LESSONS LEARNED FROM THE API 14.1 GAS SAMPLING RESEARCH PROJECT
AN OVERVIEW OF COMMON CAUSES OF GAS SAMPLE DISTORTION AND INFORMATION NEEDED FOR PROPER GAS SAMPLING

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Introduction

Over the past ten years, the Gas Technology Institute (GTI), the American Petroleum Institute (API) and the United States Minerals Management Service (MMS), have co-sponsored an extensive natural gas sampling methods research program at the GTI Metering Research Facility (MRF), located at Southwest Research Institute (SwRI). The results of this research provided a basis for the revision of Chapter 14.1 (i.e., *Collecting and Handling of Natural Gas Samples for Custody Transfer*) of the API Manual of Petroleum Measurement Standards (MPMS). The last revision was published in 2001, and work is beginning in 2005 on a new edition that will incorporate the latest research findings.

The API Chapter 14.1 Working Group, a research steering committee consisting of natural gas sampling experts from major oil and gas companies, provided input that helped focus the project on improving current field practices. The research identified several causes of natural gas sample distortion, as well as techniques for avoiding gas sample distortion. The research data illustrated how errors in calculated gas properties, such as heating value and density, can occur as a result of poor sampling technique.

The 2001 Revision of API Chapter 14.1

The 2001 revision of Chapter 14.1 of the API MPMS provides guidance for obtaining representative samples of natural gas through spot, composite, and continuous sampling methods. It focuses on the practical application of thermodynamic principles that, if ignored, can cause a gas sample to become distorted, resulting in a biased gas analysis. If a biased analysis is used to calculate the heating value or other properties of the sampled gas, errors in excess of 10 percent may occur.

The revised Chapter 14.1 builds on the knowledge contained in the previous version by identifying several specific causes of natural gas sample distortion. Chapter 14.1 discusses gas sample distortion in detail and provides recommendations for avoiding it. The standard is suitable as an instructional tool and as a guide to sampling system design and sampling techniques. The standard is written primarily for field personnel. It provides the technical background necessary to understand and apply basic hydrocarbon mixture thermodynamics to natural gas sampling in order to avoid gas sample distortion.

This paper draws on the information in the revised Chapter 14.1 and presents an overview of three common causes of gas sample distortion: (1) sample distortion due to equipment and processes that cause the sample gas temperature to drop below the hydrocarbon dew point temperature, (2) sample distortion caused by dirty or contaminated sampling systems and (3) sample distortion caused by sampling system components fabricated from materials known to affect the integrity of a natural gas sample. Recommendations for avoiding gas sample distortion according to the revised Chapter 14.1 are presented below. This paper begins with a discussion of the importance of the hydrocarbon dew point in gas sampling methodology and sampling system design, followed by an introduction to the natural gas phase diagram.

Hydrocarbon Dew Point

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[1], 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[2], 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 influence on heating value. This distinction should be

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[1] This process is known as an *isobaric* (or constant pressure) temperature reduction. It is the process that occurs when using a "chilled mirror device" 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.

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 characteristic of natural gas and should be considered 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. The 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.
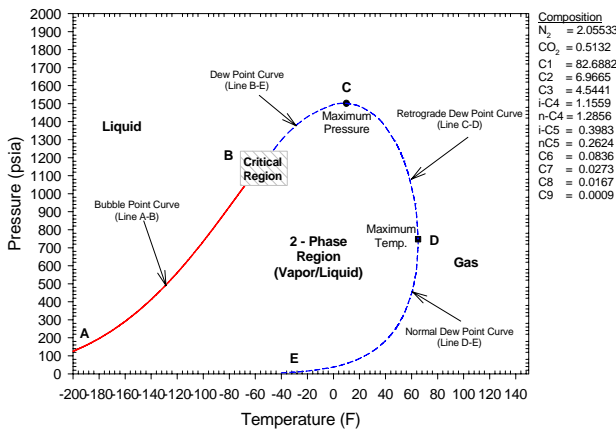

Figure 1.   A typical natural gas phase (P-T) diagram.

