RESEARCH TOPICS INFLUENCING CHANGES TO THE API 14.1 STANDARD

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Introduction

The American Petroleum Institute (API) Manual of Petroleum Measurement Standards (MPMS) Chapter 14.1, *Collecting and Handling of Natural Gas Samples for Custody Transfer*, provides practical guidance for gas sampling in custody transfer applications. It is intended as a collection of lessons learned and best practices, and as such, it is a living document.

In support of this, API, the Gas Technology Institute (GTI), the United States Minerals Management Service (MMS), and the Pipeline Research Council International (PRCI) co-sponsored an extensive natural gas sampling research program at the Metering Research Facility (MRF), located at Southwest Research Institute (SwRI®). The body of this research was conducted between 1999 and 2005 and supported the most recent revision of API 14.1, published in 2006.

Research into natural gas sampling has continued after the closing of the API 14.1 research project, and the standard will continue to be updated as the body of knowledge progresses.

The Importance of the Hydrocarbon Dew Point

In natural gas sampling applications, it is important to be familiar with the hydrocarbon dew point (HDP) and to be aware of how it can affect your sample's accuracy. This is different from the water dew point, which is another topic of concern, but will not be discussed in this paper. An example image of the HDP as viewed in a chilled mirror device is shown in Figure 1.

The HDP is defined as the temperature for a given pressure at which hydrocarbon condensation begins (1). The HDP is often plotted on a temperature versus pressure chart as shown with the dashed blue line in Figure 2. To the right of the HDP curve and above the critical temperature, no liquids will be present. As the pressure-temperature state moves to the left of the HDP curve, liquids will condense, and a natural gas sample will contain gas and liquid phases simultaneously.

Figure 1. Gas at the Hydrocarbon Dew Point in a Chilled Mirror Device

In the image above, faint droplets are visible on the mirror with an iridescent ring around the perimeter of the mirror. This indicates that the HDP has been reached (1).

Note that the curve passes through or near common pipeline operating temperatures and pressures in a variety of locations. A common process that causes a gas to condense is known as the Joule-Thomson (J-T) effect and is caused by a gas cooling as its pressure drops. This process can be encountered in sampling systems if a gas sample flows through a restriction such as a partially open needle valve. If this is the case, the gas and equipment must be warmed enough to counteract the J-T cooling effect. Many of the guidelines outlined in API 14.1 are aimed at avoiding this transition during sampling.

The HDP curve shown in Figure 2 below is an approximation, and the true HDP curve can be difficult to predict accurately for some pipeline gases. Because different components condense at different temperatures and rates, crossing the HDP curve will change the density, heating value, and many other properties of the remaining gas. Generally, heavy hydrocarbons condense before lighter components causing a drop in the measured heating value and density – two key measurements in custody transfer applications.

