

## LESSONS LEARNED FROM THE API MPMS, CHAPTER 14.1 GAS SAMPLING RESEARCH PROJECT

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### **Introduction**

Between 1999 and 2005, the Gas Technology Institute (GTI), the American Petroleum Institute (API), 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 results of this research provided a basis for the most recent revisions to the API Manual of Petroleum Measurement Standards (MPMS) Chapter 14.1, *Collecting and Handling of Natural Gas Samples for Custody Transfer*. The research supported revisions that produced both the 5<sup>th</sup> edition of the standard, published in 2001, and the 6<sup>th</sup> edition, published in February 2006.

The API Chapter 14.1 Working Group, a research steering committee consisting of natural gas sampling experts from major oil and gas companies, guided the project in order to improve current field practices. The research identified several causes of natural gas sample distortion, field techniques for avoiding gas sample distortion, and potential sources of error in the characterization of natural gas samples [References 1 through 6]. The research results were used to develop guidelines in API MPMS Chapter 14.1 for obtaining and analyzing representative samples of natural gas. The standard focuses on the practical application of thermodynamic principles that, if ignored, can distort a gas sample and result in a biased gas analysis. As will be shown in this paper, such a biased analysis can produce errors in heating value or other gas properties in excess of 10 percent.

As with the preceding editions, the 6<sup>th</sup> edition of API Chapter 14.1 [Reference 7] built on the knowledge contained in previous versions. The standard identifies several specific causes of natural gas sample distortion and provides recommendations for avoiding it. The 5<sup>th</sup> and 6<sup>th</sup> editions were also written as an instructional tool and a guide for proper sampling system design and sampling techniques. The standard is written primarily for field personnel and provides the technical background needed to understand and apply basic hydrocarbon mixture thermodynamics to natural gas sampling in order to avoid sample distortion. The 6<sup>th</sup> edition contains much of the same information as the 5<sup>th</sup> edition and follows the

same format, but was updated to reflect the results of research since 2001 on hydrocarbon dew point prediction and preparation of natural gas standards for calibrating gas chromatographs (GCs).

This paper begins with a discussion of the importance of the hydrocarbon dew point in gas sampling methodology and sampling system design. The discussion includes an introduction to the natural gas phase diagram, an example of the impact of distorted gas samples on heating value accuracy, and an example of the need to characterize correctly a gas sample for dew point calculations. This paper then describes the additions and changes to API Chapter 14.1 appearing in the 6<sup>th</sup> edition, along with the results of research supporting many of these changes.

### **The Importance of Hydrocarbon Dew Point in Natural Gas Sampling**

**Definitions.** The hydrocarbon dew point is defined as the pressure and temperature at which hydrocarbon constituents in a natural gas mixture begin to change phase. For instance, if the temperature of a natural gas mixture is reduced while the pressure remains constant<sup>1</sup>, the temperature at which hydrocarbon condensation begins to occur is the hydrocarbon dew point temperature. If the pressure of a natural gas is increased while the temperature remains constant<sup>2</sup>, the pressure at which hydrocarbon condensation begins is the hydrocarbon dew point pressure.

The hydrocarbon dew point of a natural gas differs from the water dew point in that the latter describes the pressure and temperature at which water vapor contained in the gas mixture begins to condense. Some gas mixtures will reach the water dew point temperature before reaching the hydrocarbon dew point temperature during an isobaric temperature reduction. This paper focuses on the hydrocarbon dew point because of its

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1. This process is known as an *isobaric* (or constant pressure) temperature reduction. It is the process that occurs when a "chilled mirror device" is used to determine dew point in the field.

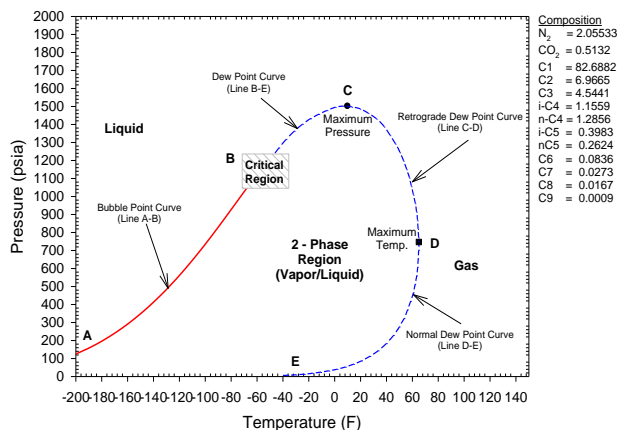
2. This process is also known as an *isothermal* (or constant temperature) pressure increase and is similar to processes used for determining the dew point in a laboratory.

influence on heating value. This distinction should be kept in mind during any discussion of natural gas thermodynamics.