The line B-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-D represent the pressures and temperatures at which retrograde condensation occurs. The points on this line represent retrograde phase behavior. Retrograde condensation can occur during common natural gas sampling processes.

The 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.

Hydrocarbon Dew Point and Natural Gas Sampling

The hydrocarbon dew point is perhaps the single most important property in natural gas sampling. If the sample temperature is allowed to drop 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 the impact of dropping below the hydrocarbon dew point temperature contributes to increased random and bias error in the calculated heating value and density. The phase diagram shown on Figure 2 illustrates how different processes common in natural gas sampling can cause the temperature of the sampled gas to fall below the hydrocarbon dew point.
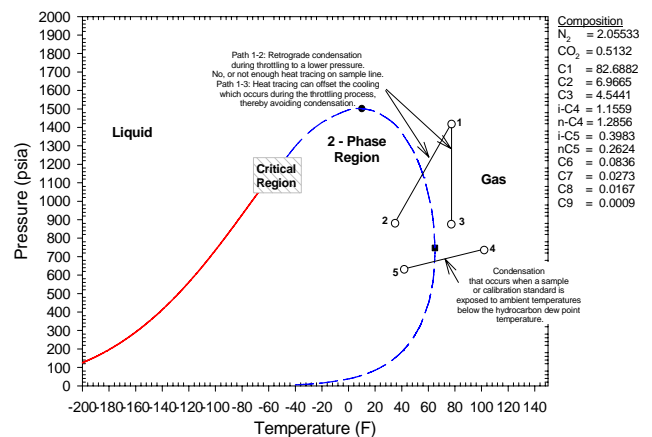

Figure 2.   A typical natural gas phase (P-T) diagram showing several processes common in natural gas sampling. These processes can cause condensation – a fundamental cause of gas sample distortion.

Path 1-2 represents the process that occurs when natural gas flows through a regulator or partially closed valve. The cooling associated with the pressure reduction is known as the Joule-Thompson effect. Condensation and sample distortion can occur during this "throttling" process.

The cooling can be offset through the application of heat to the sampling system. Path 1-3 shows the potential impact of adding sufficient heat to the system to offset the cooling effect.

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

The potential impact of condensation on the heating value of natural gas can be illustrated graphically. Figure 3 shows the potential effect of 41^OF gas sampling equipment on a 1,500 BTU natural gas with 0.85 mole percent n-hexane through n-decane (labeled as C_6+) components and a hydrocarbon dew point of 91^OF. Table I shows the gas composition associated with the figure.
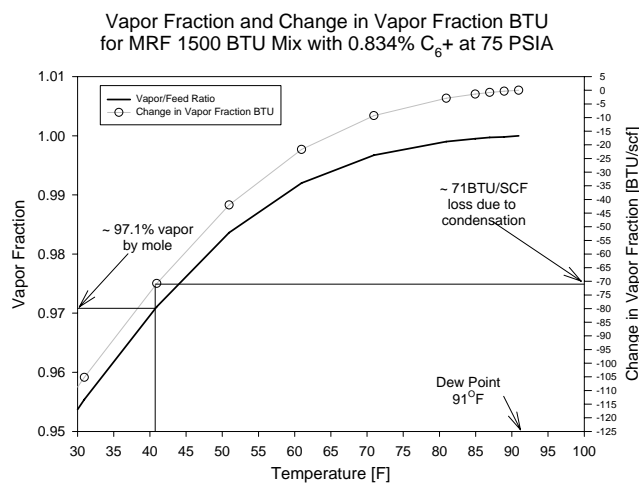

Figure 3. The vapor fraction and change in vapor fraction BTU associated with condensation of a 1,500 BTU/SCF natural gas mixture.

The vertical axis on the left shows the vapor (gas) fraction, on a molar basis. The liquid fraction is simply 1 minus the vapor fraction. The vertical axis on the right shows the change in vapor fraction BTU.

As the temperature is reduced below the hydrocarbon dew point temperature, hydrocarbon constituents condense in order of decreasing molecular weight. This condensation causes the vapor fraction of the mixture to decrease and a corresponding decrease in the heating value of the vapor fraction.

