COLLECTING AND HANDLING OF NATURAL GAS SAMPLES FOR CUSTODY TRANSFER

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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. Though gas sampling should not be performed without fully reading the standard, this paper is designed to provide supplemental information, illustrative examples, and guidelines for how best to use API 14.1. Specific sections of the standard are highlighted and broadened with additional detail. Special emphasis is put on the accurate sampling of an unknown gas stream.

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.

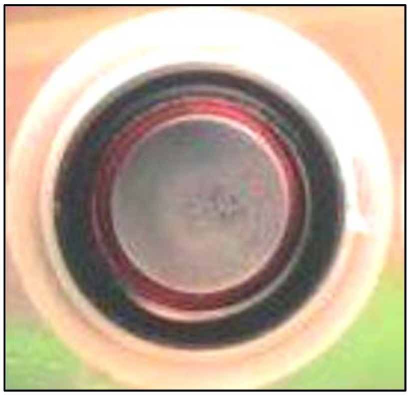

Figure 1. Gas at the Hydrocarbon Dew Point in a Chilled Mirror Device
In the image above, faint droplets are visible on the mirror with an iridescent ring around the perimeter of the mirror. This indicates that the HDP has been reached (1).

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 Chapter 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.

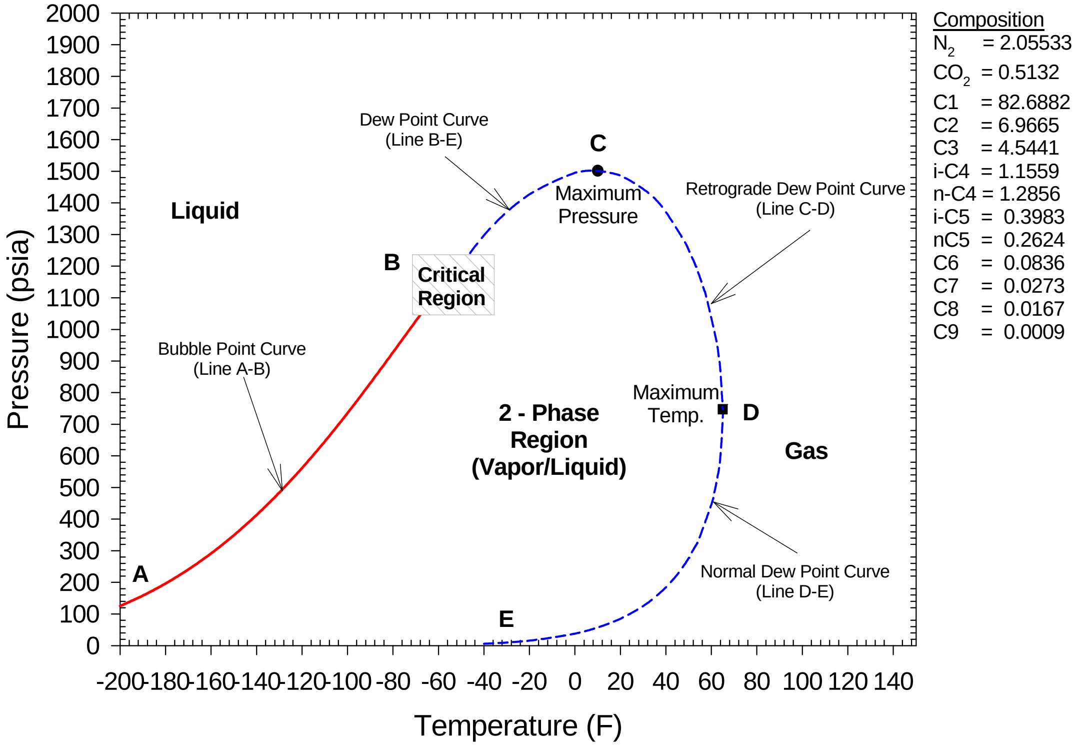

Figure 2. Pressure vs Temperature Plot of a Hydrocarbon Dew Point Curve

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

Care must be taken in the handling of a sample after it is collected to avoid condensation and distortions in the sample properties. 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 50°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**

GUIDELINES FOR INITIAL SAMPLING OF A GAS STREAM OF UNKNOWN HYDROCARBON DEW POINT AND COMPOSITION

Sampling an unknown gas stream for custody transfer poses unique risks. Without knowledge of the gas stream composition, samples may be collected improperly, and J-T cooling or exposure to ambient temperatures can drop the sample temperature below its HDP. A gas stream below its HDP can lose heavy hydrocarbons through condensation, and the liquids can be trapped in the sample connections or in the cylinder itself. This can lead to several issues:

- A sample analysis that indicates a lower (or higher) energy content than the actual gas stream, leading to lower (or higher) custody transfer revenue.
- Pipeline natural gas that violates custody transfer tariffs, but is not recognized as being in violation.
- Equipment problems such as damaged turbines, flooding of burners, and poor combustion.