Retrograde condensation is a phenomenon that occurs in many common natural gas mixtures. It is characterized by the presence of two hydrocarbon dew points at a given pressure or temperature. Retrograde condensation can occur during isobaric temperature *increases*, or during isothermal pressure *reductions*. Retrograde behavior is a characteristic of natural gases and should be considered both when sampling a natural gas stream and when designing gas sampling systems.

**The phase diagram.** A phase diagram, or phase envelope, describes the phase change behavior of a natural gas mixture. It can be used to illustrate the effect of natural gas sampling processes on natural gas.

Figure 1 shows a typical phase diagram for natural gas. Line A-B is the bubble point curve. The bubble point is reached when an infinitesimal amount of gas appears during an isothermal pressure reduction of a liquid hydrocarbon mixture.



**Figure 1. A typical natural gas phase (P-T) diagram.**

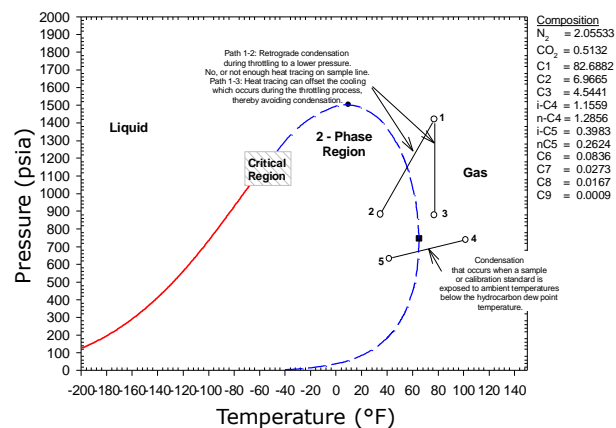
Line B-C-D-E is the dew point curve. It represents the range of pressures and temperatures at which gas/liquid phase changes occur with a natural gas mixture. The points along line B-C-D represent the pressures and temperatures at which retrograde condensation occurs, that is, condensation during temperature increases at constant pressure or during pressure reductions at constant temperature. Note that the range of pressures and temperatures of the retrograde dew point curve can be encountered during common natural gas sampling processes.

Line D-E is the lower, or normal, dew point curve. Condensation associated with the conditions defined by this curve may occur during a pressure increase, such as when compressing a gas sample from a vacuum gathering system into a sample cylinder, or during a temperature

reduction, such as occurs when a full sample cylinder is exposed to cold ambient temperatures.

**Hydrocarbon dew points and sample distortion.** The hydrocarbon dew point is perhaps the single most important property to consider in natural gas sampling. If the sample temperature drops below the hydrocarbon dew point temperature, a significant loss in hydrocarbon content can occur, resulting in errors in volumetric flow rate, heating value, and other gas property calculations.

Tests conducted at SwRI on spot sampling methods showed that allowing the gas sample to drop below the hydrocarbon dew point temperature contributes to increased random and bias errors in the calculated heating value and density. The phase diagram shown in Figure 2 illustrates how different processes common to natural gas sampling can cause the temperature of the sampled gas to fall below the hydrocarbon dew point.