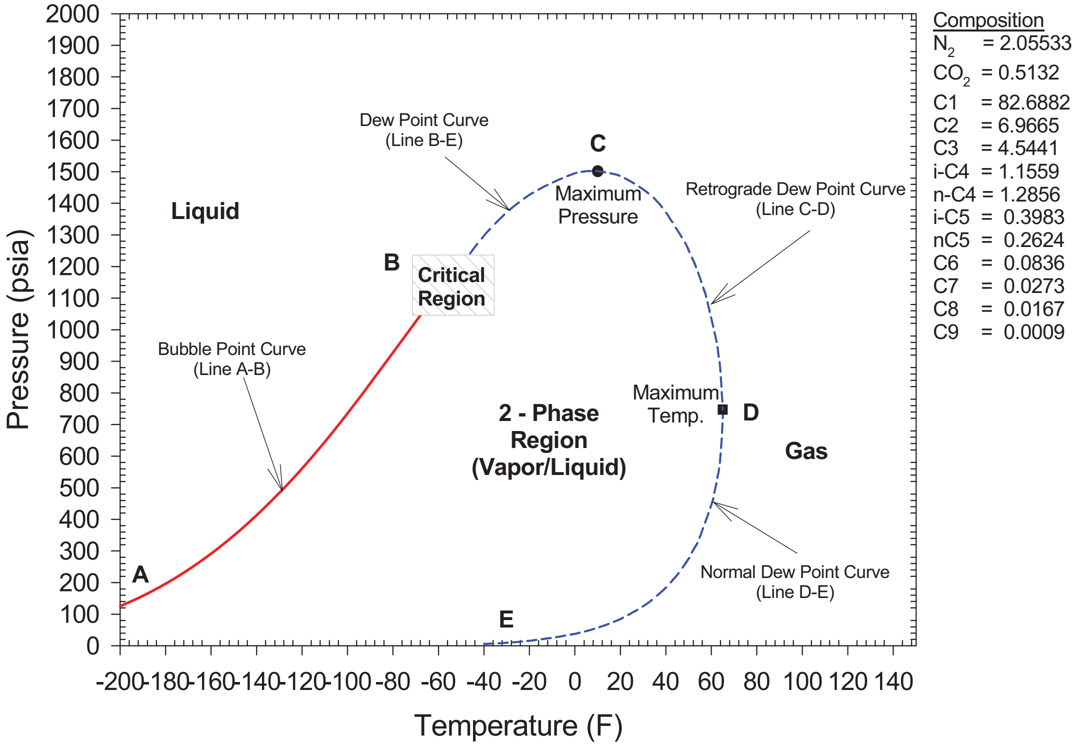

Figure 2. Pressure vs Temperature Plot of a Hydrocarbon Dew Point Curve

An example plot of a phase boundary curve for a typical natural gas mixture is shown. The blue line represents the HDP curve (2).

If a gas sample has changed phase within the sample cylinder, and the cylinder has not been opened, the condensation process may be reversed. This is accomplished by heating the sample cylinder above the predicted HDP for enough time to revaporize all of the condensation. The standard requires that the sample cylinder be held at 30°F above the HDP for at least two hours. This revaporization must be conducted before any liquid or gas has been removed from the sample cylinder, or the gas sampled by the GC and that remaining in the cylinder will both be distorted.

As an example of the effects of condensation, consider a mix of 1,500 Btu/scf gas with the components shown in Table 1. This gas is rich but is well within the range of natural gases found upstream of processing stations. If this gas were at 75 psia, the HDP would be roughly 91°F. A drop of 40°F below the hydrocarbon dew point would cause condensation and would cause the remaining gas to have a heating value 70 Btu/scf lower than the sampled gas stream. This would coincide with only a 3% drop in vapor fraction. If this occurred in a 300 cc cylinder at 75 psia, the condensed liquid would be less than 1/1,000 of a pound, a small enough amount to easily avoid detection (2). If this condensation were to occur in a crevice or other difficult to clean area, it could contaminate a later sample and increase its measured heating value (3).

Table 1. Composition of an Example Gas Mixture with a Heating Value of 1,500 Btu/scf

Component	Mole Percent
Methane	64.107
Ethane	10.330
Propane	7.128
Iso-butane	2.174
Normal butane	6.386
Iso-pentane	1.874
Normal pentane	2.307
Normal hexane	0.538
Normal heptane	0.187
Normal octane	0.086
Normal nonane	0.023
Normal decane	0.016
Nitrogen	3.939
Carbon dioxide	0.906
Total	**100.001**

Changes to API 14.1 for the 2006 and Later Revisions

Several changes were made to the most recent edition of API 14.1, most of which were aimed at collecting and preserving representative gas samples. These changes respond to continuing research and the changing compositions of gas found in nontraditional sources that are more and more common. They also address increased flow rates through larger diameter lines and associated challenges.