In short, sampling an unknown gas stream requires care and attention to avoid potentially significant costs to the operator and/or the end user of the natural gas.

Measuring HDPs before Sampling

When faced with sampling an unknown gas stream, the preferred technique is to measure the HDP and keep the temperature of the sample (and the sampling equipment) above the HDP. HDP measurement can be done manually using chilled mirror devices or automatically with a variety of automated analyzers.

Manual HDP measurement has been standardized in Annex G of the seventh edition of API Chapter 14.1 (1). The annex references the ASTM D1142 standard for measuring water dew points using a chilled mirror device (8). The annex expands on this standard by providing guidelines for measuring the HDP of natural gas mixtures using the same device. The procedures were developed using a combination of practical industry knowledge and applied research. Notably, the annex provides uncertainty values for HDP measurements made with chilled mirrors (5).

Annex G also illustrates different types and amounts of condensation that an operator could see within a chilled mirror device during normal use and while diagnosing problems. A few of these illustrations are shown in Figure 3. It should be noted that manual measurement, though standardized, is still subjective, since different operators can obtain different results on the same gas stream.

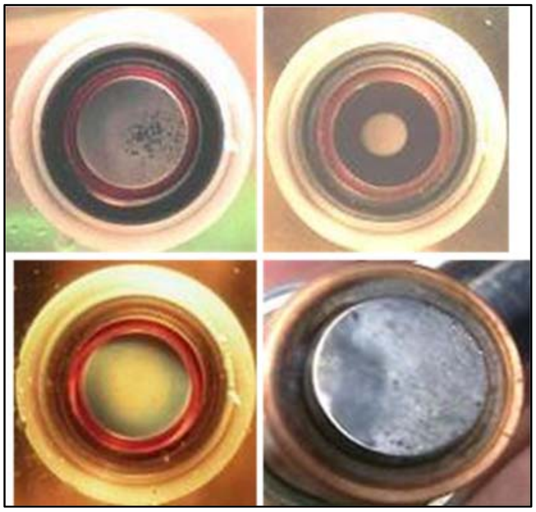

Figure 3. Example Images of Condensation Observed on a Chilled Mirror Device

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

Automated HDP measurement devices can vary greatly in operating methods. Examples include optical detection of condensate on a chilled mirror, spectroscopic analysis of a gas stream and correlation to HDP, and gas chromatographic analysis and equation of state HDP calculation. Automated HDP measurement devices are objective and are often more repeatable than manual measurements. However, they can suffer from measurement interference and other sources of bias.

Sampling Without Direct HDP Measurements

When the HDP is impractical to measure, gas samples can be taken, but the samples should be checked to confirm that the gas in the pipeline is above its HDP. API Chapter 14.1 describes various approaches to collecting samples when the HDP is unknown. Most of these approaches require the use of an equation of state (EOS) to predict the HDP from an analysis of the sample. From most to least preferred, the recommended sampling methods are listed below.

1. Take a constant pressure spot sample at or above the flowing gas temperature, perform an extended analysis, and calculate the HDP temperature using the analysis and an EOS.
2. Use a pressure-reducing sampling method, perform an extended analysis, and calculate the HDP temperature using an EOS.
3. Use historical information, including past analyses and dew point measurements from a similar source.
4. Take a spot sample at line pressure, heat the sample gas to at least 30ºF above the flowing temperature at the time of the sample, perform an extended analysis, and calculate the HDP temperature using an EOS.

If the HDP temperature calculated from one of these samples is above the flowing temperature, the sample is suspect and cannot be considered representative of the gas stream. Direct measurement of the HDP is recommended before any further gas samples are taken.

USE OF EQUATIONS OF STATE (EOS)

As noted above, EOSs may be used with sample analyses to predict the HDP of a gas stream. Several EOSs are used by the natural gas industry to predict the properties of natural gases with a given composition at a known pressure. The Peng-Robinson (P-R) EOS and Soave-Redlich-Kwong (SRK) EOS are two EOSs commonly used by the natural gas industry to predict the HDP of natural gases. These have been found to predict the HDP well for leaner gases, but often under-predict the HDP for richer gases, particularly at higher pressures. This is illustrated in Figure 4, where both EOSs are compared to experimental data for a representative production gas with a heating value of 1,325 Btu/scf.