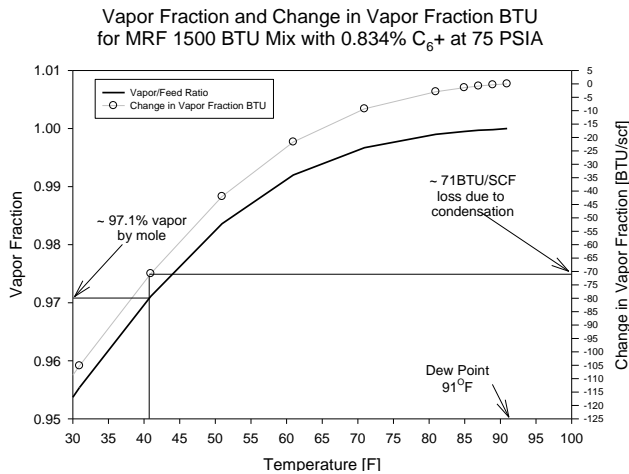
**Figure 2. A natural gas phase diagram showing several common processes in natural gas sampling that can cause condensation and gas sample distortion.**

Path 1-2 represents the cooling process, known as Joule-Thomson cooling, which occurs when natural gas flows through a regulator or partially closed valve and undergoes a pressure reduction. Condensation and sample distortion can occur during this “throttling” process. The cooling can be offset through the application of sufficient heat to the sampling system, as shown by Path 1-3.

Path 4-5 shows how condensation of a sample can occur if the sample container is exposed to an ambient temperature below the hydrocarbon dew point temperature.

**The effect of a phase change on heating value.** With the concepts behind hydrocarbon dew points and phase change introduced, the potential impact of phase change on natural gas heating value can now be illustrated graphically. Figure 3 shows the potential effect of 41°F gas sampling equipment on the 1,500 Btu/scf natural gas

composition listed in Table 1. This gas contains 0.85 total mole percent of components n-hexane through n-decane (commonly labeled C<sub>6+</sub>), and has a hydrocarbon dew point of 91°F, 50 degrees above the equipment temperature.



**Figure 3. The change in vapor fraction and vapor fraction heating value associated with condensation of a 1,500 Btu/scf natural gas mixture.**

In Figure 3, the horizontal axis shows the temperature of the gas or gas-liquid mixture. The vertical axis on the left shows the vapor (gas) fraction on a molar basis. The liquid fraction is simply one minus the vapor fraction. The vertical axis on the right shows the change in vapor fraction heating value, in Btu/scf, as liquid condenses from the gas sample.

| 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          |
| <b>Total</b>   | <b>100.001</b> |

**Table 1. The 1,500 Btu/scf natural gas mixture used to calculate the values in Figure 3.**

Assume that a representative sample of the natural gas in Table 1 is contained in a standard 300 cc constant volume sample cylinder. Suppose that the sample is collected at a temperature above the hydrocarbon dew point, but then the cylinder and its contents are exposed to an ambient temperature of 41°F. The process described in this example is similar to the process shown by Path 4-5 in Figure 2. As the temperature is reduced below the hydrocarbon dew point temperature, hydrocarbon constituents condense, preferentially in order of decreasing molecular weight (heaviest components first). This condensation causes a decrease in the vapor fraction of the mixture and a corresponding decrease in the heating value of the vapor phase. Because the heavier components condense first, Figure 3 shows that a small amount of liquid condensation is associated with a large decrease in heating value. At a temperature of 41°F, the loss in heating value amounts to over 70 Btu/scf.

The weight of the condensed liquid in this simple example can be estimated. The total mass of gas (vapor) in the cylinder at the original conditions of 75 psia and 91°F is approximately 0.0045 lb<sub>m</sub>. When the temperature is reduced to 41°F, condensation occurs and the vapor fraction decreases by approximately 2.9 mole percent. The percent decrease in the mass of the vapor fraction for this particular gas mixture is 7.5%. When this mass condenses, the liquid contained in the cylinder will be approximately 0.00034 lb<sub>m</sub> -- only a fraction of the weight of a dime. This small amount of liquid can account for significant losses in the heating value of the gas sample, yet clearly, it is difficult to detect without sensitive laboratory instruments.

Now suppose that this very small amount of condensed hydrocarbons is located within a component of a sampling system, such as a sample valve. The cooling process that creates this condensate could occur during the pressure reduction process described by Path 1-2 in Figure 2, as the sample flows through the equipment toward the sample cylinder. If this small amount of condensed hydrocarbons is swept into a sample cylinder during a subsequent sample, a significant *increase* in heating value, rather than a decrease, can result. This would most likely occur if the sample cylinder is kept heated and the condensate revaporizes into the sample.