Equipment Heating Requirements

One of the changes most relevant to avoiding the HDP is the change to equipment heating and insulation requirements. The previous editions of API 14.1 called for samples to be maintained at 20-50°F above the predicted HDP. This requirement was separate from the heating required to compensate for Joule-Thomson cooling. It covered all equipment that comes in contact with the process gas and was intended as a safety margin that would ensure that the gas was above its true HDP. The standard also gives guidance as to how to properly heat or insulate equipment in order to consistently meet the required temperature.

The 2006 edition of API 14.1 addresses recent research showing better agreement between the HDP predicted by common equations of state (EOS) and that measured experimentally (4; 5). The research found that common EOS could under predict HDPs of common natural gas streams by as much as 30°F, with larger errors for richer gases and higher pressures. Accordingly, the 2006 edition requires that sampling equipment be kept at least 30°F above the predicted HDP. It does allow operators to use a lower margin if the difference between experimental and predicted hydrocarbon dew points has been shown to be less than 30°F for the gas of interest. This requirement is once again separate from the heating requirements imposed by Joule-Thomson cooling.

Sample Probe Length and Location

As natural gas production has increased, flow rates through existing pipelines have correspondingly increased. As a consequence, industry has witnessed large diameter pipelines flowing gas at higher pressures and velocities than ever before. This combination of longer probes required by larger diameter pipelines and higher velocities has increased the fatigue loading on probes as they begin to resonate. If not accounted for by the probe designer, fatigue loading can cause probes to fail catastrophically and to be swept downstream into other equipment.

API 14.1 gives equations and other guidance for selecting sample probes appropriately to avoid these failures. For example, in Table 2, the maximum length for probes is recommended based on common probe diameters. The new edition of API 14.1 clarifies many of these guidelines based on recent research findings. Probes should be mounted vertically at the top of a straight run of pipe. If the gas is not near its HDP, the probe may be placed at any axial location in a meter run that doesn't interfere with the performance of the primary metering element (1). However, if the gas is at or near its hydrocarbon dew point, the probe should be at least five nominal diameters downstream from any major disturbances. This is designed to avoid ingesting liquid droplets that could be condensed out of the gas or swept into the gas in the wake of the disturbance. Some of the major disturbances listed are orifice plates, elbows, tees, and flow conditioners (1).

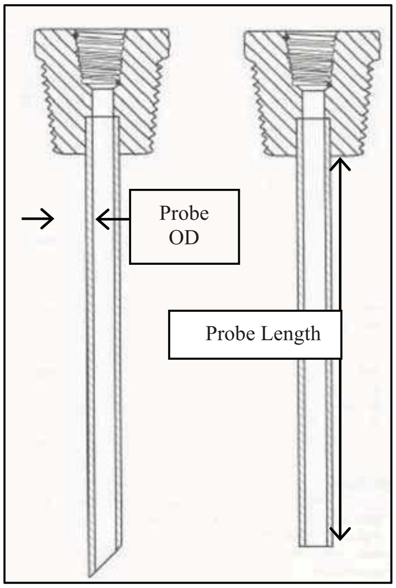

Figure 3. Two Example Sample Probes
Sample probes are shown with beveled (left) and straight-cut (right) ends. Straight-cut probes are preferred over beveled probes (1). Recommended values for the labeled dimensions are shown in Table 2.

Table 2. Maximum Probe Length Recommendations for Common Probe Diameters

Probe Outer Diameter (in)	Recommended Max Probe Length (in)
.250	2.00
.375	3.25
.500	4.25
.750	6.50

Sampling Methods

API 14.1 references GPA Standard 2166 (6) regarding spot sampling methods, and API 14.1 was updated in the 6th edition to reflect changes in the corresponding GPA document. The main change in this portion of the standard is related to the fill-and-empty method of sampling. In this sampling method, a length of tube must be installed downstream of the sample cylinder with a flow restriction at the end of the tube. This flow restriction forces the pressure drop to occur at the orifice instead of inside of the sample cylinder and reduces the risk of condensation inside the cylinder itself. The previous edition of the standard required that this flow restriction be a drilled plug. The new method allows for other flow restrictions and specifically calls out the devices with a flow coefficient (Cv) between 0.09 and 0.53. One device specifically called out is a partially-open needle valve, although any device is allowed as long as it meets the requirements for thermal isolation and throttling.

