." (Sampling Challenges Associated with Unconventional Sources – Mark Firmin)

Phase Curve and JT Effect

It is imperative to have a good understanding of the gas as it exists at the extraction point. Illustrations for the basic parts of a generic natural gas phase boundary are shown in Figure 3. Equations of state software is an extremely useful tool for calculating the phase boundary based upon the composition of the source. The phase diagram provides a means to see how the source temperature and pressure conditions relate to the phase boundary of the fluid. This is essential in determining the analytically

correct complement of equipment that should be used to extract and precondition the sample. Selection of the most appropriate sampling equipment based upon the relation of source conditions to the phase boundary is illustrated by the phase diagram in Figure 3.

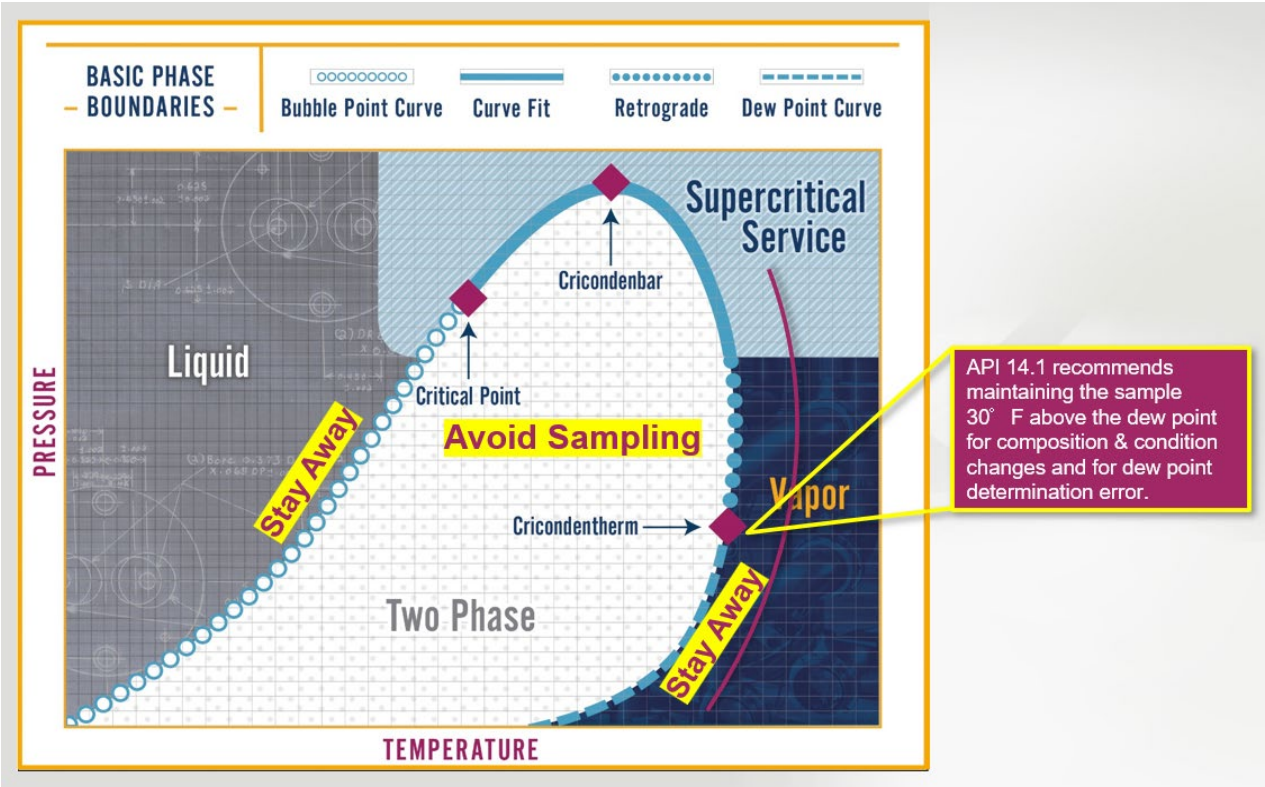


FIGURE 2. Natural Gas Phase Boundary.