This section has illustrated the magnitude of the impact of phase changes on natural gas samples. In practice, the effect of a distorted gas sample on calculated gas properties is very difficult to predict. The effects of poor sampling technique on gas samples taken under actual laboratory and field conditions are far more complicated and cannot be accurately predicted using current technology.

## Research on Natural Gas Sampling and Analysis

**Hydrocarbon dew point predictions by equations of state.** Clearly, it is crucial that a natural gas stream be kept above its hydrocarbon dew point during sampling to avoid sample distortion. The Bureau of Mines chilled mirror dew point tester [Reference 8] can be used to measure dew points of natural gas streams at field sites, but its use may not always be practical. If data on the gas composition – such as an analysis from a process gas chromatograph (GC) – is available before the sample is taken, the dew point can instead be estimated using any of a number of commercial software packages. Sampling equipment can then be heated above the estimated dew point to avoid condensation and sample distortion.

Small amounts of heavy hydrocarbons, n-hexane and heavier, can strongly affect the hydrocarbon dew point of a gas. Unfortunately, many process GCs today cannot identify these heavier components separately, and only report a “lumped C<sub>6+</sub> fraction” for the gas being analyzed. Research at SwRI has looked for a useful, accurate method for predicting hydrocarbon dew point temperatures using only process GC data through C<sub>6+</sub>.

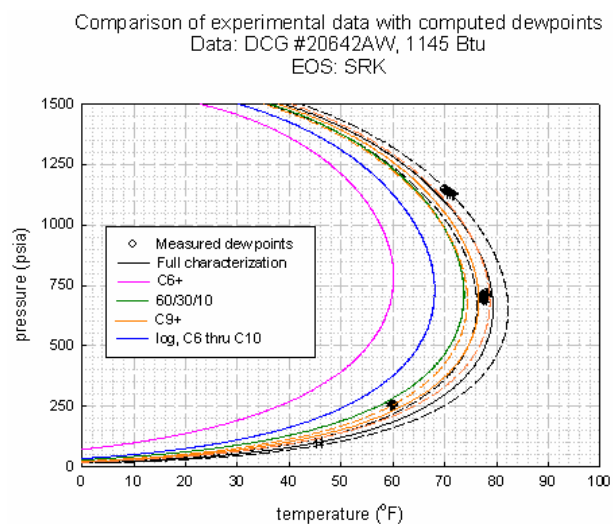
Hydrocarbon dew points and phase diagrams can be computed using any of several software programs. Gas compositions can be input to the software using different “characterizations” of the heavy hydrocarbons in the gas mixture. These characterizations make assumptions about the relative amounts of hexanes and heavier components in the lumped C<sub>6+</sub> fraction. For a given software program, the user may have the option of various equations of state (equations that predict the behavior of a gas mixture with temperature and pressure changes). Advanced software programs may also provide the user with a choice of different binary interaction parameters, or BIPs (constants taken from experimental data that predict how different hydrocarbon molecules interact with one another).

Research [Reference 4] compared experimental hydrocarbon dew point data to values predicted with different software packages, equations of state, C<sub>6+</sub> characterizations, and BIPs. Table 2 shows the observed influence of the different options on the predicted hydrocarbon dew points. Not surprisingly, the C<sub>6+</sub> characterization method had the largest influence on the accuracy of the predicted phase diagram.

| Calculation Options              | Observed Variations in Predicted Dew Point Between Options Tested |
|----------------------------------|-------------------------------------------------------------------|
| C <sub>6+</sub> characterization | Exceeding ±35°F                                                   |
| Equation of state                | ±5°F                                                              |
| Software package                 | ±5°F                                                              |
| Binary interaction parameters    | ±4°F                                                              |

**Table 2. Effects of calculation options on predicted hydrocarbon dew points.**

Figure 4 shows an example of several phase diagrams for a single gas composition, all computed by assuming different characterizations for the hexanes and heavier hydrocarbons. The results were compared to the experimental hydrocarbon dew point data for the same gas composition to determine the potential errors due to poor characterizations. The worst result was produced by treating the lumped C<sub>6+</sub> fraction as 100% normal hexane. Using this characterization gave computed dew points as much as 35°F below the experimental data. As shown above, allowing a gas sample to cool below its hydrocarbon dew point by this amount can lead to condensation of heavy components and significant errors in properties determined from the sample analysis. The best characterizations in this example either used the certified gas composition, or used the certified composition through nonane (C<sub>9</sub>) and treated the heavier components as a “lumped C<sub>9+</sub>” fraction.



