The Physics of Natural Gas Sampling

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Accurate compositional analysis of natural gas is critically important to the natural gas industry for many reasons. Accurate measurement of water vapour content can help identify the potential for pipeline corrosion damage. Hydrocarbon dew point (HDP) temperatures determined from gas analyses can help assess if hydrocarbon condensate might form in what is intended to be a dry gas stream. In the United States, accurate gas quality data can also be crucial when introducing new gas supplies (such as shale gas, biogas, and landfill gas) into the natural gas transmission grid. Natural gas samples that do not represent the true composition of a flowing gas stream can cause unnecessary shut-ins of gas supplies that, in reality, meet safety and tariff requirements.

Industry-funded research has identified several physical and chemical causes of distorted sample compositions, which in turn has led to improved techniques for sampling natural gas streams for hydrocarbon and moisture content. Many improvements are documented in applicable industry standards, such as references [1] and [2]. The procedures in these standards are not "cookbook approaches." Rather, they are guidelines for those who design and use natural gas sampling equipment. These standards include descriptions of the physical phenomena that can produce inaccurate samples. For those unfamiliar with these phenomena, this article reviews the physics of natural gas sampling, including phenomena such as adsorption and desorption, vapour-liquid equilibrium, and Joule-Thomson cooling, and how these can be addressed.

Phenomena Affecting Sample Accuracy

Natural gas streams are routinely analysed for heavy hydrocarbons, water vapour, HDP temperatures, diluents, sulfur-containing compounds, and other components. The equipment used to analyse the stream can range from manual chilled mirror dew point analysers, to automated moisture analysers and gas chromatographs, to sample cylinders used to transport a sample to an offsite laboratory. It is critically important that all gas samples extracted from a pipeline and sent through a sample line to a container or analyser be representative of the flowing gas stream.

Distortion of natural gas samples is possible because natural gas is not a pure substance, but rather, a mixture of organic and inorganic gases. When certain components in the mixture are lost from the sample, for whatever reason, the mixture is no longer representative of the flowing gas stream. Depending on the physical mechanism that results in sample distortion, it may be the heavier hydrocarbon components, the water vapour, or the sulfur compounds that are removed from or added to the sample.

Adsorption and Desorption

One such distortion mechanism is adsorption, which is the attraction and "sticking" of gases or liquids to solid surfaces through chemical or physical processes [3]. The reverse process, the release of gas or liquid molecules from a solid surface, is desorption. Adsorption should not be confused with absorption, which is the penetration of a gas or liquid into another body, such as water into the pores of a sponge. Figure 1 shows an example of adsorption and desorption of molecules at a solid wall. Often, this adsorbed layer of gas phase molecules is no more than one molecule thick [4].

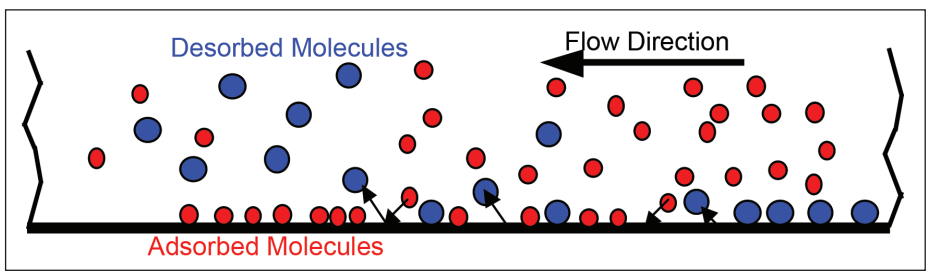

Figure 1. Adsorption and Desorption of Different Molecules at the Wall of a Sample Tube [5]

Two different kinds of adsorption affect natural gas sample collection – chemical and physical. Chemical adsorption, a chemical reaction between solid surface molecules and gas phase molecules, can be avoided by choosing materials for the inside surfaces of sampling equipment (tubing, fittings, containers, coatings, etc.) that will not chemically react with gas sample molecules. Stainless steel is a common equipment material for this reason. Viton® is a common material for o-rings and other seals, as it minimises heavy hydrocarbon adsorption. API MPMS, Chapter 14.1 recommends that sample cylinders used in sour and/or corrosive gas service should be coated with epoxy, or otherwise be passivated.