As the gas temperature is reduced below the hydrocarbon dew point, there is a large decrease in heating value associated with a small amount of liquid condensation. At a temperature of 41 ^{O}F, the loss in heating value amounts to over 70 BTU/SCF.

MRF 1,500 BTU Mix	
Component	**Mole Percent**
Methane	64.107
Ethane	10.33
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**

Table 1. The 1,500 BTU/SCF natural gas mixture used to calculate the values in Figure 3.

The mass and weight of liquid produced by condensation of the natural gas in Figure 3 can be estimated. Assume that a representative sample of natural gas is contained in a standard 300 cc constant volume sample cylinder. When the temperature is reduced to 41^OF, 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 percent. The total mass of gas (vapor) at 75 psia and 91^OF is approximately 0.0045 lb_m. If 7.5 percent of the mass condenses, then the liquid contained in the cylinder will weigh approximately 0.00034 lb_f. This is only a fraction of the weight of a dime. This small amount of liquid can account for significant losses in gas sample heating value, yet it is difficult to detect without sensitive laboratory instruments.

The process described is similar to the process shown by Path 4-5 in Figure 2 and illustrates how a phase change can cause a *decrease* in heating value. Now consider a very small amount of condensed hydrocarbons (weighing less than a dime) located within a component of a sampling system, such as a sample valve. This could occur during the pressure reduction process described by Path 1-2 in Figure 2. If the small amount of condensed hydrocarbons is swept into the sample cylinder during sampling, a significant *increase* in heating value can result.

This discussion illustrates 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.

The Need to Correctly Characterize the Gas When Computing Hydrocarbon Dew Points

Clearly, it is crucial for a natural gas stream to be above its hydrocarbon dew point during sampling to avoid sample distortion. If enough is known about the gas composition before the sample is taken, the dew point can be estimated using any of a number of commercial software packages. Small amounts of heavy hydrocarbons, n-hexane and heavier, can strongly affect the dew point of a gas. Unfortunately, many process gas chromatographs (GCs) cannot identify these heavier components separately, and only report a "lumped C_6+ fraction" in their results. Using this lumped fraction incorrectly can lead to a significant underestimate of the dew point, and to sample distortion.

Ongoing research at SwRI has sought a useful, accurate method for predicting hydrocarbon dew point temperatures using only process GC data through C_6. Phase diagrams have been computed using several software programs, different equations of state (equations that predict the behavior of a gas mixture with temperature and pressure changes), and 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_6+ fraction. Not surprisingly, the characterization method had the largest influence on the accuracy of the predicted phase diagram.

Figure 4 shows an example of several phase diagrams for the same gas, all computed by assuming different compositions for the hexanes and heavier hydrocarbons. The results were compared to the phase diagram computed from the certified gas composition, to determine the potential errors due to poor characterizations. The worst case was obtained by treating the lumped C_6+ fraction as 100% normal hexane. Using this characterization gave computed dew points as much as 35°F below the curve computed from the certified gas composition. The best characterization in this example used the actual composition of the gas through nonane (C_9), and treated the heavier components as a "lumped C_9+ fraction."

Comparison of experimental data with computed dewpoints
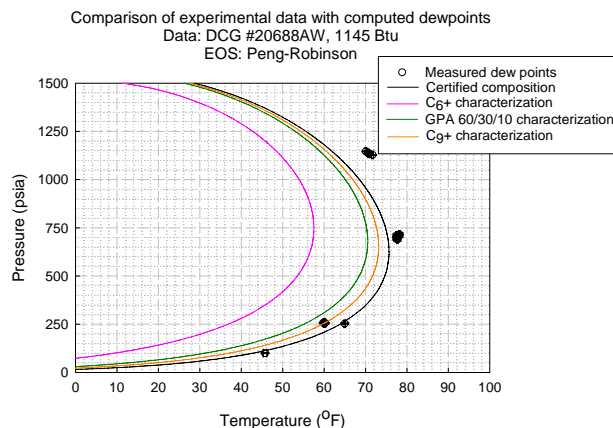Data: DCG #20688AW, 1145 Btu
EOS: Peng-Robinson

Figure 4. Potential errors in phase diagrams computed using incorrect characterizations of heavy hydrocarbons.