**Figure 4. Effect of using various C<sub>6+</sub> characterizations on predicted hydrocarbon dew point curves.**

In general, the SwRI research indicated that a typical natural gas composition must be known through nonane for its dew point to be computed with reasonable accuracy. This information can be obtained by analyzing the stream using a GC capable of detecting hexanes and heavier hydrocarbons separately. This may require a sample to be carefully obtained and sent offsite for analysis. Treating a lumped C<sub>6+</sub> fraction as pure hexane will consistently cause the dew point to be under-predicted and can lead to sampling errors.

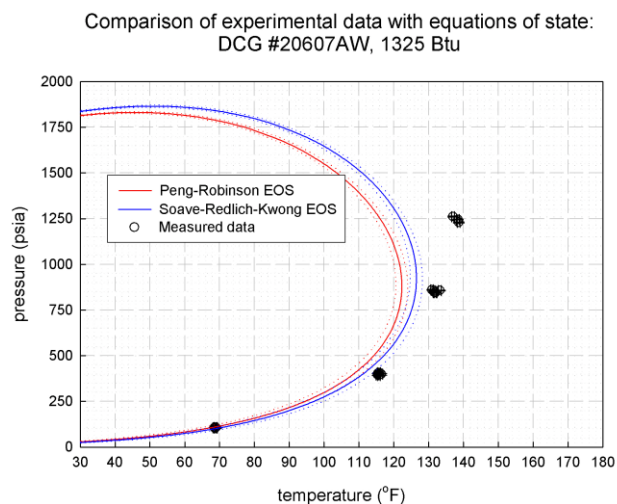
**Dew point under-predictions for rich natural gases by equations of state.** Experiments were also performed at SwRI to gather data on a variety of natural gas compositions similar to transmission and unprocessed production gases [References 4 through 6]. Data were gathered for each gas over a range of pressures to

characterize the complete hydrocarbon dew point curve, and to provide data for the assessment of dew point prediction methods described above.

For the leaner test gases, the general shape of the experimental dew point curves followed the shape of the curves predicted by equations of state. Figure 4 above compares data collected for an 1,145 Btu/scf gas to phase diagrams predicted by equations of state. In general, for the leaner gases, predictions using a  $C_{9+}$  characterization and common cubic equations of state agreed with the data at all pressures to within 15°F.

For richer gas blends, however, equations of state were found more likely to under-predict the measured hydrocarbon dew points, particularly at higher pressures. Figure 5 compares data collected for a 1,325 Btu/scf gas blend to the hydrocarbon dew point curves predicted using common equations of state and the certified gas compositions. Again, the predicted curves and the measured dew points follow the same general trends, but the calculations under-predict the measured values by as much as 30°F at the highest pressure. As shown above, allowing a gas sample to drop below its hydrocarbon dew point by this margin can lead to significant errors in analyzed properties due to condensation of heavy components.

Similar under-predictions have also been seen in other research [Reference 9]. Research is underway at SwRI and elsewhere to identify the cause, which is currently believed to be related to the gas properties used by the equations of state. In the meantime, based on these research results, changes have been made in the latest edition of API Chapter 14.1 to provide a realistic margin of error in the use of software packages to estimate hydrocarbon dew points.



**Figure 5. Example of observed errors in predicted dew point curves for rich natural gases.**

**Preparation of natural gas blends for use as GC calibration standards.** Once a natural gas sample has been collected in the field, it is typically taken to a lab for analysis. Accurate analysis of the gas sample by gas chromatography requires that the GC be calibrated against a reference gas blend that has been accurately prepared. Research [Reference 10] has reviewed methods for preparing natural gas blends used as chromatography calibration standards. The results were used to provide guidance in the 6<sup>th</sup> edition of API Chapter 14.1 on preparing reference gas blends, verifying the blend, and reporting the composition to the user.