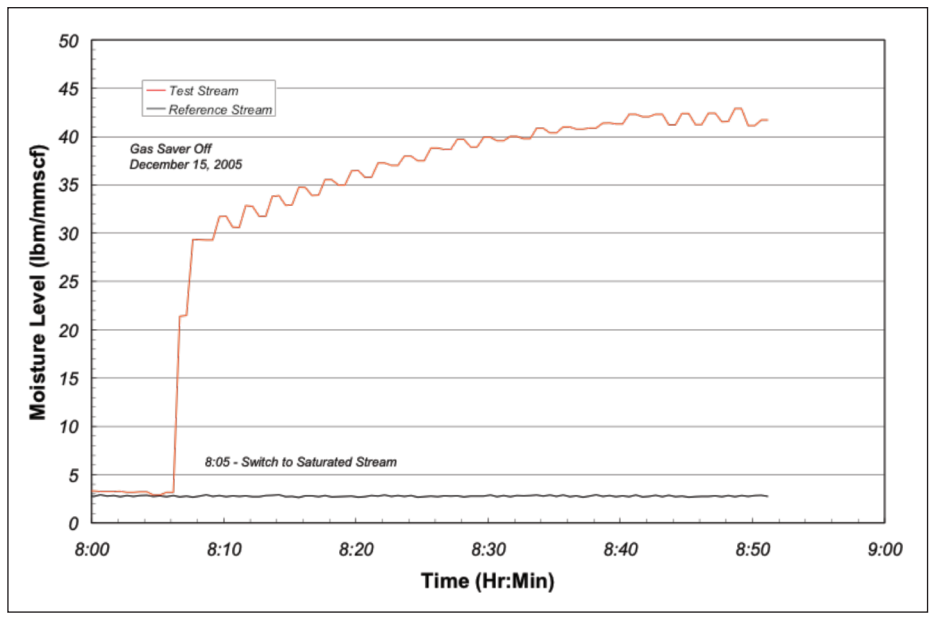

Figure 2. Response of a Real-time Moisture Analyser to the Introduction of a Moisture-saturated Gas Supply [6]

Physical adsorption is much more persistent and more difficult to deal with. Figure 2 shows how adsorption can affect the response of an online moisture analyser. In this test [6], the analyser drew gas samples from a pipeline through a heated, stainless steel sample line. After moisture-saturated gas was introduced at the sample point, the analyser took 45 minutes to register the true moisture content of the saturated gas. The delay was caused by water vapour molecules leaving the sample stream and physically adsorbing to the inside of the sample line. As the walls of the sample line gathered more and more water vapour molecules, less and less moisture was drawn from the stream. The moisture adsorbed on the sampling hardware eventually reached equilibrium with the moisture in the sample stream, and the analyser eventually registered the true moisture content of the supply. The small oscillations in moisture content were due to cycles in the heating of the sample line.

Heavy hydrocarbons and other components of a gas stream can also adsorb and desorb to equipment walls. Temperature and pressure influence adsorption equilibrium for many natural gas components, since gas molecules are more likely to physically adsorb to solid surfaces at low temperatures and high pressures. Changing the sample stream temperature and/or pressure will tend to shift the equilibrium and adsorb/desorb gas phase molecules until a new equilibrium condition is reached.