Guidelines for Laboratory Analysis

API 14.1 gives guidance on laboratory sample analysis, and the 6th edition adds guidance to the preparation of gas chromatograph (GC) calibration standards. For example, it requires that laboratories meet the GPA operational requirements laid out in GPA Standard 2198 (7). API 14.1 now requires that GC calibration standards be prepared according to GPA 2198-98 and calls out specific requirements from that standard. It requires that gases must be gravimetrically prepared; that is, each component must be weighed as it is added to the mixture. It requires that those measurements be traceable back to NIST or an equivalent standards body. API 14.1 requires that each component of a given GC calibration mixture be screened for impurities and that any impurities be accounted for in the final composition. It also calls out the required accuracy of the composition as shown below in Table 3. This guideline requires that the accuracy of each component's concentration fall within the specified ranges based on the nominal concentration. Please note that important changes to this table are currently being considered and may appear in future versions.

Table 3. Required Blending Accuracy

The table below illustrates the required accuracy for GC calibration standards. These guide the required accuracy for each component based on what percent of the total composition it comprises (7).

Percent Concentration (mole %)	Percent Accuracy
0 to 0.099%	5%
0.10 to 9.999%	2%
10.0% to 100%	1%

Auto-Ignition Addendum

A new addendum was included in the 6th edition to reflect industry concerns regarding auto-ignition in sample containers. There is a theoretical possibility of auto-ignition if a sample cylinder is not properly purged and filled. Specifically, if a sample cylinder is stored at a low pressure and then is rapidly pressurized with gas, a shockwave could occur within the cylinder. This shockwave would compress the gas at its forefront and correspondingly heat it. If this heating brought the gas above its auto-ignition temperature and the cylinder had also contained oxygen before the rapid filling process, a combustion process could occur. This process would require an inlet valve with a large flow area that was opened very quickly, as with a large quarter turn valve. API 14.1 notes that API is not aware of this actually occurring in the field, but the process is possible in theory (1).

Measuring Hydrocarbon Dew Points

One of the newest additions within the 6th edition of API 14.1 is an addendum containing guidance on experimentally determining the HDP for a specific gas. The addendum references the ASTM D1142 standard for measuring water dew points using a chilled mirror device for general design and use guidelines for such a device (8). The addendum expands on this standard and applies its guidelines to the measurement of the HDP in gas mixtures (1).

These guidelines also require a visual observation port, meaning that automated devices do not meet the requirements of the addendum. The procedures recommended were developed using a combination of practical industry knowledge and applied research. This research investigated various methods of using and maintaining chilled mirror devices and established uncertainty values for the use of chilled mirrors (5). The addition to API 14.1 provides illustrations of different observations that an operator could make within a chilled mirror device during normal use and while diagnosing problems. A few of these examples are shown in Figure 4.

Figure 4. Example Images Collected Using a Chilled Mirror Device

Clockwise from the top left, these images show hydrocarbon condensation, water condensation, glycol contamination, and alcohol condensation (5).

Checklist for Inspecting Field Sampling Locations

The Bureau of Land Management will be referencing API 14.1 within its regulations and has requested a standard checklist for inspecting field sampling locations. This checklist has been added as an addendum to API 14.1.

Current Research and Future Topics

Heavy Hydrocarbon "Lumping" Models

One persistent challenge within hydrocarbon measurement is the measurement of hydrocarbons heavier than hexane. The hydrocarbons are often not measured individually by a GC and are reported as a combined total. These hydrocarbons comprise a small portion of common natural gas mixtures but have a significant impact on the mixture's density, heating value, and HDP; therefore, various models have been developed for characterizing these components.