In the study, several companies that supply calibration standards to the natural gas industry were visited and surveyed to understand their preparation techniques. The study sought out the accuracy achievable in certified gas compositions, and worked to identify “best practices” for companies to follow. The review found that relative uncertainties of 1%, at the two-sigma confidence level, are routinely attainable in hydrocarbon components from methane through isobutane and normal butane. Uncertainties of less than 1% in heavier hydrocarbons are achievable by companies that use gravimetric analyses and high-precision balances in their preparation process.

The study identified specific preparation techniques and equipment that can cause errors in the blending process, such as storing raw materials in areas that are not climate-controlled, or failure to clean equipment used to transfer raw materials from storage to the blending cylinder. Several practices were also identified that are suggested as “best practices” for limiting blend contamination, removing measurement bias, or reducing uncertainty in blend compositions. These included checking raw materials for impurities before use, enclosing scales and balances to minimize fluctuations caused by drafts of air in the preparation room, multiple-point calibrations of GCs used to verify blends, and the use of quality control charts to track the performance of equipment used in the blending process. These best practices were considered in preparing the latest revision of API Chapter 14.1, which now gives additional guidance on the preparation and use of calibration gases.

#### **Additions and Changes to API MPMS, Chapter 14.1**

During preparation of the 6<sup>th</sup> edition of API MPMS Chapter 14.1, the previous edition was updated in five specific areas. These updates were based on research results obtained by SwRI, and on concurrent revisions to other relevant standards.

**Equipment heating requirements.** The previous edition of API Chapter 14.1 required that sampling equipment be heated well above calculated hydrocarbon dew points to avoid condensation and sample distortion. This safety margin was a result of concerns about the ability of equations of state to predict accurately hydrocarbon dew



points. The 5<sup>th</sup> edition of the standard recommended that the gas being sampled be maintained at 20 to 50°F (11 to 28°C) above the expected hydrocarbon dew point throughout the sampling system.

In the 2006 revision of the standard, this operating margin was reduced to reflect research on the accuracy of hydrocarbon dew point calculations. The 6<sup>th</sup> edition recommends that sampling equipment be maintained at least 30°F (17°C) above the expected hydrocarbon dew point. This margin can be reduced further where data (such as the data in Figures 4 and 5) show that differences between calculated and measured hydrocarbon dew points for the gas composition of interest are less than this 30°F margin.

This operating margin shall be applied to all equipment that comes into contact with the gas sample, including sample probes, sample lines, regulators, filters, valves, and sample containers. This can be achieved with heated sample probes, heat trace, catalytic heaters, and/or insulation. If the operating margin requires equipment to be heated above 125°F (52°C), care should be taken that temperature limits on elastomeric seals and any other heat-sensitive materials in the sampling assembly are not exceeded.

If a sample has been collected following these guidelines, but the sample cylinder is exposed to temperatures below the expected dew point after the sample is collected, API Chapter 14.1 states that sample integrity can be restored by heating the cylinder to at least 30°F above the expected hydrocarbon dew point for two hours before opening the cylinder for analysis. Guidance contained in the 2006 edition also states that the predicted dew point can be based on the sample pressure in the cylinder if the sample pressure is different from the pipeline pressure. This could occur, for example, if the sample line is regulated between the pipeline and collection point.

**Sample probe length and location.** Additional guidance has been added to the 6<sup>th</sup> edition of API Chapter 14.1 on avoiding probe failure due to flow-induced vibration. Sample probes within a flowing pipeline can vibrate as the flow forms vortices (eddies) behind the probe. If the probe is too long, the vibration frequency can eventually cause the probe to break off in the pipeline due to high-cycle metal fatigue.