In general, the SwRI research indicates that a 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_6+ fraction as pure hexane will consistently cause the dew point to be underpredicted, and can lead to sampling errors.

Gas Sample Distortion Due to the Sample Gas Temperature Dropping Below the Hydrocarbon Dew Point Temperature – Laboratory and Field Test Results

The Gas Processors Association (GPA) spot sampling methods and three composite samplers were tested with several gravimetrically prepared natural gas mixtures in static (non-flowing) conditions. The deviations in calculated heating value and density for the gas samples obtained during the tests are shown in Figure 5.
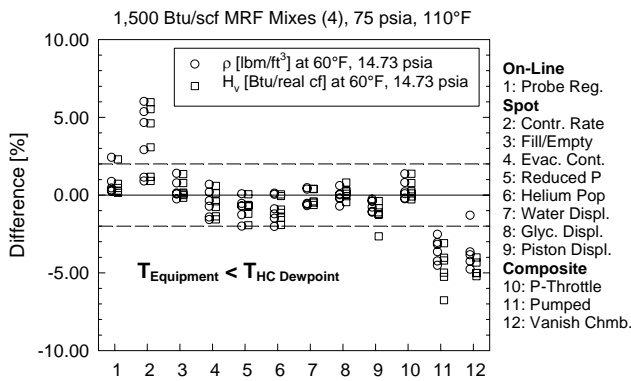
Figure 5. **The deviation in calculated heating value and density using analyses obtained from samples taken with equipment at temperatures below the hydrocarbon dew point temperature.**

Figure 6. **Composite sampler field test results showing the effect of placing a heated enclosure around the sampling system.**

When the temperature of the sampling hardware was below the hydrocarbon dew point, all methods produced distorted gas samples. Some sampling methods produced samples that were enriched, causing an increase in the sample heating value and density. Other methods produced samples that were depleted, causing a decrease in the sample heating value and density. All of the methods produced highly variable results, suggesting that a phase change occurred during sampling.

The results from the composite sampler tests in Figure 5 (Methods 10, 11 and 12) led to subsequent field tests to better understand the operational limits of composite samplers. *In-situ* tests were conducted at a gas pipeline site in northwest Colorado. Four composite samplers were installed on a pipeline that was flowing 1,100 BTU/SCF natural gas, and exposed to ambient conditions 60-70°F below the hydrocarbon dew point. The composite samples were analyzed and the calculated heating value and density of each sample were compared to the average values acquired from on-line gas chromatograph (GC) analyses. After approximately six months of testing, heated enclosures were installed on the composite sampling systems to stabilize the ambient air temperature around the samplers at approximately 100°F.

Test results from one composite sampling system are shown in Figure 6. Results after the heated enclosures were installed showed a significant improvement, with each system providing samples with heating values and densities that agreed with the reference to within +/- 0.75%, nominally.
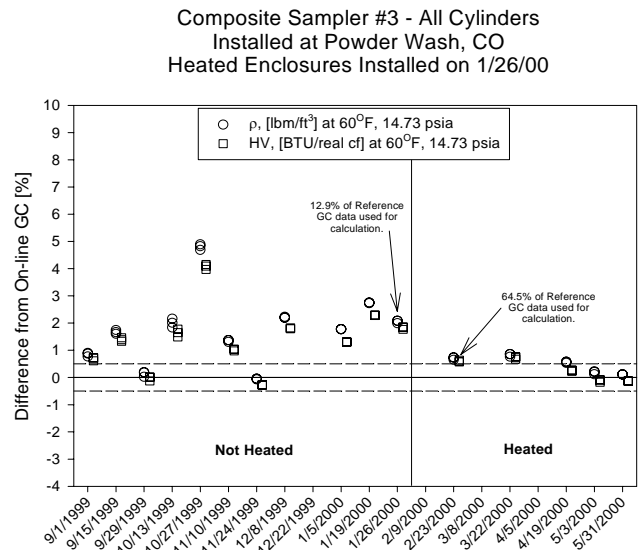
The 2001 revision of Chapter 14.1 of the API MPMS states that the sample gas temperature must remain 20-50°F above the hydrocarbon dew point temperature at all times during sampling. If the sampling process involves a pressure reduction, additional heat must be added at or upstream of the point of pressure reduction to offset the Joule-Thomson effect (approximately 7°F per 100 psi of pressure decrease).