A more recent EOS, developed at Ruhr-Universität Bochum (the University of Bochum) in Germany, is known as GERG-2008 (10). This equation uses a thermodynamic property known as the Helmholtz free energy to predict various properties of gas mixtures, including HDPs and phase boundaries. Limited tests of this equation have shown better agreement with existing HDP data than the P-R and SRK EOSs at higher pressures and for richer gases, as shown in Figure 4.

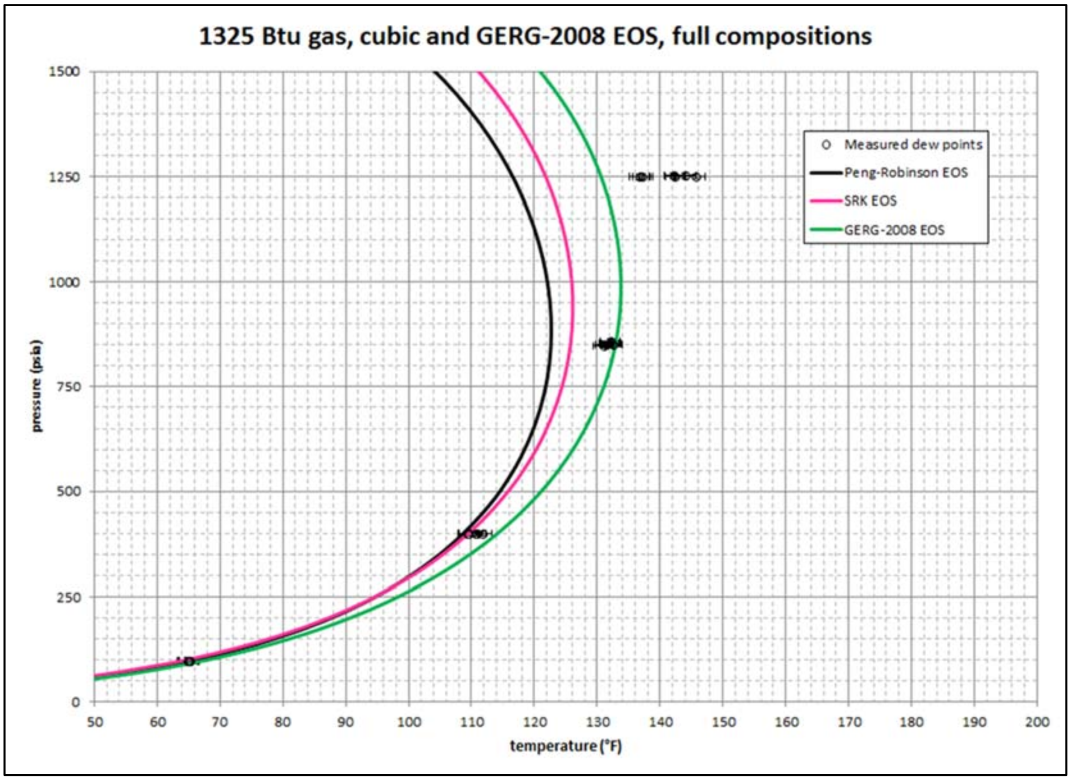

Figure 4. Predicted versus Experimental Hydrocarbon Dew Point

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 demonstrates the tendency of the P-R and SRK EOSs to under-predict the HDP of rich gases, such as production gases, at higher pressures.

Heavy Hydrocarbon "Lumping" Models

One persistent challenge in the use of EOSs to predict HDPs (and other natural gas properties) is the need for data on hydrocarbons heavier than hexane. Often, these components are not measured individually by a field GC, but are reported as a combined total, or a "C_{6+} fraction." 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 predicting the HDP of all gas streams (5). The research did show that treating the C_{6+} fraction as normal hexane did not accurately predict the HDP and could cause the HDP to be under-predicted by as much as 70°F. Many field GCs use the GPA 60/30/10 method of characterizing the C_{6+} fraction (60% n-hexane, 30% n-heptane, and 10% n-octane). This approach, and similar standard fraction distributions, can accurately characterize the density, heating value, and many other properties of many natural gas streams. However, these same distributions generally predict the HDP of typical gas streams only to within ±25°F (5). There are other characterization models available, but questions remain about how well they work when used with different EOS to predict HDPs (9). Where possible, a periodic extended analysis of a gas stream to at least C_9 is recommended for accurate HDP predictions.