API Chapter 14.1 gives formulas for selecting the maximum probe length to avoid probe failure due to flow-induced vibration using information extracted from a European standard [Reference 11]. Table 3 shows examples of the maximum allowable probe lengths for probes of various diameters. The maximum lengths were computed assuming a maximum gas velocity in the pipeline of 100 ft/s (30.48 m/s), probe wall thickness of 0.035 inches, and 316 stainless steel as the probe material. Probe lengths should still be chosen to place the probe tip within the center one-third of the pipe cross section.

| Probe Outer Diameter (inches) | Recommended Maximum Probe Length (inches) |
|-------------------------------|-------------------------------------------|
| 0.25                          | 2.00                                      |
| 0.375                         | 3.25                                      |
| 0.50                          | 4.25                                      |
| 0.75                          | 6.50                                      |

**Table 3. Examples of maximum recommended probe lengths to avoid vibration failure [Reference 7].**

Guidance on the location and orientation of sample probes in the pipeline has been clarified in the 6<sup>th</sup> edition of the standard. Probes should be mounted vertically at the top of a straight run of horizontal pipe. If the gas stream is not near its hydrocarbon dew point, any probe location within a meter run that meets this requirement is satisfactory so long as the probe does not interfere with the performance of the metering element. Straight-cut probes are preferred over probes with beveled open ends.

If the gas stream is near its hydrocarbon dew point, and the sample probe is located downstream of an element or device that disturbs the flow (such as another sample probe or a flow conditioner), the distance from the disturbing element to the sample probe should be at least five times the maximum diameter of the disturbance. For major disturbances that change the flow profile of the stream, such as orifice plates, elbows or flow conditioners, the distance to the probe should be five times the inside pipe diameter at the disturbance. This requirement is intended to prevent liquid droplets that form in the flow behind the disturbance from potentially distorting the gas sample.

**Sampling methods.** The 6<sup>th</sup> edition of API Chapter 14.1 refers to several sampling methods described in GPA Standard 2166 [Reference 12]. With the revision of GPA 2166, changes were also made to API Chapter 14.1 to reflect this revision. The API document cites the expected accuracy of gas heating values and densities determined from samples taken with each method. These accuracy values come from results of experiments in which known reference gases were sampled using each method, analyzed, and the results compared to the reference gas values.

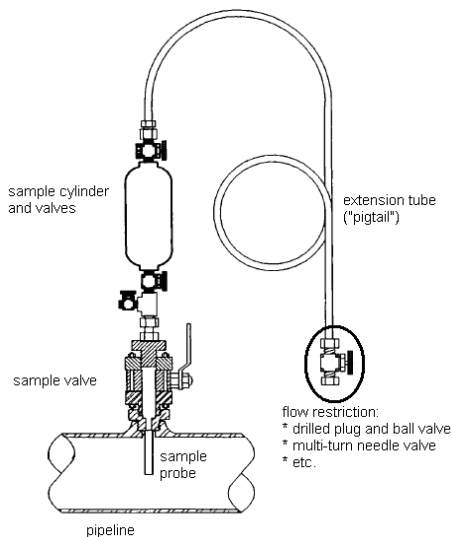
API Chapter 14.1 refers readers to GPA 2166 for sampling procedures and equipment specifications, and in some cases, provides supplemental suggestions for using a particular sampling method. For example, where floating piston sample cylinders are used to gather samples at constant pressure, API Chapter 14.1 recommends that the cylinder be pre-charged with an inert blanket gas to a pressure equal to or greater than the

pipeline pressure, and that the piston be moved flush with the inlet end cap to ensure that the cylinder volume is zero at the start of the sampling procedure. The 6<sup>th</sup> edition of API Chapter 14.1 recommends that inlet piping not be purged using a fill-and-empty method, but that a purge valve be installed on the cylinder end cap or the sample line to allow a flow-through purge.

One significant change in sampling equipment has been specified by the new editions of API Chapter 14.1 and GPA 2166. When samples are collected using the fill-and-empty method, these standards previously required a drilled plug to be placed at the end of a “pigtail” to control the sample flow rate (Figure 6). The purpose of the flow restriction and pigtail is to move the throttling process and associated Joule-Thomson cooling far from the sample cylinder, so that condensation in the sample cylinder is avoided. API Chapter 14.1 and GPA 2166 now allow for other flow restrictions, such as a multi-turn needle valve, to be placed at the end of the pigtail. This addition to the method is based on tests of the fill-and-empty method at SwRI that used needle valves instead of drilled plugs to shorten the fill-and-empty cycle time [Reference 4].

API Chapter 14.1 gives specifications on pigtail geometries and of throttling devices that will work well in this application. In particular, API Chapter 14.1 recommends that the throttling device have a flow coefficient  $C_v$  between 0.09 and 0.53.