Research has shown that currently there is no single characterization method that works best for all gas streams (5). The research did show that C6+ lumping did not provide sufficient resolution to accurately predict the HDP and could bias the predicted HDP by up to 70°F. This is more than three times greater than the differences between various EOS. It was shown that C9+ characterization was adequate to predict the HDP to within ±25°F in most cases. Where this is not possible because of GC limitations, the GPA 60/30/10 method of characterizing heavy hydrocarbons also generally predicted the HDP with accuracies within ±25°F (5). There are other characterization models available, and questions remain about the various characterization models and how well they work when used with different EOS (9).

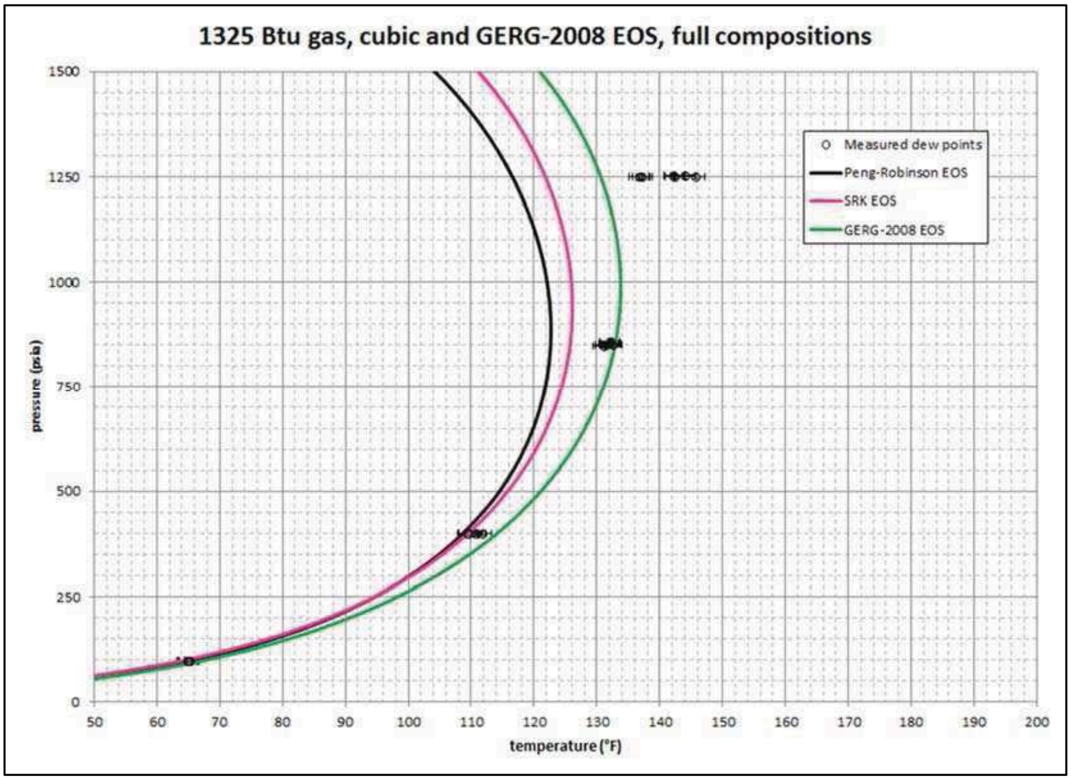

Figure 5. Predicted versus Experimental Hydrocarbon Dew Point

The above plot compares experimentally-measured hydrocarbon dew points to the P-R EOS (black line), the SRK EOS (pink line), and the GERG-2008 EOS (green line). This is for a typical natural gas mixture at common pipeline pressures

New Equations of State (EOS)

EOS are used within the oil and gas industry in order to predict the HDP for a gas when given its composition and pressure. Research into a general EOS for natural gas applications has been ongoing for several decades and continues today. As discussed earlier, these equations only predict the HDP to within tens of degrees at pipeline conditions. Current models such as the Peng-Robinson (P-R) EOS and Soave-Redlich-Kwong (SRK) EOS predict the HDP well for lighter gases at lower pressures, but often under-predict the HDP when these conditions change. This is illustrated in Figure 5 above where both EOS are plotted with experimental data for comparison. These two EOS were developed using different data sets and; therefore, one will generally match a certain composition of gas better than the other.