Differences between Calculated and Measured HDPs

Users should be aware of the differences between HDPs predicted by an EOS and measured HDPs. An EOS predicts the temperature at which the first few heavy hydrocarbon molecules in the gas stream theoretically condense out to form liquid. A device used to measure the HDP will register the temperature at which the smallest amount of condensate can be detected. In the case of a Bureau of Mines chilled mirror device, the HDP will depend on the skill and eyesight of the operator.

Both HDPs predicted by EOS and HDP measurements are subject to biases. For HDPs calculated from a sample analysis, these can include biases in the sampling procedure, biases in the sample analysis, and biases in the EOS and its parameters. HDP measurement biases are commonly related to the detection method, but may also be related to the method of transporting the sample to the instrument.

Measured HDP temperatures tend to be a few tenths to a few degrees Fahrenheit less than a calculated HDP, since an instrument requires more than a few molecules to detect condensation. In general, as the gas composition becomes richer, the differences between measured and calculated HDPs tend to decrease, because more heavy hydrocarbons will condense out from a richer gas as the temperature falls below the HDP.

EQUIPMENT HEATING REQUIREMENTS

To avoid sample condensation and the errors discussed above, API Chapter 14.1 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 separate from the heating requirements imposed by Joule-Thomson cooling. The requirement covers all equipment that comes in contact with the gas sample, and is intended as a safety margin to ensure that the gas stays above its HDP as it travels to the sample cylinder. API Chapter 14.1 also gives guidance on how to properly heat or insulate sampling equipment to consistently keep it at the required temperature.

SAMPLE PROBE LENGTH AND LOCATION

Besides precautions to avoid sample condensation, the length and location of the sample probe should also be examined. 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 Chapter 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 (see Figure 5). API Chapter 14.1 gives several other guidelines for probe installation.

- 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).
- If the gas is at or near its HDP, 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).

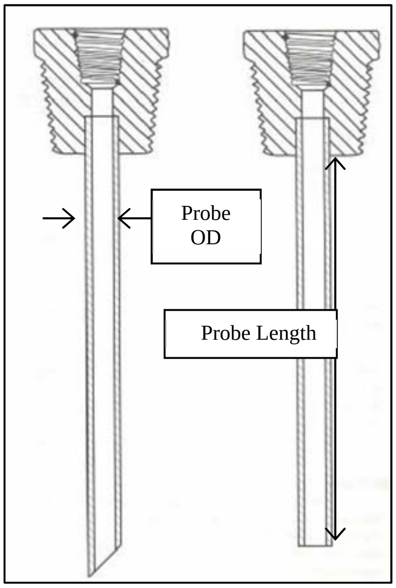

Figure 5. Two Example Sample Probes

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 the reader is referred to that standard for details of the various methods. One change of note to the GPA standard that may not yet be commonly used is related to the fill-and-empty method of sampling. In this 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 GPA 2166 required that this flow restriction be a drilled plug. The standard now allows for other flow restrictions and specifically discusses the use of devices with a flow coefficient (Cv) between 0.09 and 0.53. One device specifically mentioned that can meet this specification 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

To help ensure that natural gas samples are both properly collected and analyzed, API Chapter 14.1 gives guidance on laboratory sample analysis, with specific 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 Chapter 14.1 also requires that GC calibration standards be prepared according to GPA 2198 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 Chapter 14.1 also 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 in Table 3. This guideline requires that the accuracy of each component’s concentration fall within the specified ranges based on the nominal concentration.

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

API Chapter 14.1 Section 16 reflects industry concerns regarding auto-ignition of natural gas 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 Chapter 14.1 notes that API is not aware of this actually occurring in the field, but the process is possible in theory (1).

CHECKLIST FOR INSPECTING FIELD SAMPLING LOCATIONS AND PROCEDURES

The seventh edition of API Chapter 14.1 includes a checklist (Annex H) for inspecting field sites where natural gas is sampled, the sampling methods used, and the procedures used to analyze samples in the lab. The checklist is recommended for use by field personnel, company auditors, and training instructors to ensure that API Chapter 14.1 guidelines are followed and that natural gas samples are collected according to API Chapter 14.1 requirements. In 2017, the Bureau of Land Management (BLM) referenced API Chapter 14.1, Annex H in its regulations for the measurement of natural gas produced on federal lands, and this checklist will be used by BLM inspectors as well.

CONCLUSION

API 14.1 serves the natural gas industry as the standard for best practices in the collection and handling of gas samples in custody transfer. In support, this paper has expanded on several important sections of the standard, providing background information, examples, and guidelines.

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