**Guidelines for laboratory analysis.** Significant additions to Section 16 of API Chapter 14.1 give new guidance for laboratories that analyze gas samples. For instance, API Chapter 14.1 states that laboratories shall meet GPA operational requirements or requirements of other recognized standards organizations, so that analyses are performed in accordance with their procedures.



**Figure 6. Sampling apparatus for the GPA Fill-and-Empty method (adapted from Reference 13).**

New to API Chapter 14.1 for the 6<sup>th</sup> edition are the accuracy requirements for preparation of calibration standards. As a minimum, calibration gases shall be gravimetrically prepared; that is, components shall be weighed out as they are added to the gas blend. Such measurements shall be traceable to NIST or a similar standards body. Raw materials used to prepare calibration standards shall be screened for impurities. The certificate for the calibration standard gas shall include estimated uncertainties for the final composition, computed from uncertainties in instruments used to prepare the gas, biases observed during calibration of the instruments, and other significant sources of uncertainty. Accuracy requirements for the final blend composition are also stated, taken directly from GPA Standard 2198 [Reference 13]. These requirements are shown in Table 4.

| Concentration of Component (mole %) | Required Relative Accuracy of Certified Concentration |
|-------------------------------------|-------------------------------------------------------|
| 0 to 0.099%                         | 5%                                                    |
| 0.10 to 9.999%                      | 2%                                                    |
| 10.0% to 100%                       | 1%                                                    |

**Table 4. Required accuracy of calibration standard gas blends from API Chapter 14.1 and GPA 2198.**

Other guidelines discuss the use and handling of these calibration standards by analysis laboratories. For instance, cylinders containing calibration standards shall be kept at least 30°F above the hydrocarbon dew point of the gas blend at its fill pressure, or if necessary, above the cricondentherm of the gas. API Chapter 14.1 recommends that after one year, a standard should either be replaced or re-analyzed to confirm that its certified composition is still correct. Analyzing the standard to confirm its certified composition before it is first used is also recommended.

**Addendum on auto-ignition.** An addendum to the 2006 edition addresses the theoretical possibility of auto-ignition of mixtures of natural gas and air in sample cylinders. Although there have been no reports of natural gas explosions occurring during the filling of sample cylinders, this addendum makes users aware of the theoretical possibility and provides guidance to avoid the problem.

If natural gas enters the sample cylinder at the speed of sound, the shock wave created by the gas entering the cylinder can theoretically act like a piston, rapidly compressing any contents of the cylinder until it reaches its auto-ignition temperature. If the cylinder already contains air, and the resulting air/gas mixture ratio supports combustion, a fire or explosion could occur

inside the cylinder. To mitigate the theoretical possibility of auto-ignition, the addendum to API Chapter 14.1 states that (1) all air or oxygen must be removed from the cylinder or (2) the velocity of gas entering the cylinder must be kept below the speed of sound. This must be accomplished in a manner that does not introduce sample distortion. Avoiding the use of valves with large openings that can be opened quickly, such as a quarter-turn, full-port valve, can mitigate the chances of auto-ignition.

### **Ongoing Gas Sampling Research and Future Modifications**

This paper has reported on the results of research into natural gas sampling and analysis, and discussed changes in the 2006 edition of API Chapter 14.1 that reflect the results of that research. However, questions remain to be answered, and the natural gas community can expect to see future revisions to API Chapter 14.1 and related standards that will put the findings of continuing gas sampling research into practical use.

The mission of the API Chapter 14.1 Working Group has been expanded to include sampling for moisture content and other properties related to gas quality. A new Appendix to API Chapter 14.1 is being balloted that will provide improved guidance on measuring both hydrocarbon and water vapor dew points. This appendix will be based on research on the accuracy of automated dew point instruments performed since the publication of the 6th edition, as well as research that has noted the impact of different “types” of hydrocarbon dew points that correspond to different amounts of condensate.

The Bureau of Land Management plans to incorporate API Chapter 14.1 into its regulations by reference, and has asked the Working Group to include a checklist for inspecting field sampling locations. Users can also expect to see a new Appendix similar to the Laboratory Inspection Checklist for reviewing field sampling locations, equipment, and sampling practices.

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