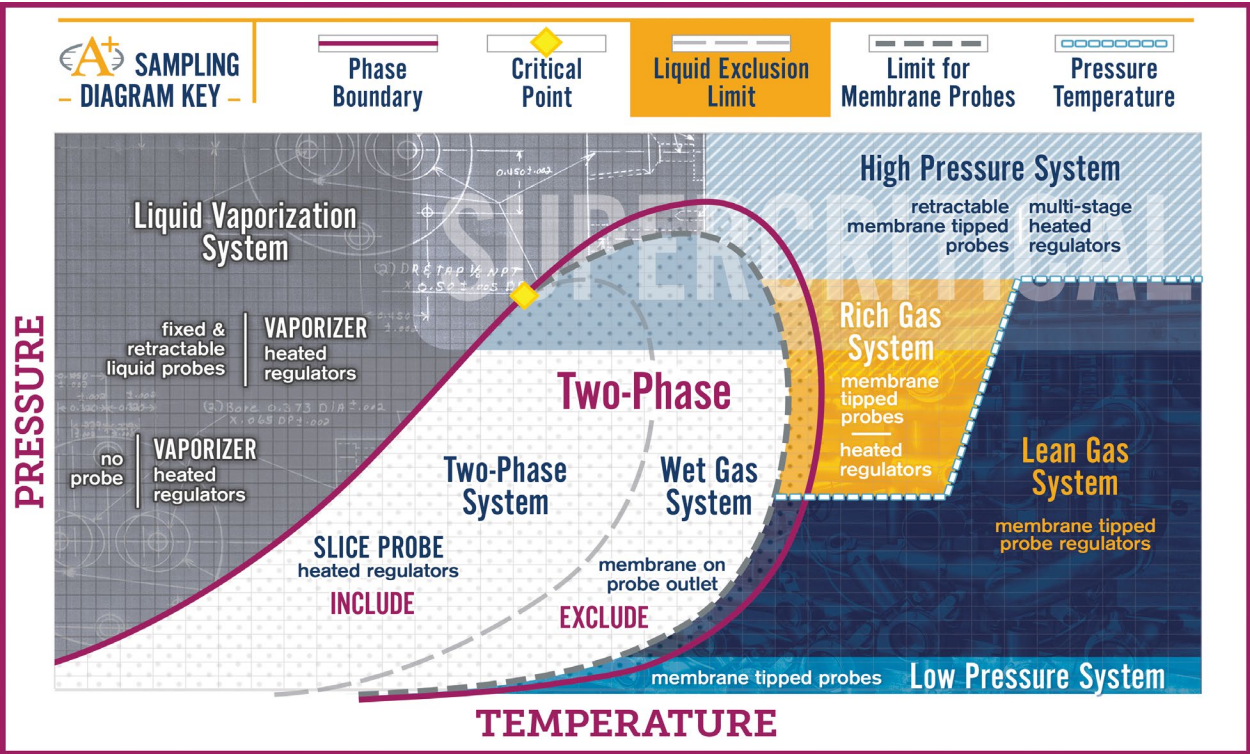


FIGURE 3. Sampling Equipment Selection with a Phase Diagram.