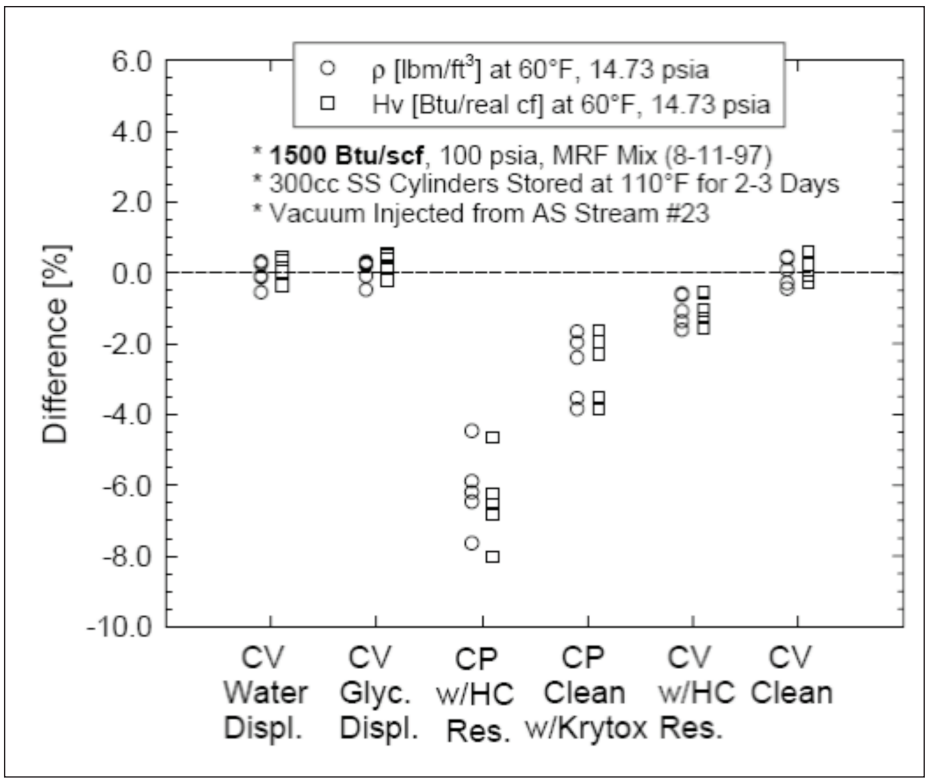

Figure 3. Effect of Residual Liquids in Sample Cylinders on the Density and Heating Value of 1,500 Btu/scf Natural Gas Samples [7].

Physical adsorption cannot be eliminated entirely from sampling systems, but several actions can minimise the sample distortion it causes. These include minimising surface areas in contact with the sample stream, avoiding porous materials such as plastics, increasing sample flow rates to speed up adsorption/desorption equilibrium, lowering the sample pressure through a regulator to promote desorption, and actively heating equipment to desorb gas molecules from the walls.

Gas Components Dissolved into Liquids

Certain liquids can dissolve significant amounts of natural gas sample components out of the gas phase. These liquids may find their way into the sampling system as residue from previous sample streams, or as solvents left behind from equipment cleaning procedures. As a rule, liquid residue with the same or similar chemical composition as components in gas samples will dissolve those components from the samples and distort the sample compositions [7].

Figure 3 shows the impact of liquids on gas sample integrity. Samples of a rich natural gas were placed in constant-volume (CV) and constant-pressure (CP) sample cylinders containing several liquid residues. The liquids included water and glycol left over from sampling procedures, a liquid hydrocarbon (HC) mixture of n-paraffin hydrocarbons and compressor oil, and DuPont Krytox® lubricant. After storage in the cylinders for two to three days, the samples were analysed to determine if components had dissolved into the contaminants and affected the sample compositions. The water and glycol liquids did not absorb heavy hydrocarbon components from the samples, and caused no notable distortion of the gas sample. In contrast, the liquid hydrocarbon residues absorbed hydrocarbon components from the gas, lowering the sample density and heating value by as much as 8%. In the test with Krytox, it was found that the cylinder seals had previously been exposed to liquid hydrocarbons. This residue was responsible for the sample distortion, not the Krytox itself.

As with adsorption/desorption, the amount of a particular component dissolved in the liquid residue will depend on pressure and temperature conditions of the sample and the amount of the component present in the sample. Similar distortion also is possible when the liquids are in a flowing sample line. When the stream pressure and temperature change in the sample line, the flowing gas sample will undergo a similar composition change as the equilibrium between component levels in the stream and in the liquid changes.

Filters are recommended to prevent undesirable liquids from reaching the sample line, analysers, regulators, or any other equipment intended for gas-only analyses. If liquids do enter sampling equipment, sample systems should be designed for thorough and easy cleaning. Research has found wet steam to be the most effective cleaning agent for removing heavy hydrocarbon liquids from sampling equipment, provided the steam does not contain treatment chemicals or corrosion inhibitors that could also contaminate the equipment [7]. Solvents that do not leave a residue after drying, such as acetone and liquid propane, are also effective.