In order to address these inaccuracies, many organizations continue to attempt to develop EOS that will accurately predict the HDP for the variety of compositions and pressures witnessed in modern pipelines. New and promising EOS were developed at Ruhr-Universität Bochum (the University of Bochum) in Germany and are known as GERG-2008 (10). The equation uses a thermodynamic property known as the Helmholtz free energy in order to predict the properties of gas mixtures. Using this property as a key variable, GERG-2008 predicts properties of gas mixtures that can be used to determine phase boundaries. This equation has shown improved agreement with existing data, especially at higher pressures and for richer gases (see Figure 5 above). GERG-2008 is becoming more commonly used within the industry and will be included in the newest version of AGA-8.

Conclusion

API 14.1 serves as a living document that operators can use as a reference for practical guidelines related to natural gas sampling in custody transfer applications. As a living document, it continues to be revised in order to reflect modern technologies and changes in the natural gas industry. As natural gas production from nontraditional sources continues to increase, the technology will continue to improve, and API 14.1 will grow and improve accordingly.

References

1. API Manual of Petroleum Measurement Standards, Chapter 14 – Natural Gas Fluids Measurement, Section 1 – Collecting and Handling of Natural Gas Samples for Custody Transfer, American Petroleum Institute, Washington D.C., February 2006.
2. George, D. L. and Kelner E., *Lessons Learned from the API MPMS, Chapter 14.1 Gas Sampling Research Project*. Houston, TX, Proceedings of the 2014. American School of Gas Measurement Technology.
3. Metering Research Facility Program: Natural Gas Sample Collection and Handling-Phase I, Behring, K.A. III and Kelner, E., GRI Topical Report No. GRI-99/0194, Gas Technology Institute, Des Plaines, Illinois, August 1999.
4. Metering Research Facility Program: Natural Gas Sample Collection and Handling-Phase V, George, D. L., Burkey, R. C., and Morrow, T. B., GRI Topical Report No. GRI-05/0134, Gas Technology Institute, Des Plaines, Illinois, March 2005.
5. Metering Research Facility Program: Natural Gas Sample Collection and Handling-Phase IV, George, D. L., Barajas, A. M., Kelner, E., and Nored, M., GRI Topical Report No. GRI-03/0049, Gas Technology Institute, Des Plaines, Illinois, January 2005.
6. GPA Standard 2166, Obtaining Natural Gas Samples for Analysis by Gas Chromatography, Gas Processors Association, Tulsa, Oklahoma, 2005.
7. GPA Standard 2198, Selection, Preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends, Gas Processors Association, Tulsa, Oklahoma, 2003.
8. ASTM Standard D 1142, *Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew Point Temperature,* ASTM International, West Conshohocken, PA, 1995.
9. Laughton, A., *Use of the GERG-2008 Equation of State for Hydrocarbon Dew Point Calculation*. Grapevine, TX, Proceedings of the 2015 American Gas Association Operations Conference.
10. Kunz, O., Klimeck, R., Wagner, W., and Jaeschke, M., *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures.*, GERG TM 15, 2007.
11. Metering Research Facility Program: Natural Gas Sample Collection and Handling-Phase II, Kelner, E., Britton, C. L., Behring, K.A. III and Sparks, C. R., GRI Topical Report No. GRI-01/0069, Gas Technology Institute, Des Plaines, Illinois, January 2003.
12. Metering Research Facility Program: Natural Gas Sample Collection and Handling-Phase III, Kelner, E., Sparks, C. R., and Behring, K.A. III, GRI Topical Report No. GRI-01/0070, Gas Technology Institute, Des Plaines, Illinois, August 2002.