Natural Gas Phase Diagram

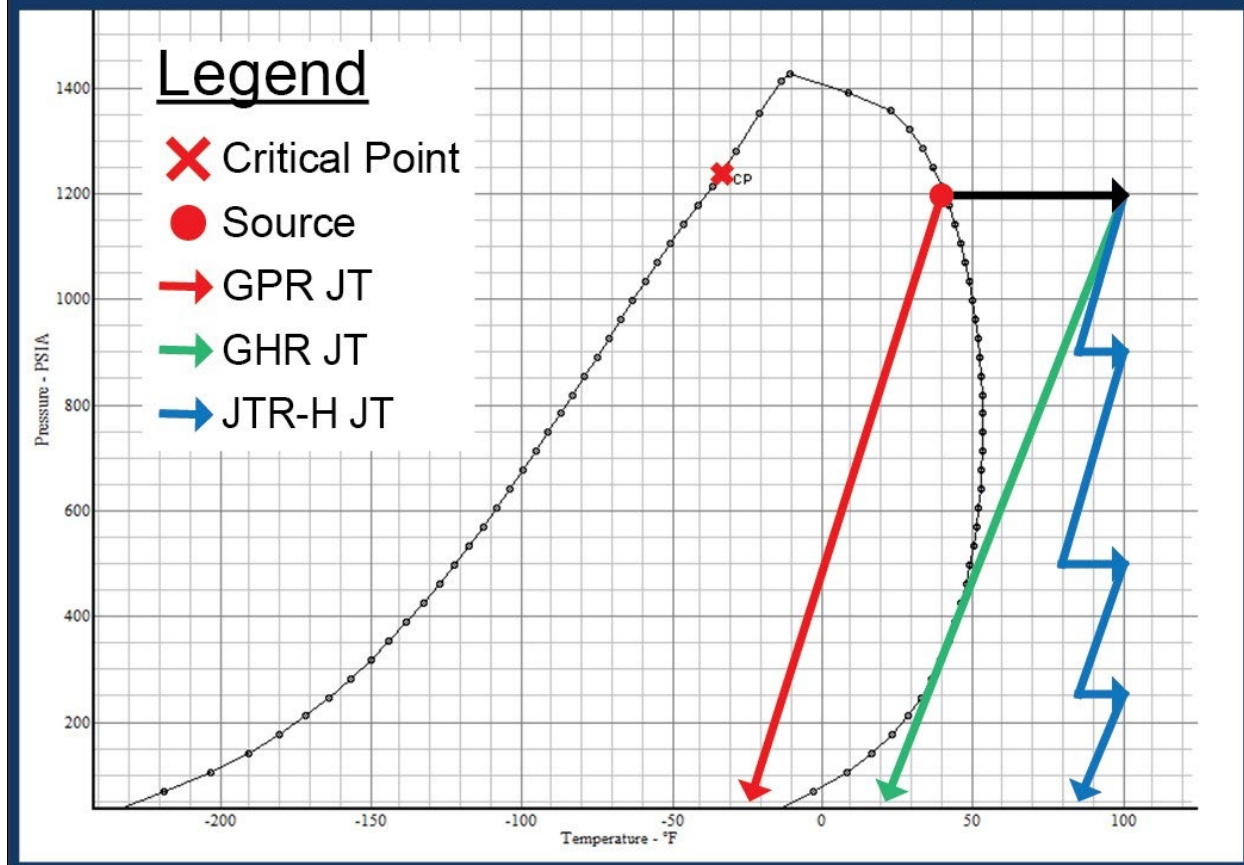


Figure 4. JT Effect with different regulation options.

+++Get updated equipment selection curve+++

The standards also recommend that gas sample temperature be maintained above the hydrocarbon dew point. Good sample system design practice is to use the conservative value of 30°F because of the uncertainty associated with hydrocarbon dew point determination. It follows that if the sample source temperature is within 30°F of the hydrocarbon dew point then the sample will need to be heated before the sample pressure can be reduced. Any liquids in the sample will of course need to be separated from the gas before it is heated, or the gas composition will be altered.

Joule-Thomson (JT) cooling occurs when compressed gas is allowed to expand in such a way that no external work is done. The JT cooling for natural gas is approximately 7° for every 100-psi dropped. Phase curves are a good tool for providing a visual representation of the JT cooling as it relates to the phase boundary. Best practice is to design a sample system that can provide a gas sample without coming within 30°F from the calculated hydrocarbon dew point while starting from the highest pressure and coldest temperature. These conditions represent the largest pressure drop closest to the dew point. A probe regulator has become the de facto standard for natural gas sampling, but it was not designed for applications where there is not enough heat to offset the cooling that would take place on a significant pressure drop. External, multistage, or multiple heated regulators in unison will. As shown in equipment selection in Figure 3 and example of choosing a multistage regulator in Figure 4. It is also imperative to reduce the pressure as close as possible to the extraction point. Not to do so would expose the sample to more likely hood of condensing out the heavier hydrocarbons and distorting the sample. Many over engineered sample systems consist of multiple “sample conditioning panels” remote from the extraction point. Transporting line pressure further than necessary with these system setups could create errors in analysis.

Sampling for BTU Determination

API 14.1 and GPA 2166-05 both advise separating the liquids from the sample in the pipeline under the operating pressure and temperature to ensure a representative sample. This is still a fundamental best practice and can be achieved accurately using a phase separation membrane tipped probe as recommended by the standards. This is imperative when hydrocarbon liquids are present because any change in the pressure or temperature of a sample of gas and liquids prior to the separation will upset the vapor liquid equilibrium of the sample and thus rendering it unrepresentative of the actual sample being measured.