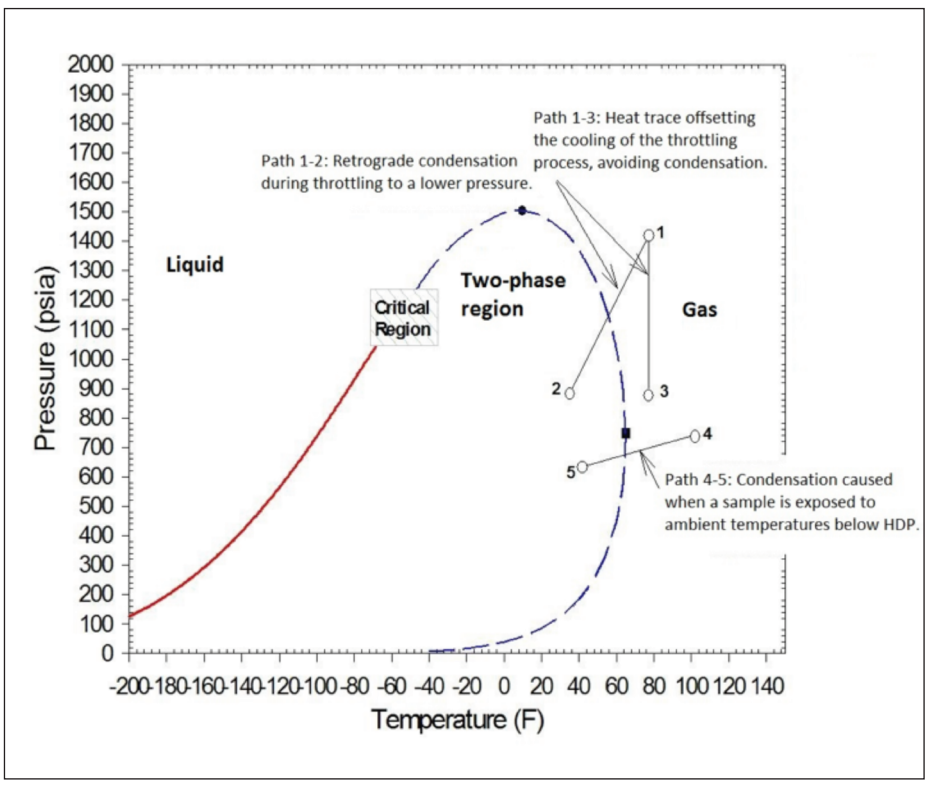

Figure 4. Natural Gas Phase Diagram Showing Common Sampling Processes that can Cause Condensation and Gas Sample Distortion [8].

Phase Changes

Ideally, a natural gas pipeline will not contain any liquids, and samples of the gas stream will remain in the gas phase during the sampling process. However, in some instances, condensation of certain natural gas components from the gas sample into the liquid phase can corrupt the gas sample. Those responsible for collecting samples should know the temperature and pressure conditions at which such condensation can occur, and control sampling conditions accordingly.

In natural gas applications, the dew point is the pressure and temperature at which specific components in a natural gas mixture begin to condense from the gas and form a liquid phase [8]. The temperature and pressure condition at which hydrocarbons begin to condense from the gas phase is known as the hydrocarbon dew point (HDP), while the condition at which water vapour begins to condense from the mixture is called the water vapour dew point (WVDP). As the pipeline pressure changes, the temperature of each type of dew point changes also, creating dew point curves that vary with the content of the natural gas, as well as with temperature and pressure.

The HDP curve is considered critical to sample integrity. Research has confirmed that allowing the gas sample pressure and temperature to cross the HDP curve into the gas-liquid two-phase region will distort the sample composition, and will lead to errors in properties such as heating value and density calculated from the sample analyses. Several processes common to natural gas sampling can cause the temperature and pressure of the sample to cross the HDP curve, as shown in Figure 4. These include the Joule-Thomson cooling that occurs when natural gas is "throttled" through a regulator or partially closed valve (path 1-2 on Figure 4), and the cooling that can occur if the sample container and its contents are exposed to an ambient temperature below the hydrocarbon dew point temperature (path 4-5). Such cooling can be avoided by applying sufficient heat to the sampling equipment, as shown by path 1-3.

The effects of poor sampling technique on gas samples taken under actual laboratory and field conditions are complicated and cannot be accurately predicted using current technology. However, if the hydrocarbon dew point has been reliably measured, or the gas stream has been sampled and reliably analysed using equipment heated well above the flowing stream temperature, the dew point curve or phase diagram can be used to select appropriate equipment for future sampling and analysis applications.

Conclusion

This article has reviewed several chemical and physical phenomena that can change the composition of a natural gas sample, thereby corrupting the sample and leading to inaccurate analysis of the gas properties. Research has led to techniques and standards for preventing these phenomena and avoiding their possible adverse effects on sample accuracy. Proper use of the phase diagram and knowledge of thermodynamics of the flowing stream will allow users to select equipment that will avoid significant losses in hydrocarbon content and underestimates of water vapour content, which in turn can cause unnecessary production shut-ins or inequities in custody transfer.

References

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