Chapter 14.1 recommends the use of steam, hot water, or electrical heat tracing, catalytic heaters and insulation to provide heat to the sample gas. If the ambient temperature will keep the sample gas at 20-50°F above the hydrocarbon dew point temperature, heating is not required. Previous research suggested that the fill-and-empty spot sampling method might heat the sample cylinder enough to avoid hydrocarbon phase change problems in cold ambient conditions. Experiments were conducted in 2001 and 2002 to monitor the sample cylinder temperature during the fill-and-empty process, and determine the method's self-heating ability at different line conditions and ambient temperatures. It was found that the method does heat the sample cylinder, especially in cold weather, but does not generate enough heat to be used on saturated gas when the initial sample cylinder temperature is lower than the pipeline gas temperature.

If sample cylinders are exposed to temperatures below the hydrocarbon dew point temperature *after* sampling (Path 4-5 in Figure 2), the sample can be recovered by heating it to 140°F or 20-50°F above the hydrocarbon dew point temperature, whichever is lower, for at least two hours prior to analysis.

Gas Sample Distortion Caused by Dirty or Contaminated Sampling Systems

The previous discussion showed that the presence of liquid hydrocarbons affects the integrity of a natural gas sample. Liquid hydrocarbon contaminants are not always natural gas constituents. Occasionally, heavier hydrocarbons contained in compressor or machine oil contaminate sampling equipment. Figure 7 shows the impact of several residues left in a sample cylinder. The hydrocarbon residue is a 50/50 mixture of SAE-30 compressor oil and n-hexane through n-decane. The liquid hydrocarbon residue caused a reduction in the heating value and density of the gas sample.
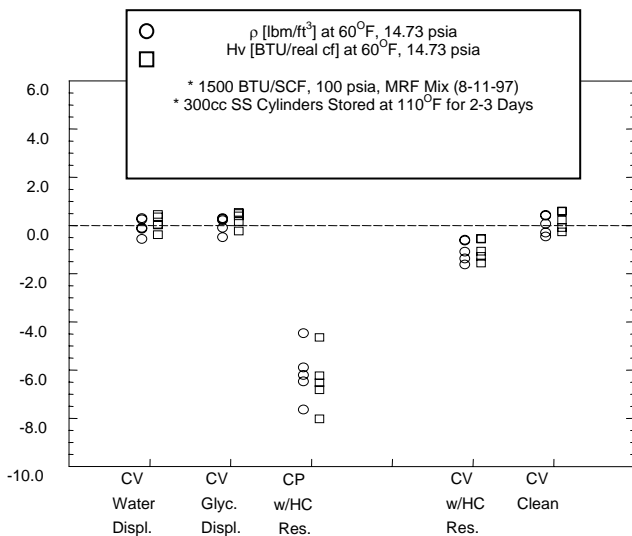
Figure 7. The impact of several residues left in a sample cylinder. The hydrocarbon residue is a 50/50 mixture of SAE-30 compressor oil and n-hexane through n-decane.