The standards have not changed their stance as there had not been technology developed that is capable of being repeatable under field conditions outside of a laboratory or economical in scale to validate the expense. Sample systems that are designed not using a membrane tipped probe will almost never provide a representative sample due to vapor liquid equilibrium in combination along with the process of extracting the sample along with slippage of the extracted sample through the system. Extracting a sample of both liquid and vapor is difficult because liquid exists in a different location in the pipeline. Liquids can be present:

1. Entrained on the pipe wall with other fluids.
2. In significant percentages before and after obstacles like thermowells that shear the films of the pipe.
3. At even higher volumes where pooling may occur in dips in the pipe or build up in front of meters.
4. High presence of the flowing gas before and after an orifice.

There has been and will be a desire to extract natural gas as well as the natural gas liquids together. Extracting a sample of both liquid and gas is also problematic due to the velocity of the 2 states. A sample of both will quickly disassociate as slippage will occur. Liquids will travel significantly slower than the vapor they are extracted with. This means that even if a sample system is using a vaporizing regulator to provide a solely vapor sample for analysis, the sample will not be represented as the liquid and vapor being vaporized is not the same combination that was extracted and thus does not represent the actual source flowing through the pipeline.

A representative sample of natural gas vapor and liquids can be achieved but only if very specific requirements are met. The first requirement is to extract gas and liquid from the flowing sample and eliminate the previously mentioned hurdles. It is key to have a proper probe location 5 diameters downstream of a disturbing element or at the most laminar flow location available. The probe being used needs to be designed to allow for the flowing sample to enter and extract a small volume of the vapor and liquids. This can be achieved by having a small slit or slice on the tip facing upstream and allowing the sample to enter. It is imperative at this point to make sure the sample path sizing is comparable to capillary tubing which will prevent the liquid and gas sample from disassociating from slippage. If and only if all these steps are followed in the proper sequence, then the sample that will be vaporized using a vaporizing regulator and will be representative of the sample flowing in the pipeline.

Everything discussed is extracting gas and entrained hydrocarbon liquids. Any other liquids or contaminants present in the source will need to be confirmed capable of being vaporized by the selected vaporizing component. Extracting from a sample containing a heavy presence of contaminants that will damage the sampling components or are unable to vaporize should then use a membrane tipped probe as it will work a physical protection but still allow for a representative sample to be extracted from the source.

Sampling for Moisture Measurement

Sample systems for measuring moisture should always use a membrane and preferably at the probe tip. Moisture measurements do not happen where liquid water is present so any liquids in the line will be contaminants or liquid hydrocarbons making the "wet gas" not wet with water. A sample system designed for measuring moisture as well as BTU should only use membrane tipped probe as we will not want to use a slice type probe which would allow contaminants. An alternative solution could be available with a membrane external from the probe tip and preferably at the top of the probe if the only component being measured is moisture. This option should be considered only if there is enough entrained contamination in the sample line to make service on the probe an excessive inconvenience. Moving the membrane to a larger separator at the top of the probe will require the contaminant to pass up through the probe and be gravity drained back down the probe removing the need for a bypass or fast loop for the contaminants. This also may allow an ease of maintenance on those heavy contaminated lines but would be a deviation from the standards and is not recommended for BTU as the separation is not occurring under the operating pressure and temperature of the pipeline and render the sample not representative of the source.

Sampling for H₂S Measurement

Sampling considerations are similar to moisture measurements. A membrane tipped probe is the first choice and the only choice if 1 system is providing a combination with BTU. The largest deviation here is on common moisture measurement there will

not be liquid water however H₂S levels can vary from very low trace levels to very high percentages. Membranes that are chemically inert and separate liquids from gas based off of surface tension do a very good job of rejecting entrained H₂S. The “sticky” characteristics of H₂S though cause it to stick and coat a membrane. This is problematic for sampling as it reduces the surface area and can clog a membrane tipped probe possibly requiring a significant amount of servicing. In cases like this and others where a higher presence of contaminants on a sample for a single component, a deviation from the standards can be chosen and use a membrane separator at the top of the probe. As stated above, this allows for ease of service for the technician in the field as it will not require him to fully retract the probe or use a fixed probe. Both of which are further beneficial as an application like this containing a significant amount of H₂S can be dangerous so an isolated and easy to service.