If there is reason to believe that any part of the sampling system has been contaminated, the system must be thoroughly cleaned to obtain a representative natural gas sample. Several cleaning methods were tested on contaminated sample cylinders during the research project. Figure 8 shows the results of one series of cleaning tests. The results indicate that most methods leave *some* residual. Steam cleaning was the most robust method evaluated during the research.
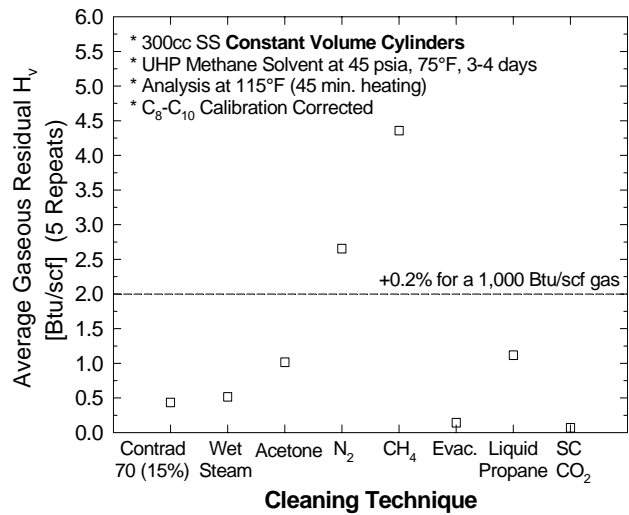
Figure 8. Cylinder cleaning tests conducted with 300 cc constant volume sample cylinders.

If a gas sample is taken using a cylinder that has not been sufficiently purged, or if air or other contaminants have leaked into the sampling system, then the integrity of the sample will be compromised, even if the sampling method is performed correctly. Figure 9 shows the effect of a nitrogen leak on the heating value and density of a gas sample obtained during sample cylinder cleaning tests at SwRI. The nitrogen increases the density and reduces the heating value of the sample. The errors can be significant and might not have been discovered if only the heating value of the sample was considered. The effect is similar if air is introduced into the system during sampling.
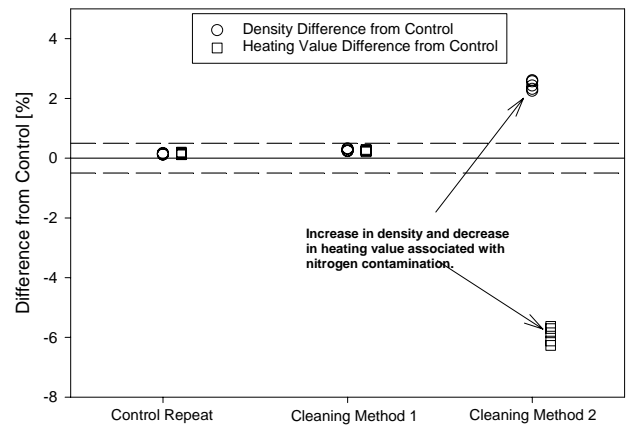
Figure 9. The effect of nitrogen that has leaked across the seals of a floating piston cylinder during a particular set of tests.

The 2001 revision of Chapter 14.1 recommends that sample systems be designed so that they can be thoroughly cleaned and that a procedure for cleaning sampling systems and sample containers be established. Chapter 14.1 recommends that sample cylinders be cleaned prior to each sample collection.

Steam is identified as the most effective sample system cleaning agent. Water containing corrosion inhibitors or other chemicals that may contaminate the sampling system should be avoided. Solvents, such as acetone and liquid propane, that do not leave a residue after drying are considered acceptable. Decon Contrad 70[®], or equivalent, is also acceptable. Other cleaning methods may be used, if testing can prove their effectiveness.

Sample containers and sampling systems must be dried and purged, or evacuated, after cleaning. Nitrogen, helium, and dry instrument-quality air are acceptable for drying sample containers and sampling systems. Blanket gases may be used to pre-charge sample containers. The blanket gas must be selected so that the analytical device will not interpret it as part of the sample.

Gas Sample Distortion Caused by Sampling System Components Fabricated from Materials Known to Affect the Integrity of a Natural Gas Sample.

Many materials commonly used to fabricate sampling system components can distort gas sample integrity. Highly porous materials and components with large surface areas are likely to cause adsorption or 'sticking' of hydrocarbon molecules to the surface of the material, that produce a corresponding reduction in heating value. If the temperature and/or pressure of the system changes, adsorbed molecules can be released from the material surface and can re-enter the sample stream, causing an increase in the heating value. This phenomenon cannot be eliminated by cleaning the sampling system.

Several common tubing materials of different diameters and lengths were tested to determine the impact on gas sample integrity. Clean stainless steel tubing was found to have little or no impact. Most plastic tubing materials had an impact on sample integrity, with polyethylene causing a reduction in heating value and density of over 6 percent. This is believed to be caused by solid-surface adsorption. Nylon 11 was the only plastic tubing material tested that did not adversely impact the gas heating value and density determination (Figure 10).
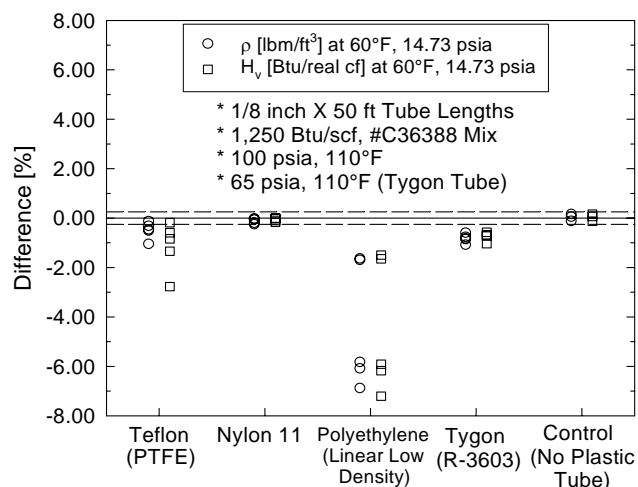

Figure 10. The effect of several types of plastic tubing on a 1,250 BTU/SCF natural gas.

The 2001 revision of Chapter 14.1 recommends the use of inert and non-porous materials in gas sampling systems. 304 or 316 stainless steel is generally recommended as a suitable material for sampling systems. Carbon steel is not recommended because of the potential for chemical reactions with the components in the gas, which can result in sample distortion. Furthermore, carbon steel is susceptible to high corrosion rates, particularly when used in wet or sour gas sampling. The use of dissimilar materials is discouraged due to the potential for high corrosion rates and gas sample distortion.

Valve seats, o-rings, and other types of seals should be made of elastomers that will not degrade when the sample gas makes contact. With the exception of Nylon 11, or its equivalent, Chapter 14.1 does not recommend the use of plastic tubing in natural gas sampling systems.

For sour gas applications, Chapter 14.1 recommends the use of special linings or coatings, such as epoxy or other suitable coatings. Soft metals, such as brass, copper, and aluminum are not recommended.

Conclusions

Unrepresentative (distorted) natural gas samples can be collected through improper sampling methods and poorly designed sampling systems. Errors derived from the calculation of gas properties, such as heating value and density, based on analyses of distorted gas samples may exceed 10 percent. These errors will propagate through the energy flow rate equations, resulting in an error in the calculated energy flow rate.

Gas sampling research conducted at SwRI over the last seven years has identified several causes of gas sample distortion. Three causes of gas sample distortion are (1) sample distortion due to equipment and processes that cause the sample gas temperature to drop below the hydrocarbon dew point temperature, (2) sample distortion caused by dirty or contaminated sampling systems and (3) sample distortion caused by sampling system components fabricated from materials known to affect the integrity of a natural gas sample.

The 2001 revision of Chapter 14.1 (i.e., *Collecting and Handling of Natural Gas Samples for Custody Transfer*) of the API Manual of Petroleum Measurement Standards includes discussions of these and other causes of gas sample distortion. Chapter 14.1 provides recommendations for obtaining representative gas samples by avoiding gas sample distortion. It emphasizes the importance of avoiding the hydrocarbon dew point temperature and recommends the use of the hydrocarbon phase diagram as a design tool to keep sampling equipment temperatures above the hydrocarbon dew point temperature. The revision also emphasizes the critical need for sampling equipment cleanliness and recommends that sampling system designs include features that allow them to be thoroughly cleaned in a timely manner. Chapter 14.1 also addresses the importance of avoiding components fabricated from materials known to cause gas sample distortion, such as many types of plastic tubing.

Technicians and engineers responsible for obtaining natural gas samples should be aware of the factors that cause sample distortion. The causes of sample distortion, such as the hydrocarbon dew point temperature, sampling equipment material selection, and equipment cleanliness should be considered when obtaining gas samples and when designing gas sampling systems.

References

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