Trace Measurement and Adsorption

Trace measurement for both Moisture and H₂S offer another avenue of sample improvement to adsorption. Adsorption is the process in which the atoms of a substance adhere to the surface. Moisture molecules will adsorb to the sampling components and tubing and will adsorb more if the sample pressure increases or temperature decreases. A moisture analyzer may produce very different results from day and night cycles. The more extreme the conditions the larger the deviation, especially on a line that is not heat traced. The molecules will desorb from the wall of the components as the temperature rises and adsorb again if the day cools or as the sun sets and temperature continues to drop through the night. This example is significant for standard moisture analysis and systems recommend using heat trace to not only protect against the cooling of the sample for hydrocarbon purposes but for adsorption as well. Regarding trace measurement, this example would be catastrophic. Trace measurement for moisture H₂S or any component should use the smallest and least components possible in the sample system. This is reduced tubing size, probe internals, valving, and filtration. Process and refining applications often require exotic materials be used for sampling due to chemical compatibility as well as adsorption but in the gas industry coatings on stainless 316 and the smallest size applicable allows for the best and economically reasonable solution for analysis. Coatings improve inertness and reduce the adsorption of molecules. Certain industry coatings are more effective than others for specific applications. Examples of these are Dursan® for moisture and SilcoNert® for H₂S.

Sampling Supercritical Fluid and General Elastomer Selection

Supercritical Fluid as a substance does not have a state like liquid or vapor. The phase is indistinguishable. This fluid is created when the pressure and temperature of a liquid and/or gas is driven past the critical point. Once the substance is supercritical, it can diffuse through solids like a gas and dissolve materials like a liquid making it imperative to select seals that are specifically designed for use in supercritical gas service. Supercritical fluid has no surface tension. This means that a membrane tipped probe will be unnecessary from an analytical standpoint however if there are any other contaminants in the process, filtration will be required, and it is still best practice to leave entrained contaminants in the source than to extract them and must remove them and treat the sample after extraction. Super critical applications are not exclusive to: Rich compositions, offshore or deep drilling locations, or what some people may call “high pressure” applications as that perspective will vary from applications and experiences. Lastly, the presence of contaminants such as H₂S, CO₂, and others are not consistently present. Supercritical applications may not be exclusive to these situations and examples but quite often will occur in them. Phase curves with full composition and plotted conditions can preemptively help with soft material selections.

Elastomer selection should ultimately be up to the end user. Even the concept of “standard pipeline quality natural gas” is a misnomer that can and does vary significantly even within the same company. The party responsible for the equipment once installed needs to do their due diligence to identify any contaminants that may cause issues with components. The damage supercritical fluid can inflict has been previously explained. Elastomers successfully used in this application have been Rapid Gas Decompression (RGD) elastomers. Another substance that can impact elastomer selection is CO₂. CO₂ will swell or attack different elastomers. Instances of compatibility may not be as drastic as destroying the elastomer while in service. The percentage of CO₂ may not affect the components while in use but may impact elastomers that are removed during routine maintenance and not allow the servicing technician to reuse them. An example would be if an O-ring is removed to change a membrane from a membrane separator and is unable to fit back in the groove it was previously in. This should lead the customer to explore other elastomer options.

Conclusion

Industry standards are important guides to proper sampling for traditional pipeline quality gas. Further exploration of the best probe depth as well as the expansion of wet gas categories will benefit the industry and sampling. Using equations of state software to generate a phase curve is a great tool for designing proper sample systems to account for proper regulation options but also to identify the presence of liquids and supercritical applications. Sampling for BTU determination requires the customer to first decide whether they wish to include or exclude the entrained liquids. Separation of the hydrocarbon liquids under the

prevailing pressure and temperature is the safest and surest way to extract a representative sample. Trying to include the liquids will distort the sample and put the analyzer at risk if specially designed, low volume system components are not selected. Moisture and H₂S measurement and other single component measurements best practice is to use a membrane tipped probe. Applications and systems that have heavy contaminants that require unrealistic servicing requirements may lead to the use of non-standard systems however best practices must be followed and never if 1 sample tap is providing a sample in combination with BTU. The purpose of the analysis should be considered, and Trace measurement is an example of the benefits of designing a system per the application. The use of low volume components and special coatings to reduce adsorption will greatly increase accuracy. Sampling from the Supercritical region requires proper regulation and elastomer selection to be done safely and properly. Other components in the gas may require different elastomers and the end user's due diligence in association with working with sample system and analyzer companies will yield the best selection of successful systems